

HARNESSING THE COMPLEXITY OF COMPLEX OXIDES

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Abstract

Human prosperity is driven by technology. And over the past 50 years, much of the tremendous progress in human prosperity has been driven by information technology, especially the semiconductor transistor and Moore’s law. But today Moore’s law is ending. Going forward, humanity faces two broad possibilities: either stick with the transistor and settle for a reduced rate of progress in computer hardware or, as has been done many times in the past, develop a new computing paradigm with more initial difficulty but higher ultimate potential.

One candidate materials platform for a future computing paradigm is complex oxides, whose complexity is both boon and bane. On the one hand, the complexity of complex oxides is responsible for their wide range of tunable properties, such as ferromagnetism, ferroelectricity, and superconductivity. But on the other hand, their complexity makes them difficult to synthesize reliably and difficult to understand.

For my PhD, I studied how the behavior of $3d$ electrons can be tuned in thin films of complex oxide materials. In my first major project, I studied how electrical conductivity could be turned on and off at the interface of $\text{LaAlO}_3/\text{SrTiO}_3$. And in my second major project, I studied how ferromagnetism could be turned on and off in $R\text{CoO}_3$, where R is a rare earth element.

In my $\text{LaAlO}_3/\text{SrTiO}_3$ project, despite the interface’s wide variation in reported electrical properties, I highlighted a scaling relationship between sheet carrier concentration and mobility common to nearly all research groups. I also discovered that the electrical transport is robust to the presence of magnetic and spin-orbit scatterers (Tm and Lu) at a 2% concentration in LaAlO_3 . Lastly, I grew subcritical films used to build a SketchFET, the world’s first nanoscale GHz-speed writeable transistor (with potential applications in high-speed molecular sensing).

In cobalt perovskites, I extended the phase diagram of thin film magnetism, exploring the roles of both chemical pressure (through A-site doping) and epitaxial strain. I discovered that although tensile epitaxial strain from SrTiO_3 is enough to induce ferromagnetism in LaCoO_3 and PrCoO_3 , it is not enough to induce ferromagnetism in $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$, which has a smaller and less cubic unit cell. X-ray magnetic circular dichroism revealed that although the Co ions $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ are not ferromagnetic, they still possess magnetic moments, suggesting that the lack of ferromagnetism comes from a lack of exchange rather than a lack of magnetic moment. These results highlight the

importance of chemical bonding in stabilizing a ferromagnetic ground state and demonstrate new ways to tune magnetic order.

Together, these projects provide new insights toward understanding and controlling the behavior of correlated $3d$ electrons. And they bring us a few steps closer to harnessing the complexity of the complex oxides.

Acknowledgments

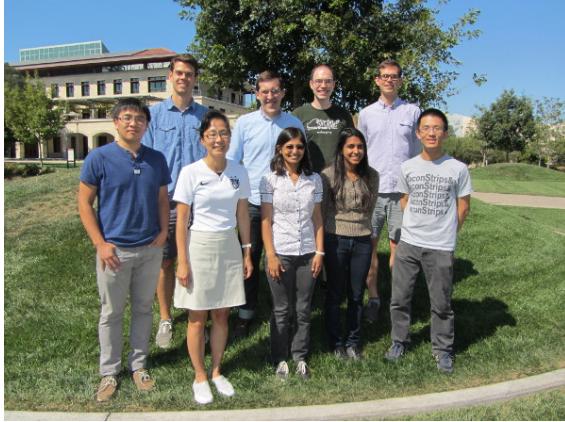
I owe many thanks to those who enabled my PhD. Together, they changed the course of my life.

First, I acknowledge my advisor, Yuri Suzuki, who guided me without a leash. From her six years of support, I learned the life-cycle of a materials research project, from identifying a research question, to materials synthesis, to measurement, to theorizing, to publishing. Without her personal guidance, funding, and laboratory, I never would have been able to write this dissertation. Thank you, Yuri.

Second, I acknowledge the National Science Foundation. Although its annual R&D budget is only about two submarines, it still scrounged the cash and courage to financially support me for three years through the NSF Graduate Research Fellowship Program. I also credit its mandate of broader impacts for spurring me to volunteer for so many science outreach efforts throughout graduate school. Thank you, NSF.

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Fourth, I acknowledge my labmates, who long labored alongside me: Urusa Alaan, who had the lab's loudest voice despite her quiet volume; Matt Gray, whose mastery of plumbing deserves the envy of Mario and Luigi; Charles Flint, who never let himself be compressed by the burden of the Evercool compressor; Purnima Balakrishnan, whose endless patience was finally rewarded in the MRS caricature line; and Mike Veit, whose good and trusting nature came in handy when I needed a victim upon whom to dump the Cryogenics machine. Thanks, everyone!



(a) By day



(b) By night

Figure 1: Members of the Suzuki Lab

Fifth, I acknowledge my family, who shaped me without constraining me. Without them, I (and my work) would be so nonexistent that its mere concept would never have even for a moment crossed anyone’s imagination. I owe my family greatly, not only for creating me physically, but also for creating me mentally. Mom, Dad, Hillary: I love you. Thank you for everything.

Sixth, I acknowledge all the great inquirers who came before me, upon whose giant shoulders I stand. Thanks Isaac, Carl, Albert, Emmy, and friends.

Seventh, I acknowledge you, the reader, for caring enough about me and the work I did to read this dissertation (or at least the second page of its acknowledgment section). I only get to live life once, and a sizable fraction of my one life was spent making this, for you. I hope you find it worthwhile.

Thank you.

Dedication

This dissertation is dedicated to the people of the future, whose happiness is the reason we do long-term basic research.¹ May you all flourish peacefully.

¹Well, happiness of future people is the *ostensible* purpose behind government funding of research. Personal curiosity, reputational status, and high salaries certainly motivate many of the scientists themselves.

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Chapter 1

Introduction

“Somewhere, something incredible is waiting to be known”

—Sharon Begley (though often misattributed to Carl Sagan)[\[1\]](#)

Six years in the making, my PhD in Applied Physics has focused on understanding how electrons interact in thin films of complex oxide materials. Although the day-to-day labor felt mundane at times, my research took place at the frontier of human knowledge and ability. I synthesized new materials never before seen in history, in layers so thin that I counted their atoms one by one. Then I took those new materials and measured them in extreme conditions: at temperatures less than a degree above absolute zero, in magnetic fields stronger than on the surface of the sun, and in pressures lower than those faced by spacewalking astronauts.

However, before I describe my research projects in detail (Chapters [3](#) & [4](#)), I'll discuss why this sort of research is worth doing (Chapter [1](#)) and the modern experimental methods that have made it possible (Chapter [2](#)). At the end, I'll tie these threads together and discuss their implications for the future (Chapter [5](#)).

1.1 Technological innovation

The ostensible purpose of my PhD research is to better understand materials in order to one day develop new technologies. This first section is devoted to a broad discussion of technological innovation: why it matters, how it is constrained, how it can be analyzed, how it can be predicted, and where my research fits in.

1.1.1 Technological innovation drives human prosperity

By nearly every metric, we humans are better off today than at any prior point in history. Life expectancy is longer[\[2, 3\]](#), farms are more fertile[\[4, 5, 6\]](#), violence has declined[\[7\]](#), and poverty has

become the exception rather than the rule[8].

Notably, this tremendous human progress, both economic[9] and moral[10], was *not* a story of slow and steady improvement across the ages. Rather, the majority of progress was concentrated into an extraordinary era so brief and so recent that it spans fewer than ten generations. Called the Industrial Age by some scholars, this era is the one we live in now. Although it is difficult to explain why the Industrial Revolution began around 1800 in the United Kingdom,¹ its impact on the world is indelible. Supported by new scientific understanding, new technologies were invented to amplify human labor, allowing people to flourish in unprecedented ways. The development of new technologies is the source of our modern prosperity, and developing yet newer technologies will be the source of our future prosperity.

Technological innovation drives economic growth

In the neoclassical Solow-Swan model of economic growth, the long-run growth of an economy is driven by the rate of technological innovation.⁴[22, 23] Although the Solow-Swan model treats technological innovation as an exogenous variable, it's clear that the rate of technological innovation

¹Explanations for the spark that lit the Industrial Revolution include newly high levels of literacy, printing, population, seafaring, scientific method, inherited intelligence, state competition, cultural superiority, surface coal, high wages, and even fashion[11, 12]. However, none of these explanations are by themselves unambiguously convincing, and any satisfactory explanation should also explain why the Industrial Revolution did not begin in China, which shared many of these features centuries earlier, during the Ming and Qing dynasties.[13, 14] History is often too multifactorial to accurately compress into simple narratives. Even the concept of the Industrial Revolution is not as simple or discrete as its name suggests.

²Technically, this should be world GP (gross product), rather than world GDP, to reflect the fact that that some wealth is generated outside of national borders, such as in international waters, Antarctica, and space. Even world GNP slightly mismeasures total output, since some workers hold no citizenship anywhere. But because all of these measures are about equal, I chose to title the plot with GDP for its familiarity.

³Surprisingly, even information capital appears to depreciate, prompting the invention of concepts such as the half-life of knowledge,[17] the half-life of facts,[18] and software rot[19] (not to be mistaken for actual physical degradation of storage media).

⁴Actually, in the Solow-Swan model, there is one other exogenous driver of the steady-state economy: population growth. Because of this second variable, it is more correct to say that technological innovation drives *per capita* long-run economic growth. And while technology-driven economic growth dwarfs population-driven economic growth today, for most of recorded human history it was actually the other way around. Population growth, not technological innovation, contributed the most to pre-industrial economies. (Then again, much of the explosion in human population after

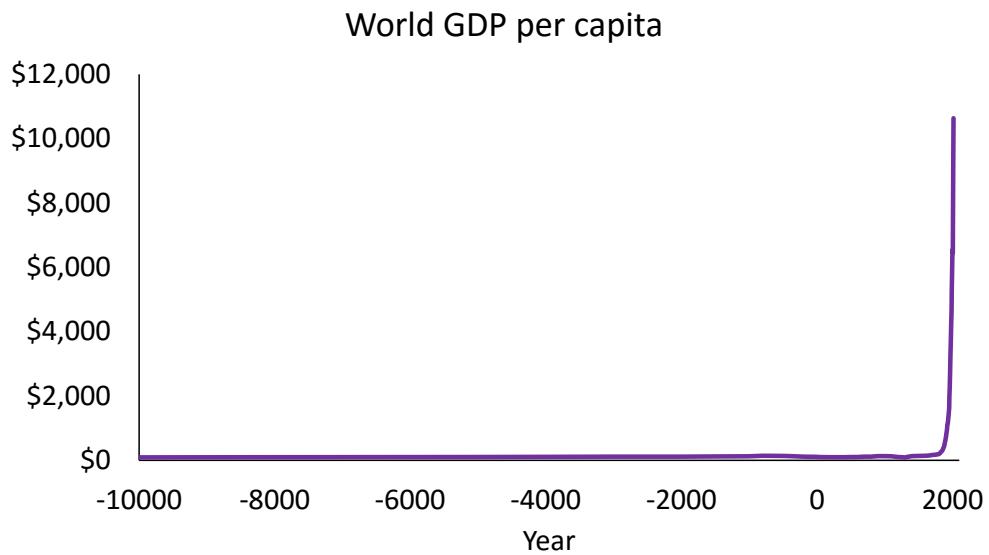


Figure 1.1: World GDP² over the past 12,000 years (measured in 2000 Int'l.\$).[15, 16] Although reducing the complexity of human experience down to a single number is impossibly crude and full of uncertainty, the shape of this plot still illustrates the superexponential progress of modern humans. Even when plotted on a log scale, this curve retains the same hockey stick-shape, with the same inflection point around 1850. (Fun fact: although the Gregorian calendar has no year 0, astronomical year numbering defines 1 BCE to be year 0.)

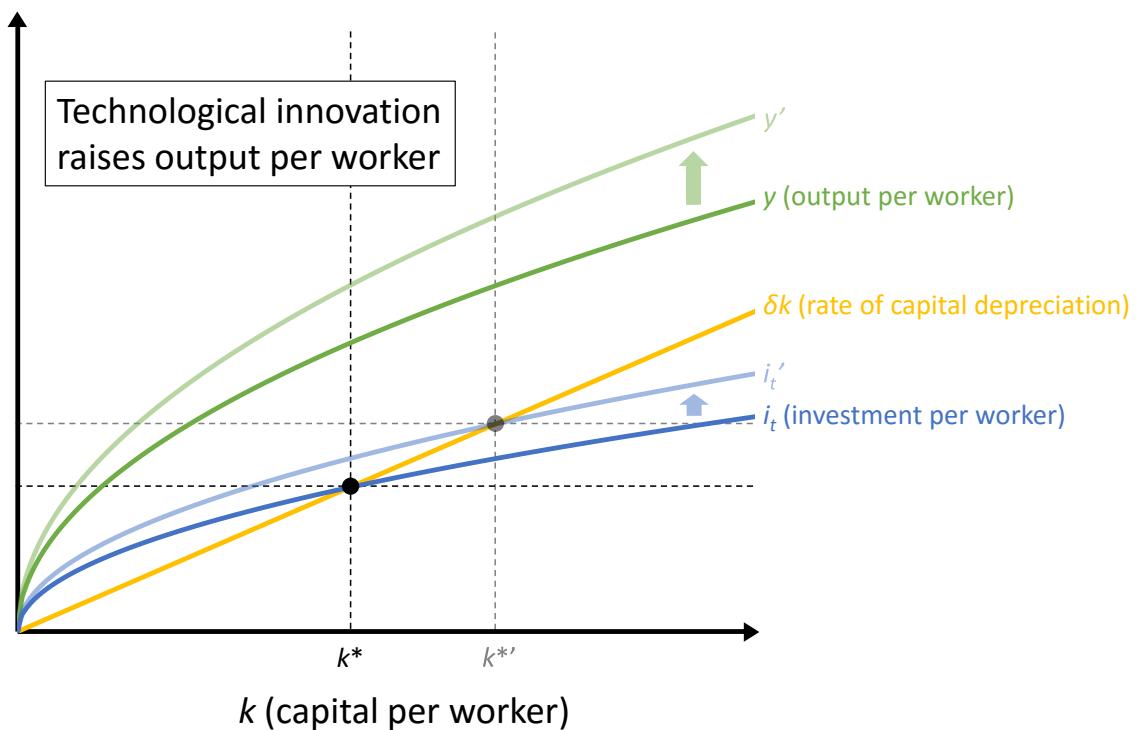


Figure 1.2: Because capital has diminishing returns and also depreciates,³ economic growth cannot be permanently sustained by capital accumulation. According to the neoclassical Solow-Swan model of economic growth, the steady-state output per capita of an economy can only be increased through improved technology.

depends on how much a society chooses to invest in technological R&D. Societies that invest more in technological R&D will tend to be richer in the long run.

Nevertheless, technological innovation is not purely a function of investment. Throwing money at a problem is no guarantee that a solution will be found: indeed, some problems may have no solution. A perpetual motion machine will never be built regardless of how much money is invested, because the laws of physics limit what can be achieved.^{5,6} Therefore, it is important for a society to understand these physical limits and strategically target R&D investment toward technologies with the greatest potential.

1.1.2 Technological innovation is constrained by physics

“When a distinguished but elderly^a scientist states that something is possible, he [or she] is almost certainly right.

When he [or she] states that something is impossible, he [or she] is very probably wrong.” “In physics, this means over thirty.”

— Arthur C. Clarke, *Hazards of Prophecy*[25]

What are the ultimate physical limits of technology? Answering this question with confidence

5000 BCE[20, 21] was driven by agriculture, itself a technological innovation.)

⁵Then again, let’s not be *too* hasty. Perhaps even free energy will be possible in the far future. The continuous expansion of the universe is constantly increasing the energy of bound matter, at least according to today’s best models.

⁶Also, and this may be a bit of a tangent, it depends what you mean by perpetual motion machines. One clever way of classifying perpetual motion machines is by which of the first two laws of thermodynamics they violate: the first law, the second law, or neither law (or, for completeness, both laws, but such excessive disregard for the laws of physics is rare).[24] A perpetual motion machine of the first kind violates the first law of thermodynamics, doing work without input of energy. A perpetual motion machine of the second kind violates the second law of thermodynamics, doing work with the input of thermal energy (this violation is more subtle because while it obeys energy conservation it does not obey entropy/information conservation). And a perpetual motion machine of the third kind is one that simply moves forever without violating any laws of thermodynamics. In my opinion, a hydrogen atom qualifies as a perpetual motion machine of the third kind. Friction cannot slow down a quantum mechanical system in its ground state. Some might argue that a hydrogen atom still doesn’t count as a perpetual motion machine because eventually it, like everything else, will decay or be sucked into a black hole or meet some other fatal end. However, I dislike this particular criticism because it implies that nothing can be a perpetual anything, robbing the word *perpetual* of its value.

warrants caution.⁷ Many answers given by brilliant minds of history have proved to be comically wrong, sometimes within mere years of their assertion.[26] Even when apparent limits are justified by correct laws of physics, the limits have a funny way of being circumvented in unanticipated ways.

In 1920, a New York Times editorial[27] proclaimed that space rockets were impossible because nothing can push against a vacuum. The editorial correctly understood Newton's third law and the conservation of momentum, but failed to imagine expelled propellant.⁸ A few years later, in 1926, Professor A. W. Bickerton also asserted the impossibility of space rockets but in a different way, arguing: "The energy of our most violent explosive—nitro-glycerine—is less than 1,500 calories per gramme. Consequently, even had the explosive nothing to carry, it has only one-tenth of the energy necessary to escape the earth.... Hence the proposition appears to be basically impossible." [25]⁹ To his credit, Professor Bickerton correctly interpreted the laws of gravity and energy conservation, but what he failed to imagine is that the fuel need not be carried to space along with the payload. Despite these and similar proclamations of spaceflight's impossibility, only a few decades later, *and with no fundamental paradigm shifts in mechanics or chemistry*, humankind set foot on the moon.

⁷Arthur C. Clarke wrote a marvelous essay, Hazards of Prophecy, which looks at why and how so many experts were wrong about the future, with many examples coming from predictions made about flight and spaceflight in the early 1900s. He classifies poor pessimistic predictions into two categories: failures of imagination, in which the relevant laws of physics were not yet known (but still could have been imagined), and failures of nerve, in which the relevant laws of physics were known (but other barriers were perceived).

⁸The New York Times eventually printed a retraction in 1969, as Armstrong, Aldrin, and Collins were on their way to the moon.[28]

⁹Although Bickerton's errant prediction has been pointed out by Arthur C. Clarke and other authors, according to Wikiquote, it's possible that this quotation of his was arguing specifically against projectile launches into space rather than rocket launches into space. And if so, while Bickerton's prediction was still technically wrong—in 1966, a projectile was indeed launched into space (though not orbit)—in practical terms, Bickerton was correct. Despite a history of attempts, projectile launches into space are not presently feasible due to the tremendous drag (which costs energy and makes aiming hard), the tremendous forces experienced by the projectile (meaning the payload needs to be extremely rugged and human-free), and the remaining requirement for a propulsion system so that the payload can change course into an orbit (otherwise it will crash, which is guaranteed to happen in a gravitationally bound two-body system without propulsion).[29]

These stories¹⁰ illustrate that even when the relevant laws of physics are known, claims of impossibility by eminent experts are by no means guaranteed to be true.¹¹ These stories also raise an important epistemological question: If expertise in physics is not enough to avoid mistaken proclamations of physical impossibility, then upon what foundation can today's physics experts ground their confidence in their own judgments, given that their judgments are similarly undergirded by expertise in physics? Are there any technological impossibilities we can be 100% sure of? Or is it just too fundamentally difficult to reason about technologies not yet invented?

Perhaps the most classic example of physics-limited technology is the heat engine, which is limited by the laws of thermodynamics to operate below the Carnot efficiency ($1 - T_{cold}/T_{hot}$). Yet even the esteemed Carnot efficiency limit may not be absolutely ironclad. In principle, a good enough measuring system may enable work to be extracted from waste heat, thereby circumventing the Carnot limit. This idea was first conceived by James Clerk Maxwell in 1867 and later came to be known as Maxwell's demon.[31]¹²

A second well-known example of a physical limit is the speed of light,¹³ which sets a minimum

¹⁰Despite including these stories about poor spaceflight predictions, I wish to emphasize how challenging it actually is to learn by grading predictions of the past. So many people have made so many claims throughout history, that it's equally easy to find to foolish quotations as prescient ones. Without a systematic and unbiased aggregation of all past predictions, everything we see is coming through a selective filter. And without knowing how that filter of history distorts the data, it's difficult to know what people believed and how often they were wrong.

¹¹Of course, many claims of impossibility *have* stood the test of time, including those regarding time travel, faster-than-light communication, invisibility, antigravity, etc. Antigravity research has a particularly interesting history, having been the subject of the Gravity Research Foundation, which was established by Massachusetts businessperson Roger Babson, who blamed gravity for his sister's childhood drowning.[30] After Babson's death, the pseudoscientific foundation transitioned into legitimacy and now exists to award annual prizes for essays on gravity. These prizes have been won by a number of scientific luminaries, including Stephen Hawking, Roger Penrose, Julian Schwinger, Frank Wilczek, and George Smoot III (the only winner of both a Nobel prize and the TV show *Are You Smarter than a 5th Grader*).

¹²In fairness, I am aware that a number of different experiments have recently claimed to measure the Landauer limit, which has been proposed as a way of reconciling Maxwell's demon with the second law of thermodynamics. However, from an admittedly less-than-thorough reading, I remain personally unconvinced.

¹³Confusingly, the speed of light is a speed limit on everything, not merely light. And extra confusingly, light can travel below the speed of light, and in fact, because no true plane waves exist, it always does. (Though it sort of depends on how you define speed. If I run a quarter-mile loop at a track in one minute, is my speed nonetheless zero, given that I haven't gone anywhere? There

on the time it takes to get from one place to another.¹⁴ As anyone who has driven down a highway during rush hour knows, we are far from hitting the speed-of-light limit when it comes to the transportation of matter. However, when it comes to the transportation of information, our technology is already brushing against this limit, as you might notice when communicating with someone on another continent. Because it takes about 100 milliseconds for light to go around the Earth, any communication to someone on the opposite side of the Earth will always have a minimum lag of 100 milliseconds, no matter what future clever device our descendants can come up with. Even a billion years hence we can be confident that communication technology will be a little laggy on Earth-scales (~ 0.1 seconds), annoyingly laggy on Earth-to-moon scales (~ 1 second), and awfully laggy on Earth-to-Mars scales (~ 1000 seconds).¹⁵

It's worth noting that the speed of light is not only a limit on technologies that traverse long distances. It's also a limit on technologies that go very fast. In the time it takes your computer's 3 GHz computer chip to go through one clock cycle (1/3 of a nanosecond), an electric signal only has time to travel along a few centimeters of wire.

In any case, it seems hard to imagine a world where the speed of light can be exceeded. And yet, in the 1920s, it was hard for many to imagine a world where rockets could ferry people to the moon. But a few decades later that impossibility became reality. Though it sounds utterly ridiculous today, who are we to say that the speed of light will not be circumvented in the future? And more generally, what truths of today can we epistemologically guarantee to be immune to unforeseen scientific developments of the future?¹⁶

In general, it is difficult to predict the possibilities of technology. Sometimes the laws of physics change,¹⁷ and even when they don't, technological innovation has a curious way of circumventing was no displacement over a duration, after all.)[32]

¹⁴By the way, pay no mind to any claims that entanglement or quantum teleportation or wave function collapse prove that the speed of light of light can be exceeded. Many interpretations of quantum mechanics (such as many worlds/decoherence) can explain these phenomena in a local way that never violates the speed of light.

¹⁵Then again, even this minimum lag may one day be circumvented in ways that still obey the known laws of physics. Perhaps a computer could predict what your conversation partner would say ahead of time. Or perhaps our conscious perception of time could be slowed, making a 10-minute delay unnoticeable. Or perhaps we might even attain the power to warp space itself.

¹⁶Here, I want to emphasize that I don't regard the truth of the 1920s to be equivalent to the truth of today. Today, at least in my present-biased judgment, we are unambiguously more correct, further along, and closer to the absolute truth than in the 1920s. Asimov wrote a terrific essay on this topic titled The Relativity of Wrong.[33]

¹⁷Rather, our understanding of them changes. Though for all we know they might change too.[34, 35]

apparent obstacles. However, not all laws of physics are equally vulnerable to being overturned by unforeseen scientific revolutions. And in particular, there is a certain class of physical law that is especially impervious to unanticipated changes: conservation laws.

1.1.3 The most fundamental constraints on technology are conservation laws

“It is only slightly overstating the case to say that physics is the study of symmetry” —Phil Anderson, More is Different[36]

In physics, there are some quantities that are conserved and some quantities that are not. Conserved quantities, such as energy or momentum, are quantities that can never be created nor destroyed,¹⁸ only transferred from one form or object to another. These conserved quantities stand in contrast with quantities like redness or photon number or temperature, whose totals we *can* change over time. So while cleverness in engineering may finagle a technology to produce red or photons or temperature, conservation laws mean that no cleverness will ever invent a technology that can truly produce energy (i.e., output more energy than is put in).¹⁹

The question of why some quantities are conserved and some are not has turned out to be one of the deepest and most fundamental questions in physics. Although the mathematical machinery needed to answer this question existed since the time of Newton, it was not until 1915 that Emmy Noether, while working on Albert Einstein’s theory of relativity, recognized that conserved quantities have a deep origin: they are a mathematical consequence of symmetry. Specifically, she showed that if a system’s dynamics can be described by a Langrangian, then every continuous symmetry will have an associated conserved quantity, which remains constant over time.²⁰[38]

Unlike other laws of physics, which derive from observation and experimentation, conservation laws are a mathematical fact. This means that no matter what future experiments might discover, as long as the universe’s laws of physics stay symmetric, the conservation laws will never be overturned.²¹ Conservation laws are some of the surest limits we have on technology.

¹⁸Except by big bangs and dark energy and other mysterious things that warp the space-time fabric.

¹⁹I mean, to be fair, nothing is created for free. Even increasing the redness of an object usually requires work of some sort. But this work is incidental and not essential to the changing redness of the object. (It’s actually quite hard to talk about doing things without also referencing the energy needed to do them.)

²⁰For a proof of Noether’s theorem, see Appendix B.

²¹Here, I’d like to point out that this argument has a subtle loophole, or at least a subtle qualification. Although it’s true that conserved quantities are guaranteed to exist if physical laws are

Below is a table of eight symmetries and their associated conserved quantities.²² These eight conserved quantities lay a foundation for thinking about the budgets that all technologies must work within.

Conserved Quantity	Associated Symmetry
Mass-energy	Time invariance
Momentum	Position invariance
Angular momentum	Rotation invariance
Charge-parity-time symmetry	Lorentz invariance
Electric charge	Gauge invariance
Color charge	SU(3) gauge invariance
Weak isospin	SU(2) _L gauge invariance
Probability	Probability invariance

Table 1.1: The eight exactly conserved quantities and their associated symmetries.

In addition to these eight conserved quantities, there is one more that deserves mention, even though it does not arise from a continuous symmetry: the conservation of information. Jokingly termed the minus first law of thermodynamics by Jos Uffink and popularized by Leonard Susskind,²³[39] the conservation of information is the idea that distinctions between states cannot be lost or erased over time. What this means practically is that when you erase a bit on your hard drive, that information is not truly lost from the universe, but rather ejected into the rest of the world as scrambled thermal vibrations. The conservation of information directly follows from the

symmetric, there is still room for our understanding of these conserved quantities to evolve. For example, the translational symmetry of physical laws implies that momentum is conserved. But it took physicists a long time to realize that true momentum is not just the mechanical momentum, $m\vec{v}$, but includes a contribution from the electromagnetic field as well. So although the law of momentum conservation never changed, our understanding of what momentum is did in fact change.

²²There are approximately conserved quantities and symmetries beyond these eight, but these eight are currently believed to be exactly conserved. (Though I confess, the split between exact and inexact laws may be somewhat arbitrary. As far as I can tell, the existence of dark energy means that conservation of mass-energy is slightly violated, yet for some reason mass-energy is grouped in as one of the eight exact laws. And I suppose the Big Bang violates all of these laws.)

²³At first, thermodynamics had only three laws (the first, the second, and the third). Later, when physicists recognized a deeper principle of thermodynamics, they inserted it as the zeroeth law of thermodynamics, ahead of the first three. By that logic, if the conservation of information is a yet deeper realization, then it ought to be instated as the minus first law.

laws of physics being deterministic²⁴ (or, stated in a narrower way, from the unitarity of the time-evolution operator in a Hamiltonian mechanics, leading to conservation of phase space distribution in a bounded phase space by Liouville’s theorem).

Together, these nine conserved quantities (the eight symmetry-derived quantities plus information) act as fixed budgets, limiting what we and our technology can do. For example, energy conservation means that the energy budget of our solar system is fixed. We can try to harvest more of the energy budget that’s out there, and we can try to use our energy more efficiently, but the ultimately available energy budget will never grow, no matter what fantastic technologies we might invent in the future.

Of these nine budgets, some are more constraining than others, at least in today’s world. From now on, I will narrow the focus to the three budgets that seem to be the most relevant today: matter, energy, and information.²⁵

Because we cannot create matter, energy, or information out of thin air, many of our technologies are devoted to transporting these things around to where they’re needed, in the form they’re needed, at the time they’re needed. This insight brings us to the next section, which discusses a technology framework matrix based on the outer product of these conserved quantities and ways to get them to where they’re needed.[40, 41, 42, 43]

1.1.4 Technology can be classified by constraint and function

Classifying technology is difficult. Even putting aside the thorny practical problems presented by definitions and their edge cases, classifying technology remains philosophically challenging because there are so many apparent ways to do it.

One perfectly valid classification of technology might group technologies by the materials they’re made of (e.g., stone tools, wooden tools, metal tools, etc.).²⁶ This classification is sensible for archaeologists. Another option might classify technologies by the time they were invented (e.g.,

²⁴Though some people incorrectly believe that quantum mechanics is necessarily non-deterministic, there *are* fully deterministic interpretations of quantum mechanics (such as the many worlds interpretation, which argues that all ‘possible’ outcomes occur simultaneously in a superposition).

²⁵The momentum budget is less important because the Earth acts as a giant momentum sink, allowing us to ‘create’ apparent momentum by merely pushing off the ground. Also, because momentum is a signed, directional quantity, that means we can ‘create’ large amounts of momentum in one direction as long as we ‘create’ large amounts of opposite momentum too. These two factors make momentum less of a constraint on technology than energy. Nevertheless, in space, unlike on Earth, it is important to manage momentum budgets carefully.

²⁶This is how archaeologists have done it. The periods of history we know as the stone age, the bronze age, and the iron age are not demarcated social structure or wealth or knowledge, but simply

prehistory, classical antiquity, industrial revolution, etc.). This might work well for historians. And a third possible classification might be to group technologies by the first letter of their names (e.g., starts with A, starts with B, starts with C). This third scheme is obviously less useful - unless you a reference librarian - but it is nonetheless logically valid. And when you consider schemes that may be semantically silly but logically valid, the classification possibilities become endless.²⁷

So what should make us prefer one scheme over any another? Well, the answer to that question depends on what we are trying to accomplish. Ultimately, the purpose of any classification system is to make it easier to describe patterns by compressing the space of things (technologies, in this case) into the smaller space of classes. And like any good lossy compression algorithm, we'd prefer to lose as much noise as possible while retaining as much useful signal.²⁸ I suggest that a maximally useful technology categorization scheme would possess the following qualities:

- Its categories would be mutually exclusive (so no technology is twice classified) and collectively exhaustive (so no technology is left unclassified).
- Its categories would cluster technologies that behave similarly (otherwise, the categories would have little use).²⁹
- Its categories would be comparable in size and importance (too many tiny and unimportant categories would be distracting and unhelpful).
- Its categories would not number too many (as to be overcomplicated) or too few (as to be trivial).
- Its categories would be abstract enough to apply to technologies of the past and the future (so that progress can be tracked by comparing them over time).

by the materials of excavated artifacts.

²⁷Well, maybe not technically endless. In a mathematical sense, a technology classification scheme is a function that maps elements from the space of individual technologies to the smaller space of technology classes. If one assumes that the space of technology classes, c , is no greater than the space of individual technologies, t , then the number of isomorphically unique technology classification schemes is bounded by c^t . However, such a simple expression belies its truly gargantuan exponential size. You only need to have 80 technologies or so before the combinatorial explosion of classification schemes outnumbers baryons in the observable universe, commonly guessed to be 10^{80} or so.[44]

²⁸In fact, with the insight that classification is a form of information compression, one can use Shannon's information entropy to mathematically formalize a way to rank arbitrary classification schemes.

²⁹For example, a classification scheme that categorized technologies by their first letter would mostly satisfy the other objectives and yet be completely useless.

Finding a classification scheme that satisfies these six simple properties sounds easy enough, right? After all, there are a gazillion possible schemes and only six constraints. Unfortunately, it turns out to be impossible to construct a classification scheme that simultaneously satisfies all of these priorities because hidden within them lies a fundamental incompatibility.

In general, there will always be tradeoffs whenever you try to construct a taxonomy of technology. On the one hand, to make your categories most useful, you want them equally populated and detailed. This entails basing your classification scheme on the technologies of the present day. However, the weakness of this approach is that when things change (e.g., the digital revolution and the rising importance of electronics/computers), your classification scheme falls behind and loses descriptive power.

To counter this downside, you might want a classification scheme based on abstract theoretical principles (i.e., technologies based on matter vs energy vs information) that works for all time periods. But then you end up with the opposite problem, where some of your categories are far more important and detailed than others.

Overall, it's a problem with no perfect solution. Even a scheme that tries to be flexible by adapting over time will suffer downsides, such as a lack of continuity, which stymies the ability to make meaningful temporal comparisons.

Despite there being no perfect classification scheme, I do want to share one scheme that is particularly elegant, devised by German engineer-philosophers in the late 70s.[\[40\]](#)

Remember how in the prior section we explored the idea that conserved quantities act as fixed budgets, constraining what we can do? Technology, in a sense, is like an accountant, manipulating these budgets by shifting entries in the columns of God's universal spreadsheet. For example, an airplane's turbojet engine is a technology that shifts chemical potential energy of ancient pressurized algae into the gravitational potential energy of me and my duffel bag.

Given this metaphor of technology as an accountant who manipulates budgets, we can classify the accountant's work in a straightforward way just by examining the phrase 'manipulates budgets.' First, what are the important budgets and second, what are the important ways they can be manipulated? As discussed before, there are three important budgets for technology: matter, energy, and information. And you can consider three important methods of manipulation: transformation, transportation, and storage. With these two dimensions—budgets and manipulations—and each of their three categories, we can construct a 3x3 matrix of technology categories, as shown below.



Figure 1.3: Luca Pacioli, also known as “The Father of Accounting and Bookkeeping.”^[45] He was the first publisher of the double-entry system of bookkeeping, as well as a teacher and friend to Leonardo da Vinci.

	Transformation	Storage	Transport
Matter	Mills Blast furnaces Refineries All manufacturing	Warehouses Silos Tanks Containers	Ships Trains Planes Trucks/cars
	Generators Engines/motors Lighting HVAC	Dams Thermal storage Batteries Capacitors	Wires Hydraulics Belts Axles
	CPUs Sensors Brains	Hard drives Optical discs DRAM	Wires Fiberoptics Radio waves
	Slide rule	Books	Sound waves

Table 1.2: A 3x3 classification of technology, based on constraint and function. The nine categories are filled with examples of common technologies.

Weaknesses of the constraint-function classification of technology

Although the above classification of technology is attractive for its simple, fundamental approach, I don't want to pretend that it is free of weaknesses.

One problem I see with this classification scheme is the distinction it draws between energy and matter. While this makes sense for electrical energy and a few other types,³⁰ which are carried without mass,³¹ most forms of energy (fossil fuels, food, nuclear fuel) *are* carried by mass. Chemical energy requires chemicals. Nuclear energy requires nuclei. Therefore, transporting these forms of energy necessarily requires transporting chemicals and nuclei. So when you attempt to classify a technology like coal-carrying train cars, it's not so clear whether it belongs under transportation of matter or transportation of energy.

Blurry division can even be a problem when it comes to information and matter. Although plenty of information is carried masslessly over copper wires and fiberoptic cables and even through the air, information is also sometimes carried in forms with mass, such as books or hard drives. (Semi-related fun fact: when it comes to transporting large amounts of data, a truck full of hard drives is often faster and cheaper than a lightspeed fiberoptic cable.[46])

Along the other axis of classification (the classification by function), the distinctions are also

³⁰Along with electricity, energy can also be carried masslessly by light, belts, water waves, or sound waves, to name a few.

³¹Well, mostly without mass. Einstein's $E = mc^2$ says that energy by definition always carries a little mass.

potentially blurry. For instance, storage just seems to be the base case of the other two: transformation with zero change, or transportation across zero distance. In fact, in real life, transportation is often just a storage container with wheels and a diesel engine. With all the diversity of manufacturing stuffed into the transformation column, is it consistent or useful to give two separate columns to boxes and boxes with wheels?³² Maybe yes, but it's just not so clear to me.³³

And lastly, where do service sector jobs fit into this classification? For instance, into which of these nine boxes does a butler fall? Does laying a fork on the dinner table fall under transportation of matter? Again, the answers to these questions are not so clear.³⁴

Despite these weaknesses, I nonetheless like this classification scheme. Because it's so abstract, it's an especially good framework for thinking about future technology. If a whole new type of technology is invented, odds are it won't fit neatly into the NAICS (North American Industry Classification System),^[51] but it is likely to fit into this 3x3 matrix framework.

How is technology classification relevant to my graduate research?

At this point, you may be wondering why my dissertation has digressed so far from its stated purpose of describing my graduate research. How did we get to technology classification and how is it in any way relevant to my research?

Physicists know the power of reasoning from first principles. So when it comes to thinking about how to improve the lives of humans, my reasoning starts from first principles. As I alluded to in the first section about economic growth, technological innovation is the reason we humans have it so good today. Human well-being was revolutionized with technologies like agriculture, cars, and

³²Speaking of boxes and boxes with wheels, if you'd like to read more about the global shipping industry I recommend the three following books, in order of readability: *Ninety Percent of Everything: Inside Shipping, the Invisible Industry That Puts Clothes on Your Back, Gas in Your Car, and Food on Your Plate*,^[47] *The Box: How the Shipping Container Made the World Smaller and the World Economy Bigger*,^[48] and *Prime Movers of Globalization: The History and Impact of Diesel Engines and Gas Turbines*.^[49] In their own way, each changed the way I see the world.

³³Perhaps the best approach I see for defining these categories from first principles is as follows: Storage is the category where positions in space don't change over time. Transportation is the category where positions in space change over time macroscopically. And transformation is the category where positions in space change over time microscopically (or at least on a component-level scale such that it changes the identity of the material or object).

³⁴In general, classifying services is harder than classifying manufactured goods. This is likely why industry classification schemes such as ISIC have manufacturing subcategories as deeply detailed as "manufacture of wood and cork, except for furniture" and yet group all of "wholesale and retail trade" into a single service subcategory.^[50]

clean water.³⁵ As we gaze to the future, what technologies can humanity hope for next?

Physics first principles are a great guide to predicting the future. Not only can we use physics first principles to tell us what technologies are likely impossible, but we can also use them to construct a technology classification scheme that makes it easier to reason about future technology. And reasoning about future technology is how our nation chooses to fund scientific research, such as mine.

With this classification of technologies by constraint and function, we can now begin to look at the history of each category, and to more concretely conceive of what improvements might be possible.

1.1.5 Classifying information technology highlights opportunities for innovation

“Man is the lowest-cost, 150-pound, nonlinear, all-purpose computer system which can be mass-produced by unskilled labor.”

—Often misattributed to a 1965 NASA report, it apparently originated from test pilot Albert Scott Crossfield in 1954[53]

From now on, I will focus simply on information technology, the most likely application of my research. I will examine past innovation in the three main functions of information technology: information storage, information transportation, and information transformation. From there, I will look at possible improvements, which will lead into Chapter 2 and my graduate research.

Storing information

Before computers, before the printing press, before written language itself, humans had few methods for storing information. For basic counting, notches could be carved into tally sticks,[54] but for remembering anything more complex, early humans could rely on nothing but their brains.³⁶ Still, by any standard, brains are impressive. There is evidence that some Aboriginal myths predate rising sea levels around 10,000 years ago, demonstrating the impressive longevity of collective memory based on oral tradition.[55, 56] And in the Pacific Northwest, a Klamath myth tells of the eruptions

³⁵Actually, there is serious archaeological evidence that agricultural transitions *lowered* human quality of life (as measured by health markers such as skeleton size).[52] Whether this was a good or a bad thing depends on your utilitarian calculus, considering that agriculture also increased population density.

³⁶Though in a way, our genes also store information. My natural fear of heights wasn't instilled into me by a teacher or some formative experience—it was hard-coded into me from my beginning, thanks to evolution.

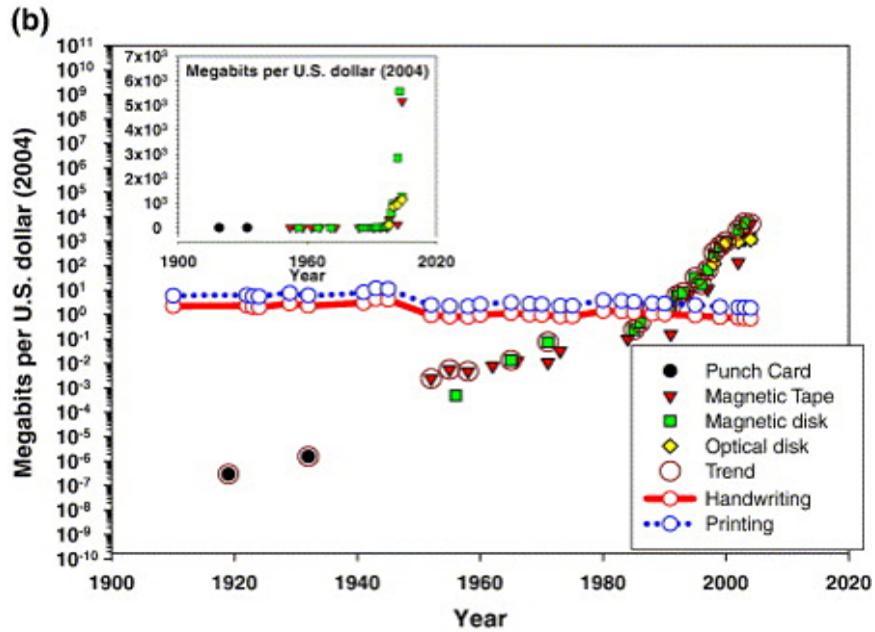


Figure 1.4: Progress in information storage over the last century. Surprisingly, perhaps, it took until 1990 or so until computer storage was cheaper than paper storage. Reproduced from Koh (2006)[42] with permission.³⁷

of Mount Shasta and Mount Mazama, which last erupted around 8,000 years ago, according to volcanologists.[57]

Since then, humanity has come a long way. Figure 1.4 shows the last 100 years of progress in information storage technology, as measured by megabits stored per dollar. As the plot shows, computer memory was actually more expensive than printed paper until around 1990! However, today computer memory is orders of magnitude better, whether stored on optical discs, magnetic drives, or in solid-state flash memory.

What are the prospects for further improvement?³⁸ Progress in optical discs, magnetic disks,

³⁷Reprinted from Technological Forecasting and Social Change, Volume 73, Heebyung Koh & Christopher L. Magee, A functional approach for studying technological progress: Application to information technology, 1061-1083 Copyright (2006), with permission from Elsevier.[42]

³⁸In the ultimate limit, the covariant entropy bound[58] (related to the Bekenstein bound[59]) roughly limits the density of information to one bit per Planck square on its bounding surface. For a 1 cm sphere, this works out to be about 10^{66} bits, incomprehensibly more dense than today's technology, which can store about 10^{12} bits in the same volume. DNA has an information density of 10^{18} bits per cubic centimeter,[60] and if we were to store one per atom in a solid,[61] then we could reach around 10^{23} bits per cubic centimeter.

and solid-state drives appears to have slowed in the past few years, but it hasn't stopped.

Magnetic hard drives have been growing exponentially denser for sixty years. Relative to the very first commercial hard disk drive in 1956, a modern drive can store more than 100 million times more bits per area. Progress has been relatively steady, but the fastest improvement came in the 1990s and 2000s, when read heads sequentially exploited anisotropic magnetoresistance, giant magnetoresistance,[62] and then tunnel magnetoresistance,[63, 64] as well as perpendicular recording. However, since 2010, the improvement trend has stalled, and industry experts forecast a permanently reduced rate.[65] Today, disk drive companies are still trying to squeeze out more marginal gains in density with approaches like shingled recording, heat-assisted magnetic recording,³⁹ helium filling, and bit-patterned media. The general forecasting consensus is that the future rate of improvement will be perhaps 10% per year, far lower than the historical rates of 50%–100% per year enjoyed in the 1990s and early 2000s. One interesting fact regarding hard drive progress is that the reading speed of hard drives has not kept pace with the stunning advancements in bit density. Sixty years after the IBM's RAMAC spun its disks at 1200 RPM[66], commercial disks today commonly spin at only 5400 RPM or 7200 RPM (though 15,000 RPM has been demonstrated).⁴⁰ As a result, memory access algorithms originally developed for specialized use on magnetic tape are now finding greater use with magnetic disk drives.

Solid-state drives also seem to be reaching maturation. In *The Bleak Future of NAND Flash*

³⁹A bit more on heat-assisted magnetic recording (HAMR): The main challenge with increasing bit density on hard drives is that as you make the magnetic bits smaller, they become less thermally stable. You can increase their stability by increasing their magnetic coercivity, but the tradeoff is that the bits become harder to write. Heat-assisted magnetic recording is a technology that makes bits easier to write, thereby making it possible to use smaller (higher coercivity) magnetic bits. This idea is not new, and in fact, enjoyed brief commercial realization in magneto-optic discs back in the 1980s. Today, Seagate is a leader in HAMR technology, but their release dates keep getting pushed back. Right now the latest word is that they'll be commercially available in 2017 2018, but who knows whether that date will stick. I've heard the main problem with HAMR now is the thermal stability of the plasmonic antenna. Because the magnetic bits are much smaller than the wavelength of laser light, conventional optics cannot be used. Instead, the head has a vertical waveguide with a plasmonic antenna at the end, which concentrates the light at the bit being written. Unfortunately, a side-effect of heating the magnetic bits is that the antenna also gets hot, and it can fail after just 100 writes. Engineers are working to solve this and it seems likely they'll succeed, but right now this is the primary problem delaying HAMR's commercial deployment, at least from what I've heard.

⁴⁰Although rotation speeds today are only 4.5–6 times faster than 1956, reading bandwidth is still much, much higher. As linear bit density increases, so too will reading bandwidth for a constant rotation speed. However, areal bit density scales quadratically with linear density, leading to a widening gap between disk capacity and reading bandwidth.

Memory, Laura Grupp et al. write: “The technology trends we have described put SSDs in an unusual position for a cutting-edge technology: SSDs will continue to improve by some metrics (notably density and cost per bit), but everything else about them is poised to get worse.” [67] Ultimately flash memory suffers from a tradeoff between density and reliability, and as silicon transistors scale down, we will get better at trading off along that price-reliability frontier, but not at pushing that frontier outward.

Despite signs that magnetic hard drives and solid-state drives are slowing their rate of improvement, many speculative technologies are peeking over the horizon, including resistive RAM, magnetic RAM, phase change memory, memristive memory, ferroelectric memory, among others.

In one sense, it’s not surprising that people have conceived of so many diverse memory technologies. For a technology to encode information, the only property it needs (at minimum) is two distinguishable states. Even a line of LEGO pieces turned either to the left or to the right could be used to encode information if you really wanted them to (and in fact, in 2012 such a machine was built in honor of Alan Turing’s 100th birthday[68]).

However, in another sense, it is somewhat surprising (at least to me), that there are so many competitive memory technologies. Although almost anything can be used to encode information, in order to do it *well* a technology must simultaneously satisfy two goals that appear opposed: it must be easy to change when you want to (writing) and it must be hard to change when you don’t want to (retention).⁴¹

Stone tablets, for example, do well at retention because stone is so durable, but do poorly at ease of writing because chiseling takes so much labor. In contrast, wet sand is easy to write on, but once written remains easy to disturb. Clay tablets were a great technological innovation because they took the best of both: while wet, clay is easy to imprint, like sand, but once dried or fired, it becomes far more durable, like stone. For the most part clay tablets were merely a read-only memory, but the tablets could be soaked in water to be recycled into new blank tablets.⁴²

For modern microscopic memory technologies, reliability is limited by thermal stability (though other factors, such as cosmic radiation, matter too). If the energy barrier between memory states is too low, thermal fluctuations may randomly flip the stored bit. Although it can depend on specifics, a general rule of thumb used in magnetic recording is that a barrier of $25 k_B T$ will last one minute, a barrier of $40 k_B T$ will last eight years, and a barrier of $60 k_B T$ will last one billion years.[69, 70]

⁴¹This apparent tension also exists for knots. A good knot must not come undone on its own, but still must be easy to tie and untie. Giant tangles of rope are not considered good knots, because although they might never jiggle loose, they are not easy to tie or untie.

⁴²In a strange way, this method of recycling clay tablets is analogous to modern flash memory, which can be read in a random-access fashion but must be erased in large blocks for rewriting.

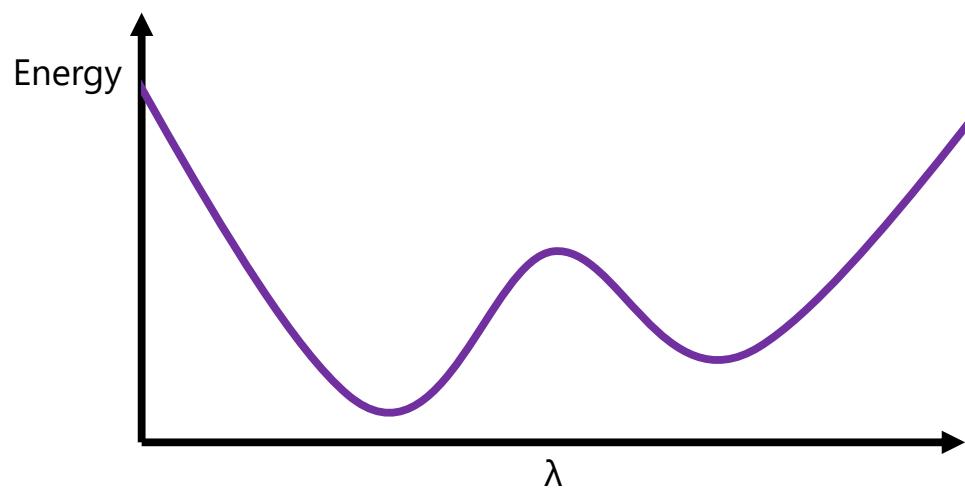


Figure 1.5: An arbitrary two-state memory technology can be modeled as a bistable potential well. Each energy well corresponds to a metastable memory state and the height of the barrier between the two states determines the memory's thermal stability in quasi-static equilibrium. λ is any parameter that characterizes the continuous transformation from one memory state to the other (in a magnetic bit, for example, it could be magnetization).

Transporting information

The trends and outlook for information transportation technologies are quite different than for information storage. Unlike information storage, which has a diverse cornucopia of competing technology options, information transportation has very few technology options worth considering. Because we'd like information to travel as fast as possible (i.e., the speed of light), right off the bat our options are limited to electromagnetic waves.⁴³ Of course, electromagnetic waves still come in a few flavors, such as free space radio transmission, free space optical transmission (requiring direct line of sight), fiber optic transmission, or wire cables.

Because electromagnetic waves are already capable of carrying signals at the universe's maximum speed, signal speed is not a very useful indicator of technological progress. Rather, bandwidth per dollar is a much better metric for evaluating progress in information transportation technology. Figure 1.6 shows progress in bandwidth per dollar, normalized by cable length, over the past 150 years.

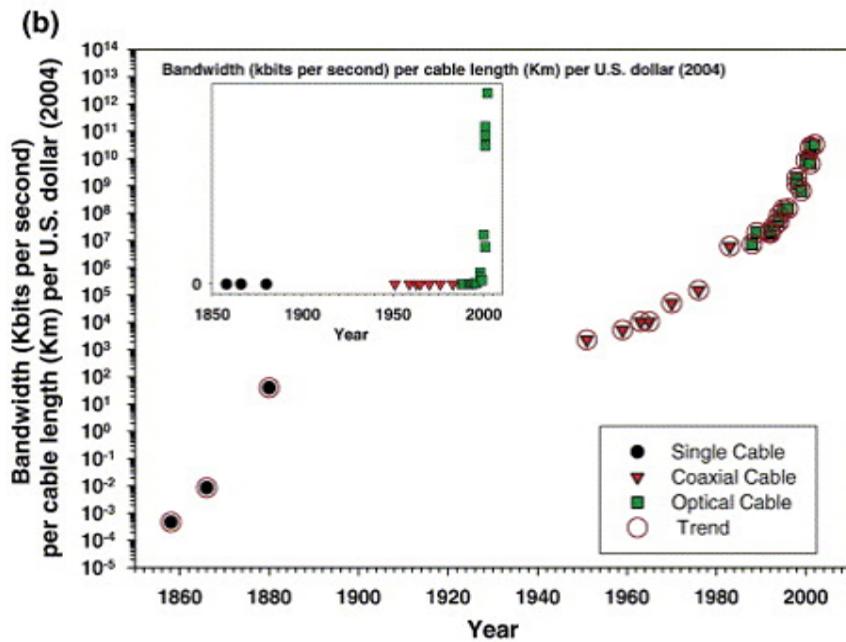


Figure 1.6: Progress in information transportation over the last century. Reproduced from Koh (2006)[42] with permission.⁴⁴

⁴³Of the three other forces, the weak and strong forces are limited by their short range, and gravitational waves require vast amounts of energy and mass for even our most sensitive detectors.[71]

⁴⁴Reprinted from Technological Forecasting and Social Change, Volume 73, Heebyung Koh & Christopher L. Magee, A functional approach for studying technological progress: Application to

The outlook for information transportation technologies appears relatively simple. For signals that travel at the speed of light, fiberoptic cables will continue to dominate as the cheapest option between two points. Engineers will continue to research how to inject and distinguish frequencies on a finer and finer scale, allowing more parallel channels of communication down a single fiber. Further progress seems likely to be evolutionary rather than revolutionary.⁴⁵

Transforming information

The third and final functional category of information technology is information transformation. Figure 1.7 shows the last century of technological process in this category.

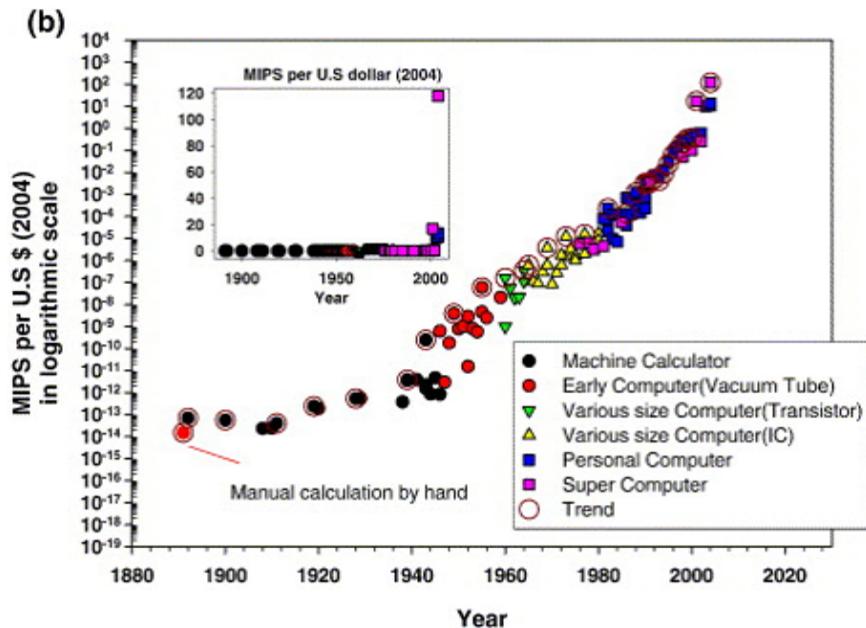


Figure 1.7: Progress in information transformation over the last century. Reproduced from Koh (2006)[42] with permission.⁴⁶ Note: while digging through the sources for this plot,[72] I discovered that the authors accidentally switched the red ‘Manual calculation by hand’ point with its nearest black neighbor. Despite their error, the main picture is unchanged.

information technology, 1061-1083 Copyright (2006), with permission from Elsevier.[42]

⁴⁵Well, further progress *along this single performance dimension* is likely to be evolutionary. New wireless technologies will continue to be developed for their advantages along other performance dimensions like mobility or ease of installation.

⁴⁶Reprinted from Technological Forecasting and Social Change, Volume 73, Heebyung Koh & Christopher L. Magee, A functional approach for studying technological progress: Application to information technology, 1061-1083 Copyright (2006), with permission from Elsevier.[42]

Many people are familiar with Moore’s law,[73, 74] which famously prescribed the rapid exponential progress of integrated circuits. However, fewer are aware that rapid exponential progress in information technology predated the integrated circuit and Moore’s 1965 prediction by many decades.

The technological enablers of transistor scaling

A common misconception about transistor scaling is that the driving force behind it was lithography changing to shorter and shorter wavelengths.⁴⁷ While it’s true that shorter wavelengths have indeed enabled smaller feature sizes, shorter wavelengths have actually provided the least improvement of the three factors in the Raleigh equation.

$$R = k_1 \frac{\lambda}{NA} \quad (1.1)$$

	Resolution (R)	k_1	Wavelength (λ)	Numerical aperture (NA)
1975[75]	2700 nm	1.00	436 nm	0.16
2016[76]	40 nm	0.28	193 nm	1.35
Improvement	68x	3.5x	2.3x	8.4x

Table 1.3: Four decades of improvement in lithography resolution. Contrary to common belief, improvement in resolution has not come primarily from shrinking wavelengths. In fact, the largest contributor in reaching smaller resolutions has been numerical aperture, whose gains were partly enabled by water immersion. (Immersing a lens in water will not by itself raise the numerical aperture of that lens; but rather, immersion allows lenses with higher numerical aperture to be usable.)

1.1.6 Moore’s law is ending

“All good things must come to an end.” —Chaucer, heavily paraphrased, 1374.[77]

Moore’s law has been so consistent for so long that some people take it as an article of faith that any engineering obstacles can and will be quickly overcome. Each time in the past that skeptics cried wolf, claiming that some limit would halt transistor scaling, the ingenuity of the semiconductor

⁴⁷A second common misconception about lithography is that the resolution limits the feature size of devices, thereby limiting their density. In fact, this isn’t quite true. What the resolution limits is the *spacing* of the devices (known as pitch in the semiconductor industry), which indeed limits their density. But the actual sizes of features can be made arbitrarily small with sensitive photoresists or reliable etch.

industry proved those cries wrong. When shrinking aluminum wires became too susceptible to electromigration, the industry switched to copper. When shrinking SiO_2 gate oxides became too electrically leaky, the industry switched to HfO_2 . So it seems entirely reasonable, when confronted with warning signs today, to shrug off the worries and keep faith in the billions of dollars being spent by the semiconductor industry on R&D.

However, just as the boy who cried wolf eventually *did* encounter a wolf (and was disbelieved), eventually Moore's law will encounter a wolf of its own. And ironically, the better we are at learning that prior wolf cries were false, the more vulnerable we become to the wolf's true arrival. So it's important not to generalize too much from the cries of past skeptics. We must always remain vigilant to the possibility that this time is different. And in my informed opinion, this time *is* different.

Of all the steps needed to make a computer chip, lithography is the most critical.⁴⁸ Lithography is what, for now, limits the density of transistors, the major driver of their cost. Historically, as transistors scaled down, the cost of lithography at each node rose. But because the cost of lithography rose more slowly than the gains from greater density, overall the move was profitable. However, as it gets harder and harder to push lithography smaller, we may be reaching the point where continued scaling fails to make economic sense.

What are the prospects for shrinking the resolution of lithography? As shown in Equation 1.1 and Table 1.3, the resolution of lithography is driven by three factors: k_1 , wavelength, and numerical aperture. Let's look at each in turn. Right now, k_1 is already at 0.28, very close to the theoretical maximum of 0.25 for two-beam imaging. So at best, there's only room for 12% more improvement in k_1 . Numerical aperture also seems to be as good as it's going to get, with limited room for improvement. Although it is possible reach values slightly higher than 1.35 by using oil instead of water, it is very difficult to find oils that meet the stringent requirements of transparency, lack of bubbles, lack of impurities, high flow speed, and photoresist compatibility.[75] Given that k_1 and NA appear maxed out, the most promising route to better resolution seems to be shrinking the wavelength further. 157-nm F_2^* lasers were attempted many years ago but were eventually abandoned after they proved too problematic for a variety of reasons (such as their incompatibility with water immersion). So instead, the industry has placed big hopes (and big bets) on an even more extreme option, 13.5 nm, which practically falls into X-ray territory, but, perhaps for marketing appeal, is known as extreme ultraviolet (EUV). Using a wavelength as small as 13.5 nm is a challenge because it requires many components of lithography to be simultaneously reinvented.

⁴⁸One way to quantify this is to compare the market capitalization of ASML, the dominant seller of lithography tools, with Applied Materials, the dominant seller of most non-lithography tools. As of May 2016, ASML's market capitalization is \$42 billion and Applied Materials's market capitalization is \$22 billion. Even combining Applied Materials with Tokyo Electron (about \$10 billion) and Lam Research (also about \$10 billion) just manages to equal ASML. It's telling that the market value of lithography tools is comparable to all other tools combined.

Transmissive optics are not compatible with such short wavelengths, so now everything, including the mask itself, must be made from reflective multilayer mirrors. Old photoresists won't work with this new wavelength, so new photosensitive polymers must be invented with all the properties needed to be spun homogeneously and then chemically developed. Lastly, entirely new sources are needed to generate this short wavelength radiation. Although some have suggested building miniature synchrotrons, the leading technology for producing radiation involves shooting a CO₂ laser pulse at individual drops of molten tin as they fall in a vacuum. The drops explode into a plasma, releasing high energy radiation which is then filtered and collected into a beam for lithography.

Despite the billions of dollars poured into extreme ultraviolet lithography, the technology remains many years behind schedule. In 2003, Intel expected EUV would be ready by 2007.^[78] In 2007, Intel thought EUV would be ready by 2011.^[79] And by 2011, the target for EUV had slipped to the 2013–2015 range.^[80] Although progress is still being made, many components of the system are behind where they need to be. The biggest problem in particular seems to be getting the power of the light source high enough for high throughput. Coupled with the general risk and cost of radical process changes, it's not clear whether EUV lithography will *ever* make it to production. And if it doesn't, then we may be at the end of the road for lithography. Further scaling may be possible by double, triple, or quadruple patterning, but these methods seem less likely to generate the cost savings that finer lithography has achieved in the past.

So if this truly is the end of the road for lithographic scaling and Moore's law, how could we tell? What might it look like? Well, if Moore's law were ending, I would expect to see more delays, more R&D layoffs, and more mergers. What do we actually see? Let's review: Intel's 10-nm node is severely delayed (until late 2017 at best). Their famous tick-tock development model has been abandoned. And recently in April 2016, Intel laid off 12,000 employees during a period of economic expansion. On the GPU side, NVIDIA and AMD have been stuck on the 28 nm node for five straight years.⁴⁹ EUV lithography remains years behind schedule and is far from production readiness. The ITRS roadmap is vaguer than it's ever been. Giant mergers are up (Intel+Altera, Applied Materials+Tokyo Electron,⁵⁰ KLA Tencor+Lam Research, etc.), concentrating the industry more than ever. And ultimately, a 5-year-old PC still works just fine. I submit that this is what the end of Moore's Law looks like.⁵¹

⁴⁹Though, to be fair, they are at last on the cusp of getting 14/16 nm products to market.

⁵⁰The proposed merger between Applied Materials and Tokyo Electron was blocked by the US Department of Justice over antitrust concerns, but I still count the attempt as a sign of a maturing, concentrating industry.

⁵¹Moore's law means many different things to different people. Although Moore defined the law to refer to the number of components in an integrated circuit,^[73] many have broadened its meaning to refer to the consistent exponential progression of information technology.^[81] And even Moore himself later adjusted his law's exponential rate.^[74] When I say that Moore's law is dying or Moore's law is

If Moore's law really is ending, then what comes next? Will our computing technology plateau, still slowly improving, but at a much reduced rate? Or, as in past eras, will we find a new technology to replace our mature incumbents and thereby continue the long-term improvement trend in information technology?

No one knows.

1.1.7 What comes next?

What will future information technology be built of? At a fundamental level, there aren't many options. Apart from dark matter, everything we know of comes from the 17 particles of the Core Theory, shown in Figure 1.8.⁵²

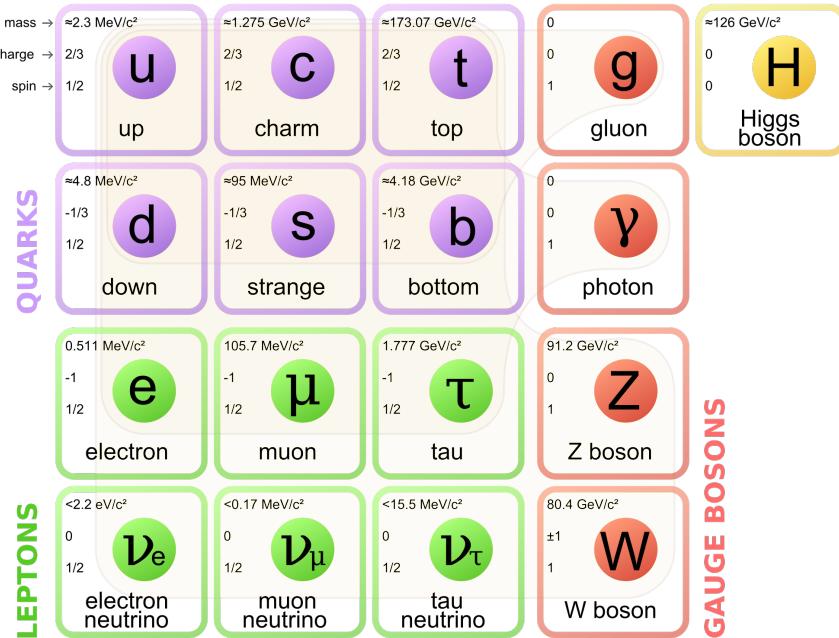


Figure 1.8: The known particles of the Standard Model (or, as Frank Wilczek and Sean Carroll prefer to call it, the Core Theory). Picture by MissMJ, distributed under a [CC-BY-SA 3.0 license](#), via Wikimedia Commons.

From these 17 particles arise stable bound neutral clumps that we know as atoms. Triplets of

ending, I don't mean that all progress will stop for all time. What I mean is that the rate of progress in the near future will fall significantly and distinctly below the rates of the past few decades. No doubt, in the short term, progress will continue along many dimensions. In the long term, I expect nothing specific, only that I'll be surprised.

⁵²Or, if you're a string theorist, strings.

Group → 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
↓ Period																		
1	1 H															2 He		
2	3 Li	4 Be														10 Ne		
3	11 Na	12 Mg														18 Ar		
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	54 Xe	
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	86 Rn	
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

Figure 1.9: The periodic table. Almost all technology comes from combinations of these hundred or so building blocks. Picture by Sandbh, distributed under a [CC-BY-SA 4.0 license](#), via Wikimedia Commons.

quarks are bound together to make protons and neutrons, which themselves are bound together into nuclei, around which negatively charged electrons orbit. Of the 118 elements ever observed, around 80 are radioactively stable. Almost all technology comes from different combinations and configurations of these hundred or so elements.

Further limiting the atomic building blocks available for technology are the rarity of some heavy elements, which make them expensive to extract. Figure 1.10 shows the relative abundances of elements in the Earth’s crust. Abundance is an imperfect measure of cost, since cost also depends on the local concentration in ore deposits and the selectivity of various physical and chemical purification methods, but it nevertheless reflects the general trend. Rare earth elements in particular are more expensive than their abundance suggests, due in part to the fact that their highest energy *f* electrons barely participate in chemical bonding, causing them all to react very similarly (their chemical similarity makes them more difficult to purify).⁵³

Ideally, any new information technology will be composed of abundant atomic matter. But apart from that physical and economic constraint, there is an exponentially large space of materials to search for new technological possibilities. Furthering this search (in a small and specific way) is the

⁵³In fact, the chemical similarity of the rare earth elements is one reason why it took so long to identify them as separate elements.

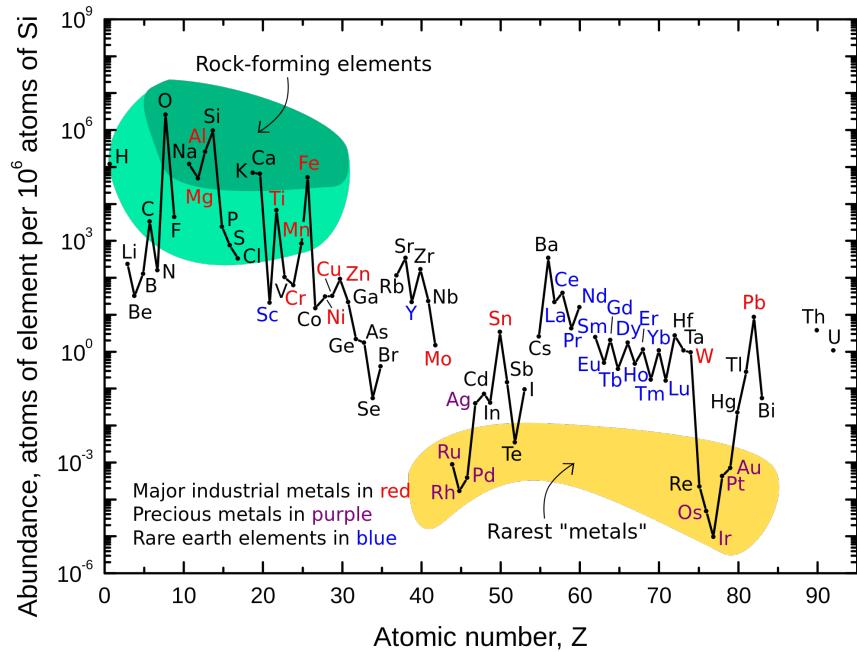


Figure 1.10: The abundances of elements in the Earth’s crust vary tremendously. Oxygen, the crust’s most abundant element, is about a trillion times more common than Iridium, the crust’s rarest element. Rarer elements are less common in technology because they typically take more work to find and purify. Interestingly, the abundances of elements in the Earth’s crust do not mirror those of the rest of the solar system, partly because heavier elements sank to the core of the Earth. With asteroid mining, these heavy elements may become cheaper someday.[82] Picture adapted by michbich from USGS Fact Sheet 087-02, distributed into the public domain, via Wikimedia Commons.

focus of this dissertation and the past six years of my life.

1.2 Searching for new materials and new physics

As we search for new materials to build new technology, it's worth thinking about the features that made past materials so successful. For instance, what was it about the semiconductor that made it so useful for information technology? The answer to this question, in my opinion, is the power of "sometimes."

1.2.1 The power of "sometimes"

If you owned a computer that only "sometimes" turned on, placed Amazon orders that only "sometimes" arrived, and had friends who only "sometimes" kept their promises, you'd live in a state of frequent frustration. Fortunately for most us, we don't live in such a world. All around us, products and processes have been designed to be reliable.⁵⁴

However, when it comes to electronic and magnetic materials, reliability - at its literal extreme - is not necessarily a good thing.⁵⁵ Transistors that are always conducting won't make a good computer chip. Magnetic bits that always point up won't make a good hard drive. And photochromic lenses that always stay dark won't make good eyeglasses. Common to each of these technologies are

⁵⁴In my opinion, the significance of reliability is too often underappreciated in our modern world. Let me explain why. Complex technology, nearly by definition, is composed of smaller, more fundamental parts that work together. So for a complex piece of technology to function, it typically needs all of its components functional at once. For instance, for a car to operate, it needs wheels AND tires AND an engine AND gasoline AND a driver AND so on, for thousands of critical components. If any one of those components fails, the entire car will fail. Because complex technology depends on components whose functionality is logically ANDed together, reliability becomes vastly more important as technology becomes more interdependent. A single component failing will not only halt its own output, but it will halt the output of every other component that indirectly relies on it. For this reason, the reliability of components acts as a limit on how complex and interdependent our technology can get. Without reliable components, the human race would be stuck with relatively primitive technologies. This is why reliability is so important. Without it, the combinatorial[83, 84] technological explosion of the industrial revolution(s) might never have been possible.

⁵⁵In fact, the power of "sometimes" even extends to biology. Some researchers believe that thermal noise is not necessarily a hindrance to cells, but actually helps in some fundamental ways.[85] There is evidence for this in genetics[86] and neurons[87], and some researchers even hypothesize that cell size has evolved to be in the Goldilocks sweet spot of thermal noise, big enough to overcome the major problems of noise but still small enough to derive some benefit.

materials that “sometimes” work one way and “sometimes” work another way. This is the power of the “sometimes.”

1.2.2 A brief history of semiconductors

No class of materials is more emblematic of the power of “sometimes” than the semiconductor,⁵⁶ which sometimes conducts electricity and sometimes does not. The controllable conductivity of semiconductors forms the foundation of modern electronics, from computer chips to photovoltaics to wireless communications to the laser.

However, the semiconductor was not always such a star material. It wasn’t until 1910 that the term was coined,[91] and even decades afterward, many physicists questioned whether semiconductors even existed. In 1931, future Nobel laureate Wolfgang Pauli wrote to his colleague Rudolf Peierls: “On semiconductors one should not do any work, that’s a mess, who knows whether there are semiconductors at all!”[92] His attitude was hardly uncommon at the time. Another physicist of that era complained “What are semiconductors good for? They are good for nothing. They are erratic and not reproducible.”[93] Among scientists, semiconductors had gained a nasty reputation for being difficult to study because their electrical properties seemed to vary uncontrollably from

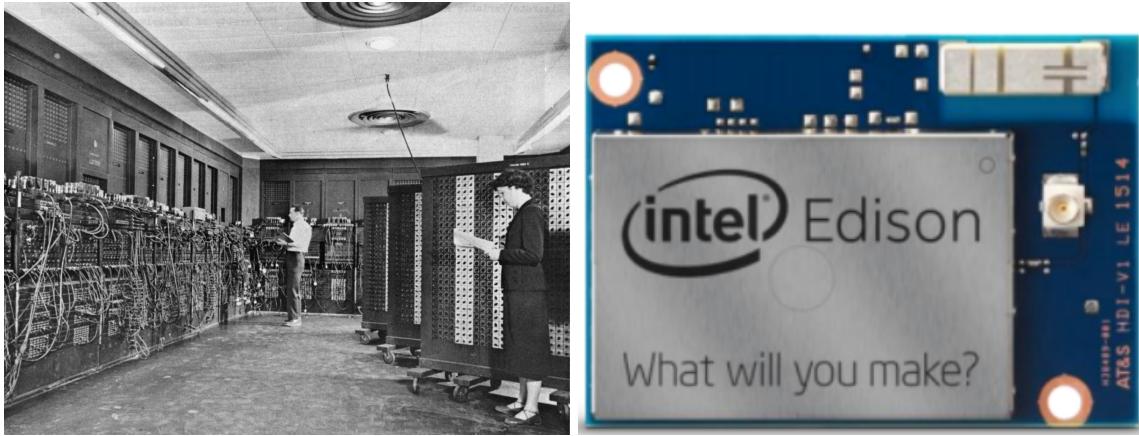
⁵⁶Surprisingly, the definition of semiconductor is not wholly agreed upon. A fair number of professors and textbooks define a semiconductor to be a material with conductivity in between a conductor and an insulator.[88] Others define a semiconductor to be a material with a small band gap,[89] where small is perhaps 3 eV or less. However, these definitions are fuzzy and fail to drive home what makes a semiconductor fundamentally distinct from an insulator. The definition that I prefer and advocate is as follows: a semiconductor is a material that can be doped with charge carriers.⁵⁷ This definition emphasizes the true essence of semiconductors, which is that their conductivity can be controlled by chemical doping and electrostatic gating. And this is the fundamentally unique property of semiconductors that leads to the more superficial properties described by the other definitions. Because charge carriers can only persist when their energy is less than the energy of compensating electrostatic defects, the band gap typically needs to be small (and how small is not an arbitrary cutoff like 3 eV, but will vary depending on the material’s particular defect chemistry). Furthermore, having a small band gap will typically cause a material’s conductivity to lie in between that of conductors (which have no band gap) and that of insulators (which have a large band gap).

⁵⁷For materials that can only be doped one way, with electrons but not holes, or holes but not electrons, I propose the following term: *semisemiconductor*. SrTiO_3 is an example of a semisemiconductor, because although it can be doped n-type by La^{3+} or Nb^{3+} or oxygen vacancies, attempts to dope non-transient holes into the system will be stymied by the formation of compensating oxygen vacancies. Because of this mechanism of compensating oxygen vacancy formation, a fair number of complex oxides are semisemiconductors.[90]

sample to sample, sometimes differing by as much as 7 orders of magnitude. Considering that reproducibility is a bedrock principle of the scientific method, it was extremely challenging to study materials that could not be reproduced reliably.

Progress in the field of semiconductors remained sluggish until World War II,[94, 95] when the military's well-funded desire for radar systems stoked demand for semiconductor diode rectifiers. Around the same time, scientists finally began to reliably control the doping level of semiconductors, focusing on materials like silicon and germanium, which were doped by chemical impurities, rather than self-doping materials like copper oxide, which were doped by chemical vacancies.

And the rest is history.



(a) ENIAC required a staff of six full-time engineers and broke down about once a day. (b) Edison requires a staff of zero full-time engineers and breaks down about zero times a day.

Figure 1.11: ENIAC and Intel's Edison board, side by side. (Not even close to scale.)

	Year	Cost (2015\$)	Power consumption	Tubes/transistors
ENIAC[96]	1946	\$6,000,000	174,000 W	17,468
Intel's Edison[97]	2014	\$50	0.5 W[98]	5,000,000,000[99]

Table 1.4: 70 years of progress stimulated by the semiconductor transistor.

1.2.3 What will be the semiconductor of the 21st century?

As Moore's law ends and semiconductor-based computing matures, we face two possible futures: either we settle for a reduced rate of technological progress or, alternatively, we invent new materials and paradigms that are capable of circumventing the physical limits of traditional semiconductor transistors. Although the second option of new technology and high performance sounds more

exciting, it's quite possible that it simply won't pan out.⁵⁸ Perhaps there really isn't anything better than the semiconductor transistor. And even if we do invent a radically superior transistor, it will still take a long, long time to catch up to the semiconductor industry in terms of supply chain management, factory tooling, worker education, technological compatibility, economies of scale, etc. So in the short run, over the next 20 years at least, I'd put my money on the continued dominance of the semiconductor transistor. But projecting far out, say, in 100 or 1,000 years, are we really going to be using the same general transistor technology as today?⁵⁹ Nobody knows. But framed this way, it certainly seems quite plausible that we could discover a superior alternative.

Therefore, if I had to frame the goals of my research field into a single question, it would be this:

What will be the semiconductor of the 21st century?

That is, what will be the next paradigm shift,[100] the next disruptive[101] materials platform that leaps ahead of the semiconductor transistor? And in answering that question, in seeking new materials for future computers, what generalizable lessons can we learn from the success of semiconductors to guide our search? And, perhaps just as important, but less commonly asked, what lessons *shouldn't* we learn from semiconductors? I.e., which idiosyncratic features of the semiconductor might we profitably discard in constructing a new and improved technological paradigm?

Here, I wish to highlight two important lessons from the semiconductor, and then illustrate how they apply to the family of materials known as complex oxides. Lesson one: Controllable variation is valuable. The properties that made the semiconductor so successful were its variability and our eventual control of that variability by chemical doping. Therefore, in a research program looking for future computing materials, it makes sense to seek materials with high variability (perhaps along different properties than conductance) and then learn to control them. Complex oxides, as a family, possess a tremendously wide range of properties, properties that can be controlled not only by chemical doping, but also by structural modification. Lesson two: Poor understanding of a material is actually a positive signal of its usefulness, because the materials with the most variability are naturally the last to be understood. As I discussed earlier, semiconductors were known for many

⁵⁸In all of history there has been nothing quite like the blistering technological progress of integrated circuits over the past 60 years. The astounding success of the semiconductor transistor has instilled confidence in many people, who extrapolate out and expect progress to continue. However, viewed from another perspective, the astounding success of the semiconductor transistor makes it that much harder to be surpassed by a new challenger. As we target technological R&D, how much sense does it make to aim at supplanting one of the most successful technologies of all time? Given the transistor's dominance, perhaps we'd better off investing less in alternatives and more in its continued development.

⁵⁹Some technologies, like the wheel, have been dominant for thousands of years. There is a nonzero probability that the same will be true of the semiconductor transistor.

decades before finally being put to use in diodes and transistors. The reason this took so long is twofold. First, the variability of semiconductors made them naturally harder to study. And second, because they were harder to study, very few scientists even attempted to study them, which further slowed the pace of scientific understanding. As a result, this materials family with so much technological potential was sitting right under our noses for decades. Similarly, complex oxides have been known for decades, yet remain relatively difficult to understand. It seems quite possible that they will follow a similar arc as the semiconductor, where at first their complexity stymies our understanding until eventually that complexity is understood and harnessed for new purposes unachievable by the materials that came before.

1.3 Harnessing the complexity of complex oxides

A complex oxide is a chemical compound that contains oxygen and at least two other elements (or oxygen and just one other element that's in at least two oxidation states).^[102, 103] Complex oxide materials are notable for their wide range of magnetic and electronic properties, such as ferromagnetism, ferroelectricity, colossal magnetoresistance, and high-temperature superconductivity. Although the space of complex oxides is far too combinatorially large to survey in a single paragraph, or even in an entire book, I will highlight a few classic examples that illustrate the diversity of correlated-electron phenomena. Most of the world's commercial hard ferromagnets, such as those in electric generators and motors, are ferrites, such as $\text{SrFe}_{12}\text{O}_{19}$.^[104] Commercial ferroelectrics, used commonly in actuators and positioning systems, are commonly titanates,^[105] such as $\text{PbZn}_x\text{Ti}_{1-x}\text{O}_3$ ^[106] and BaTiO_3 . Less commercially valuable but still interesting is the phenomenon of colossal magnetoresistance. Colossal magnetoresistive materials include LaMnO_3 and other manganites.^[107] And classic examples of superconductivity include $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ^[108] and other cuprates. Common to all of these materials—ferrites, titanates, manganates, and cuprates—are the facts that they possess (1) transition metal ions, (2) oxygen, and (3) complex chemical formulas. This is no coincidence. Correlated-electron phenomena often arise from semi-localized electrons in d orbitals, whose potential can be unlocked by ionic oxygen bonding and tuned by alloying and doping. The rest of this section will briefly explain why these unique circumstances make complex oxides so interesting and potentially useful in information technology.

1.3.1 The paradigm of orbital localization

In general, if you want a material to exhibit any sort of useful dynamic behavior, it must, by definition, be in different states at different times. In semiconductors, the different states that we exploit are different levels of conductivity, which are controlled by the concentrations of electrons and holes. In complex oxides, though, I wish to focus on a dichotomy that is superficially similar in ways but is fundamentally quite different: the dichotomy of localized and delocalized electron

orbitals.

All of the complexity of atomic matter and chemistry and life itself come from valence electrons, which can inhabit a very limited set of orbitals.⁶⁰ The principal quantum number, n , ranges from 1 to 7, and the azimuthal quantum number, l , ranges from 0 to 3 (often labeled by the letters s , p , d , and f for historical reasons).⁶¹ It's amazing that such complexity arises from such simple components.

A solid's properties are determined by the electrons that bond it together. In general, a solid with electrons in delocalized orbitals (such as those in the s , p , or $5d$ orbitals) will tend to be metallic and well-described by band theory. These correspond to the blue region on Figure 1.12. On the other end of the spectrum, a solid with localized electrons (such as those in the $4f$ orbitals) will tend to be insulating with local-magnetic moments and well-described by molecular orbital theory.⁶² These correspond to the red region in Figure 1.12. However, for electrons in orbitals with middling localization (such as $5f$, $3d$, and $4d$), it's much harder to predict how they will behave. In this regime, electrons cannot easily zoom by one another, so they often end up exhibiting complex, correlated behavior. This results in uncommon ordered properties such as ferromagnetism, ferroelectricity, high-temperature superconductivity, charge ordering, and more.⁶³ Although this correlated behavior is much harder to model, it may have potential for future technology.

1.3.2 The importance of oxygen in complex oxides

By themselves, transition metals and rare-earth metals do not necessarily exhibit correlated electron phenomena from their semi-localized d or f orbitals. This is because these metals also have extended s orbitals (or for lanthanides, $6s$ and $5d$ orbitals) that participate in bonding and conduction, masking the effects of the d or f orbitals underneath.

⁶⁰Again, I am relying on the simple but useful fiction of single-electron orbitals. These do not exist in real life, but because they make talking about chemistry so much easier, I will continue to rely on them. In your mind, feel free to substitute the word ‘orbital’ with the wordier ‘counterfactual low-energy multi-electron excitation.’

⁶¹Of course, in theory, these numbers can go higher. But such atoms are extremely unstable.

⁶²Although this range of properties, from metallic to insulating, sounds superficially like semiconductors, the causes are quite different. In semiconductors, the variation in conductance is caused by the variation in the concentration of electrons or holes. However, in complex oxides, the variation in conductivity can be caused by the variation in orbital localization. As a result, there can arise many correlated electron phenomena not seen in semiconductors.

⁶³Although electron correlation can lead to emergent properties of materials, it is by no means required.[109] The fractional quantum Hall effect in graphene comes from a system filled with relatively uncorrelated sp^2 electrons.

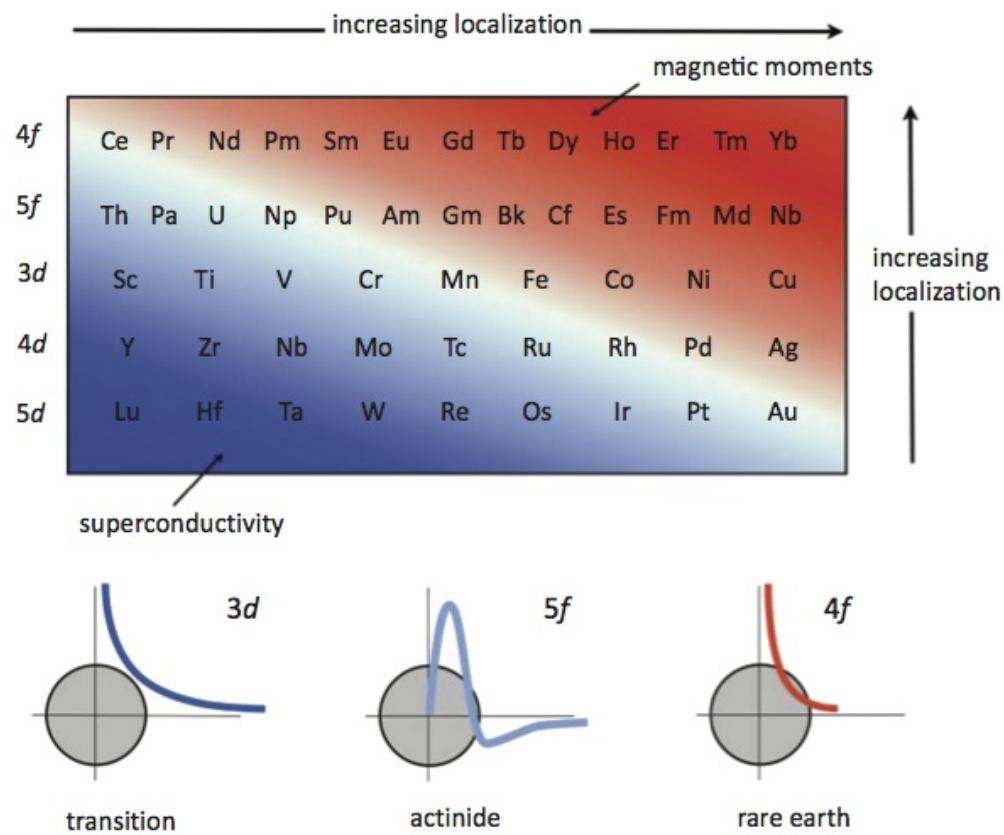


Figure 1.12: A Kmetko-Smith diagram,[110] copied from P. Coleman's *Introduction to Many-Body Physics*.[111]

The best way to pull off these extended electrons is to bond the transition or rare-earth metal with oxygen. Oxygen is the perfect element for this task: it has the highest electronegativity behind fluorine, but unlike fluorine it is safe and abundant. It also is better than fluorine at bonding with multiple atoms in a solid.

Without oxygen, the complex oxides would not exhibit complex, correlated electron behavior. Oxygen is necessary to pull off the valence *s* electrons, leaving the key *d* or *f* electrons behind as the new valence shell.

1.3.3 Controlling bonding in crystals of complex oxides

Having now emphasized how the chemical bonding of electrons drives materials properties, it's worth considering what options we have for designing new materials by controlling their chemical bonding and structure.

Top-down design versus bottom-up

Because atoms are so small, placing them one-by-one into an imagined crystal structure would take an inordinate amount of time to get any appreciable quantity of material. Therefore, nearly all techniques for synthesizing materials rely on bottom-up approaches, where nanoscale physical interactions help guide the atoms into their desired places.

Chemical composition

One of the most powerful tools for creating materials is thermodynamic equilibrium. A collection of atoms can be heated into a relatively homogeneous liquid and then slowly cooled, resulting in an equilibrium crystal that is controlled by the initial collection of atoms. This technique was used by early humans to produce bronze and other materials, and today it is still very common, being used to produce alloys and ingots of many different crystals. In my research, crystal substrates were synthesized using the Czochralski process,⁶⁴ a specific technique that broadly relies on equilibrium thermodynamics and chemical composition to create large, homogeneous crystals.

In general, thermodynamic techniques require lots of heat and time, which makes them relatively simple and potentially expensive.

Non-equilibrium processing

In the vast space of possible materials, those that are thermodynamically stable inhabit just a tiny fraction of it. Therefore, it is important to find non-equilibrium processing techniques that allow us to create useful meta-stable materials. Quenching is a classic technique that exploits slow kinetics

⁶⁴As with many scientific and technological advances, the process was discovered by accident, when Czochralski dipped his pen in molten tin instead of his inkwell.[112]

as a strategy for avoiding a material's equilibrium state.[113] Quickly quenching carbon-rich steel through its eutectic point makes it much stronger by limiting the rate at which carbon precipitates out of the material.

In contrast to equilibrium techniques, non-equilibrium techniques must avoid heat or time.

One relevant technique for reaching non-equilibrium, meta-stable materials is thin-film deposition. The next few subsections discuss ways in which thin-film deposition can be exploited to reach materials states that are unreachable by conventional equilibrium techniques.

Epitaxial strain

In terms of materials properties, the most straightforward advantage of thin-film deposition is epitaxial strain. Epitaxial strain is a type of strain that occurs in thin films, caused by the bonding force of the substrate's atoms acting on the atoms of the the thin film. If the substrate has an atomic structure with wider atomic spacing than the film, the substrate's atoms will pull the thin film's atoms further apart in the two in-plane directions. Conversely, if the substrate has an atomic structure with closer atomic spacing than the substrate, the thin film's atoms will be pulled closer together in the two in-plane directions. Typically there is an elastic response in the out-of-plane direction that helps accommodate the modified spacing. These structural distortions can be quantitatively described by ϵ and σ , the second-order strain and stress tensors, respectively.

$$\epsilon = \begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{bmatrix} \quad (1.2)$$

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \quad (1.3)$$

The strain tensor can be additively decomposed into three parts: the volume dilation, the orthorhombic distortion, and the shear strain.

$$\epsilon = \epsilon_{volume} + \epsilon_{orthorhombic} + \epsilon_{shear} = \begin{bmatrix} \epsilon_{11} + \epsilon_{22} + \epsilon_{33} & 0 & 0 \\ 0 & \epsilon_{11} + \epsilon_{22} + \epsilon_{33} & 0 \\ 0 & 0 & \epsilon_{11} + \epsilon_{22} + \epsilon_{33} \end{bmatrix} + \frac{1}{3} \begin{bmatrix} 2\epsilon_{11} - \epsilon_{22} - \epsilon_{33} & 0 & 0 \\ 0 & 2\epsilon_{22} - \epsilon_{11} - \epsilon_{33} & 0 \\ 0 & 0 & 2\epsilon_{33} - \epsilon_{11} - \epsilon_{22} \end{bmatrix} + \frac{1}{3} \begin{bmatrix} 0 & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & 0 & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & 0 \end{bmatrix} \quad (1.4)$$

For [001] epitaxy, the type I used in my research, the applied strain is orthorhombic (with in-plane spacing differing from out-of-plane spacing) and, depending on the elastic response, volumetric as well. For epitaxy on other crystal planes, the decomposition will be different.

One of the most successful examples of strain engineering is strained silicon, incorporated into modern transistors in the mid-2000s. By depositing silicon thin films next to silicon-germanium, the spacing between the silicon atoms is increased, allowing for higher electron mobility and consequently higher electronic performance. In fact, over the past decade or so, the use of strained silicon has been a bigger driver of performance than traditional scaling.

Epitaxial structure-transfer

For crystals with a complex structure, the effects of epitaxial strain can be similarly complex. When atoms get pushed toward one another, complex crystal structures can accommodate this pushing in a number of ways. In many perovskite-based crystal structures, for example, biaxial compression is accommodated by octahedral rotations, where bond angles are what primarily change, rather than bond lengths. Bond angles are especially important in superexchange magnetism, and the paradigm of strain-induced octahedral rotations has become increasingly recognized as a tool for understanding and manipulating the properties of materials.[\[114\]](#)

1.3.4 The astounding success of band theory

Mass education is great. On an individual scale, mass education has provided the poor a path out of poverty, allowing the children of farmers and laborers to leverage their intelligence in more productive occupations. On a societal scale, investment in mass education has likely contributed to the rise of modern democracy, productivity, and peace.[⁶⁵](#)

However, mass education has downsides. Efficiently standardizing myriad human accomplishments into book chapters and homework assignments often has the regrettable side effect of deadening a proper sense of surprise and awe. In my opinion, band theory is one of these victims.

Each year, thousands of undergraduate students are dryly taught band theory, which, after some simplifying assumptions, allows one to calculate how electrons act in solids. As the students advance, they may be taught how these assumptions break down in some materials, where band theory fails to apply. However, there is an aspect to band theory that few students are ever taught: it's a surprise that it works at all!

⁶⁵Speaking of schooling and peace, some well-meaning education reformers (and others) argue that the roots of modern compulsory education lie in the Prussian ‘factory’ model of schools, invented at the dawn of the industrial age to make more obedient soldiers and workers out of the population. But scholars of education history dispute this narrative, calling it sloppy and crudely reductionist.[\[115\]](#)

To accurately calculate the properties of a material, one must solve the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = H\psi(\mathbf{r}, t) \quad (1.5)$$

where, for a solid with some assumptions,⁶⁶ the Hamiltonian H is

$$H = \sum_i \frac{\vec{p}_i^2}{2m_e} + \frac{1}{2} \sum_{i,i'} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_{i'}|} + \sum_j \frac{\vec{p}_j^2}{2m_j} + \frac{1}{2} \sum_{j,j'} \frac{Z_j Z_{j'}}{4\pi\epsilon_0 |\vec{r}_j - \vec{r}_{j'}|} + \frac{1}{2} \sum_{i,j} \frac{e Z_j}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \quad (1.6)$$

where the terms are, in order, the kinetic energy of electrons, the potential energy from electron-electron repulsion, the kinetic energy of the nuclei, the potential energy from nucleus-nucleus repulsion, and the potential energy from electron-nucleus attraction. i is the index for electrons, \vec{p} is the momentum operator, m_e is the mass of the electron, e is the elementary charge, ϵ_0 is the dielectric constant, \vec{r} is the position operator, j is the index for nuclei, and Z_j is the charge of the nucleus.

The brevity of this equation belies its truly monstrous size. Even if you were to ignore all of the nuclear terms and all of the core electrons, this equation is still impossibly difficult to solve, requiring the diagonalization of Hamiltonian with roughly 10^{46} terms. And even if such a computation were magically possible, the mere task of inputting initial conditions or reading the output would be an impossibly immense task.

Therefore, many different approximations to this equation have been developed.[116, 117, 118] One of the simplest and most fundamental is band theory. Band theory's key assumption, which makes the model solvable (at the cost of being wrong in ways), is the assumption that electrons are non-interacting. With this assumption, the solid's wavefunction can be factored into single-electron states (and then rebuilt into a multi-electron state by applying the Pauli exclusion principle through Fermi-Dirac statistics).

From here, one approach is to ignore the nuclei as well, and lump the single electron's interactions into an effective periodic potential V that depends only on space and no other particles.⁶⁷ This makes the equation much simpler:

$$H = \frac{\vec{p}^2}{2m_e} + V(\vec{r}) \quad (1.7)$$

Alternatively, after making the independent electron assumption, one can perturb the Hamiltonian by introducing a tight-binding term, H_{TB} , where the atomic orbitals are the starting basis then

⁶⁶ Already this Hamiltonian ignores relativity, ignores all forces except electromagnetism, ignores the energy of the electromagnetic field, and assumes nuclei are point particles.

⁶⁷ In this approach, it is important to choose a good effective potential, and many methods have been invented to generate such potentials.

mixed by transfer integral terms proportional to t_{ij} . If only nearest-neighbor terms are considered, this approach predicts band structures with cosine dispersion.

$$H_{TB} = - \sum_{i,j} t_{ij} (c_i^\dagger c_j + c_j^\dagger c_i) \quad (1.8)$$

Overall, band theory has been wildly successful at explaining the electronic properties of many materials. But when you stop to consider how unreasonable and unphysical it is for band theory to assume that electrons are non-interacting, it's astonishing that the theory works at all. Although I regard this as a somewhat open problem, I believe that it can be answered by a deep understanding of statistical mechanics, where it turns out that the lowest-energy excitations of multi-particle wavefunctions end up being remarkably similar to the lowest-energy excitations of single-particle wavefunctions, even though the states are totally different.⁶⁸

1.3.5 The not-so-astounding failures of band theory

Given band theory's strong assumption of electron independence, it should come as little surprise that its predictions are sometimes violated. The most classic example are Mott insulators, materials that band theory predicts to be metals but turn out to be insulators. This class of materials was highlighted by Mott in 1949 when he hypothesized that electron repulsion prevented the flow of charge in NiO.[119]

1.3.6 Progressing beyond the independent electron assumption

One of the most successful approaches for moving beyond the independent electron assumption is the Hubbard model, which extends the tight-binding model of band structure with a term that models the on-site repulsion of electrons, the strength of which is scaled by the parameter U .

$$H_H = - \sum_{i,j} t_{ij} (c_i^\dagger c_j + c_j^\dagger c_i) + \sum_i U_i n_{i\uparrow} n_{i\downarrow} \quad (1.9)$$

However, the Hubbard model, with its ‘effective’ repulsion scaled by U , is relatively crude. In *Condensed Matter Physics*, Michael Marder writes of the Hubbard model: “there is no better illustration of the difficulties involved in progressing systematically beyond the one-electron pictures of solids.”[118, 120]

There is a vast body of literature detailing the theoretical and experimental attempts to construct models that are more accurate at the cost of more complexity. I will not attempt to describe even the sliver of that vastness within my ken, but merely wish to emphasize that cutting-edge goes

⁶⁸I cannot personally prove this statement myself, but it comes from extended discussion a few years back with UC Berkeley Physics Professor Dung-Hai Lee.

far beyond what I've briefly shared here. However, simple models such as the Hubbard model are nonetheless important because their framing of the problem is the foundation for many of these more complicated and specialized techniques.⁶⁹

1.3.7 The role of experiments

It is precisely because of the difficulty of theoretical prediction that scientists perform experiments. Oftentimes, the easiest way to discover a material's properties is not to calculate them, but to measure them. And once many such properties have been measured, emergent patterns can be identified, even if they are fully untethered from first principles physics equations. This is the role of experiments, performed by experimentalists like myself.

The hope is that by synthesizing and measuring new and interesting materials, we can identify technologically useful phenomena or patterns. These measurements can also constrain the space of physical models, raising the likelihood that new and better models will be developed. These were the scientific goals of my two major PhD research projects, described in detail in Chapters 3 and 4.

1.4 Magnets

Much of my PhD research involved magnetism, one of the most classic examples of correlated electron behavior. For reasons that I will touch on later, there is hope that information technology based on magnets can surpass the semiconductor transistor in energy efficiency. This section of my dissertation provides relevant background information about magnetism and magnets, but for an in-depth explanation of these topics, I suggest reading a textbook, such as Spaldin's *Magnetic Materials: Fundamentals and Device Applications*[121] or Stoehr's *Magnetism: From Fundamentals to Nanoscale Dynamics*[122] or Coey's *Magnetism and Magnetic Materials*[123].⁷⁰

1.4.1 Magnets are prominent in physical and information technology

The first known use of magnets in technology took place in China around 300 BCE. Spoon-shaped pieces of lodestone (a rock rich in Fe_3O_4) were used like compasses to point south. Although at first

⁶⁹Another reason that simple models are important is that it's important to know which features of a model are necessary for modeling some complex behavior. If a simple model can model some system as well as a complex model, then it means the complexity of the complex model is not explaining very much.

⁷⁰Spaldin's book is accessible, Stoehr's book is comprehensive, and Coey's book has decent coverage of applications and their markets. However, be aware that Coey's book is in the first edition and contains many errors, errors that he seems uninterested in correcting on his errata page, which has not been updated in years despite my repeated emails.

these spoons' only uses were geomancy, feng shui, and fortune telling, eventually improved versions found use in navigation.

Since then, magnets have spread. They are in computer hard drives, in generators, in motors, in wireless communication electronics, in voltage transformers, and more. Magnet technologies can be classified into three major categories: permanent (hard) magnets, soft magnets, and magnetic recording. Each category is roughly a third of the global market for magnets, which in 2010 totaled \$30 billion.[123]

Hard magnets, defined by their high magnetic remanence and high coercivities, are useful for converting between electrical energy and mechanical energy.⁷¹ They are used in generators, electric motors, actuators, holding devices, and sensors. Production is dominated by ferrites, though high-performance applications use rare-earth magnets.⁷²

Soft magnets, defined by their low coercivities and low magnetic remanence, are useful for efficiently amplifying magnetic fields. They are used in the cores of transformers, in radiofrequency and microwave circuits, and in other electronics. Transformers typically use Fe-Si alloys, whereas high-frequency applications, which require high resistivity for low losses, use soft ferrites.

Magnets used in magnetic recording tend to have middling coercivities. Hard drive disks are perhaps the biggest market today, but this technology family includes magnetic tape (both for archival data storage as well as audio and video cassette) and magnetic stripes. If anything, this market seems less healthy now than in the past. Although data centers demand more and more information storage each year, much of this growth has been absorbed by solid-state drives, a high-performance alternative with steadily dropping costs. Audio and video cassettes are already obsolete, and it's likely that fate will similarly befall magnetic card strips, which face competition from EMV Chip and PIN technology as well as smartphones.

Although the commercial applications of my research are vague, the high cost of its materials and fabrication techniques make high-value information technology its likeliest application. This could be information storage, information processing, or sensors.

1.4.2 What is a magnet?

Like some other branches of science, magnetism lacks a full vocabulary to label its phenomena, and as a result, sometimes a single word can be overloaded with multiple meanings. For example, what does it mean for a material to be magnetic? Does it mean the material exhibits a response in an applied magnetic field? If so, then all materials are magnetic, be they diamagnets, paramagnets,

⁷¹Or, put another way, between magnetic fields and torque.

⁷²Although you might reasonably expect rare-earth magnets to primarily consist of rare-earth elements, in fact they are mostly iron. The common rare-earth magnet neodymium iron boride ($\text{Nd}_2\text{Fe}_{14}\text{B}$) is only 12at% rare earths.

ferromagnets, or otherwise. Does it mean that the material's electron magnetic moments exhibit long-range order? Then diamagnets and paramagnets would be left out, but antiferromagnets, which also possess very little net magnetic moment, would remain included. Does it mean that the material is presently exhibiting long-range ordering? If so, then ferromagnets above their T_c would be excluded. Ultimately, the question of what is a magnetic material has no correct answer. It depends entirely on what the asker means. For this chapter, I will use the word magnet to mean ferromagnet.⁷³

Magnetic materials can be categorized in many ways. They can be itinerant, where the valence electrons are mobile, or they can be local, where the valence electrons cannot easily move from atom to atom. Local magnets are easier to describe than itinerant magnets. All of their magnetic behavior can be expressed in terms of how their microscopic magnetic moments order. If they form domains and tend to align in a common direction in the absence of a magnetic field, then the material is a ferromagnet. Else, if they point in random directions in the absence of an applied magnetic field, then the material is a paramagnet.⁷⁴ If the electron spins point in no direction at all (i.e., there are no unpaired electrons), then the material is a diamagnet.⁷⁵ These three basic forms of magnetism

⁷³The word ‘ferromagnet’ is itself overloaded. Narrowly defined, a ferromagnetic material is one whose microscopic magnetic moments all align in the same direction. But broadly defined, a ferromagnetic material is any material that exhibits a spontaneous net magnetic moment. This broader definition encompasses orderings that are not strictly ferromagnetic, such as ferrimagnetic ordering, in which unequal microscopic magnetic moments alternate their alignment, resulting in a net magnetic moment.

⁷⁴The dividing line between ferromagnets and paramagnets is actually rather subtle (and to a newcomer, it's not even obvious that there ought to be a sharp dividing line rather than a gradual transition). In a ferromagnet, because of thermal fluctuations, the local moments will never be fully aligned, and at temperatures just below T_c the microscopic ordering can look quite patchy. In a paramagnet, on the other hand, the local moments will never be fully randomly aligned; short-range interactions may align small patches, just as in a ferromagnet. In fact, by eye, it is impossible to tell the difference between a patchy ferromagnet and a patchy paramagnet. The property that divides them is whether their ordering is long-range or just short-range. E.g., if you start at one local moment and then move a long distance away, how accurately can you predict the alignment of your new location? If you can only predict it with 50% accuracy, the material is a paramagnet. If you can predict it with more than 50% accuracy, the material is a ferromagnet. The question of where to draw the dividing line between ferromagnets and paramagnets is handled with more sophistication in the study of phase transitions and critical exponents in field of statistical mechanics.

⁷⁵Really, any material with a magnetic susceptibility that is (mostly) well-defined, negative, and independent of temperature is a diamagnet. There are some conductors and semiconductors with unpaired electrons that are nevertheless diamagnetic because their conduction electrons have low

are plotted in Figure 1.13, though of course many more complicated patterns exist as well.

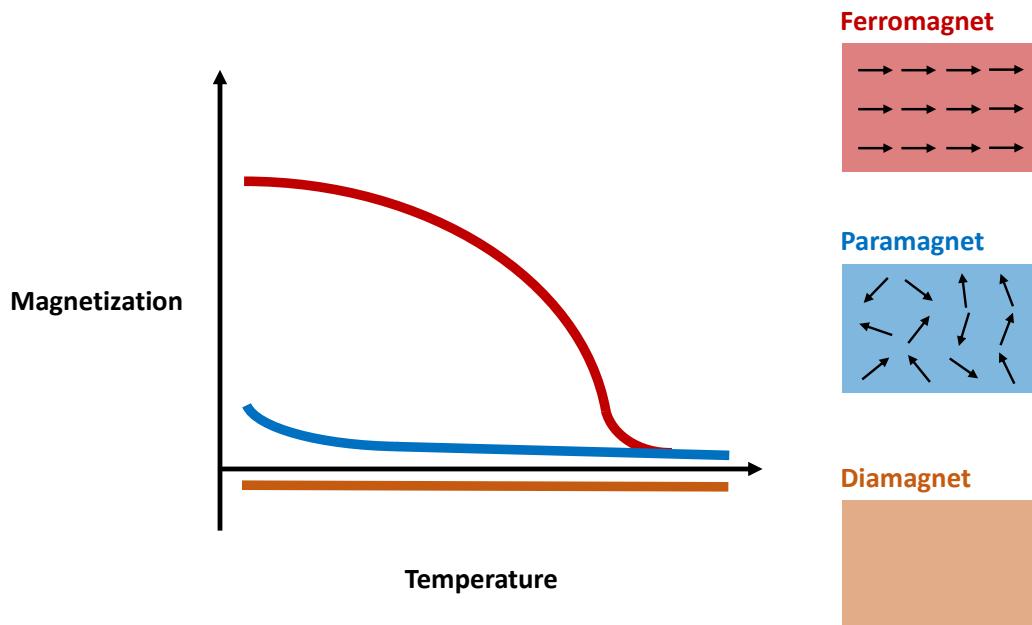


Figure 1.13: Three common forms of magnetism and their dependence on temperature.

1.4.3 Magnets require two ingredients: magnetic moments and exchange

Ferromagnetism, the alignment of many microscopic magnetic moments, requires two ingredients. First, it requires that a material has magnetic moments in the first place. And second, it requires that the exchange interaction is strong enough for those microscopic magnetic moments to cooperatively order.

1.4.4 Magnetic moments

Fundamentally, electron magnetic moments come from two sources: spin angular momentum and orbital angular momentum.⁷⁶ Spin, denoted S , is the quantum mechanical angular momentum intrinsic to particles. Orbital angular momentum, denoted L , comes from the orbit of the electron around its atom. Sometimes their total, denoted J , is a good quantum number to use.

effective masses, amplifying their diamagnetic response.

⁷⁶A third source is from classical motion through space. This effect is weak and opposes applied magnetic fields, resulting in diamagnetism. Because it is so weak, it only clearly appears in materials with no unpaired electrons or in materials where the conduction electrons have small effective mass.

The Zeeman effect describes how electron magnetic moments feel a torque that tries to align them with an applied magnetic field. Because this torque is relatively weak, it takes very low temperatures and very high magnetic fields to overcome thermal fluctuations and fully align an individual electron magnetic moment. However, with the exchange interaction between neighboring electrons, they can stay aligned at warmer temperatures and in zero applied magnetic field.

1.4.5 Exchange

The exchange interaction is a quantum phenomenon that explains why electron spins align with one another. Because fermions have wavefunctions that are antisymmetric under identical particle exchange, either their spatial component or spin component is antisymmetric too (but not both). Antisymmetric spatial wavefunctions tend to keep the particles further apart from one another, which is energetically favorable because electrons repel. Since the spatial part of the wavefunction is antisymmetric, the spin part of the wavefunction must be symmetric. This is why wavefunctions with aligned spins have lower energy.

The strength of the exchange interaction depends strongly on the overlap between the individual electron orbitals. Electrons in orbitals with a high degree of overlap will experience a strong exchange interaction. However, if the orbital overlap is too large, the electrons will tend to delocalize and conduct, diminishing the exchange effect.

Direct exchange

When two electron orbitals overlap directly, this is known as direct exchange, or sometimes just exchange. This is the common mechanism of exchange in elemental metals like iron and gadolinium.

Superexchange

In many oxides, such as the ones I study, $3d$ transition metal ions are not adjacent in their crystal lattice, but separated by O_2^{2-} ions. Nonetheless, exchange can occur through the intermediary oxygen ion. This is known as superexchange. Whether the interaction aligns the magnetic moments parallel or antiparallel depends on the bond angles and orbital filling, and can be described by the three Goodenough-Kanamori-Anderson rules.[\[124, 125, 126, 127\]](#)

Antisymmetric exchange

Antisymmetric exchange, also known as the Dzyaloshinski-Moriya interaction, is another type of exchange that occurs in low-symmetry materials with spin-orbit coupling.[\[128, 129\]](#) It is responsible for magnetic skyrmions.[\[130\]](#)

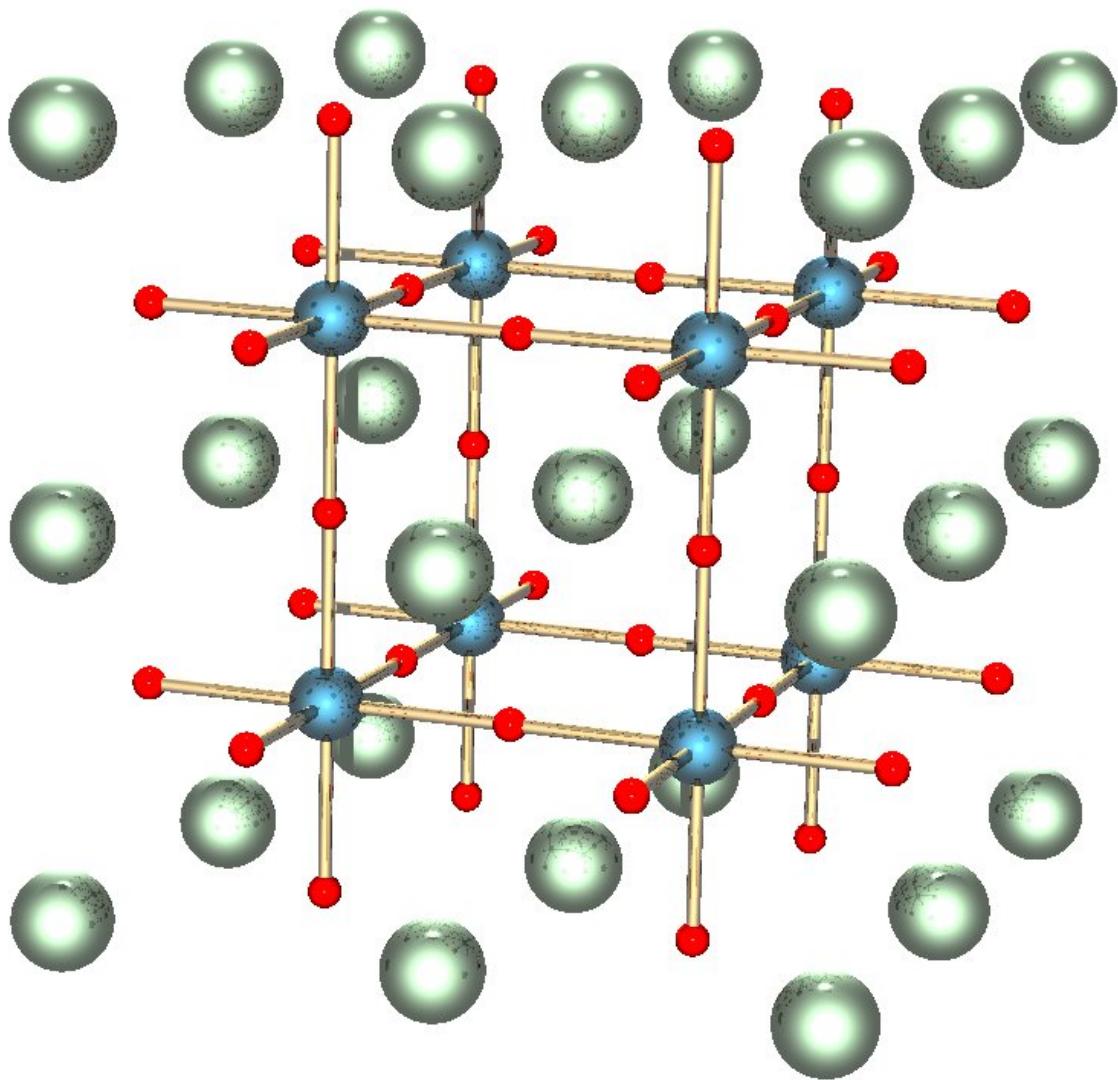


Figure 1.14: The materials I studied have the perovskite crystal structure. Perovskites are oxides with the chemical formula ABO_3 . The green spheres represent the A-site atoms, the blue spheres represent the B-site atoms, and the red spheres represent oxygen atoms. For many perovskites, the interesting action takes place on the B-site atoms and depends sensitively on the chemical bonding between the B-site atom and the six oxygen atoms that surround it. In particular, the magnetism of insulating magnetic perovskites often comes from the superexchange interaction through oxygen atoms in each B-O-B chain. Perovskite picture in the public domain, released by user Cadmium at English Wikipedia.

Double exchange

Double exchange is an interesting mechanism that takes place between mixed-valence $3d$ ions with both localized and itinerant electrons. A classic example are the manganese perovskites, such as $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, which has a mixture of Mn^{3+} and Mn^{4+} ions.

1.4.6 Spintronics

Digital electronics are commonplace in modern life, and becoming more commonplace with each passing year. They have transformed the workplace, increasing productivity so much that some economists have deemed it the third industrial revolution.⁷⁷[133]

Digital electronics work by encoding information in the position of electrons.⁷⁸ Today, the best and cheapest way to shuttle electrons around is inside of conducting material (i.e., wires). Unfortunately, moving electrons through a material costs energy each time an electron collides with the material's atomic lattice.^{79,80} This fundamental, nearly inescapable energy cost is why electronics consume so much energy. Alternative, lossless materials like superconductors or topological insulators or even vacuums are a possible way to circumvent this problem of electron scattering, but

⁷⁷However, economists do not entirely agree on what makes an industrial revolution an industrial revolution. I have seen economists suggest as many as six independent industrial revolutions[131] and as few as zero,[132] though one, two, and three seem to be the commonest counts.

⁷⁸Annoyingly, at least to me, many scientists working on spintronics introduce their research carelessly by saying that spintronics encodes information in the spin of the electron while electronics, in contrast, uses charge. But this is ridiculous—the charge of the electron is constant! What isn't constant is the wavefunction of the electron, and the wavefunction is factored into a spatial component and a spin component. Therefore, I think it's natural to say that electronics encodes information in the spatial positions of electrons (leading to voltage and current) whereas spintronics encodes information in their spins (leading to magnetism). Of course, I'm not being totally fair. A more macroscopic view might say that electronics exploits charge density whereas spintronics exploits spin density. And in this macroscopic view based on density, then the spin vs. charge dichotomy is more defensible.

⁷⁹Incidentally, this fundamental property of electrical conduction is why voltage is needed to sustain current.

⁸⁰Also, this explains why transmission lines are operated at high voltages and made of metal. By delivering high voltage electrons, you need to send fewer for the same amount of power, and fewer electrons sent means fewer collisions which means less power loss. Secondly, by making power lines out of conductive metal, collisions are less frequent (for a fixed current). That said, in real power line design there are other constraints too, like cost and weight, which favor aluminum over its more conductive cousins, such as copper, silver, and gold.

none have easy paths to success. So instead, another plan is to start using electron spin instead of electron position to encode information. This avoids the central power loss issue of electronics because it avoids the problem of electron scattering.

For these reasons, spintronics has the potential to be more energy efficient than electronics. However, we're a long way from a world of magnet-based computers. And even if we do get there, electronics won't be over. We'll still need ways to interface magnetic components with electrical components as way to bridge new technology with old.

Information can be encoded in many ways. In transistors, information is encoded by either many or few electrons in the transistor gate (or equivalently, by any property that is concomitantly controlled by the gate electrons). Magnets, on the other hand, store information in very different ways. Magnets are especially well suited to encoding binary information - single electrons naturally have two spin states. However, configurations of many spins can encode information in other ways too (domain wall positions, skyrmions, vortex polarity, resonance etc.).

Today's most well-known magnetic technology is the hard drive. To convert an electric signal to a magnetic signal, it uses a small electromagnet. To convert a magnetic signal back to an electric signal, it uses tunnel magnetoresistance.

Another magnetic technology, still on the horizon, is MRAM (magnetic random access memory). In MRAM, electric signals are usually converted to magnetic signals by spin transfer torque. Converting a magnetic signal back to an electric signal uses tunnel magnetoresistance, just like a hard drive.

Right now, the best way to turn a magnetic signal into an electric signal seems to be tunnel magnetoresistance, in which flipping the magnetization of a material can scale its resistance by up to a factor of 6 or so at room temperature. Going the other way, the best way to turn an electric signal to a magnetic signal is probably spin transfer torque, although the inverse spin hall effect has potential too. But can we do better?

Ferromagnetism needs two ingredients: spins and exchange (and the exchange needs to be stronger than destabilizing thermal noise). So if you want to turn ferromagnetism on and off, you need to turn either spin on/off or exchange on/off.⁸¹

The most common approach is to use an electric field to affect exchange (or, how exchange competes with bandwidth). Ferroelectric materials can change their crystal structure in response to an electric field, and a change in crystal structure can lead to a change in the strength of the exchange interaction.

You can classify technologies into three functional categories: transportation, storage, transformation (you can also include production as a subset of transformation). This applies to digital information technology reasonably well. Production of information (from the system's perspective)

⁸¹You cannot really turn exchange off, but you can make it weak enough so that the ordering it would induce is too weak to survive thermal noise.

comes from input devices like keyboards or sensors. Transportation of information occurs along wires and fiber optic cables. Storage of information occurs in hard drives and RAM. And information is transformed in processors built of transistors.

Where can spin be used best? Let's look at each category one by one, starting with transportation.

What about transportation? For transportation, there aren't many technological options. Wires and fiber optics seem best (and in the sense that they harness electromagnetic waves, they are basically the same, just operating at different frequencies with different dielectric losses). There have been ideas of using nanomagnets in a cascading domino configuration, but in my honest opinion the reliability engineering seems totally impractical without wild jumps in our fabrication abilities. Over shorter distances, spin currents can carry spins encoding information.

How about storage? Magnets are already used in hard drives, and possibly MRAM. With both of these, the cost of production is relatively fixed, meaning that the cost per bit varies inversely with the density. So the question is, how dense can these go? With hard drives, as far as I can tell, the limits seem to be driven the size of write head, read head, and magnetic media. Assuming the first two can be made arbitrarily small, the third will limit you, and it has a limit based on how stable you want your memory to be. However, if you can keep boosting your coercivity, you can keep shrinking the bits (though high coercivity might require new writing technologies like HAMR). Also if bits can refreshed as they are in RAM, then you might also be able to go smaller (assuming the relaxation process is nonlinear).

Really though, the grand prize lies in information transformation. When people complain about the high power of electronics holding back computer chips, they are talking about electrical transistors and the subthreshold slope problem. Here, spintronics may be the next evolution. The most famous proposal is the SpinFET, proposed in 1990 by Datta and Das.[\[134\]](#) But 25 years later, and we're still far from making them. What else might be out there? Really it all depends on how we represent information with spins and how we get those spins to interact with each other in a low noise way. But it seems safe to assume that materials that can convert magnetism to electricity and vice versa will be essential building blocks.

1.5 Connection to my research

Although my introduction has spent time broadly examining the technological landscape for spintronic devices, my actual research has been focused at a much lower level. My goal has been to help understand the fundamental physics and materials science of complex oxides, a class of materials which exhibits many correlated-electron phenomena not seen in *sp*-band semiconductors. The hope is that by understanding these complex phenomena, we can provide the asphalt to pave the way to a superior spintronic future.

The rest of this dissertation is dedicated to discussing my specific efforts in detail. Chapter 2 will describe the major experimental tools that enabled me to deposit thin films and then measure their crystal structures, elemental compositions, surface topography, electrical properties, and magnetic properties. Chapter 3 will detail my efforts to understand the conductivity and magnetoresistance of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface and modify it through the use of rare-earth dopants. Chapter 4 will then detail my efforts to understand the magnetism of cobalt perovskite thin films, and in particular how I used SQUID magnetometry and X-ray magnetic circular dichroism, in combination with X-ray diffraction, to measure how chemical pressure and epitaxial strain can affect the magnetism of these materials. Finally, Chapter 5 will summarize my major results and present some thoughts on the future.

Chapter 2

Experimental techniques

This chapter is organized into two parts: first, sections 2.1 and 2.2 cover how I synthesized the materials in my research, and second, sections 2.3 and beyond cover how I characterized the materials in my research.

2.1 An overview of thin film deposition techniques

We are surrounded by technologies that rely on thin film deposition. Thin films are used in industries and applications as diverse as semiconductors (computer chips, hard drives, solar cells, light-emitting diodes), optics (mirrors, antireflective coatings), automotive/aerospace (paints, other protective coatings), food (food-safe coatings in cans and bags), and even pharmaceuticals (thin-film drug delivery[135]).

The ability to deposit materials in thin layers has many advantages. Products can be made thinner, lighter, and cheaper. But the truly exciting advantage of thin film deposition arises when the thickness of a material approaches the length scale of relevant materials physics, such as the wavelength of light (100 nm–1000 nm), the wavelength of electrons (1 nm–10 nm), the diffusion length of electrons, the mean free path of electrons (1 nm–100 nm), or the strain relaxation length (1 nm–100 nm). On these scales, thin film deposition can be used to unlock entirely new materials properties.

Dozens of thin film deposition techniques have been invented over the past century to accommodate a diverse set of materials and needs. These techniques can be classified along a number of dimensions, such as whether the technique is physical or chemical, whether it uses gases or liquids or solids, or whether the atoms arrive at high energy or low energy. One possible classification tree is displayed below:

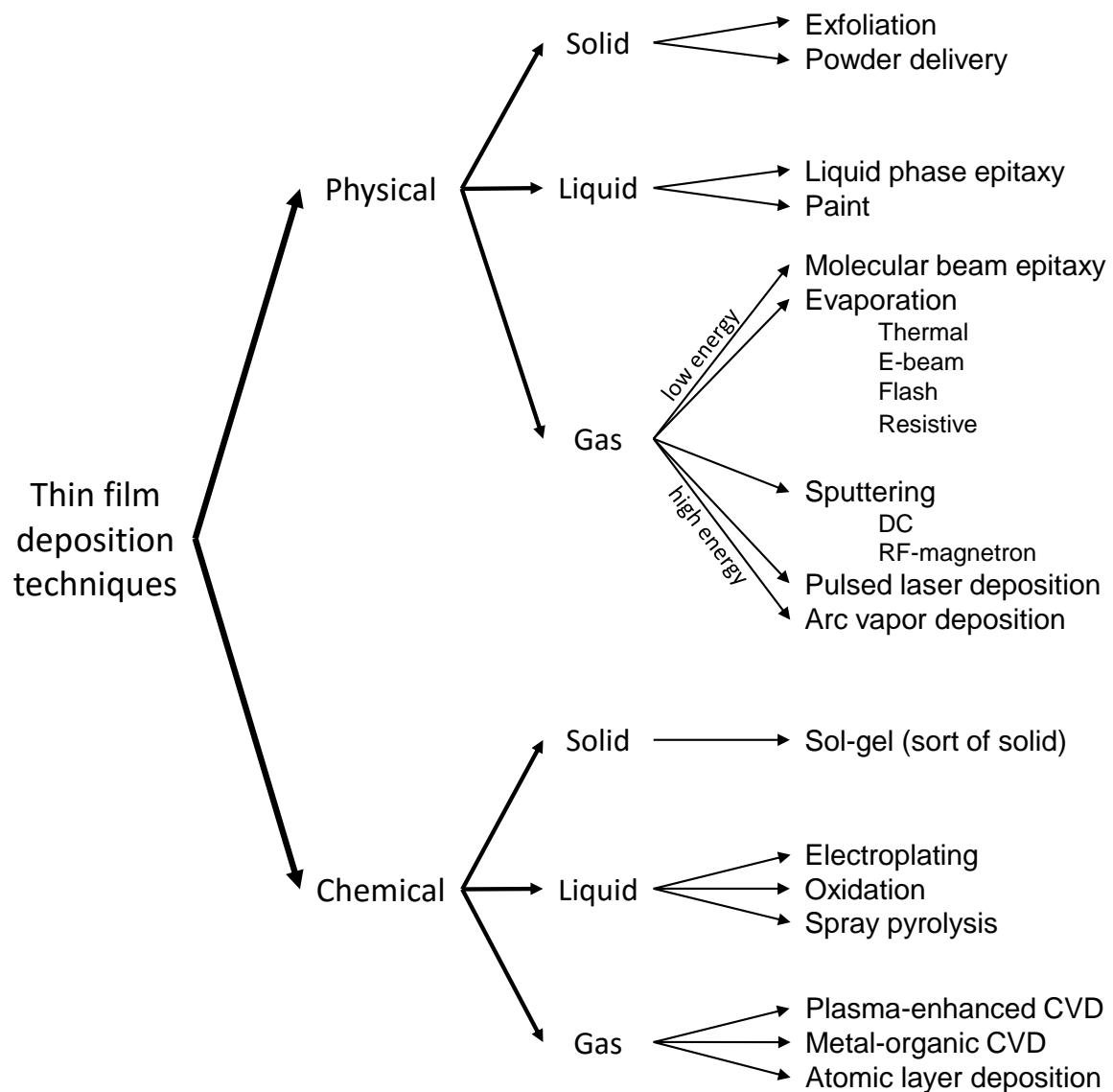


Figure 2.1: A hierarchical classification of thin film deposition techniques. This tree is not even close to comprehensive (and may reflect my experience with and bias toward physical vapor deposition), but it illustrates the wide variety of methods that have been invented to move a bunch of atoms onto a flat surface.

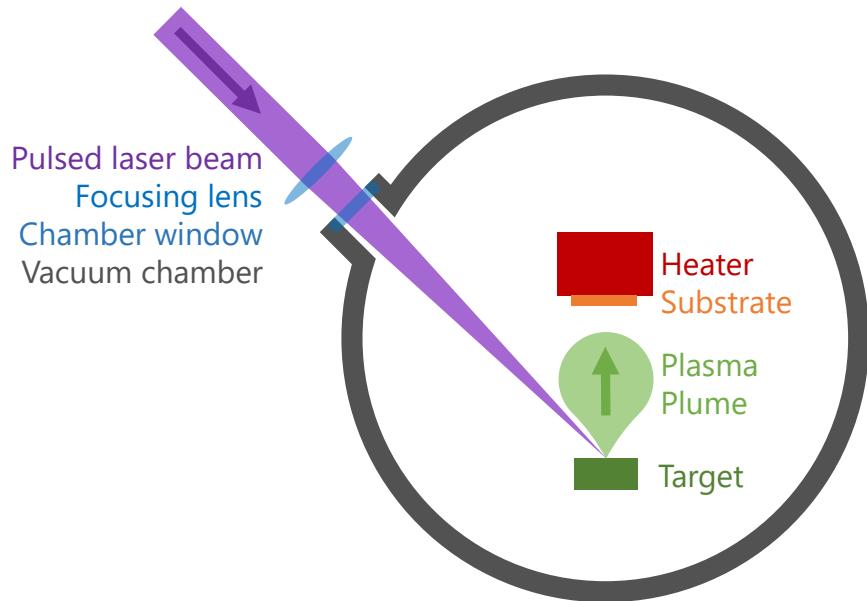


Figure 2.2: A simple diagram of pulsed laser deposition.¹ In reality, a vacuum chamber for pulsed laser deposition may be outfitted with many other parts, such as a turbomolecular pump, a backing roughing pump, pump valve controls, gas inlets, gas flow controls, capacitive pressure sensors, ion gauges, thermocouples, a heater controller/power supply, a water cooling system, a target rotation system, a substrate mounting system, a *in situ* reflection high-energy electron diffractometer system, a laser-synchronized particulate fan, or a load lock.

In my research, I synthesized thin films with a single one of these techniques: pulsed laser deposition. (However, for lithographic patterning and wire contacts, I also occasionally used e-beam evaporation, sputtering, and spin coating.)

2.2 Thin films were synthesized by pulsed laser deposition

Pulsed laser deposition, sometimes abbreviated PLD, is a thin film deposition technique that rose to prominence in the late 80s and early 90s as a simple but effective method for depositing high-temperature superconductors, which are normally difficult to deposit because of their complex chemical compositions.[136, 137, 138] Though its use today remains mostly confined to academic research, pulsed laser deposition has become a popular technique for synthesizing a wide variety of oxide materials, as well as other chalcogenide and nitride materials. My research in particular has focused on depositing thin films of the oxides LaAlO_3 and PrCoO_3 (detailed in Chapters 3 and 4, respectively).

¹This figure may look plagiarized from the Wikipedia article on pulsed laser deposition, but in fact I authored the figure in that article. So I suppose it's self-plagiarized.

Pulsed laser deposition works as follows: high-power laser pulses are fired at a target material, vaporizing its surface. As the vapor expands outward, some of it condenses on a nearby substrate material, forming a thin film on its surface. It's that simple! A single laser pulse will deposit only a fraction of a monolayer, making it possible to control the thickness of thin films with atomic precision.

In my lab, which uses a typical setup, the laser pulses were generated by a KrF excimer laser.² KrF produces ultraviolet light with a wavelength of 248 nm (5 eV), which lies in an absorptive sweet spot that's energetic enough to ablate many solid materials³ but not so energetic as to be absorbed by oxygen in the air.⁴ Each pulse has a duration of about 30 nanoseconds and a total energy of up to 1 joule⁵, meaning that the instantaneous power reaches a tremendous 40 MW (enough to power a small town), all of which is focused down onto a 10 mm^2 spot. However, since the pulses only last 30 nanoseconds and are fired at a rate of 1 Hz–10 Hz, the *average* power flux ends up being a modest 1 W/cm^2 – 10 W/cm^2 (about 10–100 times as bright as a sunny afternoon).

Compared with other techniques, such as those classified in Figure 2.1, pulsed laser deposition has a unique combinations of advantages and disadvantages that define its technological niche.

2.2.1 Advantages of pulsed laser deposition

In my mind, pulsed laser deposition has four major advantages: it's good for multi-element films, it's compatible with many materials, it's easy to set up, and it's scalable (both up and down).

It can deposit films with complex stoichiometry

The primary advantage of pulsed laser deposition is that it can easily deposit materials with complex stoichiometries, such as the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Unlike thermal evaporation, which due to its gentle heating evaporates different elements at different rates, the violent power of the laser pulse ablates every element roughly equally. So if you can synthesize a solid chunk of some material to use as the target, then pulsed laser deposition can stoichiometrically transfer the material from target to substrate. (Of course, the full story is more complicated, but that's the gist.)

²Incidentally, excimer lasers are also used in laser eye surgery, in which case the target material being ablated is the lens of your eyeball.

³To be specific, insulators with band gaps less than 5 eV (otherwise the light will be transmitted) or metals with plasma frequencies less than 5 eV (otherwise the light will be reflected).

⁴Absorption by air is not a deal-breaker, but constructing a vacuum tube for your laser beam adds extra cost and complexity, which often aren't worth it.

⁵For scale, 1 joule is the energy it takes to lift a 100-gram banana up by 1 meter.

It's versatile

A second advantage of pulsed laser deposition is its versatility. Because laser ablation is such a physically violent process, it is relatively insensitive to the chemistry of the target and the chemistry of the background gas. For this reason, pulsed laser deposition is compatible with a wide range of materials, a wide range of background gases, and a wide range of gas pressures. Versatility is especially advantageous in research settings, where scientists may want to explore a variety of materials on the back of only a single investment.

It's easy to set up

A third factor in the popularity of pulsed laser deposition is that it's relatively straightforward to set up. The parts are common, the setup is somewhat modular, and the deposition conditions take less time to optimize than with molecular beam epitaxy or other multi-source techniques.

It's scalable

Lastly, pulsed laser deposition is scalable. Not only can it be scaled *up* for mass production,[139]⁶ it can also be scaled *down* for exploratory research. Unlike some techniques that require large material targets for uniformity (such as sputtering), pulsed laser deposition can use targets as small as a square centimeter.

2.2.2 Disadvantages of pulsed laser deposition

Of course, pulsed laser deposition is not perfect. Indeed, it has significant disadvantages that have prevented it from becoming a mainstream manufacturing method.

It can deposit particulates

Although high-energy laser pulses are ideal for stoichiometrically blasting elements with equal efficiency, this energetic blasting comes with an unfortunate downside: nonuniform subsurface boiling can launch small chunks of material from the target surface, which then land on the substrate, resulting in a film dotted with small particulates. Although techniques have been developed to ameliorate the problem of particulates (e.g., dual laser,[140] fan shutters, high-uniformity targets), they remain a challenging downside of the technique, particularly for manufacturing complex devices, which require high film uniformity.

⁶That being said, just because it can be scaled up, doesn't mean it will be. Many barriers, primarily cost, make pulsed laser deposition unattractive for commercial applications.

It's relatively expensive

A second major downside of pulsed deposition is its cost. Excimer lasers are not cheap, and neither are their halogen gas mixtures, which must be replaced regularly. Because fluorine gas is so extremely reactive, it continually reacts with other elements, causing the concentration of fluorine to drop over time and the concentration of fluorine-compound impurities to rise over time. My lab's laser, which is used far less frequently than it would be in a manufacturing setup, requires a fresh gas fill every three weeks.

⁷

It can be difficult to go from good to great

The ease and versatility of pulsed laser deposition make it great for prototyping and exploring new materials. However, for high volume-manufacturing, these attributes have lower value. What matters there is growing materials with high quality at high volume, consistently. And unfortunately, while pulsed laser deposition is great at growing decent films right away, these films are not always high quality. Stoichiometric transfer, the great advantage of pulsed laser deposition, is never perfect in reality, especially at higher gas pressures, where different elements will be scattered differently by collisions with the background gas.^[141] Fine-tuning the deposition conditions for very high-quality growths can be just as time-consuming as for alternative deposition techniques, like sputtering or molecular beam epitaxy. So while pulsed laser deposition may have an advantage in its ability to deposit good films quickly, it has considerably less advantage in its ability to deposit very high-quality films. (To be clear, I am not saying pulsed laser deposition has a disadvantage in high-quality films, just that its edge fades. Anyway, the meaning of “high-quality” is nebulous, so don’t place too much confidence in this point always being true. I just hope to convey the general idea that the materials versatility of pulsed laser deposition is valuable for exploration, but not so much for manufacturing.)

2.2.3 The history of pulsed laser deposition

Of all the technology needed for pulsed laser deposition, the laser is the most critical piece. For this reason, the history of pulsed laser deposition is closely entwined with the the history of the

⁷The price of excimer laser gas has skyrocketed over the past few years due to the unrest in Ukraine caused by Russia’s military incursions. Premixed gas for our laser has gone from costing about \$1,000 per cylinder to \$10,000 per cylinder. For reasons unbeknownst to me, Ukraine was the world’s leading supplier of neon, the primary buffer gas mixed in with our KrF. Since neon is distilled straight from the atmosphere, it seems odd that global production would be so geographically concentrated, but it is. Perhaps it is a story of cheap energy, cheap labor, economies of scale, experience curve progress, and path dependence.



Figure 2.3: My lab's excimer laser, a Coherent LPX Pro 305F, used to make many of the thin films in this dissertation.

laser (and specifically pulsed UV lasers based on excimers). However, even though the foundational technology had been invented by the mid 1970s, it wasn't until the high-temperature superconductor craze of the late 80s that pulsed laser deposition took off as a popular research technique. Here's a brief timeline⁸ of key events in the development of pulsed laser deposition:

- 1905: Photoelectric effect explained with light quanta (by Einstein)[142]
- 1916: Stimulated emission theoretically proposed (by Einstein)[143]
- 1953: Maser invented (by Gordon, Zeiger, and Townes)[144, 145]
- 1960: Laser invented (by Maiman)[146]
- 1962: Laser used to ablate material (by Breck and Cross)[147]
- 1965: Laser used to ablate material and deposit it as a thin film (by Smith and Turner)[148]
- 1970: Ultraviolet excimer laser invented[149]⁹
- 1975: Noble gas-halide excimer laser invented
- 1987: Thin films of the superconductor YBCO deposited by pulsed laser deposition, kicking off the technique's growth in popularity[150]

2.2.4 The detailed stages of pulsed laser deposition

Although the basic setup of pulsed laser deposition is conceptually simple, its dynamics are quite complex. The absorption of so much energy in such a tiny amount of time leads to complicated

⁸Surprisingly, if you try to check the years on this timeline, you'll find that authoritative-looking sources conflict with one another. For example, both 1916 and 1917 are claimed for Einstein's theory of stimulated emission. And both 1953 and 1954 are claimed for Townes's invention of the maser. I suspect some of the discrepancies may arise when there are different dates for something first being invented versus first being published versus first being published in an official journal versus first being published in an official English-language journal. When secondary and tertiary sources were inconsistent, I tried hard to track down primary sources to identify the most likely truth. However, I may not have found the true year in all cases, so be aware that these dates, and others like them, may be off by a year or two.

⁹Technically, the excimer laser ought to be called the exciplex loser. Though early designs were based on excited dimers, or 'excimers,' today's designs are actually based on excited complexes, which we might call 'exciplexes.' Furthermore, because these devices are better described as *oscillators* rather than *amplifiers*, they should really be called losers rather than lasers. But history is history and that's the name we have.

non-equilibrium evaporation that is difficult to quantitatively model. The process of pulsed laser deposition can be divided into separate stages for analysis. There is no single correct segmentation of the process, and different authors choose different schemes, implicitly emphasizing some steps over others. My personal preference is to divide the process into four stages: light absorption, initial one-dimensional expansion of the plasma plume, continued three-dimensional expansion of the plasma plume, and growth of the thin film.[151]

Absorption and ablation

As the ultraviolet laser pulse hits the target material, electrons are accelerated by the pulse's oscillating electric field, gaining enough kinetic energy to break their chemical bonds or escape their atoms entirely.¹⁰ Very quickly, the top 10 nm or so¹¹ of the target material is vaporized into a hot glowing plasma, comprising a messy mixture of electrons, ions, neutral atoms, and larger clumps and complexes. Even after leaving the surface of the target material, the plasma will continue to absorb energy from the laser for the duration of the pulse.

The shallow ablation crater left behind by the laser pulse remains hot for a brief period of time, so to give the spot time to cool the target is usually rotated at a constant speed between pulses so that the next pulse will strike a new location. Rotating the target also has the advantage of averaging over any inhomogeneity in the target's composition.

One concern during this stage is that some elements will absorb more laser light than other elements, leading to selective deposition of those elements over others. This concern regards both the target material, where more absorptive elements will be vaporized first, and the plume, where more absorptive elements will be ionized first. However, as long as the laser pulse is sufficiently energetic to vaporize every element for many atomic layers, there should be little selectivity in vaporization. And in the plume, as long as it is energetic enough, its free electrons will exchange energy between ions, helping them stay in quasi-equilibrium with one another. These concerns are why pulsed laser deposition requires such a high power pulse and why pulsed laser deposition is so good at depositing multi-element materials.

¹⁰The details of this absorption process are complex and material dependent. Not only are there the typical considerations of direct and indirect band structures, but because of the high concentration of power, normally rare processes like multi-photon absorption or avalanche ionization must be considered as well.

¹¹Again, the exact number depends on the material (principally the material's cohesive binding energy) as well as the laser beam's power flux, but generally materials are ablated at a rate of 1 nm–100 nm per pulse.

Initial one-dimensional expansion of the plasma plume

Initially, the plasma plume is very hot and dense, with pressures as high as 10 atmospheres (despite being in a vacuum chamber).[\[152\]](#) This high pressure propels the plasma plume at high speed, pushing it from the surface of the target material in a miniature explosion. At this stage, the plasma plume is far from thermal equilibrium, and rapidly expands away from the target material.

Continued three-dimensional expansion of the plasma plume

As the plasma plume continues to expand outward, a number of things change. The plume's shape evolves as its internal pressure pushes outward in all directions rather than just off of the target material. It also starts to thermally equilibrate internally, leaving lighter atoms with higher velocity, which can again lead to off-stoichiometric film composition. At this stage, the plume also loses energy, both by radiating it away and by colliding with the background gas (if any). As the plume loses energy to the background gas, its expansion becomes more diffusive and less directional, which also changes the plume shape. Many of these details have been investigated experimentally and theoretically, but again I emphasize that this process is complex, filled with non-equilibrium shockwaves and collisions and other dynamics on a fine scale, which are challenging to model accurately.

Growth of the thin film

Once the cooling plasma arrives at the crystal substrate, a number of things can happen. Some atoms will bounce off of the substrate, some atoms will stick to the substrate, and some high-energy atoms may even sputter the substrate. Atoms that stick to the substrate will often have enough energy to continue moving atop the surface, especially if the substrate is heated, which it often is. The structure zone model explains how different combinations of atom arrival energy and substrate temperature result in different grain structure.[\[153\]](#) Another factor that influences the growth of thin films are the surface energies of the thin-film material (and substrate). If surface energies are high and surface mobility is high, the thin film will grow in 2D layer-by-layer mode, minimizing the surface area of the substrate-film system (Frank-van der Merwe growth). On the other hand, if surface mobility is low or if the substrate surface energy is low, then the film will grow in 3D islands or droplets that eventually merge as they grow larger (Volmer-Weber growth). And third, there can also be mixed growth (Stranski-Krastanov growth), where the film grows in 2D layers for the first few monolayers and after that continues to grow in 3D islands. Growing high-quality crystalline thin films often takes quite a bit of skill, effort, and luck to balance all of these factors.[\[154\]](#)

2.2.5 Parameters to control (and their effects)

Target material

The choice of target material is often driven by scientific considerations. However, any material must be compatible with pulsed laser deposition. This means the target material must have high ultraviolet absorption, with no band gaps over 5 eV (resulting in transmission) and no plasma frequencies above 5 eV (resulting in reflection). Furthermore, the target should not have air pockets (which can expand below the surface, causing large particulates to be ejected) and must be relatively homogeneous (so each plume comes out the same). The target material must be vacuum compatible (so nothing that boils or sublimates at low pressure). And ideally the target would have low thermal conductivity, so that the ablating laser pulse is absorbed in a thin, concentrated spot. For these reasons, powder-pressed ceramic targets, such as those used in my research, work great with pulsed laser deposition.

Substrate

The choice of crystal substrate is also important. The substrate can heavily influence the way that the thin film grows. For high-quality crystalline growth, a substrate should be smooth, vacuum-compatible, resistant to sputtering, stable at high temperatures, and possess a crystal structure that is compatible with the thin-film material. Often a crystal structure is chosen to specifically alter the thin film's crystal structure through epitaxial strain or octahedral rotations or similar structural effects.

Heater temperature

The substrate temperature is another factor that must be traded off. Higher temperatures are good for increasing the surface mobility of deposited atoms, helping them find an equilibrium crystal structure. However, going too high in temperature can cause a number of problems. It can cause the thin film or substrate to sublime, resulting in poor stoichiometry. It can also be difficult for practical reasons like overheating nearby equipment parts. And sometimes the point of thin-film growth is to explicitly avoid equilibrium phases of the material.

Gas pressure (affects oxygenation, stoichiometry, energy of deposited particles)

When depositing oxides, the pressure of background oxygen gas is very important. If the pressure is too low, the resulting thin films may end up oxygen deficient, which can donate electrons in semiconducting materials. Low pressure is also associated with increased sputtering, since atoms are not slowed before landing on the substrate surface. However, if the pressure is too high, the gas will rob the plume of energy before it reaches the substrate surface, making it less likely for atoms to lock in to their preferred crystal positions. Furthermore, a high background gas pressure will

selectively filter the light and heavy atoms traveling through it, resulting in poor cation stoichiometry. Sometimes multiple background gases are used to independently tune oxygen stoichiometry and background gas effects. And if oxygen stoichiometry or background gas pressure is really a problem, sometimes highly reactive ozone gas may be used instead of O₂. One additional consideration is that low gas pressure makes it easier to use *in situ* RHEED monitoring during thin film growth.¹²

Target-substrate distance

The target-substrate distance is another parameter that must be chosen for pulsed laser deposition. Its effects are related those of gas pressure, because the further the substrate is from the target, the more background gas it must travel through. Distances that are too long result in poor cation stoichiometry (from mass-dependent scattering in the gas) and worse crystal growth (from arriving atoms having less surface energy). On the other hand, distances that are too short may result in sputtering of the substrate (from high energy arrivals). The target-substrate distance is also constrained by geometry—the substrate must be far enough back so that the excimer laser pulse has a clear path to the target.

Laser wavelength

Laser wavelength is another parameter with trade-offs in either direction. Ideally, shorter wavelengths are better because shorter wavelengths are better absorbed. However, if the wavelength is too short, air will absorb the laser energy before it even reaches the vacuum chamber. For this reason, as well as chemical and economic reasons, typical pulsed laser deposition wavelengths are in the range of 200 nm to 300 nm. In particular, my lab uses a 248-nm KrF excimer laser.

Laser pulse energy

Laser pulse energy is another important parameter for pulsed laser deposition. If the laser pulse energy is too high, the plume will sputter the substrate and film, making them rougher and worsening stoichiometry. However, if the laser pulse energy is too low, the target may be evaporated rather than ablated, again resulting in poor cation stoichiometry.

¹²For the unfamiliar, RHEED stands for reflection high-energy electron diffraction, a low-angle electron diffraction technique. Watching the RHEED diffraction pattern during deposition can reveal how a thin film's surface structure changes as it grows. For layer-by-layer growths, scientists can count the number of atomic layers deposited by tracking oscillations in RHEED signal intensity. As with X-ray diffraction, it is often most useful to reason about RHEED by thinking in terms of reciprocal space. For RHEED, the reciprocal lattice can be thought of as a two-dimensional grid of columns that are intersected by a sphere with radius equal to the inverse electron radius. Their intersection produces the typical arc of spots seen in RHEED patterns.

Laser pulse frequency

The frequency of laser pulses (not to be confused the frequency of the laser light itself) typically ranges from 1 Hz–10 Hz. Faster rates of deposition allow films to be grown in less time, but at the cost of giving the target less time to cool and the surface atoms less time to migrate to their ideal crystalline positions.

Laser spot size

The laser spot size is a less important parameter, often going unreported in the literature. However, it still has an important impact on growth. The size and shape of the spot will affect the size and shape of the plume. Furthermore, the homogeneous a spot can be the better. This is why a large spot, which has a higher ratio of area to perimeter, is better than a small spot, all things equal. However, larger spots require larger lasers for a fixed energy density, so it gets expensive to make it too large.

Searching parameter space

When growing new materials it's often not clear which growth conditions to use. Therefore many scientific projects begin with by exploring the growth parameter space of the desired material. Even recipes in the published literature must often be retuned for specific growth chambers, which have some degree of idiosyncrasy. This exploration of parameter space is not a random walk, since measurements of film quality after growth will usually give clues on how to improve future growths. One important skill is decided when a recipe is ‘good enough.’ It is never possible to grow a perfect film, and often the parameter trade-offs involve minimizing two bad outcomes rather than entirely eliminating them.

2.3 Measurement introduction

Measurement lies at the heart of science. Without measurement, there is no way to learn, no way to test hypotheses, no way to generate data.

After we make our materials, it's important to measure them. The purpose of this is not only to test our theories, but also to test whether the material we made was the material we were trying to make.

What we care about can be divided into different categories. Often we want to know the structure of our material. We ask questions like: Is it crystalline? If so, what is its crystal structure? How homogeneous is the crystal structure? Is the material smooth? Is it rough? Is the roughness random or ordered?

We care too about chemical information. Does the material have the right ratio of atomic ingredients? What sites do they sit on in the crystal structure? Are there any unintended chemical impurities?

Often we're also interested in the magnetic properties of our materials. We ask questions like: Is the material magnetically ordered? If so, below what temperature? How strong is the material's magnetism? What are the coercive fields of the magnetism, if any? How does the magnetism change with temperature? How does it change with applied magnetic field? What elements are responsible for the magnetism? Is the magnetism from electrons' spin, local orbits, or free motion?

And often we're interested in the electronic properties of our materials. We ask questions like: Do they conduct electricity? What type of carriers conduct the electricity? How dense are these carrier particles? Are they arranged in two dimensions or three? How does the conductivity change with temperature? What defects scatter the carriers?

Next, I will talk in detail about the techniques I've employed to answer these important questions.

2.4 Crystal structure was measured by X-ray diffraction

X-ray diffraction is one of the most useful experimental techniques in condensed matter physics. By measuring the diffraction pattern of x-rays reflecting off of a material,¹³ the arrangement of atoms inside the material can be inferred. In my research on thin films of complex oxides, X-ray diffraction is particularly useful for measuring how the crystal structure of the thin film is affected by its substrate.

This section will discuss the general idea behind X-ray diffraction, the particular scans I employed, and some second-order insights not always found in introductory material. For a comprehensive introduction to X-ray diffraction, you should read a textbook rather than my dissertation. I hear that Cullity's *Elements of X-ray Diffraction* is quite good.[155]

2.4.1 The general idea behind X-ray diffraction

The goal of X-ray diffraction is to understand the crystalline packing of atoms in a material. X-ray diffraction can tell you the crystal's symmetry, its atomic spacing, its thickness, and more.

The general idea of X-ray diffraction is to shoot a beam of X-rays into a material, measure the X-rays that come out (the intensity at different angles), and use that measurement to draw inferences about the material's crystal structure.

An X-ray diffraction scan requires many parameters to be chosen. Relative to the sample, the incoming X-ray beam must aim at a position in space (three dimensions of control), at a particular

¹³The definitional distinction between diffraction, reflection, and refraction is not all that important in my mind. All of them arise as a consequence of light's wave nature.



Figure 2.4: A PANalytical X'Pert PRO X-ray diffractometer was used to generate some of the data in this dissertation. The left side of the figure shows its exterior and the right side shows its interior.

angle (three more dimensions to control), with a particular wavelength/spectrum, intensity, dispersion, spot width, and spot length (even more parameters to control). In addition to the incoming beam, the detector's settings must be chosen from a variety of angles with a choice of filters and collimators and slits.

2.4.2 Why X-rays?

X-rays, with wavelengths between 0.01 nm and 10 nm,¹⁴ are especially well-suited to crystal diffraction. Longer-wavelength radiation is too blurry to easily resolve the atomic diffraction pattern, and shorter-wavelength radiation is expensive to produce and interacts too strongly with matter.

2.4.3 Reciprocal space is the most important paradigm of X-ray diffraction

Although the math works out in any basis, imagining the reciprocal basis makes it easier to visualize the conditions necessary for constructive interference in X-ray diffraction off of a crystal.¹⁵ In real space, a crystal can be described by a lattice (a repeating array) and a basis (the set of atoms that

¹⁴Or, in units of energy: 100 eV to 100 keV. Or, in units of frequency: 3×10^{16} Hz to 3×10^{19} Hz.

¹⁵The reason the reciprocal basis works so naturally is that both the crystal and the X-ray are entities that repeat in space. Therefore, the mathematics is simplified when working with spatial frequencies.

are repeated at each point in the array). If you imagine shooting X-rays into this real-space crystal, it's not immediately clear what pattern of X-rays should diffract out. However, if you imagine the reciprocal space of the lattice, which is constructed by Fourier transforming the 3D real-space lattice into three dimensions with units of reciprocal length (or spatial frequency), then it becomes much easier to picture constructive diffraction conditions. Constructive diffraction will occur only when the head of the scattered beam vector lands on a point in reciprocal space. Mathematically this is described by the Laue equations:[156]

$$\frac{2\pi}{\lambda} (\vec{k}' - \vec{k}) = \vec{g}_{hkl} \quad (2.1)$$

When the equation is true (or close to true), X-ray intensity will be detected, and when the equation is false, no (or very little) X-ray intensity will be detected. λ is the wavelength of the X-rays, \vec{k}' is the scattered beam wavevector, \vec{k} is the incident beam wavevector, and \vec{g}_{hkl} is the reciprocal lattice vector indexed by h , k , and l . As an example, Figures 2.5 and 2.6 show the angles needed to observe the $\bar{1}03$ diffraction peak, for a crystal structure and X-ray wavelength similar to those in my research.

2.4.4 Beware of two common X-ray diffraction misconceptions

Although you probably don't believe these yourself, at this point I wish to emphasize two common misconceptions about X-ray diffraction that are almost true (and therefore make good conceptual shortcuts) but are not entirely true (and therefore should be treated critically when coming up with new X-ray experiments).

MYTH: A periodic atomic structure is necessary for X-ray diffraction

Because time evolution is unitary, any distinct final state can be, in principle, tracked back to its initial starting state. Therefore, diffraction off of any object, crystalline or not, is possible in principle. Even a single molecule can be imaged with diffraction. So it's not true that a periodic atomic structure is necessary for X-ray diffraction.

However, this misconception exists for a reason: it's *mostly* true. Although technically not required for X-ray diffraction, a periodic atomic structure does makes X-ray diffraction much, much easier. Because a crystal has a periodic structure, X-ray diffraction off of a crystal is concentrated in small solid angles known as Bragg peaks. And because the intensity scales as the square of the amplitude,¹⁶ concentrating the amplitude into Bragg peaks quadratically concentrates the intensity, making the diffraction pattern much easier to measure and resolve.

¹⁶Why intensity equals the amplitude squared is a deep and fundamental problem in physics. Although explanations have been proposed, none have gained popular acceptance.[157, 158]

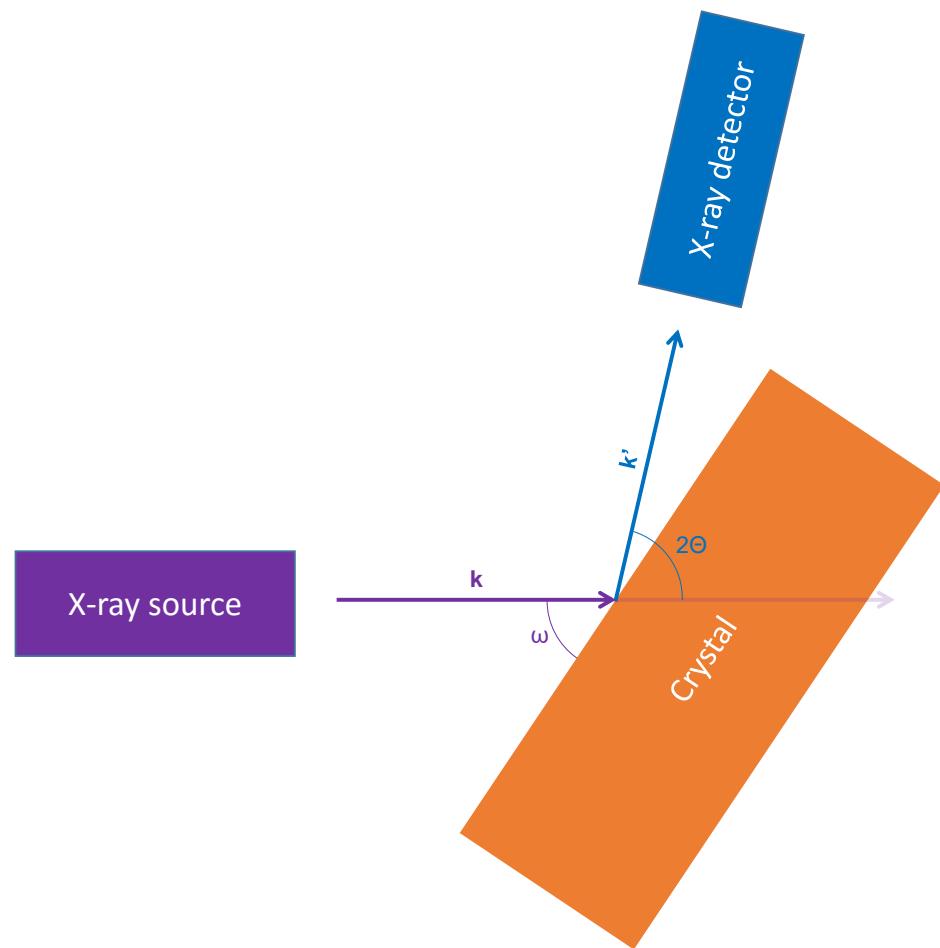


Figure 2.5: X-ray diffraction in real space. Relative to the X-ray source, ω controls the angle of the crystal and 2θ controls the angle of the X-ray detector. Not illustrated are the crystal's other degrees of freedom: x , y , z , χ (sometimes called ψ), and ϕ .

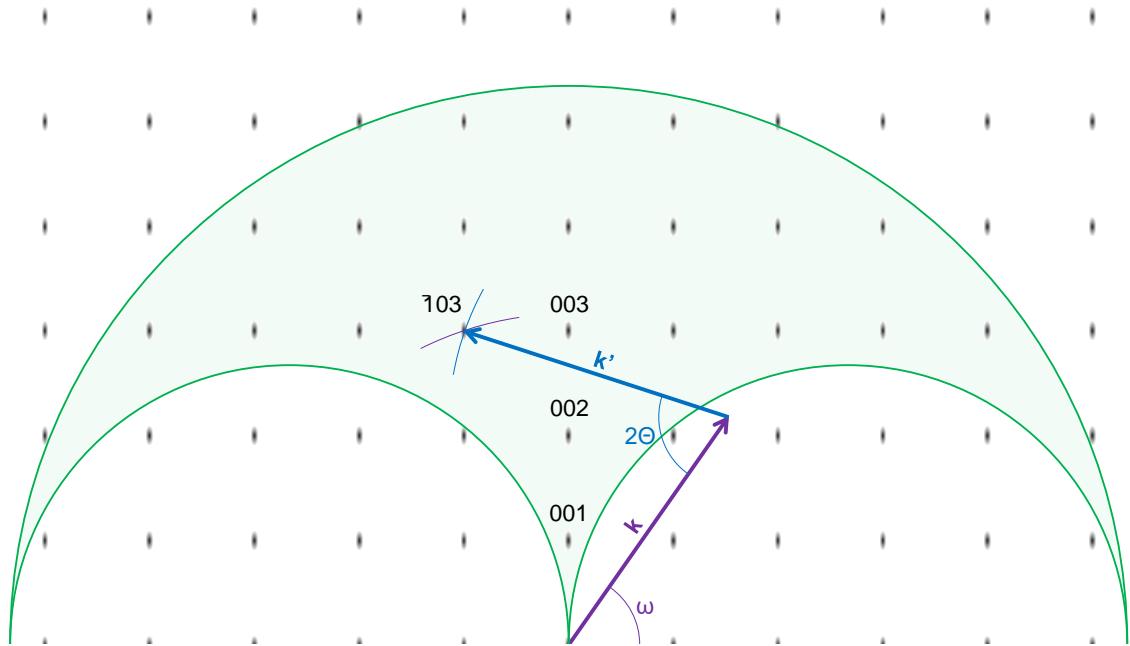


Figure 2.6: The reciprocal-space view of X-ray diffraction. The particular reciprocal lattice slice shown here, a thin film with a 0.4-nm cubic unit cell, is similar to those measured in my research. It is illuminated by a 0.15 nm beam (from a copper $K\alpha$ X-ray source) in a geometry aligned on the $\bar{1}03$ diffraction peak. The purple vector is the incident X-ray beam and the blue vector is the scattered X-ray beam. The green area covers the peaks that can experimentally measured (its outer radius is limited by the wavelength of the X-ray radiation and its inner radii are limited by the transparency of the crystal and its holder). The labeled diffraction peaks are the peaks I measured throughout my PhD research. The purple and blue arcs through the $\bar{1}03$ peak show the scans from varying one angle (either ω or 2θ) while the second is held constant. The sphere traced out by moving the scattered vector (blue) over all angles is the Ewald sphere.

MYTH: X-ray diffraction of a crystal produces its Fourier Transform

A second mostly-true-but-technically-false misconception is that X-ray diffraction produces a Fourier Transform of a crystal structure, allowing the real lattice to be inferred by observing the reciprocal lattice. While this is a useful shortcut to have in mind, it's not technically true. One easy way to see why this myth is false is to imagine a very thick crystal being bombarded by X-rays from above. The top of the crystal will contribute more to the diffraction pattern than the bottom of the crystal, because the X-rays will be heavily attenuating by the time they reach the bottom. This difference between the top and bottom of a crystal is not consistent with the purely mathematical Fourier Transform picture of diffraction, where the top and bottom ought to contribute equally.

2.4.5 Out-of-plane lattice parameters are measured by Omega-2Theta scans across out-of-plane peaks

A common scan I performed was an Θ - 2Θ scan across out-of-plane peaks (typically the 002 peak on a fine scale and the 001–003 peaks on a coarse scale). In an Θ - 2Θ scan, ω (set to equal Θ) and 2θ are changed simultaneously so that the angle of incidence always remains equal to the angle of scattering. Like rocking curves, the width of Θ - 2Θ scan peaks correspond to crystal quality, with wider peaks indicating greater variation and worse quality.¹⁷ However, unlike rocking curve peaks, the positions of Θ - 2Θ peaks also convey valuable information. The position of Θ - 2Θ peaks indicate the out-of-plane spacing between atomic layers, a common property of interest. The out-of-plane spacing between atomic layers is, assuming normal elasticity, expanded for films under compressive in-plane strain and contracted for films under tensile in-plane strain. However, it's important to keep in mind that epitaxial strain is not the only factor that affects atomic spacing. In oxides, a high concentration of oxygen vacancies can also expand the lattice significantly, so a larger than expected out-of-plane lattice parameter can sometimes be a proxy for crystal quality as well.

Wide-angle Θ - 2Θ scans were also useful, not for measuring the expected peaks, but for verifying that no unexpected peaks were present. If a poor quality growth had resulted in pockets of material with a different crystal structure and lattice parameter, then that material would cause additional peaks to show up. The absence of additional peaks was an early, rough check that a growth had gone well.

¹⁷Note that even a high quality crystal will always have some irreducible X-ray peak width from instrumental broadening and from the film's finite thickness.

2.4.6 Mosaic spread is measured by Omega scans across out-of-plane peaks

A scan for measuring mosaic spread (an indicator of crystal quality) is the ω scan, also known as a rocking curve. This scan works by first aligning to an out-of-plane diffraction peak (such as a 002 peak in a pseudocubic system), and then rocking ω back and forth while holding all other angles constant. In reciprocal space, this measures the width (in Q_x) of the diffraction peak. A wider rocking curve peak corresponds to greater variation in the alignment of atomic planes, implying a greater degree of imperfection in the crystal.

2.4.7 In-plane lattice parameters (and more) are measured by reciprocal space maps

To measure in-plane lattice parameters, it's necessary to measure reciprocal lattice peaks with an in-plane component (e.g., any peak except the 00l peaks). In my research, I commonly performed reciprocal space maps of $\bar{1}03$ peaks to measure both in-plane and out-of-plane lattice spacings. These scans provide far more information than ω scans and ω - 2Θ scans, but because they vary two parameters independently, they take far longer to run. Like an ω - 2Θ scan, a reciprocal space map scan varies ω and 2Θ , but unlike a ω - 2Θ scan, a reciprocal space map rasters over all combinations to map out an area rather than a line. The use of a line detector, which measures a whole bunch of angles in parallel, can speed up this process from many hours to under two hours.¹⁸

As Figure 2.6 shows, the $\bar{1}03$ peak is one of the easiest to access for a perovskite crystal structure.

2.4.8 Different phases of material can be detected by powder X-ray diffraction

Another X-ray diffraction technique that I used is powder X-ray diffraction. Commonly used on powders or microcrystalline samples, it is a technique that aims to fingerprint the microscopic atomic arrangements without caring about the macroscopic orientation of the crystal. Unlike the other X-ray diffraction scans I used, in powder X-ray diffraction, the sample is spun around during diffraction. This smears all the points of reciprocal space into a bunch of rings, from which microstructure can be measured and then fingerprinted against a database.

¹⁸The time spent needed for a scan varies quite a bit depending on the intensity of the peak and the desired fidelity. My scans of perovskite film peaks typically took around an hour each using a line detector.

2.4.9 Film thickness is measured by X-ray reflectivity scans

Although there are a number of ways to measure film thickness, one of the easiest techniques, at least for very smooth thin films, is X-ray reflectivity. X-ray reflectivity scans work by firing X-rays into the film over a range of shallow angles. As the intensity of X-rays reflected drops sharply with angle,¹⁹ it is modulated by a periodic signal that comes from constructive interference from reflections off of the film's top and bottom surfaces. The periodicity of this modulation can be fit or even simply Fourier transformed to calculate the thickness of the film.

2.5 Elemental composition was measured by high-energy ion scattering spectrometry

Also known as Rutherford backscattering spectrometry,²⁰ high-energy ion scattering spectrometry is a method for measuring a material's structure and elemental composition. As with many techniques, the general idea is to learn about a material by shooting something into a material and then measure whatever bounces out. And in this case, the something being shot into the material is very fast ions, typically helium nuclei (alpha particles) or hydrogen nuclei (protons) with kinetic energies on the order of MeV. The energy of backscattered ions is related to the charge Z of the nucleus that backscattered them, so by analyzing the energy spectrum of backscattered ions, scientists can infer the quantity of different elements, as well as their depth profile.

¹⁹More precisely, intensity drops as $1/Q^4$, where Q is the scattering vector.

²⁰In fact, in addition to being called high-energy ion scattering spectrometry and Rutherford backscattering spectrometry,[159, 160] the technique is also sometimes called Rutherford backscattering spectroscopy[161, 162, 163] or Rutherford backscattering[164] or backscattering spectrometry[165]. While the distinction between spectroscopy and spectrometry seems to be vague in practice, International Union of Pure and Applied Chemistry defines spectroscopy as “the study of physical systems by... radiation...” and spectrometry as “the measurement of such radiations...”[166] Although I personally try to follow this prescription, in practice the two terms often seem to be used interchangeably. For instance, mass spectrometry used to be known as mass spectroscopy back when the machines had actual physical scopes on them. When newer versions of the machines lacked scopes, the name of the technique changed to mass spectrometry.

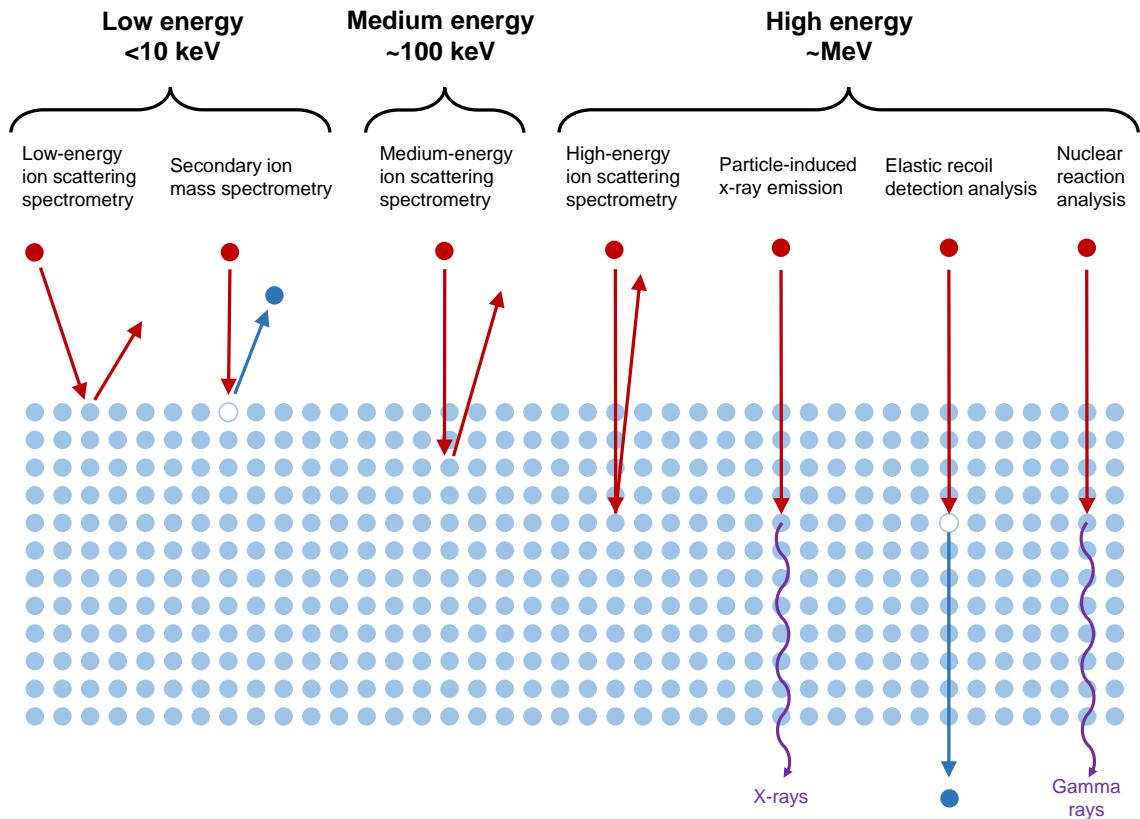


Figure 2.7: High-energy backscattering spectrometry is only one of many ion scattering spectrometry techniques. This diagram is meant to convey a general sense of the diversity of techniques and is not at all comprehensive—many other techniques and variants exist besides the ones shown here (too many to even succinctly list in text). Also, this diagram is misleading in its angles and scale and detail, and should not be taken as an exact representation of ion scattering processes. In case it is not obvious, the red circles are the incident ions and the blue circles are the atoms of a material.

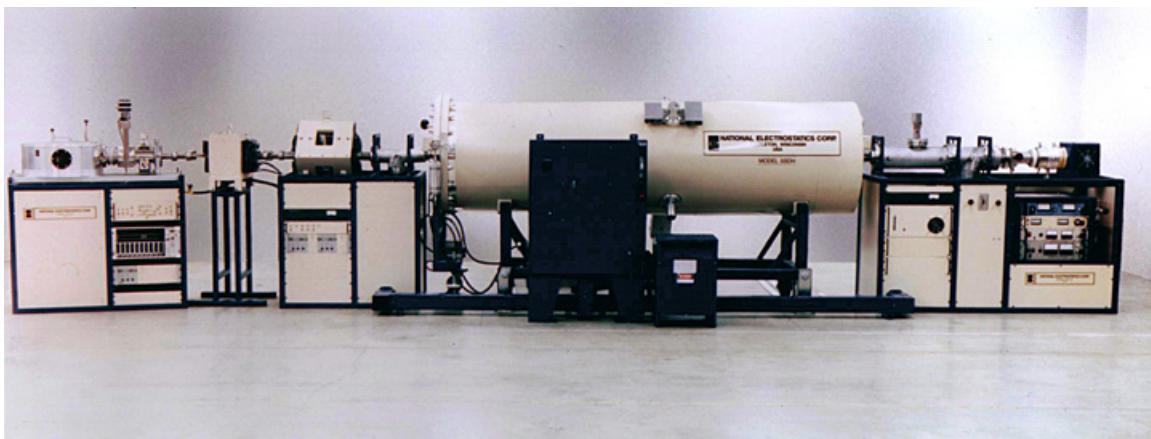


Figure 2.8: An ion beam accelerator and detector setup. This model measured all the backscattering data in my dissertation at the Lawrence Berkeley National Laboratory Ion Beam Analysis Facility.

In my research, high-energy ion scattering spectrometry with alpha particles was used to measure the elemental composition of my thin films, to confirm the stoichiometric transfer of cations during pulsed laser deposition. All measurements were performed by my trained labmates Urusa Alaan and Matt Gray at the Ion Beam Analysis Facility at Lawrence Berkeley National Lab with special help from Dr. Kin Man Yu, Dr. Andre Anders, and their graduate students. I analyzed the data using SIMNRA, a simulation program for the analysis of ion backscattering.[167, 168] The accuracy of high-energy ion scattering spectrometry is roughly 5%, but can be as poor as 10%–20% for lighter elements such as oxygen.

2.6 Surface topography was measured by an atomic force microscope

Measuring the surface topography of a film is difficult when its features are smaller than the wavelength of light.²¹ One solution to this problem is the atomic force microscope, which measures

²¹It's a common misconception that, because of diffraction, things cannot be measured or distinguished by light when they are smaller than its wavelength (400 nm – 700 nm). However, this is untrue. Because time evolution of a physical system is unitary (reversible), then even if diffraction appears to blur and mix the image, in principle (with perfect measurement and perfect computation) the true image can be extracted from any seemingly blurred data. And while this assumption of perfect measurement and computation is clearly untrue, there are nevertheless a wide variety of super-resolution microscopy techniques capable of beating and sometimes crushing the Abbe diffraction limit.[169]

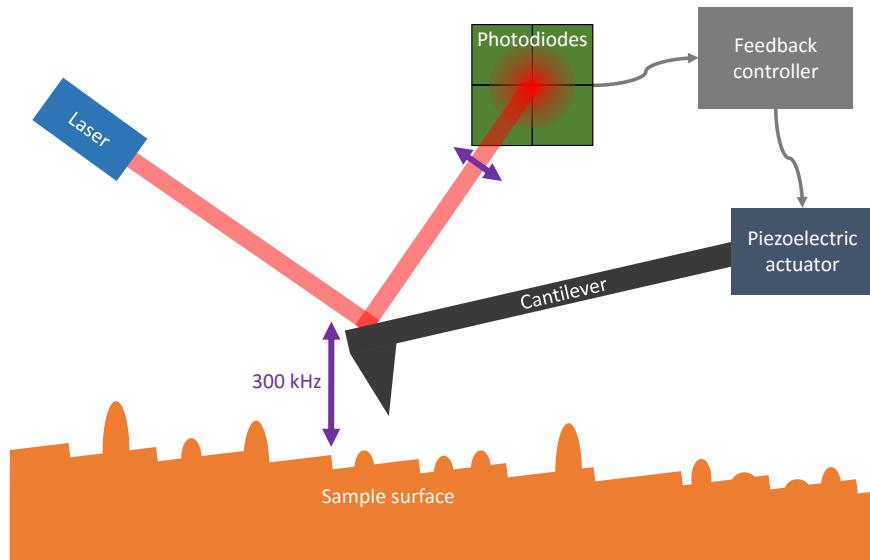


Figure 2.9: A diagram of an atomic force microscope.

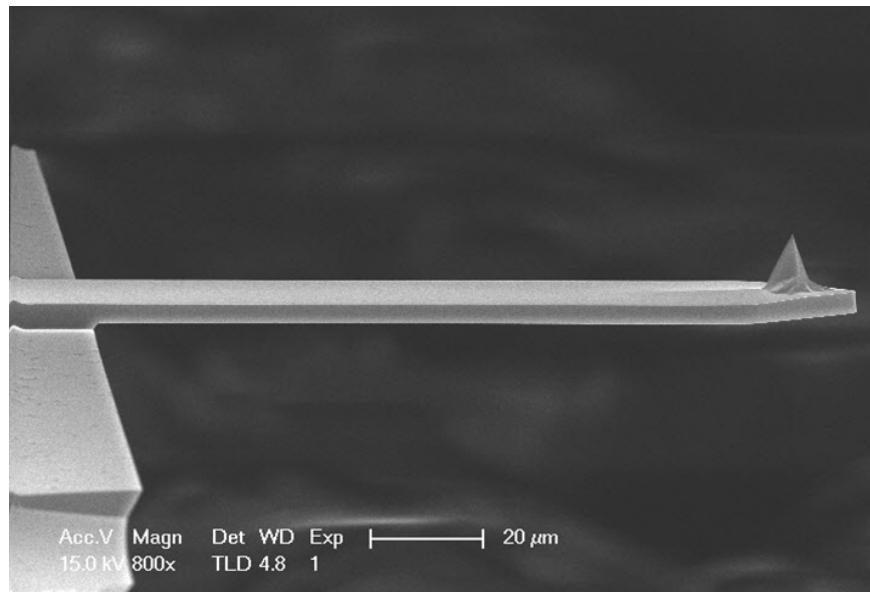


Figure 2.10: The cantilever and tip of an atomic force microscope probe. Taken from Bruker's AFM probe catalog, this image specifically is of a Bruker RTESP-300 probe. The cantilever has a nominal length of 125 μm , width of 40 μm , and thickness of 3.4 μm . The tip, at its sharp point, has a nominal radius of just 8 nm.

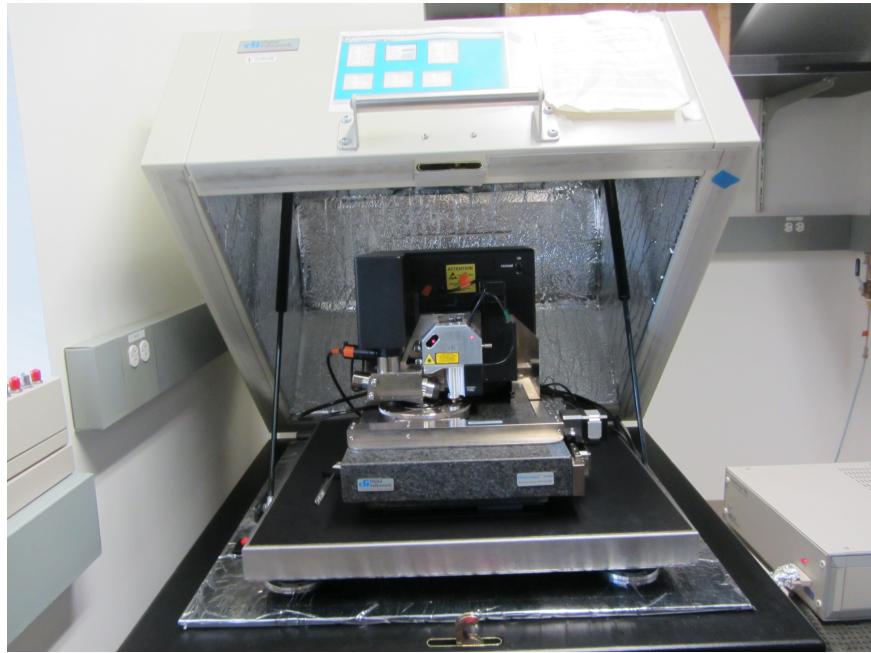


Figure 2.11: All of the atomic force microscope images in this dissertation were captured on my lab's Dimension 3100 (made by Bruker, formerly Veeco, formerly Digital Instruments). To limit noise, the scans take place on top of a vibration-isolated floating table inside of a conducting Faraday cage.

surface topography by tapping or dragging a tiny ‘finger’ across the surface. Because the wavelength of a solid material is tiny, this technique is capable of achieving much finer resolution than a typical optical microscope.

The specific procedure I used to measure my films’ surface topography is as follows: First, I inserted a silicon probe into the microscope with the tip pointed down toward sample surface. At the end of the probe was a cantilever roughly $10\text{ }\mu\text{m}$ wide and $100\text{ }\mu\text{m}$ long with a sharp pyramidal tip at the end, pointed perpendicular to the cantilever. When fresh, the tip’s radius at the point is a mere 10 nm or so. After inserting this probe, I aligned the laser beam, using two mirrors to aim it at the end of the reflective cantilever, just above the tip. Then I used two more mirrors to aim the reflected beam at a set of four photodiodes, which track the laser spot to track the motion of the cantilever. As the microscope’s piezoelectric actuator began oscillating the cantilever up and down, I scanned oscillation frequencies from 100 kHz to 500 kHz to find the resonance peak (typically around 300 kHz for the probes I used), and then set the oscillation frequency 5% below resonance. After identifying the starting heights of the probe tip and sample surface, I slowly lowered the probe tip toward the surface (along with the laser and mirrors and photodiodes, so their relative positions did not change). When the oscillation amplitude of the cantilever fell, this indicated that the tip was finally close enough to interact/touch the surface. The computer automatically controlled the height of the tip with a PID feedback loop, keeping the amplitude reduction at a constant level

(and therefore, presumably, at a constant distance from the surface). The height of the tip was then recorded as the height of the sample. More piezoelectric actuators were used to raster the tip over the sample, allowing a 2D image to be constructed. When taking measurements, I typically chose to scan in squares that were $1 \mu\text{m}$ to $5 \mu\text{m}$ on a side. Lateral resolution is limited by the width of the probe tip, around 20 nm. However, vertical resolution is where atomic force microscopes really shine. Thanks to the exquisite control of the photodiodes and piezoelectric actuator, the height of the sample surface can be measured with sub-angstrom resolution. This makes it possible for an atomic force microscope to see individual atomic terraces on solid surfaces that are very flat and smooth.

2.7 Electrical properties were measured in the van der Pauw configuration

To measure electrical properties of my thin films, I used a Quantum Design Physical Property Measurement System capable of cooling to temperatures as low as 2 K and applying magnetic fields as strong as 7 T.

Rather than patterning Hall bar circuits onto my films, which would have taken more effort and caused possible damage or edge effects, I measured electrical properties in the van der Pauw configuration. Like other electrical measurement methods, the van der Pauw is a four-point method that sources electrical current between one pair of points and measures the voltage difference between a second pair of points (shown in Figure 2.12). However, unlike other four-point methods, these points can be placed anywhere on the perimeter of a two dimensional sample and the equations derived by van der Pauw can be solved to get the sheet resistance and Hall coefficient. In my case, I wirebonded to the corners of rectangular samples, using the ultrasonic wirebonder pictured in Figure 2.13.

The van der Pauw formula,[170]

$$e^{-\pi R_{12,34}/R_s} + e^{-\pi R_{23,41}/R_s} = 1 \quad (2.2)$$

where

$$R_{12,34} = \frac{V_{34}}{I_{12}} \quad (2.3)$$

has no general closed-form solution, but can be solved with certain iterative methods.

Although no sample is perfectly two dimensional and perfectly homogeneous with perfectly small wires placed perfectly on the perimeter, the van der Pauw formula remains accurate when these conditions are violated by small degrees (say, <10%).[171, 172]

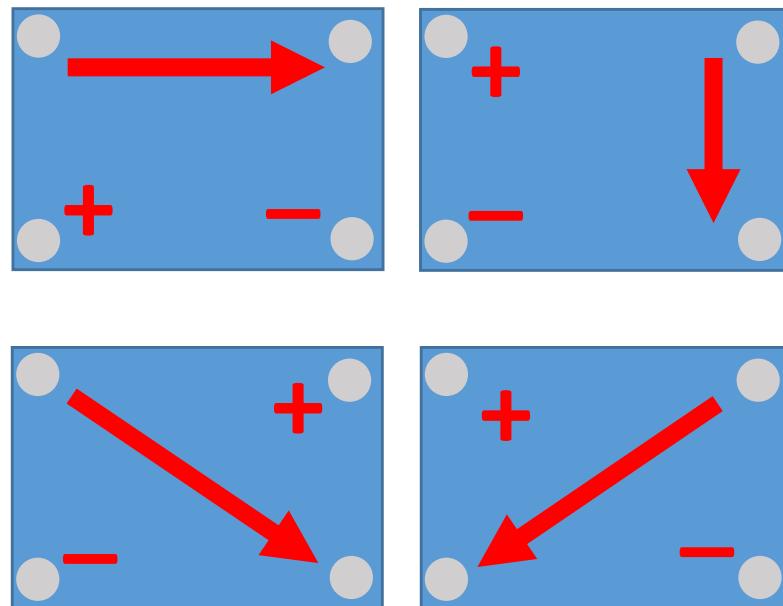


Figure 2.12: The van der Pauw configuration. The top two configurations can be used to measure the sheet resistance and the bottom two configurations can be used to measure the Hall coefficient and hence the sheet carrier concentration. Measurement accuracy is improved by averaging over the inverse and reciprocal configurations as well.

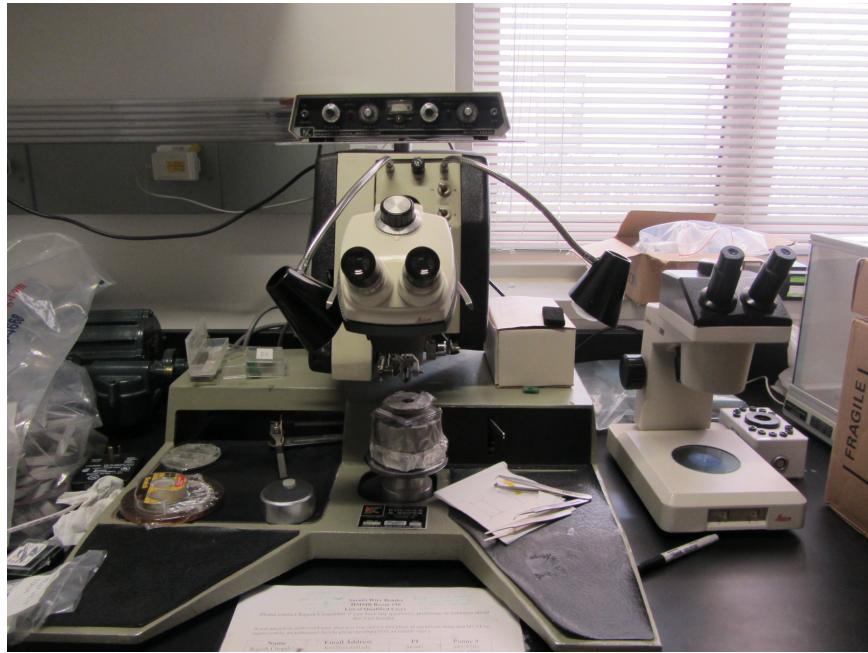


Figure 2.13: My lab's ultrasonic wirebonder, used to attach tiny aluminum wires to our thin film crystals.

Measurements were made both with direct current (DC) and alternating current (AC). An advantage of DC measurements is that current-voltage (IV) curves can be swept point-by-point to easily gauge whether they are linear. An advantage of AC measurements is that they allow the use of a lock-in amplification, an ingenious method for filtering out noise. A second advantage is that AC frequencies typically have less background noise than DC.

2.8 Bulk magnetic properties were measured by a SQUID magnetometer

Superconducting quantum interference device (SQUID) magnetometers are exquisitely sensitive devices, capable of measuring magnetic fields as small as 5×10^{-18} T.^[173]²² In my research, I performed bulk magnetic measurements with a Quantum Design Evercool Magnetic Property Measurement System, shown in Figure 2.16.²³

²²For reference, this is 13 orders of magnitude smaller than Earth's wimpy magnetic field, which is already small enough to be imperceptible while waving around a handheld magnet.

²³Overall, the commercialization and specialization of scientific tool development has been a good trend. However, one downside of commercial systems is that the companies that produce them are

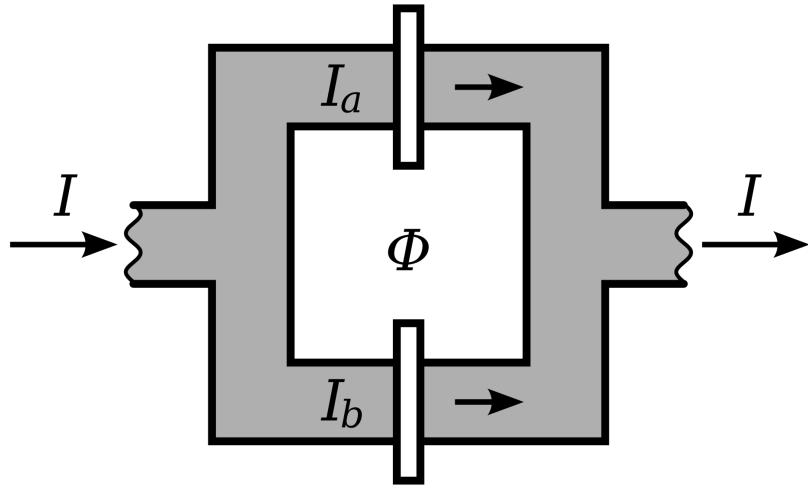


Figure 2.14: The double Josephson junction of a DC SQUID. Picture by Miraceti, distributed under a [CC-BY-SA 3.0 license](#), via Wikimedia Commons.

2.8.1 Principles of operation

Although the design of a SQUID magnetometer is complicated enough to devote entire careers and companies to, its broad principles of operation are conceptually simple.^[174, 175] A magnetic sample is attached to a stick that oscillates up and down. This generates an oscillating magnetic field, which is measured by a nearby conducting loop. In the case of a vibrating sample magnetometer, this conducting loop is made of coiled wire and a lock-in amplifier locks in to the oscillation frequency. However, in the case of a SQUID magnetometer, this conducting loop is constructed from two parallel superconducting Josephson junctions.²⁴ Normally, as more magnetic flux passes through the loop, the voltage across the Josephson junctions would oscillate. However, a real SQUID magnetometer uses a feedback controller to keep the voltage constant, and measures the magnetic flux by the amount of feedback necessary to keep the voltage constant. This measured magnetic flux can then be used to infer the magnetization of the magnetic sample.

Although the superconducting Josephson junctions must be kept at cryogenic temperatures, the magnetic sample itself can be suspended in an insulated temperature controlled chamber. Our Quantum Design SQUID system, pictured in Figure 2.16, reaches temperatures as low as 2 K (limited by the boiling point of liquid helium).

incentivized to exaggerate their sensitivity as well as downplay, deny, and poorly document known experimental artifacts.

²⁴Though I describe a SQUID magnetometer as using two Josephson junctions, this is true only for DC SQUIDs. An RF SQUID needs only one.

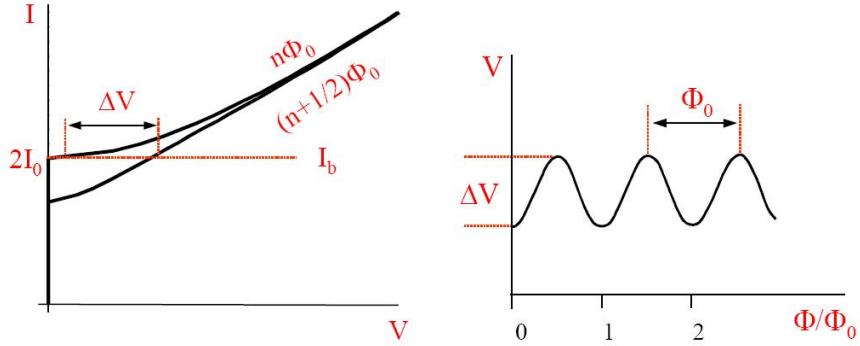


Figure 2.15: Current-voltage characteristics of a DC SQUID. The current is held fixed at $2I_0$, where increasing magnetic flux causes the voltage to oscillate (if not feedback controlled). Graphs by Janolaf30, released into the public domain, via Wikimedia Commons.

An external magnetic field can also be applied. Our Quantum Design SQUID system is equipped with a superconducting electromagnet that can reach magnetic fields as high as 7 T.

2.8.2 Common scans

Given that the magnetization of a sample can be measured at a range of temperatures and magnetic fields, it may not be surprising that the two most common scans I used were magnetization versus temperature and magnetization versus applied magnetic field.

Scans of magnetization versus temperature are useful for seeing how a magnetic material's magnetic properties change with temperature. They can reveal magnetic phases transitions, such as the Curie temperature of a ferromagnet. They can also be helpful for subtracting the diamagnetic background of crystal substrates, since diamagnetism is independent of temperature. Magnetization versus temperature scans are often performed while warming with a small but constant applied field (though sometimes it is 0 for ferromagnets) and after being cooled in a large applied field (or not, sometimes).

Scans of magnetization versus applied magnetic field are useful for measuring ferromagnetic hysteresis. They can reveal a ferromagnetic material's saturation magnetization, coercive fields, remnant magnetization, and possible exchange bias. These scans can even be used to measure a sample's paramagnetism at high fields and low temperatures, where paramagnetism becomes nonlinear with magnetic field.

2.8.3 Common sources of error

Although SQUID magnetometers are exquisitely sensitive, enough to detect nanoscale magnetism, they are also exquisitely sensitive to noise.^[176] Magnetic contaminants can come from many common

sample preparation materials, such as kapton tape, steel tweezers, plastic holders, silver paint, and more.[177, 178] Errors can also come from samples being misaligned. An off-center sample will appear to have a magnetization different from its true value.[179, 180] And even the machines themselves have error when reporting their own temperature or applied magnetic field. Hysteresis in the superconducting electromagnet can introduce errors into measured coercive fields on the order of 1 oe–10 oe, enough to ‘invert’ the hysteresis of a soft ferromagnet. When it comes to mismeasurement of temperature, Quantum Design systems in particular are known for their slow, unreported temperature drift,[181, 182] an experimental artifact which I suspect has led to false photomagnetism ‘discoveries.’

2.9 Element-specific magnetic properties were measured by X-ray magnetic circular dichroism

X-ray magnetic circular dichroism is a uniquely powerful tool for measuring magnetism. X-ray magnetic circular dichroism, as its name might suggest, is an effect where a magnetic material absorbs left and right circularly polarized X-rays at different rates.

The key advantage of X-ray magnetic circular dichroism is that, because different elements absorb X-rays at characteristic energies, this technique can associate magnetic signals with individual elements in a material, and sometimes even individual oxidation states. For example, in a piece of LaCoO₃, this technique can identify that the magnetism is coming from the cobalt ions rather than potential contamination from kapton tape, tweezer handling, plastic holders, silver paint, etc., which are otherwise difficult to rule out.[177, 178] The ability to attribute magnetism to specific elements (or even specific atomic sites or electronic states) is lacked by most magnetic measurement techniques, which only measure a materials aggregate magnetic moment.

Because X-ray magnetic circular dichroism ideally requires a high intensity beam of X-rays delivered at many possible energies, it is often performed at synchrotrons, where X-rays are emitted from a beam of electrons being accelerated in a loop. In my particular research on films of PrCoO₃ and Pr_{0.7}Y_{0.3}CoO₃, I performed X-ray magnetic circular dichroism measurements at the Advanced Light Source at Lawrence Berkeley National Lab, on beamlines 4.0.2 and 6.3.1.

2.9.1 X-ray absorption

There are many methods for measuring X-ray absorption, each with its own advantages and drawbacks. Four are illustrated in Figure 2.17 and described below. In my research, I measured L- and M-edge²⁵ absorption using the method of total electron yield, which is relatively sensitive but

²⁵L-edge absorption excites electrons from the 2p states to the 3d, and M-edge absorption excites electrons from the 3d states to the 4f. Each absorption band is split into two peaks (L₂/L₃ or



Figure 2.16: My lab's SQUID magnetometer, an Evercool MPMS made by Quantum Design.

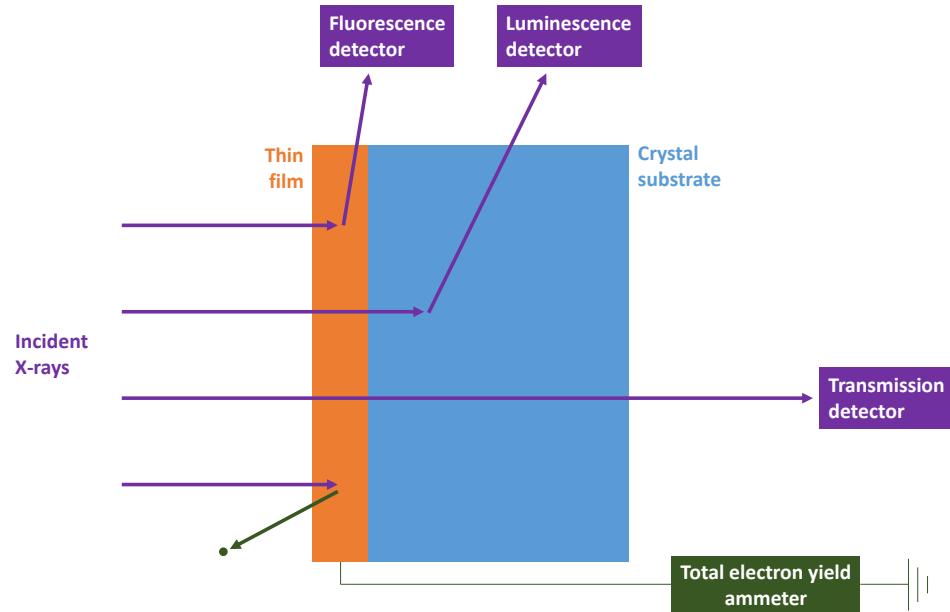


Figure 2.17: Four methods of measuring X-ray absorption.

requires a conducting sample and only measures the sample's surface.

Fluorescence

Fluorescence is one way of measuring X-ray absorption. After an X-ray excites an electron out of a core state, the state is temporarily empty. When another electron drops in to fill it, a new X-ray is emitted. These X-rays can be detected, and their intensity corresponds to the rate of X-ray absorption.

Luminescence

For thin films, luminescence is another method that can measure X-ray absorption.^[183] Rather than measuring the thin film's X-ray emission, the *substrate's* X-ray emission is measured. This gauges the intensity of X-rays *not* absorbed by the thin film.

Transmission

X-ray transmission can also be directly measured with X-ray detectors. This is similar to luminescence, in that it measures the X-ray transmission of the film, but unlike luminescence it does not require a luminescent substrate.

M₄/M₅ by the strong spin-orbit splitting of the lower energy core states.

Total electron yield

A sensitive way of measuring X-ray absorption is total electron yield. It works by measuring the electrical current needed to replace ejected Auger electrons. As before, after an X-ray excites an electron out of a core state, the state is temporarily empty. When another electron drops in to fill it, instead of emitting its energy in the form of an X-ray, it can lose its energy by transferring it to another electron. This other electron will suddenly have a huge amount of kinetic energy, and, if it is near the surface of the material, may be ejected altogether (if it's in the interior of the material it will just travel along until it loses its energy to other electrons). Every time an electron, which is negatively charged, is ejected from the material, the material becomes slightly positively charged. If the material is electrically connected to ground (neutral voltage) and if the material is itself conducting, then electrons will flow from ground to the material to replace the electrons being ejected. A sensitive current detector can measure this flow of charge and thereby measure the X-ray absorption. It's important to emphasize that because electrons are only ejected near the surface of the material (where near is something like 5 nm), this technique only measures the X-ray absorption, and hence the magnetism, of the material's surface. Depending on the goal of an experimenter, this surface sensitivity can be either good or bad.

Figure 2.18 illustrates twelve example X-ray absorption spectra (after normalization).

2.9.2 X-ray magnetic circular dichroism

The idea behind X-ray magnetic circular dichroism, illustrated in Figure 2.20, is that left and right circularly polarized X-rays are absorbed at different rates depending on the magnetization of an atom. By varying X-ray energy and measuring whether left or right circularly polarized X-rays are absorbed more, an experimenter can determine whether an element is magnetic and in which direction its magnetic moment points. In some cases, by carefully examining the absorption's spectral line shape, the magnetism of an element can even be correlated with its oxidation state.

X-ray magnetic circular dichroism only works because of the spin sensitivity offered by the spin-orbit split core states. For this reason, X-ray magnetic circular dichroism does not work for transitions from core s electrons, which have no orbital angular momentum and therefore no spin-orbit splitting. Common transitions used in X-ray magnetic circular dichroism are the $2p \rightarrow 3d$ ($L_{2,3}$) transitions for 3d transition-metal elements and the $3d \rightarrow 4f$ ($M_{4,5}$) transitions for rare-earth elements.

For an in-depth explanation of X-ray magnetic circular dichroism (and related magnetism topics), I recommend Stoehr's *Magnetism: From Fundamentals to Nanoscale Dynamics*.[\[122\]](#)

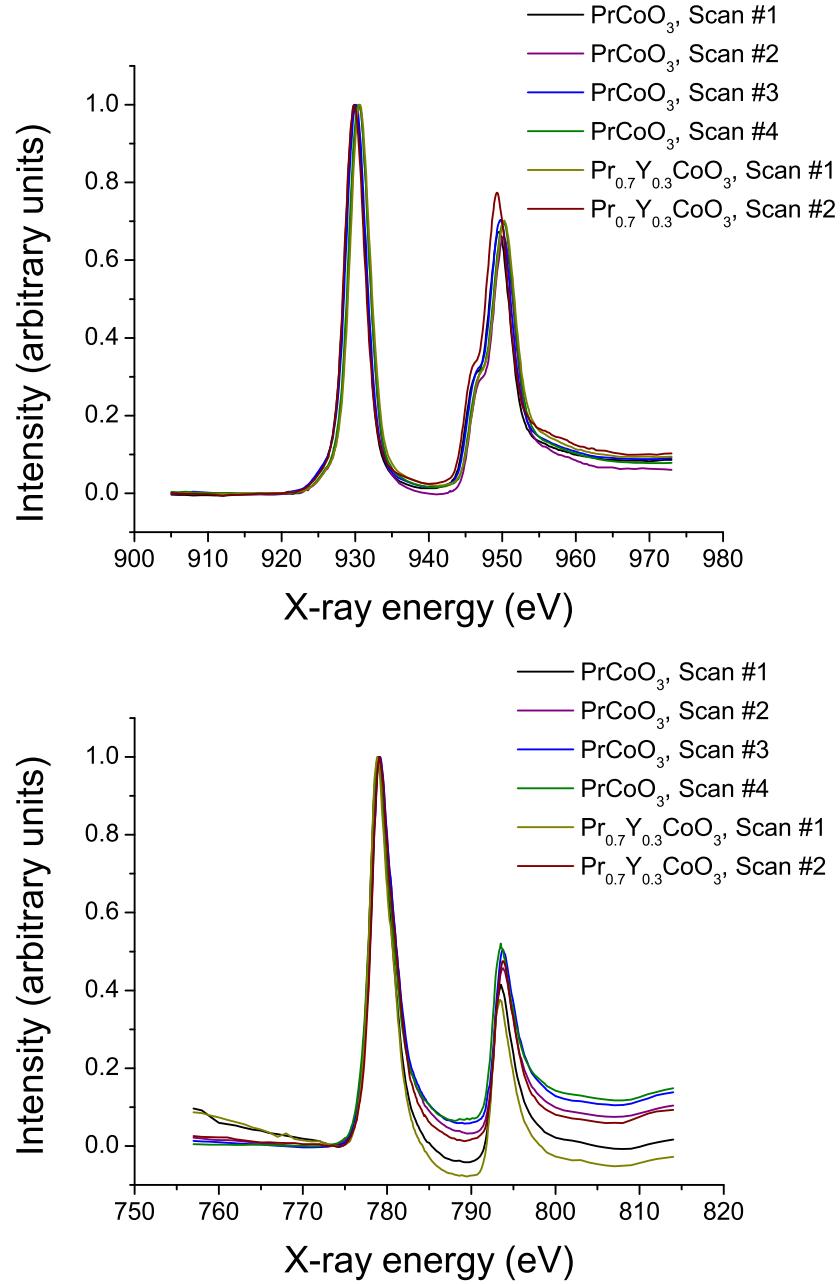


Figure 2.18: Examples of X-ray absorption spectra. The top plot shows X-ray absorption from the M_{5,4} transitions in praseodymium and the bottom plot shows X-ray absorption from the L_{3,2} transitions in cobalt. All scans have been normalized by shifting their pre-edge to 0 and then linearly scaling their maximum to 1. Despite this normalization, there is still some variation from scan to scan.

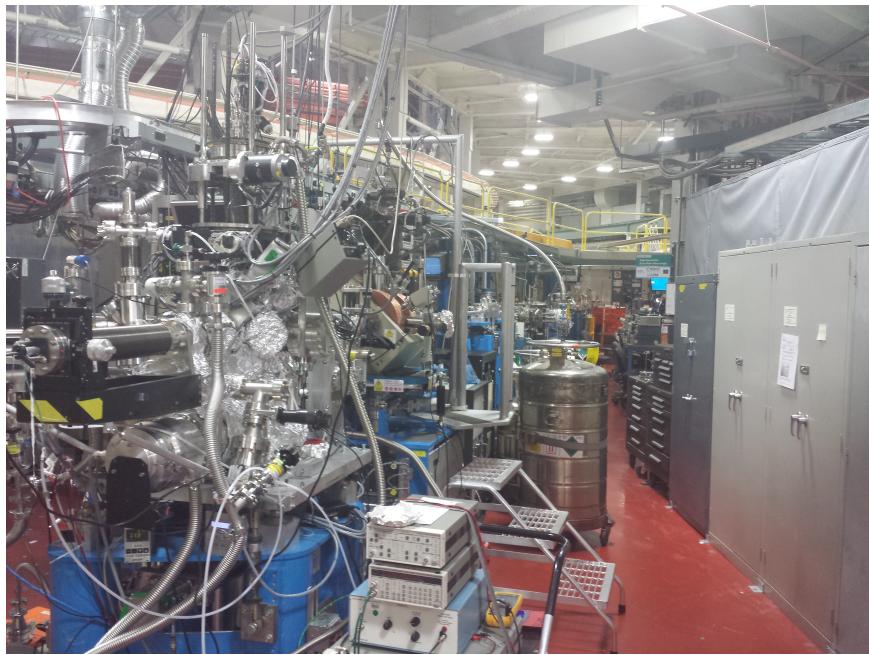


Figure 2.19: The endstation on beamline 6.3.1 at the Advanced Light Source at Lawrence Berkeley National Lab. This was one of the two beamlines where I measured X-ray absorption and X-ray magnetic circular dichroism.

2.10 Local crystal structure was measured by a scanning transmission electron microscope

In my cobalt perovskite project, the local crystal structure and local elemental composition was probed using a scanning transmission electron microscope. The measurements were performed by my expert collaborators, Dr. Maria Varela and Mariona Cabero.

Scanning transmission electron microscopes work by firing a high-energy ($\tilde{200}$ keV), narrowly focused beam of electrons at a very thin sample of material (perhaps 10 nm–1000 nm thick). An electron detector underneath the sample measures electrons that make it through the sample. In bright-field imaging, the detector is placed directly below the beam to measure the electrons that pass through with minimal scattering. In dark-field imaging, an annular detector measures the electrons that pass through with significant angular scattering. We used a particularly sensitive form of dark-field imaging called high-angle annular dark-field imaging. The angle of the annulus is made so large that no Bragg diffracted electrons are collected at all. This leaves only the electrons which have been scattered at large angles, which presumably comes from scattering off of atomic nuclei. Because they scatter off of nuclei, these high-angle electrons have intensities that are sensitive to the charge Z of these nuclei. This causes the atomic bright spots of the image to be brighter for

A magnetic field applied in the \uparrow direction aligns valence electrons in the \uparrow direction leaving more hole states in the \downarrow direction

For the L₃ transition ($2p_{3/2} \rightarrow 3d$), X-rays with \uparrow circular polarization are more likely to excite spin \downarrow electrons into the hole states than spin \uparrow electrons into the hole states

For the L₂ transition ($2p_{1/2} \rightarrow 3d$), spin-orbit coupling is opposite ($l-s$ instead of $l+s$), so the excitation's spin sensitivity is opposite

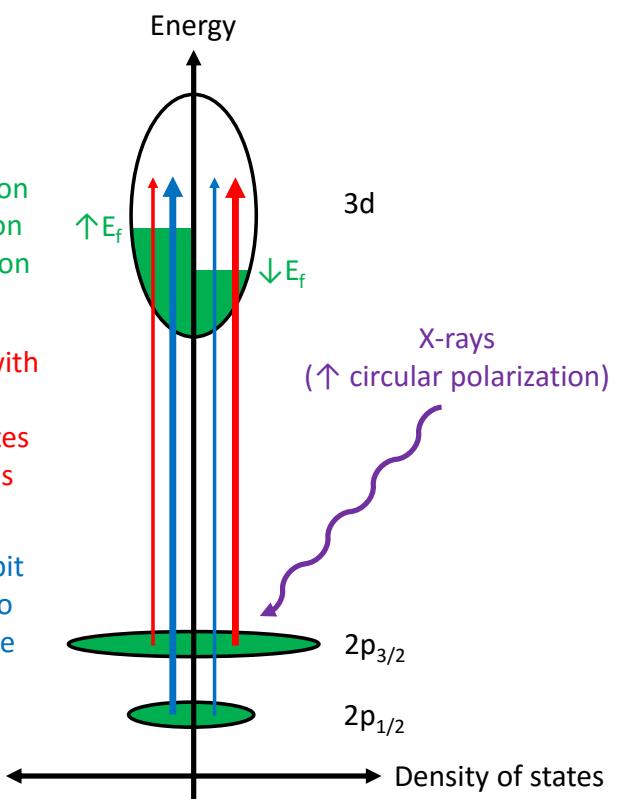


Figure 2.20: A simple diagram of L-edge X-ray magnetic circular dichroism in a partly filled 3d transition metal magnet. Not to scale. To measure dichroism, X-ray absorption must be compared to absorption with the opposite applied magnetic field or X-ray polarization. For examples of real X-ray magnetic circular dichroism data, see Figure 4.18 in Section 4.6.5.

higher- Z atoms, making it possible to distinguish the different types of atoms by their brightnesses.

2.11 Local elemental composition was measured by an electron energy loss spectrometer

A second large advantage of high-angle annular dark-field imaging is that it leaves the primary transmission beam available to be measured by an electron energy loss spectrometer. Electron energy loss spectrometers measure the energy of electrons that have passed through the thin sample. Electrons in the beam can lose energy to many sinks, but one sink in particular that they can lose energy to is the core shell excitations of the atoms they pass by (these are the same element-specific excitations exploited in X-ray absorption spectroscopy). For instance, if a beam has an energy loss peak at 780 eV, that could indicate that is passing through cobalt atoms and exciting the cobalt atoms' $2p \rightarrow 3d$ L₃ transition. Although it takes care, electron energy loss spectrometry can be used to measure the elemental composition of a sample on a local scale. And because scanning transmission electron microscope is simultaneously measuring a real-space image with high-angle annular dark-field imaging, these two maps can merged and the elemental composition data can be directly associated with features in the scanning transmission electron microscope image.

Chapter 3

The lanthanum aluminate-strontium titanate interface

3.1 Executive summary

In my LaAlO₃/SrTiO₃ project, despite the interface's wide variation in reported electrical properties, I highlighted a scaling relationship between sheet carrier concentration and mobility common to nearly all research groups (the relationship being that mobility roughly varies as carrier concentration to the -3 power). I also discovered that the electrical transport is robust against the presence of the magnetic and spin-orbit scatterers Tm and Lu at a 2% concentration in LaAlO₃.

3.2 Background

The interface between lanthanum aluminate (LaAlO₃) and strontium titanate (SrTiO₃) is a notable materials interface because it exhibits properties not found in its constituent materials. Individually, LaAlO₃ and SrTiO₃ are non-magnetic insulators, yet LaAlO₃/SrTiO₃ interfaces can exhibit electrical conductivity,[184] superconductivity,[185] ferromagnetism,[186] large negative in-plane magnetoresistance,[187] and giant persistent photoconductivity.[188] The study of how these properties emerge at the LaAlO₃/SrTiO₃ interface is a growing area of research in condensed matter physics.

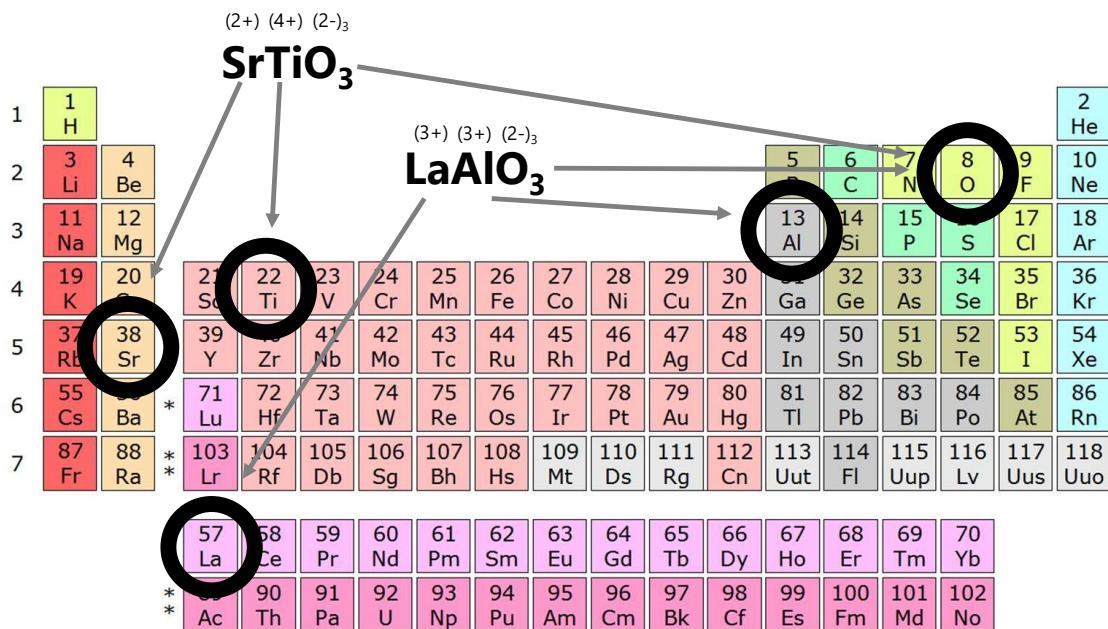


Figure 3.1: The five elements comprising $\text{LaAlO}_3/\text{SrTiO}_3$. Periodic table adapted from Sandbh (Own work) [CC BY-SA 4.0], via Wikimedia Commons.

3.2.1 Emergent properties

3.2.2 Conductivity

Under the right conditions, the $\text{LaAlO}_3/\text{SrTiO}_3$ interface is electrically conductive, like a metal. The angular dependence of Shubnikov-de Haas oscillations indicates that the conductivity is two-dimensional,[189] leading many researchers to refer to it as a two-dimensional electron gas (2DEG). Two-dimensional does not mean that the conductivity has zero thickness, but rather than the electrons are confined to only move in two directions. It is also sometimes called a two-dimensional electron liquid (2DEL) to emphasize the importance of inter-electron interactions.[190]

Conditions necessary for the conductivity

Not all $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces are conductive. Typically, conductivity is achieved only when:

- The $\text{LaAlO}_3/\text{SrTiO}_3$ interface is along the 001 crystallographic direction
- The LaAlO_3 and SrTiO_3 are crystalline and epitaxial
- The SrTiO_3 side of the interface is TiO_2 -terminated (causing the LaAlO_3 side of the interface to be LaO -terminated)[184]
- The LaAlO_3 layer is at least 4 unit cells thick[191]

Conductivity can also be achieved when the SrTiO_3 is doped with oxygen vacancies; however, in that case, the interface is technically $\text{LaAlO}_3/\text{SrTiO}_{3-x}$ instead of $\text{LaAlO}_3/\text{SrTiO}_3$.

Hypotheses for the conductivity

The source of conductivity at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface has been debated for years. SrTiO_3 is a wide-band gap semiconductor that can be doped n-type in a variety of ways. Clarifying the mechanism behind the conductivity has been a major goal of research. Four major hypotheses have been explored in the literature:

- Polar gating
- Oxygen vacancies
- Intermixing
- Structural distortions

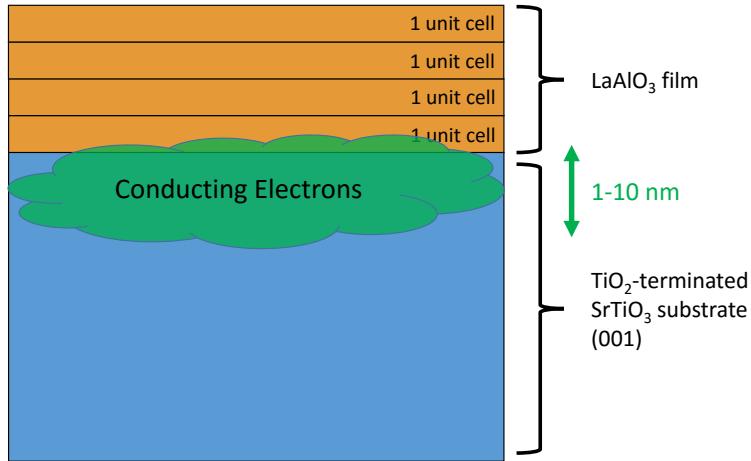


Figure 3.2: A diagram of the interface between the lanthanum aluminum oxide and strontium titanium oxide interface. Electrons begin to conduct only after depositing four or more unit cells of LaAlO₃. Not to scale.

Polar gating

Polar gating was the first mechanism used to explain the conductivity at LaAlO₃/SrTiO₃ interfaces.^[184] It postulates that the LaAlO₃, which is polar in the 001 direction (with alternating sheets of positive and negative charge), acts as an electrostatic gate on the semiconducting SrTiO₃.^[184] When the LaAlO₃ layer grows thicker than three unit cells, its valence band energy rises above the Fermi level, causing holes (or positively charged oxygen vacancies^[192]) to form on the outer surface of the LaAlO₃. The positive charge on the surface of the LaAlO₃ attracts negative charge to nearby available states. In the case of the LaAlO₃/SrTiO₃ interface, this means electrons accumulate in the surface of the SrTiO₃, in the Ti *d* bands.

The strengths of the polar gating hypothesis are that it explains why conductivity requires a critical thickness of four unit cells of LaAlO₃ and that it explains why conductivity requires the SrTiO₃ to be TiO₂-terminated. The polar gating hypothesis also explains why alloying the LaAlO₃ increases the critical thickness for conductivity.^[193]

One weakness of the hypothesis is that it predicts that the LaAlO₃ films should exhibit a built-in electric field; so far, x-ray photoemission experiments^[194, 195, 196, 197] and other experiments^[198, 199, 200] have shown little to no built-in field in the LaAlO₃ films. The polar gating hypothesis also cannot explain why Ti³⁺ is detected when the LaAlO₃ films are thinner than the critical thickness for conductivity.^[195]

The polar gating hypothesis is sometimes called the polar catastrophe hypothesis,^[201] alluding to the counterfactual scenario where electrons don't accumulate at the interface and instead voltage

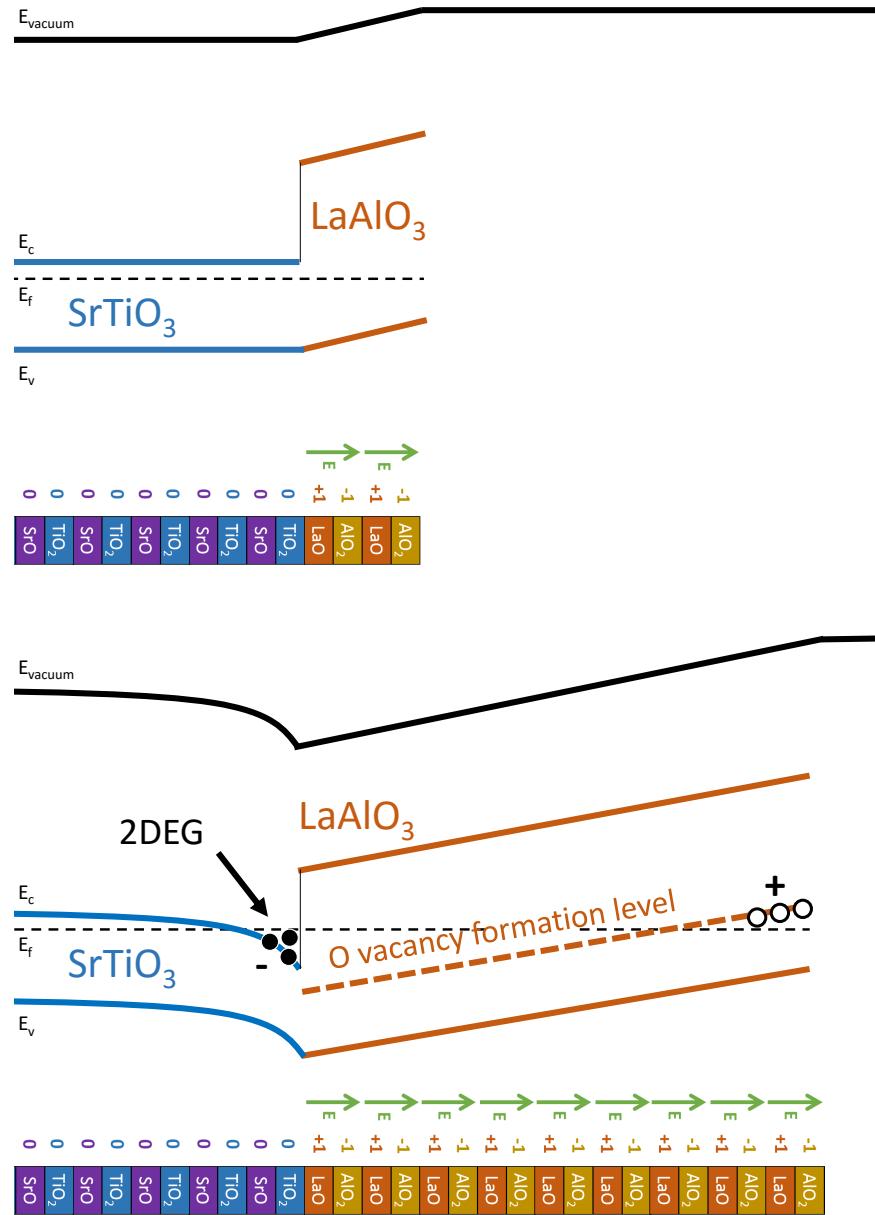


Figure 3.3: One popular theory for the conductivity in LAO/STO is that the built-in electric field of the LAO causes holes or oxygen vacancies to appear on its surface beyond a critical thickness. These positively charged holes or oxygen vacancies attract negatively charged electrons into the STO side of the interface, similar to modulation doping of other semiconductor 2DEGs.

in the LaAlO₃ builds up forever. The hypothesis has also been called the electronic reconstruction hypothesis,[201] highlighting the fact that electrons, not ions, move to compensate the building voltage.

Oxygen vacancies

Another hypothesis is that the conductivity comes from free electrons left by oxygen vacancies in the SrTiO₃.[202] SrTiO₃ is known to be easily doped by oxygen vacancies, so this was initially considered a promising hypothesis. However, electron energy loss spectroscopy measurements have bounded the density of oxygen vacancies well below the density necessary to supply the measured free electron densities.[203] (Another proposed possibility is that oxygen vacancies in the surface of the LaAlO₃ are remotely doping the SrTiO₃.[195])

Intermixing

Lanthanum is a known dopant in SrTiO₃,[204] so it has been suggested that La from the LaAlO₃ mixes into the SrTiO₃ and dopes it n-type. Multiple studies have shown that intermixing takes place at the interface;[205] however, it is not clear whether there is enough intermixing to provide all of the free carriers. For example, a flipped interface between a SrTiO₃ film and a LaAlO₃ substrate is insulating.[206]

Structural distortions

A fourth hypothesis is that the LaAlO₃ crystal structure undergoes octahedral rotations in response to the strain from the SrTiO₃. These octahedral rotations in the LaAlO₃ induce octahedral rotations in the SrTiO₃, increasing the Ti d-band width enough so that electrons are no longer localized.[207]

3.2.3 Superconductivity

Superconductivity was first observed in LaAlO₃/SrTiO₃ interfaces in 2007, with a critical temperature of roughly 200 mK.[208] Like the conductivity, the superconductivity appears to be two-dimensional.[185]

3.2.4 Ferromagnetism

Hints of ferromagnetism in LaAlO₃/SrTiO₃ were first seen in 2007, when Dutch researchers observed hysteresis in the magnetoresistance of LaAlO₃/SrTiO₃.[209] Follow up measurements with torque magnetometry indicated that the magnetism in LaAlO₃/SrTiO₃ persisted all the way to room temperature.[210] In 2011, researchers at Stanford University used a scanning SQUID to directly image the ferromagnetism, and found that it occurred in heterogeneous patches.[186] Like the conductivity in LaAlO₃/SrTiO₃, the magnetism only appeared when the LaAlO₃ films were thicker than a few

unit cells.[211] However, unlike conductivity, magnetism was seen at SrO-terminated surfaces as well as TiO₂-terminated surfaces.[211]

The discovery of ferromagnetism in a materials system that also superconducts spurred a flurry of research and debate, because ferromagnetism and superconductivity almost never coexist together.[186] Ferromagnetism requires electron spins to align, while superconductivity typically requires electron spins to anti-align.

3.2.5 Magnetoresistance

Magnetoresistance measurements are a major experimental tool used to understand the electronic properties of materials. The magnetoresistance of LaAlO₃/SrTiO₃ interfaces has been used to reveal the 2D nature of conduction, carrier concentrations (through the hall effect), electron mobilities, and more.[189]

With the field applied out-of-plane

At low magnetic field, the magnetoresistance of LaAlO₃/SrTiO₃ is parabolic versus field, as expected for an ordinary metal.[212] However, at higher fields, the magnetoresistance appears to becomes linear versus field.[212] Linear magnetoresistance can have many causes,[213, 214, 215, 216, 217, 218, 219] but so far there is no scientific consensus on the cause of linear magnetoresistance in LaAlO₃/SrTiO₃ interfaces.[212] Linear magnetoresistance has also been measured in pure SrTiO₃ crystals,[220] so it may be unrelated to the emergent properties of the interface.

With the field applied in-plane

At low temperature ($T < 30$ K), the LaAlO₃/SrTiO₃ interface exhibits negative in-plane magnetoresistance,[212] sometimes as large as -90%. [187] The large negative in-plane magnetoresistance has been ascribed to the interface's enhanced spin-orbit interaction.[187, 221]

3.2.6 Comparison to other 2D electron gases

The 2D electron gas that arises at the LaAlO₃/SrTiO₃ interface is notable for two main reasons. First, it has very high carrier concentrations, on the order of 10^{13} cm². Second, if the polar gating hypothesis is true, the 2D electron gas has the potential to be totally free of disorder, unlike other 2D electron gases that require doping or gating to form. However, so far researchers have been unable to synthesize interfaces that realize the promise of low disorder.

3.2.7 Synthesis methods

Most LaAlO₃/SrTiO₃ interfaces are synthesized using pulsed laser deposition. A high-power laser ablates a LaAlO₃ target, and the plume of ejected material is deposited onto a heated SrTiO₃

substrate. Typical conditions used are:

- Laser wavelength of 248 nm
- Laser fluence of 0.5 J/cm² to 2 J/cm²[222]
- Substrate temperature of 600 °C to 850 °C[209]
- Background oxygen pressure of 10⁻⁵ Torr to 10⁻³ Torr[209]

Some LaAlO₃/SrTiO₃ interfaces have also been synthesized by molecular beam epitaxy, sputtering, and atomic layer deposition.[223]

3.2.8 Similar interfaces

To better understand in the LaAlO₃/SrTiO₃ interface, researchers have synthesized a number of analogous interfaces between other polar perovskite films and SrTiO₃. Some of these analogues have properties similar to LaAlO₃/SrTiO₃, but some do not.

Conductive interfaces

- GdTlO₃/SrTiO₃[224]
- LaTlO₃/SrTiO₃[225]
- LaVO₃/SrTiO₃[225]
- LaGaO₃/SrTiO₃[226]
- PrAlO₃/SrTiO₃[227]
- NdAlO₃/SrTiO₃[227]
- NdGaO₃/SrTiO₃[227]
- GdAlO₃/SrTiO₃[228]
- Nd_{0.35}Sr_{0.65}MnO₃/SrTiO₃[229]
- Al₂O₃/SrTiO₃[230]
- amorphous-YAlO₃/SrTiO₃[223]
- La_{0.5}Al_{0.5}Sr_{0.5}Ti_{0.5}O₃/SrTiO₃[193]
- DyScO₃/SrTiO₃[231]
- KTaO₃/SrTiO₃[232]
- CaZrO₃/SrTiO₃[233]

Insulating interfaces

- LaCrO₃/SrTiO₃[234]
- LaMnO₃/SrTiO₃[226]
- La₂O₃/SrTiO₃[223]
- Y₂O₃/SrTiO₃[223]
- LaYO₃/SrTiO₃[223]
- EuAlO₃/SrTiO₃[228]
- BiMnO₃/SrTiO₃[235]

3.3 Introduction to my project

With my first major project in graduate school, I sought to understand the exciting yet puzzling conductivity at the interface of LaAlO₃ and SrTiO₃. By themselves, the minerals LaAlO₃ and SrTiO₃ are both transparent, electrically insulating, and non-magnetic. But when a layer of LaAlO₃ is deposited atop a SrTiO₃ substrate (under specific growth conditions), the interface between the two materials becomes electrically conductive.¹

The significance of the LaAlO₃/SrTiO₃ interface is emphasized in different ways by different scientists. Some scientist emphasize the interestingness of the interface's conductivity, superconductivity, and possible ferromagnetism. However, in my opinion, these are not all that novel. Regarding the conductivity, two-dimensional conductivity has already been studied for decades in other semiconductors. Regarding the superconductivity, it does not seem to be much different than superconductivity in plain old SrTiO₃, and while that may be interesting in its own right, its appearance in LaAlO₃ does not add much. And regarding the possible ferromagnetism at the interface, having never been able to reproduce myself, it seems likely to me that the reports in literature may be from contamination.²

¹When explaining the LaAlO₃/SrTiO₃ to a lay audience, I often tell them the parable of the salad, where lettuce and spinach come together to create bacon. A version is written out in Appendix F.

²This also seems likely considering that first, the reported observations of magnetism seem wildly inconsistent with one another[209, 186, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247] and second, scanning SQUID measurements reveal very inhomogeneous magnetism.[246, 237, 186] Of course, there is evidence on the other side too, enough to convince some minds that the ferromagnetism is intrinsic to the interface. My doubt is not 100% and I remain open-minded to new evidence and new arguments. And regardless of whether the magnetism is intrinsic to perfectly pure LaAlO₃/SrTiO₃ it would still be nice to understand.

Rather, what excites me the most about the LaAlO₃/SrTiO₃ interface are three aspects of its conductivity. First, the proposed polar doping mechanism has the potential to dope carriers into a semiconductor without disorder, in principle. Second, unlike other two-dimensional electron gases studied in other *sp* semiconductors, the two-dimensional gas in LaAlO₃/SrTiO₃ inhabits *d* orbitals, opening up new possibilities. And third, perhaps related to the other two, the two-dimensional electron gas in LaAlO₃/SrTiO₃ has an extremely high sheet carrier density relative to other two-dimensional electron gases.

3.4 LaAlO₃/SrTiO₃ interfaces doped with rare-earth ions

Adapted with permission from T.D. Sanders, M.T. Gray, F.J. Wong, and Y. Suzuki, Physical Review B **91**, 205112 (2015). Copyright 2015 by the American Physical Society.[\[248\]](#)

3.4.1 Introduction

From the quantum Hall effect to the field-effect transistor, two-dimensional electron gases (2DEGs) have been of both fundamental and technological interest. Historically, 2DEGs have been studied in covalent *sp*³-band semiconductors, but with advances in complex oxide heteroepitaxy, 2DEGs have also been created at interfaces between *d*-band oxides, such as the LaAlO₃/SrTiO₃ (LAO/STO) interface.[\[184\]](#) Because of the *d* band's relatively narrow bandwidth, the 2DEG at the LAO/STO interface exhibits strong electron-electron correlation effects not observed in conventional semiconductors.[\[249, 244, 245, 246, 239\]](#) Unfortunately, LAO/STO's low-temperature carrier mobilities (10 to 10^4 cm²/Vs) are still far inferior to those of the best covalent semiconductor 2DEGs (as high as 4×10^7 cm²/Vs).[\[250, 251\]](#) A central puzzle for the field is to understand precisely why carrier mobility is so low in LAO/STO and how it can be improved.

Over the past decade, a number of research groups have managed to boost carrier mobility in LAO/STO by a variety of methods, such as lower growth temperatures,[\[189\]](#) capping layers,[\[252\]](#) polar solvents,[\[253\]](#) high substrate miscut angles,[\[254\]](#) and conducting force microscope.[\[253\]](#) Yet despite these improvements, no one has conclusively identified the primary defect or mechanism limiting carrier mobility.

To investigate how defects limit carrier mobility in LAO/STO, some researchers have experimented with purposely doping chemical impurities at and near the interface.[\[255, 256, 257, 258, 259, 207, 260, 261\]](#) Most doping studies have doped the STO side of the interface with transition-metal dopants. Unfortunately, the results are difficult to interpret because the dopants trapped carriers, thus altering carrier concentration at the same time as they altered carrier mobility. More recently, transition metals have also been doped into the LAO side. These studies show little effect for low doping concentrations, but when the doping concentrations were high enough to distort the LAO lattice, electrical conductivity was suppressed.[\[261\]](#)

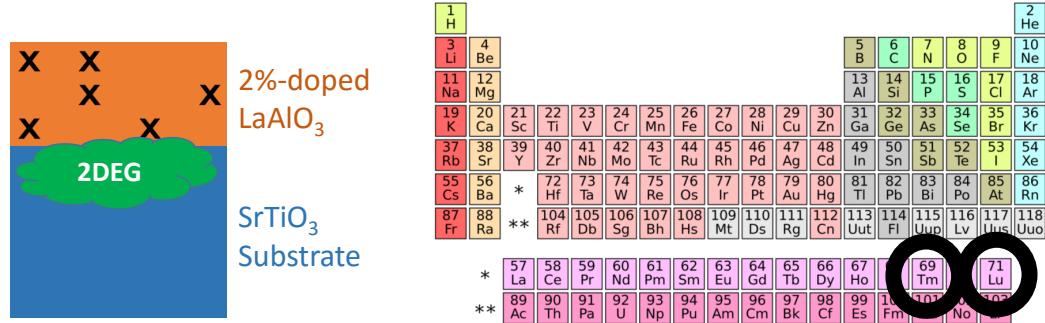


Figure 3.4: Left: A schematic diagram illustrating the relative positioning of the substrate, 2DEG, thin film, and rare-earth dopants. Right: A reminder of where Tm and Lu sit on the periodic table. Periodic table from Sandbh via Wikimedia Commons, distributed under a [CC-BY-SA 4.0 license](#).

3.4.2 Our experiment

In our experiment, we attempted to modify carrier mobility by doping the LAO side of the interface with isovalent rare earth ions (see Figure 3.4). In particular, we chose to dope 2% of the La sites with the rare-earth elements Tm or Lu. First, because Tm and Lu are isovalent with La³⁺, they should not donate or accept carriers. Second, because Tm and Lu have more protons than La (and hence larger atomic spin-orbit coupling), they may enhance spin-orbit scattering. And third, because Tm³⁺ has a magnetic moment of $2 \mu_B$, it may affect magnetic scattering.

Our main result is that doping the LAO side of the LAO/STO interface with 2% Tm or Lu has little effect on electron transport, even at low temperatures and in high magnetic fields. This result places upper limits on some types of interface scattering in LAO/STO. Our secondary result is that at low temperatures carrier concentration is anticorrelated with mobility, for both doped and undoped interfaces. This anticorrelation is too steep to be explained by ionized impurity scattering alone but may be explained by charged defects in or on the LAO film. Together these results show that electron transport in LAO/STO interfaces is robust against doping the La site with rare-earth ions, up to the 2% level.

3.4.3 Experimental methods

We synthesized LAO/STO interfaces using pulsed laser deposition. LAO films were deposited onto (001) TiO₂-terminated STO substrates at 700°C and in 3×10^{-5} Torr of O₂. To deposit the films, we focused a KrF laser at 2 Hz with an average energy density of 1.3 J/cm² onto sintered ceramic targets of the following compositions: LaAlO₃, Tm_{0.02}La_{0.98}AlO₃, or Lu_{0.02}La_{0.98}AlO₃. The target-heater

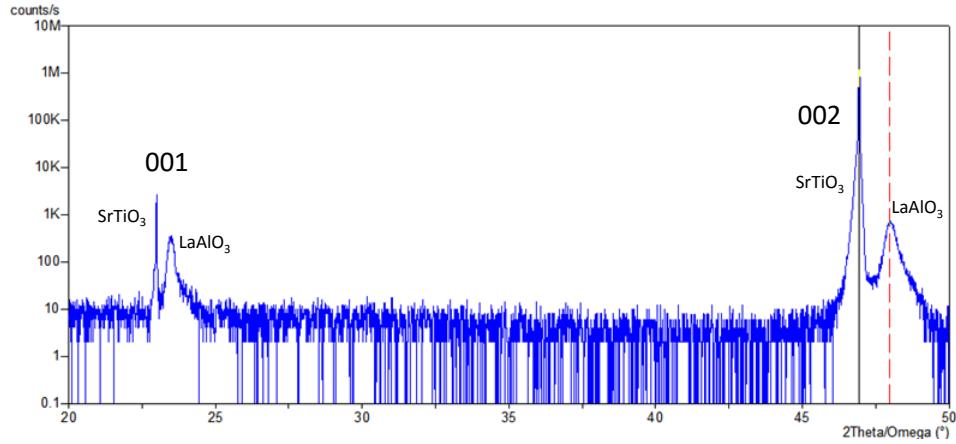


Figure 3.5: A wide-angle θ - 2θ X-ray diffraction scan reveals good crystallinity with no other crystal phases.

distance was 76 mm.

Magnetotransport measurements were performed in a Quantum Design Physical Property Measurement System in magnetic fields of up to 7 T and at temperatures down to 2 K. Samples were ultrasonically wirebonded with Al wires in the van der Pauw configuration. Carrier concentrations and mobilities were calculated using the Hall slope at low magnetic fields.

3.4.4 Results and discussion

Material quality

$\Theta - 2\Theta$ scans in X-ray diffraction showed that the films were epitaxial with excellent crystallinity. Intensity was only seen for the 00l family of peaks with no other phases or orientations present. An example wide-angle scan is shown in Figure 3.5.

Atomic force microscopy verified that the surfaces exhibited unit-cell steps. Figure 3.6 shows a representative set of three different films. The miscut angles were generally between 0.02 degrees and 0.2 degrees, making the terrace widths between 1000 nm and 100 nm. No significant correlation was seen between miscut angle and electronic properties.

The presence of dopants was verified with Rutherford backscattering spectroscopy. Figure 3.7 shows a high-energy zoom-in of the backscattering spectrum with clear peaks corresponding to Tm and Lu. The measured concentrations were consistent with the nominal expected concentrations of 2at%, given the technique's margin of error. The presence of Tm was further verified by M-edge

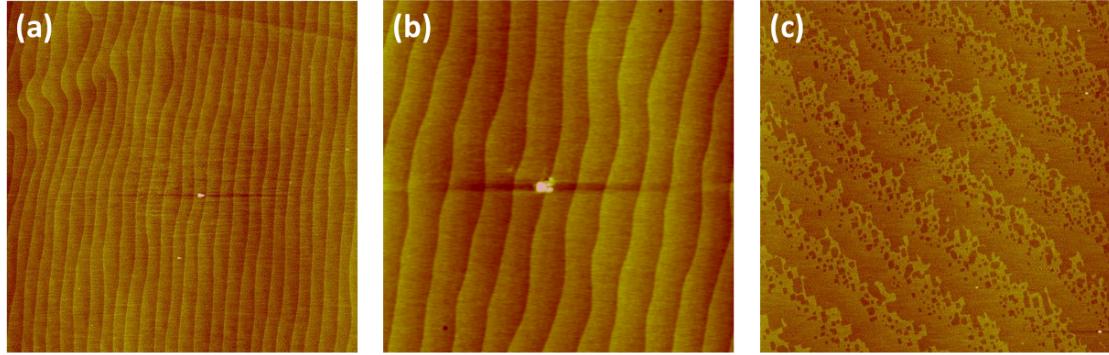


Figure 3.6: Three typical $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ atomic force microscope images of LAO/STO. The terraces (which are unit-cell height) illustrate that the surfaces of the films are atomically smooth. The defects in the middle of scans (a) and (b) are from the microscope landing on the surface of the sample. The 'swiss cheese' pattern of (c) is more common among samples with low miscut angle and wide terraces, though perhaps it could have been smoothed with a longer duration of substrate annealing.

X-ray absorption spectroscopy (not plotted). Lu was not measured because it has a full *f* shell.

Film thicknesses ranged from 1 nm to 20 nm (see Figure 3.8) and generally showed increasing carrier concentration with thickness, consistent with a polar gating scenario.

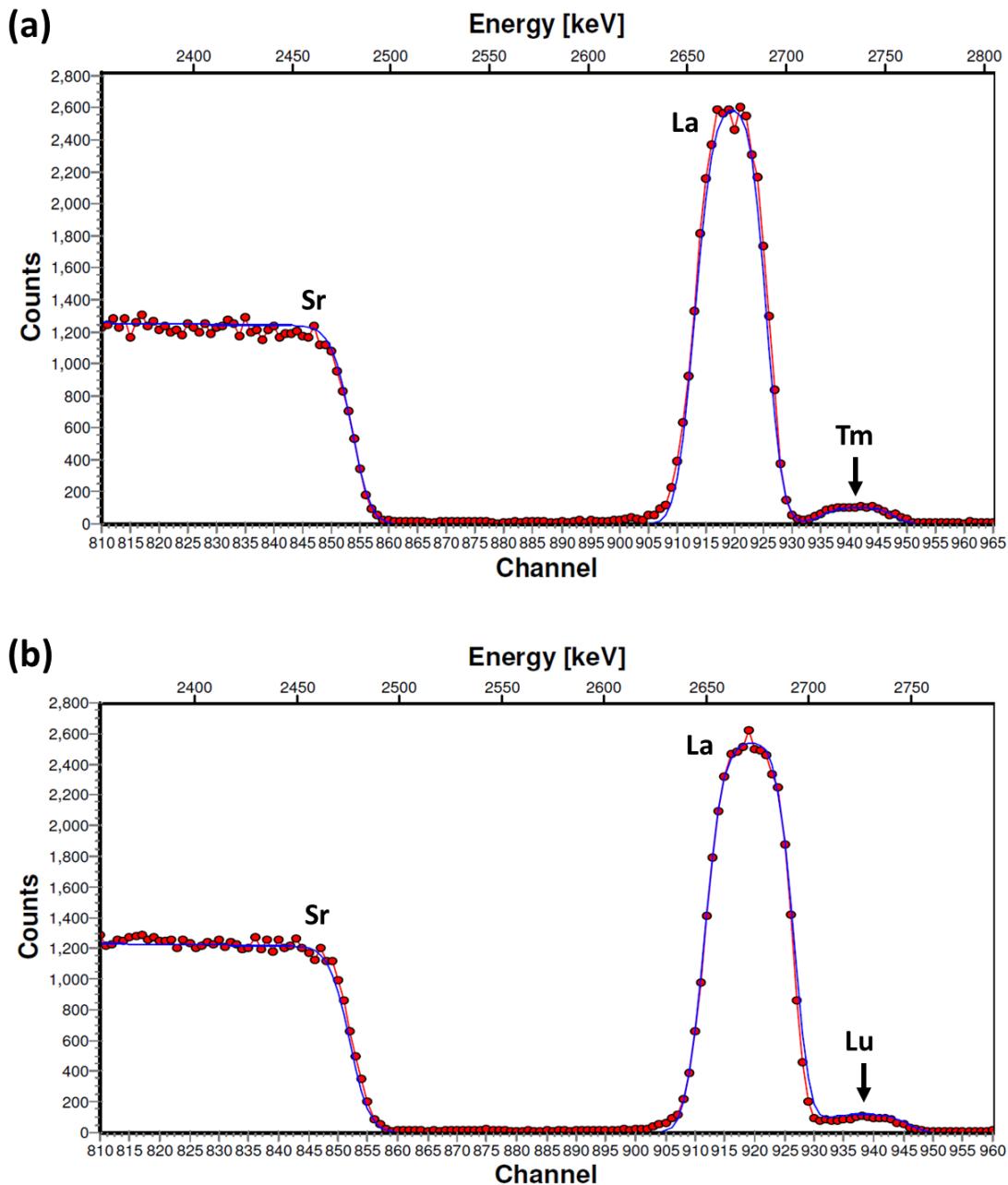


Figure 3.7: Rutherford Backscattering Spectrometry of (a) 10 nm of Tm-doped LAO on STO and (b) 10 nm of Lu-doped LAO on STO reveals that the rare-earth dopants were successfully incorporated.

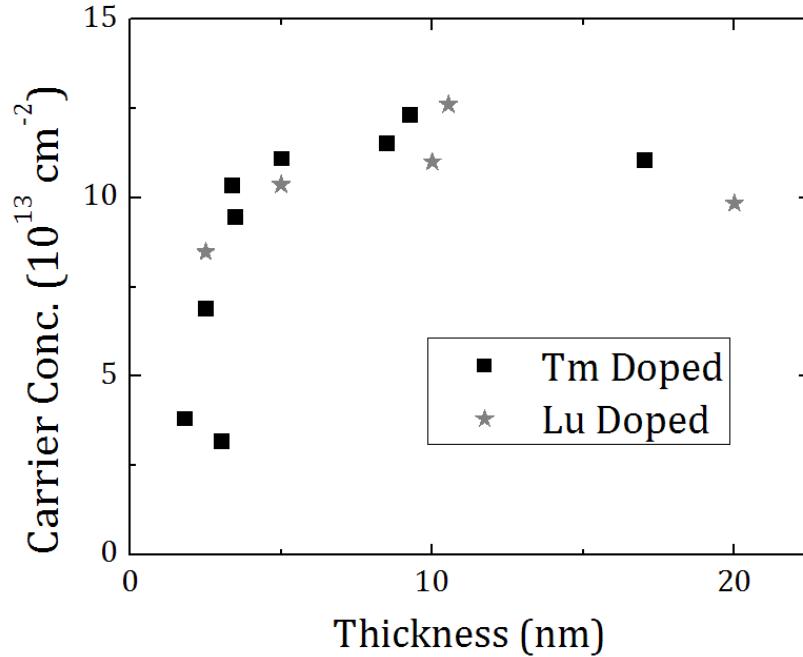


Figure 3.8: As with undoped LAO/STO,[262] we found that as film thickness grows, carrier concentration increases at a decreasing rate. This is consistent with the idea that the carriers arise from the positive surface charge generated by the naturally polar LaAlO₃ film, as shown in Figure 3.3.

Magnetoresistance

Because the rare-earth dopants Tm and Lu might increase magnetic scattering or spin-orbit scattering, we looked first for their effects on magnetoresistance (MR). We measured the sheet resistance and carrier concentration of doped LAO/STO samples and found little difference compared to undoped LAO/STO samples. The MR of a typical Lu-doped sample is shown in Figure 3.9 (Tm-doped and undoped samples are very similar). At low magnetic fields, the MR is parabolic with respect to magnetic field, consistent with ordinary magnetoresistance. However, at high magnetic fields, the MR appears to shift to a linear regime. Interestingly, this linear MR appears to be orbital in nature: when plotted as a function of mobility times magnetic field, the MR curves collapse onto a single function, in accordance with Kohler's rule[263] (see the lower plot of Figure 3.9). This high field linear MR is in agreement with measurements from other groups[212] and has also been seen in gated and ion irradiated STO,[264, 265, 266] but lacks explanation as far as we know. Theories of linear MR such as quantum linear MR,[213] classical linear MR,[214, 215] topological linear MR,[216] berry-phase linear MR,[217] phase-coherence linear MR,[218] and anisotropic-layered-metal linear

MR[219] do not seem relevant to the LAO/STO interface.³

³Apologies for the white space, but with so many figures, it's a challenge to float them all. I chose to keep the figures near their relevant text and waste part of this page rather than force you to keep flipping back and forth between figures and text that are many pages apart.

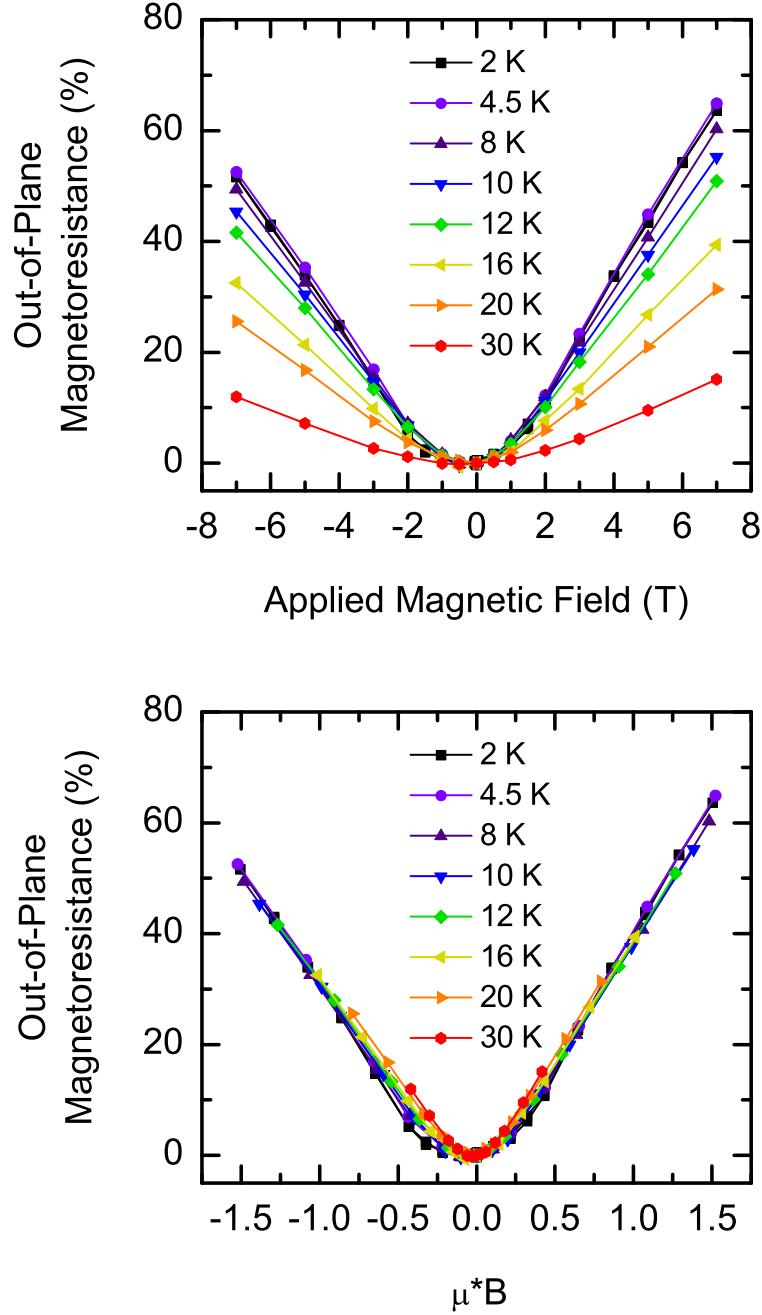


Figure 3.9: Upper: The out-of-plane magnetoresistance of a typical Lu-doped LAO/STO interface is parabolic at low field and linear at higher field, similar to undoped LAO/STO. Lower: Plotting the magnetoresistance against mobility times magnetic field ($\mu * B$) instead of B mostly collapses the magnetoresistance curves onto a single universal curve, implying that the magnetoresistance is orbital in nature and mostly due to a single carrier type.

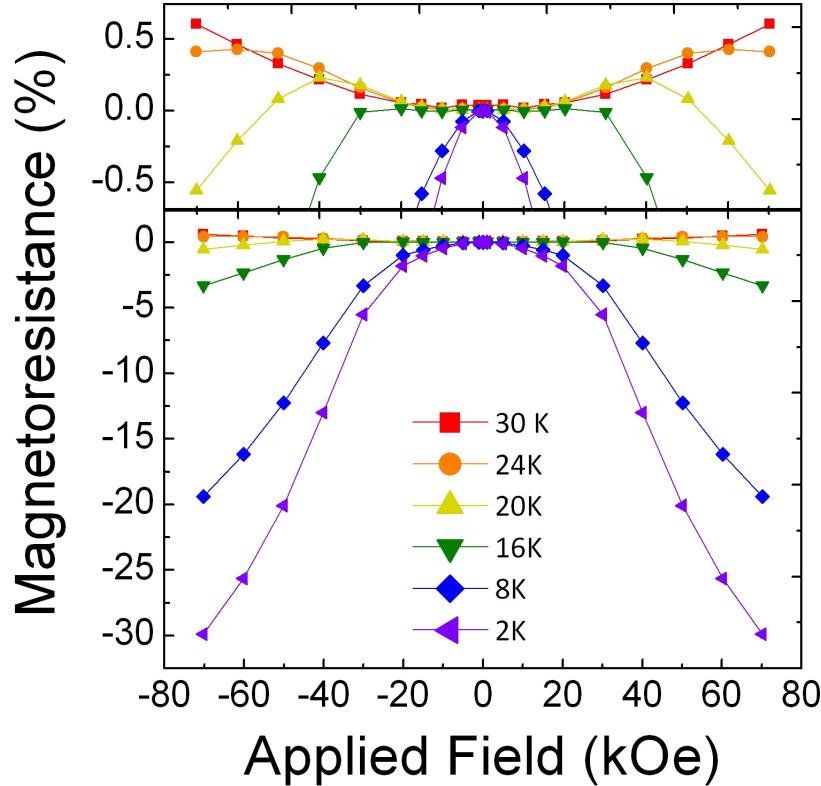


Figure 3.10: Similar to LAO/STO, our rare-earth-doped LAO/STO showed strong negative in-plane magnetoresistance at low temperatures and weak positive magnetoresistance at high temperatures. This plot is of a Lu-doped sample. Tm-doped and undoped samples looked very similar.

In addition to measuring MR with the magnetic field directed out-of-plane, we also measured MR with the magnetic field directed in-plane along the $\langle 110 \rangle$ direction (see Figure 3.10). As with the out-of-plane MR, the in-plane MR of our doped LAO/STO is very similar to that of undoped LAO/STO. At low temperatures, the in-plane MR is negative, in the range of -10% to -50% at 7 T. The temperature dependence of resistance and Hall curves is also similar among doped and undoped samples (see Figure 3.11).[260]

When the Hall curves are nonlinear (ignored by some papers but addressed by others), calculating carrier concentrations and carrier mobilities is not straightforward (see Figure 3.12). Assuming only a single carrier type, we calculated carrier concentration from the Hall slope at low magnetic fields. Although simple, this assumption seems justified because using it produces agreement with Kohler's rule, as shown in the lower plot of Figure 3.9. Even if there are multiple carrier types in reality, the agreement with Kohler's rule implies that the MR is dominated by just a single carrier type.

Using this procedure for calculating carrier concentration and mobility, we can compare our doped LAO/STO with undoped LAO/STO. Figure 3.13 shows the carrier mobilities and carrier

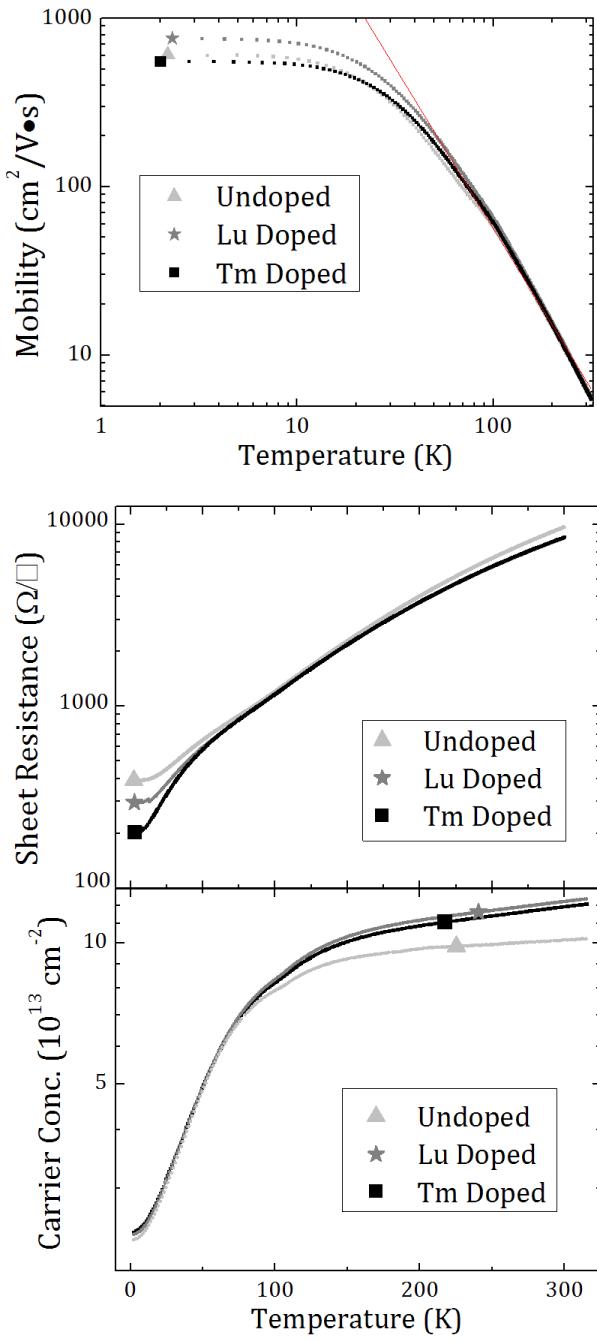


Figure 3.11: Temperature dependence of electrical transport properties in doped and undoped LAO/STO. It was messy to plot every sample we synthesized, so for narrative simplicity, only a few samples are plotted. The variation between the doped and undoped curves is much smaller than the sample-to-sample variance.

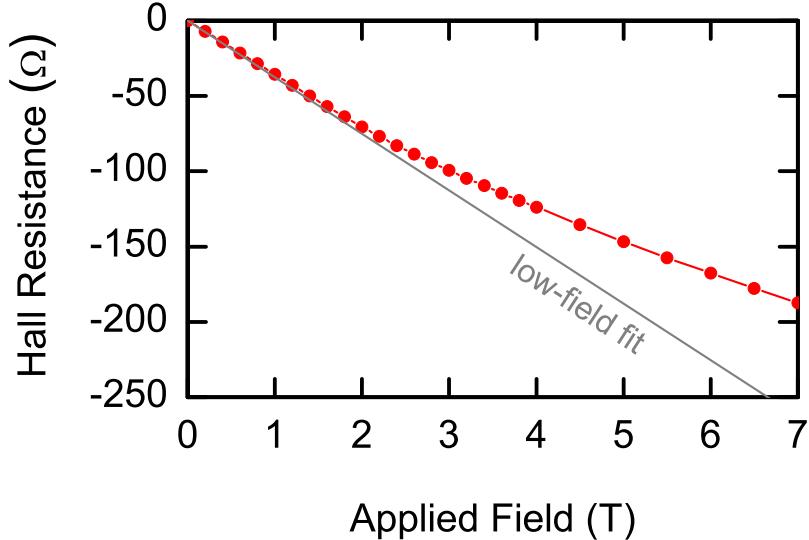


Figure 3.12: The Hall resistance of a typical Lu-doped LAO/STO interface at 2 K (Tm-doped and undoped interfaces are very similar). Although its nonlinearity suggests multiple carrier types, magnetoresistance measurements suggest that conductivity is dominated by the high mobility carriers.

concentrations of our Tm-doped and Lu-doped LAO/STO interfaces (measured at 2 K), plotted alongside undoped interfaces from our group and others (measured between 0.5 K and 15 K). Although our doped interfaces have slightly higher carrier mobility and lower carrier concentration than our undoped interfaces, the difference is smaller than the typical variance of undoped LAO/STO interfaces, making it difficult to attribute the difference to the dopants rather than target variability. Overall Figure 3.13 makes clear that the rare-earth dopants in the LAO did not have a large effect on low-temperature carrier mobility or carrier concentration.

The anticorrelation between carrier concentration and mobility

One of the most interesting relationships in our data is the steep anticorrelation between carrier mobility and carrier concentration at low temperatures (noted before by Wong et. al.[262] and Xie et. al.[253] for undoped LAO/STO). The anticorrelation is robust: we see it in both our doped and undoped samples, as well as in samples from most other groups, who use a variety of growth temperatures ($600\text{ }^{\circ}\text{C}$ to $850\text{ }^{\circ}\text{C}$), oxygen pressures (10^{-5} Torr to 10^{-2} mbar), oxygen post-annealing procedures, LAO thicknesses (4 unit cells to 37 unit cells), laser energy densities (0.6 J/cm^2 to 2 J/cm^2), laser pulse frequencies (1 Hz to 10 Hz), laser spot sizes (2 mm^2 to 10 mm^2), and electrical measurement techniques.[253, 254, 262, 267, 268, 269, 270, 271, 272, 273, 274]

The steepness of the anticorrelation between carrier mobility and carrier concentration gives

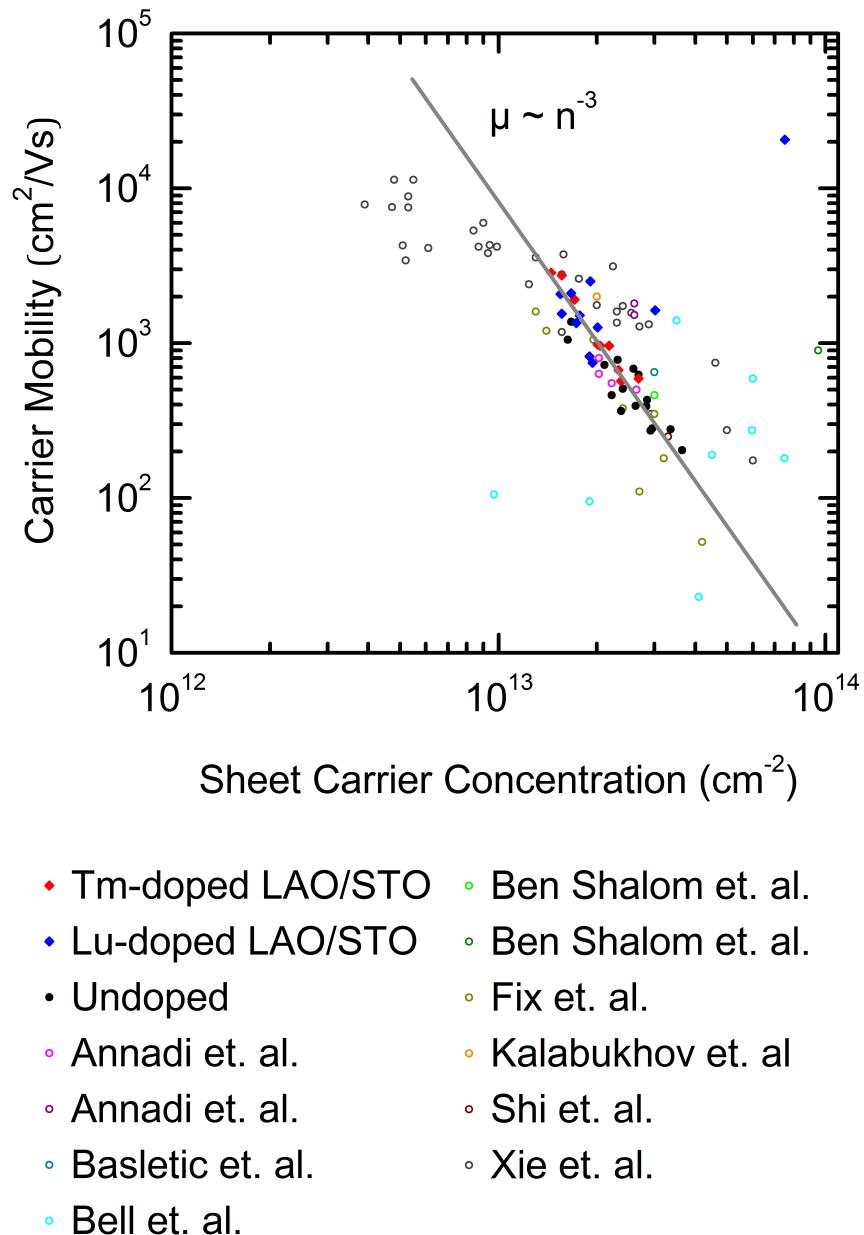


Figure 3.13: At low temperatures, carrier mobility μ is steeply anticorrelated with carrier concentration n . This is true of both our doped and undoped LAO/STO, as well as for undoped LAO/STO from other groups.[262, 267, 268, 269, 270, 271, 272, 254, 273, 274, 253] A rough power law fit to our own data shows that $\mu \propto n^{-3}$.

clues about its cause. Fitting a simple power law to our data shows that carrier mobility roughly varies as carrier concentration to the power of -3, a power so negative that it rules out otherwise plausible explanations such as ionized impurities. Ionized impurities, which both donate and scatter carriers, are often responsible for anticorrelations between carrier mobility and carrier concentration. However, ionized impurities normally result in a power law exponent of only -1, because changing the density of ionized impurities affects both carrier concentration and scattering proportionally. And in reality, the slope from ionized impurities is even shallower because additional carriers will screen the scatterers (as is the case in bulk STO, which has a power of about -0.8).[275, 276, 277]

Another plausible explanation for the anticorrelation is the two-band (or multi-band) model (see Figure 3.14).[278] The key idea is that as more carriers are added by some unspecified means, they fill a second, low-mobility band, bringing down the average mobility of the carriers. However, by itself, this explanation cannot explain the power of -3, because no matter how low the mobility of the second band, in an independent-electron band picture adding additional carriers ought to increase conductivity rather than reduce it. (Of course, if the two-band model is combined with strong electron-electron scattering then adding carriers would reduce the conductivity, in agreement with our data.)

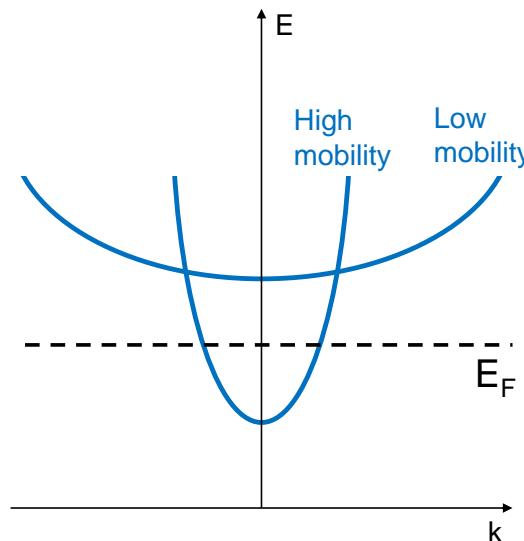


Figure 3.14: In the two-band model, as the Fermi level rises, a second, low-mobility band is filled, bringing down the average mobility of the carriers.

In general, any explanation that relies only on static defects is likely incorrect, given that other groups have been able to *dynamically* tune LAO/STO samples along this anticorrelation curve. These dynamic techniques include using a conducting atomic force microscope,[253] top gating through the LAO film,[279, 280] and using polar solvents.[253, 281] One simple fact links these

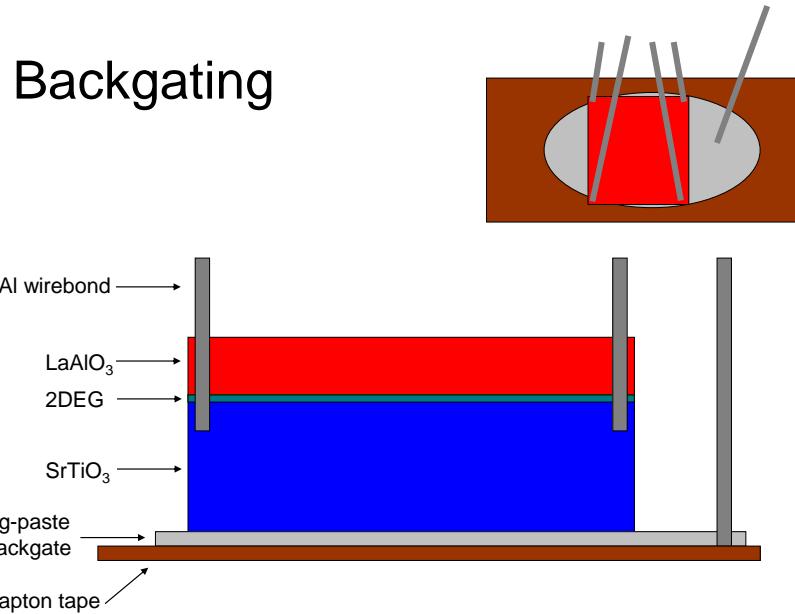


Figure 3.15: ‘Backgating’ LaAlO₃/SrTiO₃ involves applying a voltage to the backside of the SrTiO₃ substrate. Normally such a thick layer of gate insulator would diminish the effect of the gate voltage ($Q = CV$ and $C = \epsilon A/D$), but because SrTiO₃ has such a high dielectric constant at low temperature, the gate can still attract significant quantities of charge. When carriers are ‘backgated’ into the conductive interface, as opposed to top-gated, they no longer follow the anticorrelation curve.

dynamic techniques: they work by modifying the electrostatic potential from the LAO side of the interface. (Also, we emphasize that backgating through the STO substrate (see Figure 3.15), which modifies the electrostatic potential from the STO side, does not tune samples along this anticorrelation curve. In fact, backgating results in a positive correlation between carrier mobility and carrier concentration.[282] For this reason, backgated samples have not been included in Figure 3.13.)

This observation supports the notion that the anticorrelation between carrier mobility and carrier concentration is driven by the amount of positive charge in or on the LAO film (possibly due to oxygen vacancies or other defects). One possible explanation is the previously discussed two-band model combined with strong electron-electron scattering. In this model, positive charge attracts low-mobility carriers, which then strongly scatter the high-mobility carriers, strongly dropping their mobility. A second possibility relies on interface scattering (see Figure 3.16). As more positive charge in the LAO attracts more carriers, it also causes a larger interfacial electric field, pulling carriers closer to the interface where they experience more scattering and a consequently lower mobility. This phenomenon may be strongly amplified by the dielectric saturation of STO,[283] perhaps explaining why mobility varies so dramatically relative to the carrier concentration.[284]

We note that these hypotheses, which rely on positive charge in or on the LAO, are consistent

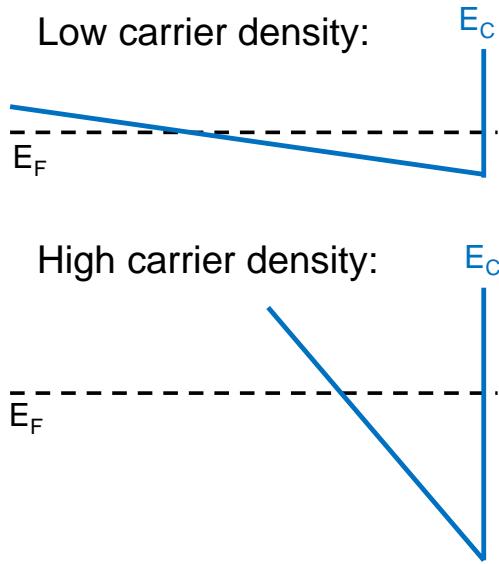


Figure 3.16: In the interface scattering model, more positive surface charge in the LAO would generate both more carriers as well as a stronger interfacial electric field, pulling the two-dimensional electron gas closer to the interface. This effect may be amplified quite strongly by STO's non-constant dielectric constant, which becomes much smaller at high electric fields.[283]

with our result that rare-earth dopants in the LAO have little effect on electron transport. If mobility is indeed determined by charged defects in or on the LAO film, then isovalent dopants would be expected to have no effect on carrier mobility, as our measurements confirm. Lastly, some theoretical papers have suggested that Ti-La hopping may be important for binding the 2DEG to the LAO/STO interface.[285, 286] However, our null results imply that Ti-La hopping is negligible, at least for electron scattering.

3.4.5 Conclusion

In conclusion, doping 2% of the La sites with Tm or Lu does not significantly alter the electron transport of the LAO/STO interface. This result is consistent with the idea that carrier mobility is determined by the positive charge in or on the LAO film. Also, as with undoped LAO/STO, we observe a steep anticorrelation between carrier mobility and carrier concentration at low temperatures. This steep anticorrelation cannot be explained by ionized impurities but seems to be driven by positive charge in or on the LAO film.

3.5 Technological applications of $\text{LaAlO}_3/\text{SrTiO}_3$

At present, there are no applications of the LAO/STO interface. However, speculative applications have been suggested, including field-effect devices, sensors, photodetectors, thermoelectrics, and even solar cells.[287, 288, 289, 290]

3.5.1 SketchFET

One of the most interesting potential applications of the LAO/STO interface is to use it as a canvas upon which circuits can be drawn with a conducting AFM. In 2008, scientists discovered that if they grew only three layers of LAO, just under the threshold for conductivity, then the interface could be coaxed the rest of the way by applying a positive voltage to the film with the conductive AFM tip.[291]

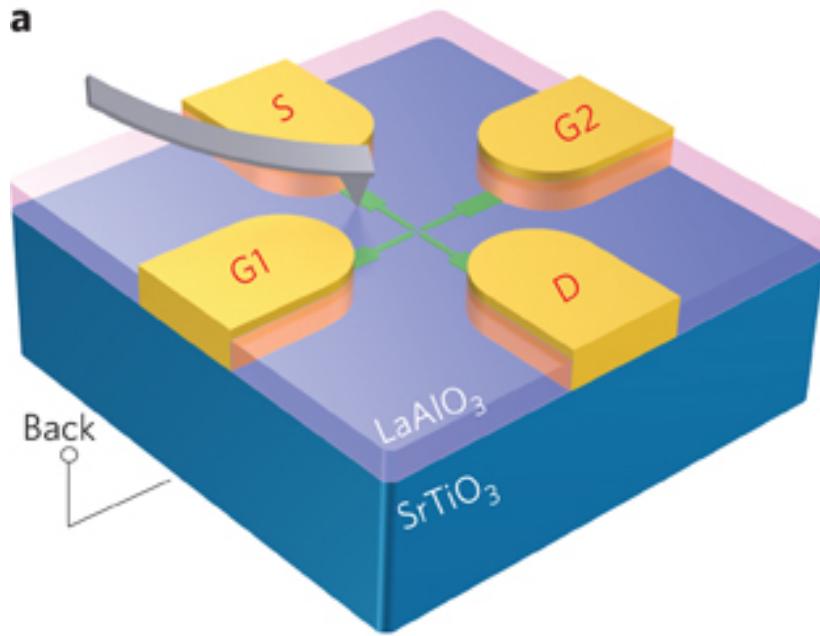


Figure 3.17: Named SketchFET, it is the world's first nanometer-scale gigahertz-speed transistor that can be 'drawn' onto a circuit by a tiny metal finger. Reprinted from P. Irvin, M. Huang, F. J. Wong, T. D. Sanders, Y. Suzuki, and J. Levy, *Appl. Phys. Lett.* **102**, 103113 (2013) with the permission of AIP Publishing under license number 3890370897085.

One application of this technology could be measuring the electrical properties of molecules. Instead of having to physically bring a molecule to a pre-designed circuit, you could, in theory, dump some molecules onto a subcritical LAO/STO 'canvas.' After finding a molecule with a microscope, you could use this technique to draw wires right up to the molecule. Rather than bringing the

molecule to the circuit, the circuit is brought to the molecule.

Chapter 4

The mysterious magnetism of cobalt perovskites

4.1 Executive summary

Because of their unique spin-state transitions, cobalt perovskites are compelling materials for electrical control of magnetism. In my project on thin films of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$, I used chemical pressure and epitaxial strain to extend the magnetic phase diagram of cobalt perovskites, revealing that ferromagnetism is promoted by both larger A-site cations and more tensile strain (see Figure 4.19). Second, by tuning the growth of PrCoO_3 thin films on SrTiO_3 , I was able to achieve a record-high T_c of 65 K. And third, my X-ray magnetic circular dichroism data suggest that the lack of ferromagnetism in $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films is due to weaker exchange rather than a lack of magnetic moment.

4.2 Background

This chapter describes my work to understand the mysterious ferromagnetism in some cobalt perovskite thin films. Hopefully one day this understanding will be used to build spintronic devices capable of outperforming today's electronic devices. Before diving into the details of my project, I'll first share some prerequisite background information on cobalt's unique magnetism and electronic structure.



Figure 4.1: Pure elemental cobalt is a magnetic metal. Photograph by anonymous, distributed under [Creative Commons Attribution 1.0 Generic License](#), via Wikimedia Commons.

4.2.1 Cobalt

Pure cobalt has the highest Curie temperature of any element, only demagnetizing above 1390 K.¹ Cobalt's strong ferromagnetism is due in part to its position on the periodic table. Flanked by iron and nickel on the periodic table's first row of transition metals, cobalt has valence electrons that occupy the fairly localized $3d$ orbitals, which lie at the magnetic sweet spot of orbital localization. These $3d$ electrons are localized enough to form local magnetic moments, but also delocalized enough to interact between atoms and order over long ranges.²

4.2.2 Cobalt's electronic structure

Although cobalt ($[Ar]4s^23d^7$ when neutral) can take many oxidation states (as low as -3 and as high as +5), it typically exists with a charge of +2 ($[Ar]3d^7$) or +3 ($[Ar]3d^6$) or sometimes +4 ($[Ar]3d^5$). These electronic states are important for thinking about cobalt's electronic structure and magnetism.

In an isolated cobalt atom, knowing the charge state—along with Hund's rules—is good enough to determine the cobalt atom's electronic structure.

However, in a solid material, cobalt atoms are *not* isolated. Nearby atoms impinge on the cobalt

¹Being ferromagnetic at room temperature in elemental form is rare by itself. Only three other elements share this distinction: iron, nickel, and (just barely) gadolinium.

²Given cobalt's proclivity for magnetism, it's no surprise that one of its main applications is as an ingredient in magnetic alloys. Every modern magnetic hard drive stores its 1s and 0s in a magnetic alloy made from cobalt.

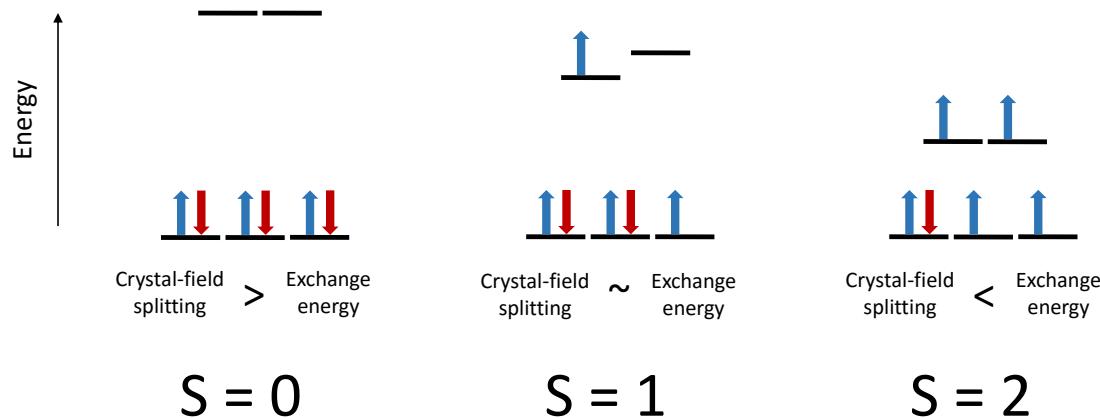


Figure 4.2: In Co^{3+} , which has six valence electrons spread between six t_{2g} states and four e_g states, tuning the crystal-field splitting can potentially tune Co's magnetic state from a diamagnetic $S=0$ state to a magnetic $S=2$ state. Understanding and controlling this phenomenon of Co^{3+} is the key idea behind my research project.

atom, affecting some cobalt electron orbitals more than others. For instance, in a perovskite crystal structure where cobalt sits on the B-site surrounded by an octahedron of oxygen atoms, the two antibonding e_g orbitals are raised in energy above the three t_{2g} orbitals.³ This effect is known as crystal-field splitting.

And it turns that Co^{3+} , by having six valence electrons, exactly equal to the six t_{2g} states (with two spin states for each of three orbitals), is uniquely affected by crystal-field splitting. If crystal-field splitting is large (relative to intra-atomic exchange), then all six of Co's valence electrons will pair up in the low-energy t_{2g} orbitals, resulting in an $S=0$ diamagnetic state. However, if crystal-field splitting is small (relative to intra-atomic exchange), then the electrons will fill both the t_{2g} and e_g orbitals, resulting in a $S=1$ or $S=2$ magnetic state, as shown in Figure 4.2.

4.2.3 Cobalt's unique spin-state transition

Oftentimes in physics a thing can be well-studied yet poorly understood. The magnetism of LaCoO_3 is one such example. Despite being the subject of detailed study since the 1960s, the magnetism of this cobalt perovskite is still a puzzle, a puzzle that researchers have not yet given up on.

³I feel a little unclean talking about single-electron orbitals when in reality they do not exist. However, it's much harder to talk about multiparticle wavefunctions, so for conceptual simplicity, I will continue to lean on this useful fiction.

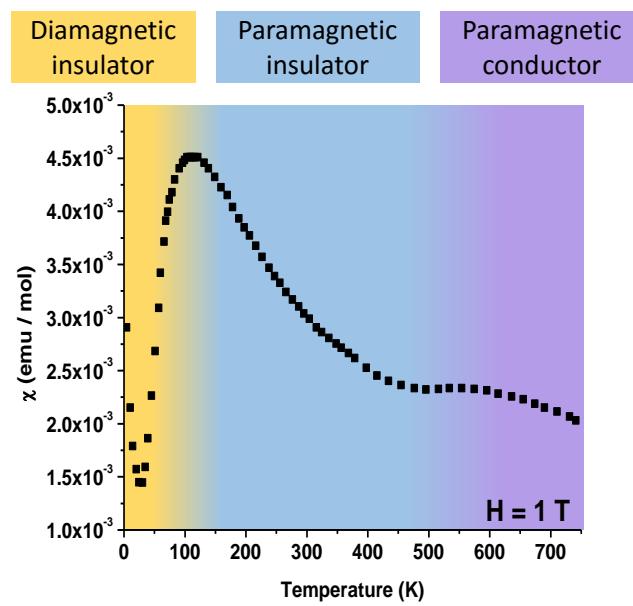


Figure 4.3: The magnetic susceptibility of LaCoO_3 versus temperature, adapted from Senaris-Rodriguez et al.[292] It is very rare for a material's magnetic susceptibility to rise with temperature, as LaCoO_3 's susceptibility does below 100 K.

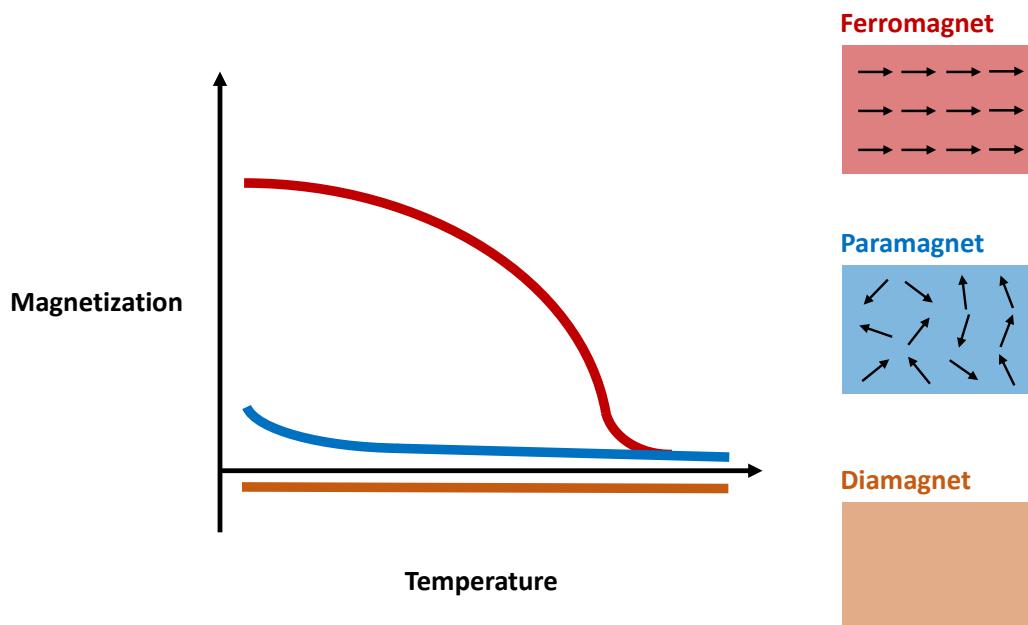


Figure 4.4: Three common forms of magnetism. First shown in Figure 1.13 in Chapter 1.

Plotted in Figure 4.3 is the magnetic susceptibility of LaCoO_3 over a range of temperatures. Unlike a simple diamagnet, paramagnet, or ferromagnet (see Figure 4.4), LaCoO_3 has a magnetic susceptibility that evolves in a complicated way with temperature. The three background colors of the susceptibility plot highlight three different phases of the material. At high temperatures, above 500 K, LaCoO_3 is paramagnetic and electrically conducting. However, as it cools below that point, the material turns insulating (or semiconducting, more accurately) and, although it remains paramagnetic, its paramagnetism becomes weaker.⁴ Cool the material further, below 100 K, and it the magnetic susceptibility falls off a cliff. Although it never reaches negative numbers, scientists still interpret this drop to mean that most of the material has turned diamagnetic, attributing the small positive remnants to trace amounts of material imperfections that remain paramagnetic.

Why all of this happens is complicated to explain. However, what all theories share in common is the state of the cobalt in the low-temperature diamagnetic regime. Because the cobalt atoms have no positive magnetic moment, there is only a single magnetic state that's possible: the $S=0$ state, where cobalt has six electrons paired up by spin in the six t_{2g} states. Because the numbers of spin up and spin down electrons are equal, there is no net spin magnetic moment. And because the filled

⁴Although the material's magnetic susceptibility continues to grow with cooling, it doesn't grow as fast as predicted by Curie's law, which expects a $1/T$ curve shape. Instead, it seems to shift to a curve that still obeys the $1/T$ relationship but with a different, smaller Curie constant.

t_{2g} states have no orbital angular momentum (thanks to the crystal-field symmetry breaking), there is also no net orbital magnetic moment.

However, in the paramagnetic states, it's much less obvious what the electrons are doing. Are the cobalt atoms in a high-spin S=2 state?^[293] Are they in an intermediate-spin S=1 state?^[294] Are they in some mixture of states with some potentially complicated ordering?^[295] Although each of these scenarios is supported by some evidence, it is surprisingly difficult to find an experimental technique that can distinguish between them without ambiguity. Even theoretical and computational analysis does not resolve the issue, since the results are sensitive to the simplifying assumptions put into the calculations. A great, relatively up-to-date review of the back-and-forth arguments over the decades can be found in Haverkort et al.^[293], which itself makes the case for the high-spin S=2 scenario on the basis of X-ray absorption experiments.

4.3 The mystery of ferromagnetism in cobalt perovskite thin films

In 2007, everything changed. D. Fuchs et al. discovered that when thin films of LaCoO₃ were deposited on LSAT, the LaCoO₃ was no longer diamagnetic nor paramagnetic below 85 K; instead, it was ferromagnetic.^[296] On its face, this discovery was not necessarily a big deal. It is well known that some non-magnetic materials can become ferromagnetic when synthesized in a defective or non-stoichiometric manner, and in fact, when LaCoO₃ was first being synthesized and studied back in the 1960s, samples *did* sometimes exhibit small amounts of ferromagnetism.^[297] However, if the ferromagnetism in Fuchs's LaCoO₃ thin films was somehow caused by the epitaxial crystal strain applied by the LSAT substrate, then that would be particularly exciting because the strain mechanism could allow an interposed piezoelectric material to electrically control the LaCoO₃'s magnetic state.^[298]

To test whether this ferromagnetism was from epitaxial strain or a more mundane, less dynamically controllable mechanism, Fuchs et al. performed a number of important experiments that distinguish these otherwise plausible hypotheses, detailed below.

4.3.1 Growth defects do not cause the ferromagnetism

LaCoO₃'s magnetism is known to be sensitive to defects. Some early samples of LaCoO₃ synthesized in the 1960s exhibit ferromagnetic hysteresis, which the authors of the study attribute to small defective magnetic regions embedded in the larger non-magnetic bulk.^[297] It's also known that substituting La with Sr in La_{1-x}Sr_xCoO₃ can induce ferromagnetism with Sr concentrations as low as 10%–20% (and presumably other methods of hole doping could induce ferromagnetism as well).^[299] Furthermore, as discussed in Chapter 2, thin film deposition techniques tend to produce

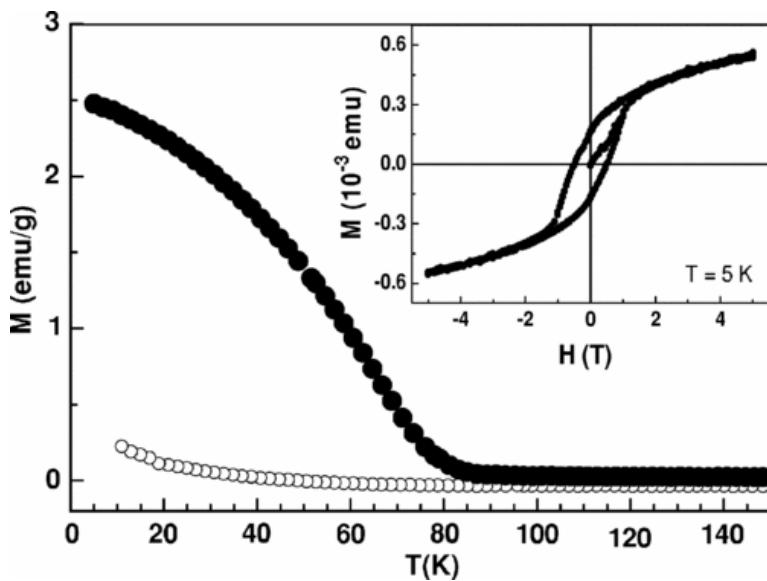


Figure 4.5: Fuchs et al.’s measurements of magnetization of LaCoO_3 thin films as a function of temperature, T , and applied magnetic field, H . The black points are for epitaxial thin films and the white points are for polycrystalline thin films. Reprinted figure with permission from D. Fuchs et al., Physical Review B **75**, 144402 (2007) under license 3871701224279. Copyright 2016 by the American Physical Society.

samples with more defects than bulk synthesis techniques,⁵ so it seems entirely reasonable that the ferromagnetism of LaCoO_3 thin films on LSAT could be from defects.

To test this hypothesis, Fuchs et al. deposited polycrystalline films using the exact same deposition conditions, except instead of depositing on LSAT, they deposited on LSAT capped with a 20-nm layer of CeO_2 , which inhibited epitaxial growth. If anything, inducing polycrystalline growth instead of epitaxial growth should increase the concentration of any defects, and thereby increase their effect on the material’s magnetism. However, not only did polycrystalline films of LaCoO_3 fail to exhibit enhanced ferromagnetism, they exhibited no ferromagnetism at all! From this, it seems unlikely that deposition-induced defects are responsible for the ferromagnetism.⁶

⁵Bulk synthesis, which is often done at very high temperature, only tends to be better when synthesizing materials that exist in thermal equilibrium. For creating materials out of equilibrium, bulk synthesis techniques are often worse than thin film techniques.

⁶Of course, this doesn’t rule out defects entirely. Defects caused by the proximity of the LSAT substrate would disappear with this CeO_2 spacer, as would defects caused by the strain from the LSAT substrate.

4.3.2 Surface states do not cause the ferromagnetism

A second possibility is that the ferromagnetism comes from some surface state. A 2004 study found that although single-crystal LaCoO_3 was not ferromagnetic, when ground up into a powder or cold-pressed (two forms with high surface area), LaCoO_3 exhibited increasing amounts of ferromagnetism.[300] It therefore seems quite plausible that thin films of LaCoO_3 are ferromagnetic simply because a thin film has a tremendously high surface-to-volume ratio.

Well, the polycrystalline experiment already showed that polycrystalline films, which have an equal amount of surface area, are not ferromagnetic. Nonetheless, it's still possible that the magnetism comes from a surface state at the interface between LaCoO_3 and LSAT. The polycrystalline film experiment is not able to falsify this hypothesis because in order to induce the polycrystalline crystal growth, a CeO_2 layer was inserted between the LaCoO_3 and LSAT.

To test whether the ferromagnetism came from an interface state or a bulk state, Fuchs et al. deposited films of varying thickness. If the magnetism comes from an interface state, the magnetization of the material should be independent of film thickness. However, if the magnetism comes from the bulk of the material, then the magnetization should scale linearly with film thickness. When Fuchs et al. measured their films, they founded that magnetization scaled linearly with film thickness, proving that the magnetism comes from a bulk state, not a surface state.

4.3.3 Epitaxial strain seems to cause the ferromagnetism

A third hypothesis is that the ferromagnetism is caused by epitaxial strain from the LSAT substrate. Although this is already supported by the polycrystalline film experiment (in which non-epitaxial films exhibited no ferromagnetism), Fuchs et al. further explored this hypothesis by depositing LaCoO_3 on a wide variety of crystal substrates, finding that the magnetism roughly correlated with the film's strain state.[301]

Despite Fuchs et al.'s evidence that the ferromagnetism of LaCoO_3 thin films is caused by strain, it was nonetheless unclear *how* that strain causes the magnetism. Epitaxial strain can result in many different changes, only some of which may be directly relevant to the ferromagnetism. As examples, epitaxial strain can increase atomic spacing, decrease atomic spacing, increase tetragonal asymmetry, induce octahedral rotations, change the energies of defect formation, cause strain gradients, and more. Since 2007, a great deal of effort has been aimed toward generating and testing models that could explain the ferromagnetism in LaCoO_3 thin films. The major ideas of the past decade are briefly reviewed in the next section.

4.4 Hypothesized models for the ferromagnetism

Explaining the magnetism in thin films of LaCoO_3 is more difficult than it might first appear. Any good model needs to successfully explain four features at once:

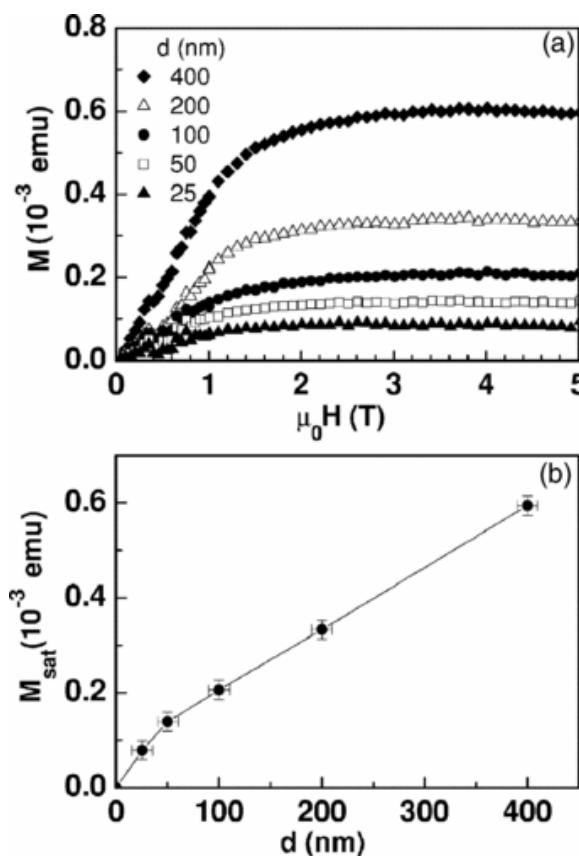


Figure 4.6: Magnetization of LaCoO_3 thin films scales with thickness. Reprinted figure with permission from D. Fuchs et al., Physical Review B **75**, 144402 (2007) under license 3871701224279. Copyright 2016 by the American Physical Society.

- Where does the magnetic moment come from?
- Where does exchange come from?
- Why is the magnetization so low?
- Why are the films electrically insulating?

Below are the major hypotheses that have been put forth to explain the magnetism in LaCoO₃ thin films. Given that many proposed models are inconsistent with one another, it is likely that most of these models will ultimately be found incorrect. The truth we eventually come to recognize could end up being a single one of these models, a combination of these models, a group of different models that each apply correctly in a different domain, or a model altogether unconsidered.

4.4.1 Jahn-Teller suppression

The original explanation for the ferromagnetism given by Fuchs et al. is that tensile strain (mostly) prevents a cooperative Jahn-Teller distortion from breaking the degeneracy of the e_g orbitals. As a result of the (near) degenerate e_g orbitals, superexchange (as described by the Goodenough-Kanamori-Anderson rules) predicts ferromagnetic ordering instead of antiferromagnetic ordering, common in single-valence perovskite oxides. In addition, Fuchs et al. proposed that the tensile strain also reduced the crystal field splitting in the LaCoO₃, causing the magnetic state of the cobalt atoms to be in an S=1 intermediate spin state rather than the S=0 low spin state that occurs in bulk LaCoO₃ at low temperatures.

4.4.2 Tetragonal strain

A second early hypothesis for the ferromagnetism in LaCoO₃ thin films was tetragonal distortion. Density functional theory calculations performed by Gupta and Mahadevan in 2009 suggest that tetragonal distortion caused by epitaxial strain (both tensile *and* compressive) stabilize an intermediate spin state that is ferromagnetic.[302] However, one problem with these calculations is that they also predicted the LaCoO₃ films should be in an electrically conducting state, which contradicts the experimental finding that the films are insulating.

4.4.3 Non-uniform tetragonal strain caused by lattice modulations from strain relaxation

In 2012, Woo Seok Choi et al. suggested that the ferromagnetism in LaCoO₃ comes from ordering of strain-induced spin states.[308] Below I will paraphrase and interpret their main findings, but for a more comprehensive take, I suggest reading their original paper from 2012[308] or their follow up from 2014[311].

Table 4.1: A scorecard of various models that have been proposed to explain the magnetism in LaCoO_3 thin films. (Don't pay too much attention to the four unspecified exchange mechanisms—they are likely to fall under the superexchange label as well. The larger point is that no models propose direct exchange or double exchange as the relevant magnetic mechanism in LaCoO_3 .

Model	Magnetic moment?	Exchange mechanism?	Low magnetization?	Insulating?
Jahn-Teller suppression[296]	Intermediate spin	Superexchange	No	Unclear to me
Tetragonal strain[302]	Intermediate spin	Unspecified	No	No
Octahedral tiltings[303]	Intermediate spin	Superexchange	No	No
Percolative network[304]	36% HS/64% LS	Superexchange	Percolative network	Yes
Tensile strain[305]	50% HS/50% LS	Superexchange	No	Yes
Spin canting[306]	50% HS/50% LS	Superexchange	Canting	Yes
Ferromagnetic clusters[307]	Clusters of non-zero spin	Unspecified	Clusters	Yes
Lattice modulations[308]	Non-zero spin in stripes	Unspecified	Minority on stripes	Yes
Orbital ordering[309]	IS and HS	Unspecified	Ferrimagnetic ordering	Unclear to me
Ordered oxygen vacancies[310]	High-spin Co^{2+}	Superexchange	Complicated pattern	Peierls-like gap

Using Z-contrast scanning transmission electron microscopy, Choi et al. observed vertical stripes (lattice modulations) in films of LaCoO_3 grown on LSAT and SrTiO_3 , substrates that apply tensile strain. Although these stripes have been identified as ordered oxygen vacancies by other groups, Choi et al. reported that their films, unlike others in the literature, did *not* exhibit significant quantities of oxygen vacancies, as indirectly measured by the lack of a Co^{2+} prepeak in X-ray absorption spectroscopy (and further buttressed by optical conductivity measurements). Further, they noted that these vertical stripes did not penetrate all the way to the film-substrate interface, but only appeared beyond the thickness at which conventional strain relaxation is calculated to occur (eight and four unit cells for LSAT and SrTiO_3 , respectively). They argue that the connection between the depths of the stripes and the conventional strain relaxation thickness, combined with the lack of any other visible strain relaxation mechanism, strongly suggests that these stripes are the mechanism by which the films are relaxing under tensile strain.

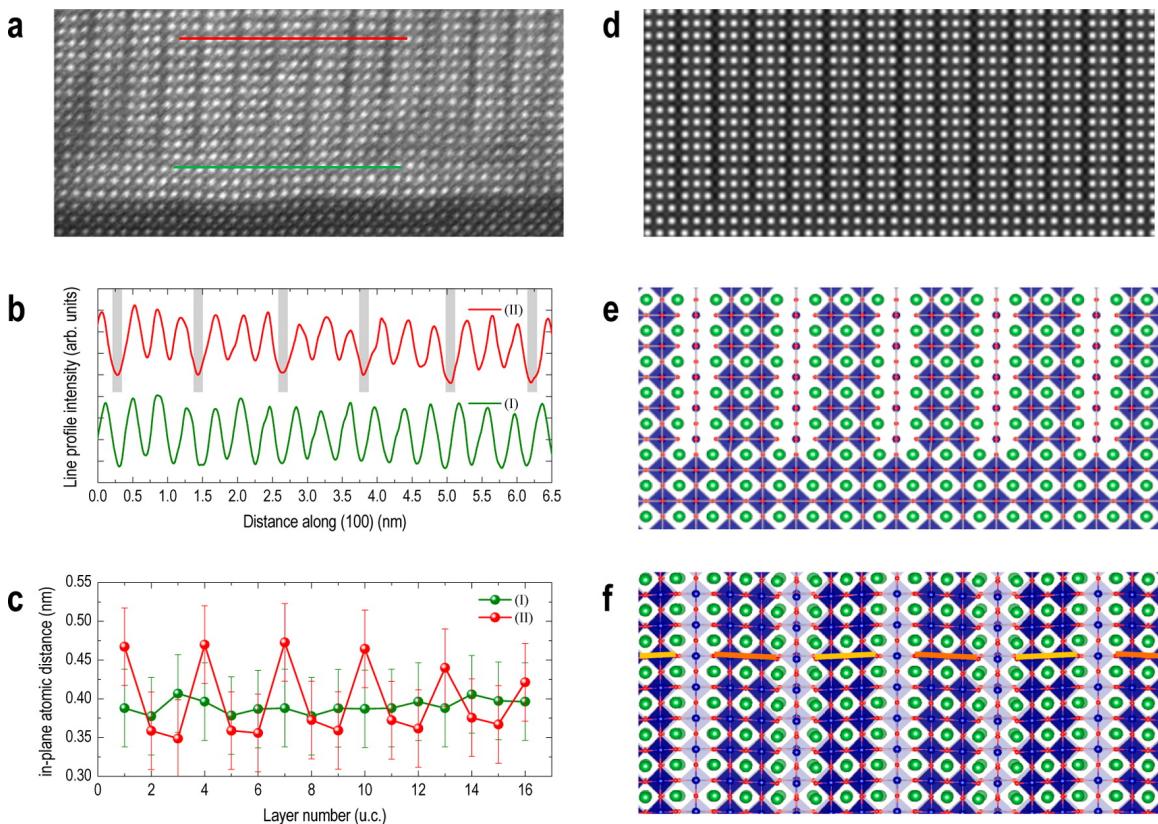


Figure 4.7: From Woo Seok Choi et al.: “(a) Experimental, cross-sectional Z-contrast STEM image for the LCO film on STO (image taken from Figure 2c). (b) Intensity profile for the lines (green for region I and red for region II) drawn in (a); gray areas indicate the dark vertical stripes for region II. (c) In-plane atomic distances between La atoms extracted from (b). (d) Simulated, cross-sectional STEM image for a LCO film on STO, clearly resembling the experimental image shown in (a). (e) Cross-sectional and (f) top views for the artificially constructed LCO film structure. Yellow and orange lines in the top-view image indicate the opposite monoclinic distortion for the neighboring domains.” Reprinted (adapted) with permission from Woo Seok Choi, Ji-Hwan Kwon, Hyoungjeen Jeen, et al., “Strain-Induced Spin States in Atomically Ordered Cobaltites”, *Nano Letters* **2012** 12 (9) 4966-4970.[308] Copyright 2016 American Chemical Society.

Having measured vertical, repeating stripes of lattice modulations, Choi et al. go on to hypothesize that the atypical coordination of the Co^{3+} atoms at the lattice modulations cause them to be in an intermediate ($S=1$) or high ($S=2$) spin state (similar to the crystal field effect I discussed earlier). These magnetic moments could then order by some mechanism, left unspecified, resulting in the ferromagnetism measured in experiments.

One advantage of this hypothesis is that it could explain why measured magnetic moments are consistently below one Bohr magneton per unit cell. Because only the Co atoms at the lattice modulations are magnetic, the remaining majority of the Co (estimated to be 60% on SrTiO_3) is

expected to be non-magnetic.

4.4.4 Oxygen vacancy ordering

Although the stripes in scanning transmission electron microscope images of LaCoO₃ films were interpreted as lattice modulations by Choi et al., others have instead interpreted the stripes as planes of ordered oxygen vacancies. Choi et al. originally considered this possibility but rejected it on the basis of not seeing a Co²³⁺ signature in x-ray absorption spectroscopy (in theory, large concentrations of oxygen vacancies should dope LaCoO₃ n-type, resulting in large concentrations of Co²⁺). However, because macroscopic x-ray absorption spectroscopy is a volume-averaged measurement, there was no direct measurement of the microscopic stripes themselves.

In 2014, Biskup et al. measured the stripes with electron-energy-loss spectroscopy.[\[310\]](#) They found that the stripes had diminished concentrations of oxygen, as shown in Figure 4.8, reprinted from their paper. In addition, by examining the Co L₃/L₂ ratio as a function of position, they found that the oxygen-donated electrons were localized on the Co atoms along the stripe.⁷

⁷It's worth noting that the coexistence of charge ordering and ferromagnetism is rare. Typically, when charge ordering is associated with any kind of magnetic order, it is associated with antiferromagnetism.[\[312\]](#)

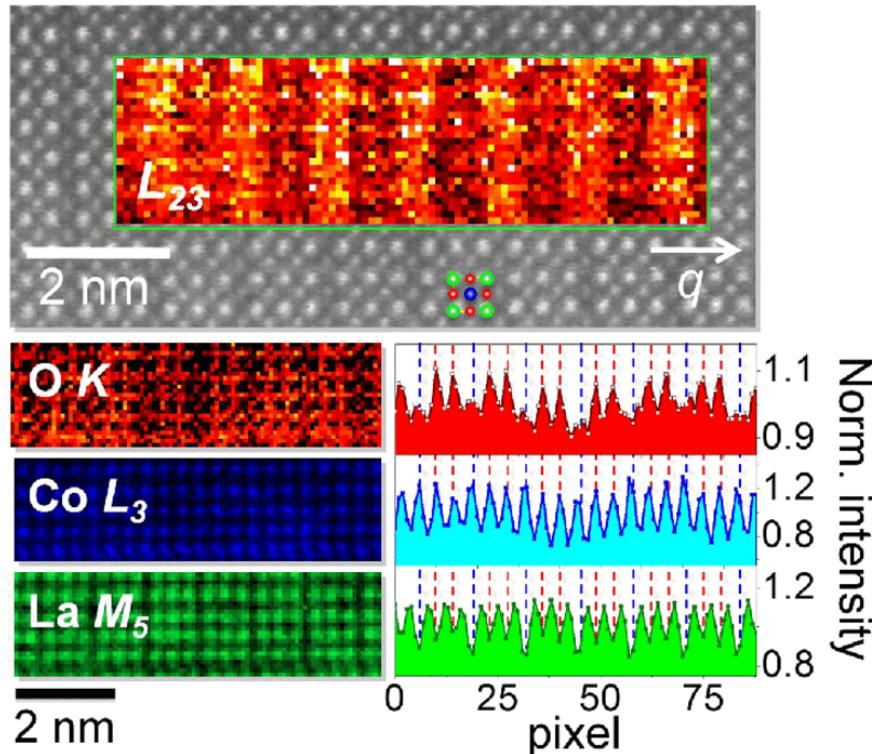


Figure 4.8: From Biskup et al.: “Top: high resolution Z-contrast image of the LCO film showing an average modulation length of three perovskite blocks. The inset shows the Co L_3/L_2 intensity ratio map for a spectrum image acquired in the area marked with a green rectangle. A schematic shows the pseudocubic unit cell (blue=Co; green=La; red=O). Bottom left: elemental chemical maps constructed by integrating the corresponding EEL spectra: O K edge (red), Co L_3 edge (blue), and La M_5 edge (green). Bottom right: normalized intensity across the O K, Co L_3 , and the La M_5 images on the left, vertically averaged across the whole images. Fully stoichiometric CoO_2 planes are indicated with red dashed lines in the background (through all three profiles), and O-deficient CoO_x planes are marked with blue dashed lines. The O intensity decreases on the latter planes as a result of the lower O content, which makes the La atoms move further apart from each other, giving rise to the dark stripes in the Z-contrast images.” Reprinted figure with permission from N. Biskup et al., Physical Review B **112**, 087202 (2014) under license 3897840427959.[310] Copyright 2016 by the American Physical Society.

Backed by density-functional theory calculations, Biskup et al. propose a new model of magnetism in ferromagnetic LaCoO_3 thin films. In their model, the Co^{2+} ions along the oxygen vacancy planes are tetrahedrally coordinated in a high-spin state, with alternating magnetic moments in an antiferromagnetic pattern. In the layers of Co adjacent to the oxygen vacancy planes, there is a checkerboard pattern of high-spin Co^{2+} and low-spin Co^{3+} , with the magnetic moments ordering ferromagnetically. Because only a fraction of the Co ions are contributing to the overall magnetic moment of the films, this proposed model is consistent with the low saturated magnetic moments measured in real-life LaCoO_3 films.

One apparent problem with the proposed model is that the model's reliance on oxygen-vacancy doping is at odds with measurements that show the LaCoO₃ films are insulating at room temperature and below. However, Biskup et al. address this, explaining that their model predicts a nonlinear, Peierls distortion-like rupture of the energy bands, which opens up an energy gap. Crucially, this mechanism seems to require a 2D Fermi surface and relaxation.

4.4.5 Orbital ordering

In 2013, J. Fujioka et al. suggested a new possible model for the magnetism, based on a ferrimagnetic, mixed-spin state with spin-orbital ordering.[309] They noted that the typical magnetization observed in films of LaCoO₃ saturates around 0.5–1.0 Bohr magnetons per Co ion, far below the 3.4 Bohr magnetons per Co ion that would be expected for a scenario with fully magnetized high-spin Co³⁺.[313] Therefore, they hypothesized that the magnetism comes from a ferrimagnetic ordering of (1 -1 1) sheets that alternate IS↑-IS↑-HS↓-IS↑-... (where IS means intermediate spin and HS means high spin). They further speculated that this spin pattern could be accompanied by an orbital ordering that goes $d_{z^2}-d_{x^2-y^2}-d_{yz}-d_{x^2-y^2}-\dots$, respectively. This ordering pattern is illustrated in Figure 4.9, excerpted from Fujioka et al.[309]

4.4.6 Spin canting

Another proposed model for the magnetism of LaCoO₃ is spin canting. In 2012, Hosung Seo et al. performed density functional theory calculations on eight unit cells of LaCoO₃ to postdict⁸ the magnetic state of strained LaCoO₃.[306] They found that for LaCoO₃ films under 2.5% tensile strain or more, a 50:50 mixture of high-spin and low-spin Co³⁺ states had a lower energy than pure low-spin states. In addition, they looked at the magnetic interactions between nearest neighbor Co ions and between next nearest neighbor Co ions in this 50:50 mixture state. Surprisingly, at least to me, they found that the nearest neighbor Co ions had ferromagnetic coupling but the next nearest neighbor Co ions antiferromagnetic coupling that was even stronger! Because of this strong antiferromagnetic coupling between next nearest neighbor Co ions, a number of complex spin patterns could plausibly arise. When Seo et al. introduce canting degrees of freedom into their model, they find a number of degenerate canted spin structures, one of which has an overall magnetization of about 0.3 Bohr magnetons per Co ion, less than most experimental measurements but still in the general ballpark.

It's also worth noting that, in addition to calculating the magnetic ordering of the mixed high-spin low-spin state, Seo et al. also calculated the magnetic ordering of a pure high-spin Co³⁺ state. According to the Goodenough-Kanamori-Anderson rules,[124, 125, 126, 127] magnetic ions with equal valences interacting through an oxygen ion from opposite sides should have an antiferromagnetic ordering. The solutions found by Seo et al. confirmed this, predicting an antiferromagnetic

⁸A postdiction is a ‘prediction’ made after the fact is already known.

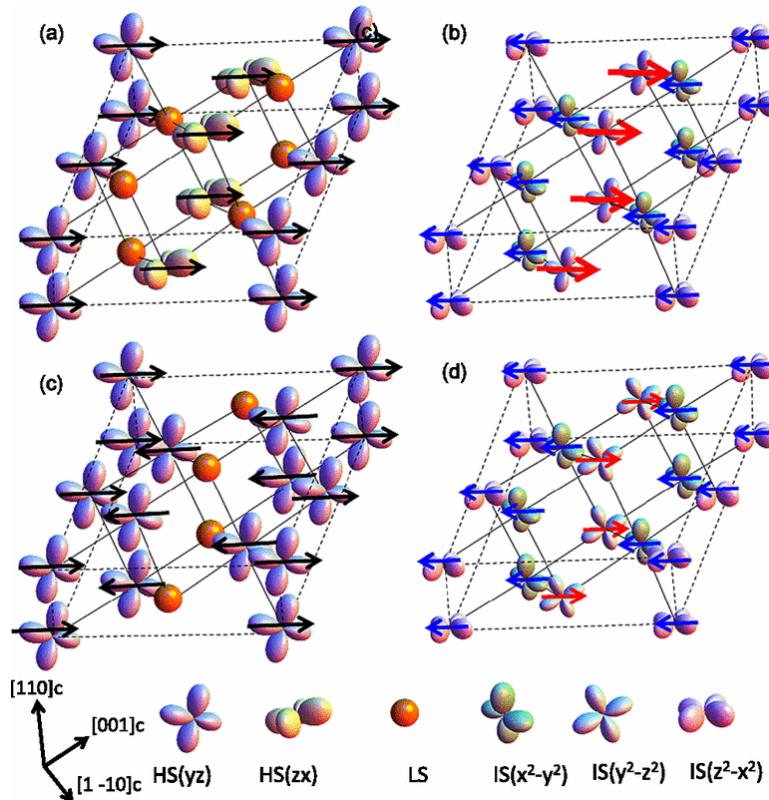


Figure 4.9: From Fujioka et al.: “The proposed models of the spin and orbital ordered structure: (a) High spin (HS)/low spin (LS)-state ordered state with the rocksalt type configuration. (b) Intermediate spin (IS)/HS-state ordered state. (c) HS/LS-state ordered state with 3/1 ratio. (d) homogeneous IS state. The lobes denote the e_g orbital of IS state and the active t_{2g} orbital of HS state. The t_{2g} orbital of IS state as well as the fully occupied, Hunds-rule coupled t_{2g} orbital is omitted for clarity. The dashed line indicates the unit cell of this spin-orbital superstructure.” Figure reprinted with permission from J. Fujioka et al., Physical Review Letters **111**, 027206 (2013) under license 3894480580398.[\[309\]](#) Copyright 2016 by the American Physical Society.

ordering. This is important because it adds to the evidence that a state of pure high-spin Co^{3+} ions cannot explain the observed ferromagnetic ordering in LaCoO_3 thin films.

4.4.7 Ferromagnetic clusters

In general, it is difficult to model the magnetism of LaCoO_3 thin films with a simple homogeneous spin state, so many hypotheses model the magnetism by proposing complex and inhomogeneous spin states. Along this direction is the hypothesis that the magnetism is coming from ferromagnetic clusters in a non-ferromagnetic background. In 2012, Sterbinsky et al. argued that the structural distortions that promote high-spin Co^{3+} (such as strain-induced changes in crystal-field splitting and Jahn-Teller-like tetragonal distortion) are insufficient to drive the material's Co ions into a homogeneously high-spin state.^[307] Because of this, Sterbinsky et al. suggest that a low concentration of intermediate- or high-spin Co^{3+} may form isolated ferromagnetic clusters, possibly resulting in spin-glass behavior (similar to mildly hole-doped $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ ^[299, 314, 315]).

4.5 So which explanation is right?

At this point, no one knows for sure which explanation is right. There is no experimental technique that allows us to directly probe the magnetism with no ambiguity. All of our knowledge comes from indirect inference, and in the case of the cobalt perovskites, there is not enough information for the field to arrive at a consensus. So for the time being, scientists will continue to piece together a picture that comes from a variety of measurements. Toward this end, I carried out the following research project, which focused on two materials similar to LaCoO_3 .

4.6 My research project

To help address the mystery of ferromagnetism in thin films of cobalt perovskites, I synthesized cobalt perovskite films similar to LaCoO_3 , namely PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$. Because of their smaller A-site cations, these two materials have slightly smaller unit cells, slightly more octahedral distortions, and slightly more crystal-field splitting.

4.6.1 Introduction

Tuning magnetism in complex oxide materials is of both fundamental and technological interest. Lattice distortions caused by chemical pressure or epitaxial strain have been shown to modify the superexchange interactions among magnetic cations and thereby enhance or suppress magnetic order.^[316] Manganese perovskites, for example, have been doped on both the A and B sites to modify the B-O-B bond lengths as well as the tilting and rotation of the BO_6 octahedra.^[317, 318] For

compositions with a ferromagnetic ground state, this A- and B-site doping can tune the Curie temperature and magnetization.

In cobalt perovskites, magnetism can likewise be tuned by substitutional doping. In $Ln\text{CoO}_3$, where Ln is a 3+ lanthanide element, Co^{3+} ions ($3d^6$) undergo a transition from being diamagnetic ($S=0$) at low temperatures to being paramagnetic at higher temperatures (with $S=1$ or $S=2$).[319, 320, 321] The temperature of this transition can be controlled by the size of the Ln ion, which affects the overlap between the Co and O orbitals. Smaller ions increase the overlap, which results in a larger band gap and spin gap. Doping the A-site with alkaline-earth ions turns the material ferromagnetic, which is attributed to a ferromagnetic double-exchange interaction.[322, 323]

As I discussed earlier, In 2007, thin films of nominally undoped LaCoO_3 were discovered to be ferromagnetic at low temperatures under certain epitaxial strain conditions.[324, 325, 326, 327] The underlying mechanisms stabilizing ferromagnetism in strained LaCoO_3 films are still controversial. Explanations of the magnetism, which generally rely on superexchange, include the methods listed in the previous section: local clusters or a percolationlike network,[304, 307] spin canting,[306] lattice modulation stripes,[308] ferrimagnetic orbital ordering, and ordered oxygen vacancies.[328, 329] Whatever the cause of LaCoO_3 's ferromagnetism, it likely applies to other cobalt perovskites too. In 2013, Mehta et al. measured ferromagnetic order in epitaxial PrCoO_3 thin films on SrTiO_3 substrates.[330]⁹

In the bulk, replacing La with the smaller ion Pr reduces the lattice parameter of the material and decreases its Co-O-Co bond angles, thereby increasing the temperature of the Co spin-state transition. Replacing La with Pr subsequently seems to reduce the ferromagnetic Curie temperature in epitaxial films from around 85 K in LaCoO_3 to 50 K–65 K in PrCoO_3 .[330] However the underlying mechanism for the stabilization of a ferromagnetic ground state is still not well understood.

To clarify the role of lattice distortions in the magnetism of cobalt perovskites, we have explored straining PrCoO_3 in two different ways: by epitaxial strain and by chemical pressure. First, to apply varying levels of epitaxial strain, we deposited PrCoO_3 films on crystalline substrates with pseudocubic lattice mismatches ranging from -2.4% to +3.1%. Our first major finding is that epitaxial tensile strain stabilizes a ferromagnetic ground state below 65 K in PrCoO_3 films deposited on SrTiO_3 substrates and sometimes on $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{TaAlO}_6)_{0.7}$ substrates (two out of seven films). In contrast, when PrCoO_3 thin films are deposited on lattice-matched or compressive substrates (LaAlO_3 or YAlO_3), they are paramagnetic down to 5 K, the lowest temperature measured. Second, to apply chemical pressure to PrCoO_3 , we substituted 30% of the Pr ions with Y, a smaller element. Our second major finding is that this substitution suppressed all ferromagnetic ordering,

⁹At the time of its publication, the authors believed their data showed a ferrimagnetic ordering. However, I discovered that their interpretation of the praseodymium moment alignment was based on a reference that used a non-standard circularity convention. As a result, their data actually supports a ferromagnetic interpretation and a correction will be issued soon.

even in films strained on SrTiO_3 . To complement the bulk magnetometry measurements of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ thin films, we performed element-specific X-ray magnetic circular dichroism measurements, which indicate that (1) the Co and Pr moments are aligned parallel to the applied magnetic field and (2) that even the non-ferromagnetic films have significant quantities of Co in a paramagnetic non-zero spin state at low temperatures.

4.6.2 A note on the pseudocubic assumption

At room temperature, bulk PrCoO_3 exhibits paramagnetic behavior with contributions from both the Co and Pr ions.^[331] It forms the GdFeO_3 perovskite structure with a space group of $Pbnm$. Despite PrCoO_3 's orthorhombic crystal symmetry, PrCoO_3 can be approximated as pseudocubic with a lattice parameter of 0.379 nm.^[332, 333] Although all the materials in this study share the same basic ABO_3 perovskite structure, they have different crystal symmetries and unit cells. Even a single material, such as SrTiO_3 , can exhibit different symmetries at different temperatures. To keep the notation consistent and simple across materials and temperatures, we will use pseudocubic crystal directions and lattice parameters for all materials. The pseudocubic [100], [010], and [001] directions will refer to vectors along the Co-O-Co bond with a length around 0.4 nm rather than the true basis vector which may be quite different in different materials or at different temperatures. This pseudocubic assumption is least suitable for YAlO_3 , which is the most distorted from cubic because of Y's small size. Therefore, in the case of YAlO_3 , we took special care to consistently define the [100] in-plane direction to be the direction with a lattice spacing of 0.372 nm.

4.6.3 Experimental methods

Pulsed laser deposition was used to deposit thin films of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$. Ranging from 9 nm thick to 54 nm thick, films were deposited on (001) single-crystalline substrates of SrTiO_3 , $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{TaAlO}_6)_{0.7}$ (LSAT), LaAlO_3 , and YAlO_3 (their structural details are shown in Table 4.2). To prevent charging during X-ray magnetic circular dichroism experiments, a few PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films were also deposited on (001) Nb-doped SrTiO_3 substrates. Before deposition, the substrates were sonicated in solvents (acetone, methanol, then isopropanol) and then heated to 700°C in 320 mTorr of O_2 . Films were deposited by focusing a 248-nm laser beam, pulsed at 3 Hz, to ablate a sintered ceramic target composed of either PrCoO_3 or $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$. The energy density averaged 1.3 J/cm² across a spot size of 10 mm². The target-substrate distance was 7 cm. Immediately after deposition, the films were cooled in 10 Torr of O_2 . These growth conditions are very similar to conditions used in two prior studies.^[330, 334]

Rutherford backscattering spectrometry was performed at the ion beam analysis facility at Lawrence Berkeley National Lab. Scanning transmission electron microscopy (STEM) observations were carried out at 200 kV in an aberration corrected JEOL JEM-ARM200cF equipped with a cold field emission gun and a GATAN Quantum electron energy-loss spectrometer (EELS). For

Substrate material	Crystal structure (room temperature)	Pseudo cubic lattice parameter (room temperature)	PrCoO_3 strain (X - 0.379 nm)/(0.379 nm)
SrTiO_3	Cubic, $Pm\bar{3}m$, 221	0.3905 nm	+3.1%
$(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{TaAlO}_6)_{0.7}$	Cubic, $Pm\bar{3}m$, 221	0.3868 nm	+2.1%
LaAlO_3	Trigonal, $R\bar{3}c$, 167	0.3790 nm	0.0%
YAlO_3	Orthorhombic, $Pnma$, 194	0.370 nm	-2.4%

Table 4.2: Structural properties of the four crystal substrates upon which PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ were deposited.

spectral imaging, the electron beam was scanned along the region of interest and an EEL spectrum was acquired for every pixel, along with the simultaneous annular dark field (ADF) signal. Random noise in the EEL spectrum images was removed using principal-component analysis.[335] Elemental maps were produced by using a multiple linear least square (MLLS) fit to reference spectra. Cross-sectional specimens were prepared by conventional mechanical grinding and polishing and Ar ion milling. Atomic force microscopy was performed using a Bruker Dimension 3100. X-ray diffraction measurements (reflectivity, $2\theta-\theta$, $\Delta\omega$, and reciprocal space maps) were performed on a Philips PANalytical X’Pert PRO using the Cu $K_{\alpha 1}$ emission line. Superconducting quantum interference device (SQUID) magnetometry was performed in a Quantum Design Evercool Magnetic Properties Measurement System. X-ray magnetic circular dichroism (XMCD) measurements were performed in total electron yield mode with 30-degree grazing incidence at beamlines 4.0.2 and 6.3.1 of the Advanced Light Source at Lawrence Berkeley National Lab.

4.6.4 The structure of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ thin films

The structure of the films was studied by atomic force microscopy, X-ray diffraction, and scanning transmission electron microscopy.

Atomic force microscopy

Atomic force microscopy verified that the films were relatively smooth, with root-mean-square roughness values ranging from 0.2 nm to 1.6 nm, with the rougher surfaces belonging to the thicker films. Films had surface structures with lateral dimensions between 10 nm and 100 nm. A typical scan is shown in Figure 4.10.

X-ray diffraction

θ - 2θ scans in X-ray diffraction indicated the films were epitaxial with intensity only from the expected 00l family of peaks. The full-width-at-half-maximum of rocking curves across 002 film peaks ranged from 0.06° to 0.4° , with the larger mosaic spreads belonging to the thicker films. An example scan is shown in Figure 4.11.

X-ray reciprocal space maps around the $\bar{1}03$ peaks, such as those in Figure 4.12, were used to measure the in-plane and out-of-plane lattice parameters of the films and thereby gauge the epitaxial coherence of the thin films. For films around 10 nm thick, the in-plane lattice parameters roughly matched the lattice parameters of their substrates, as shown for PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films in Figure 4.13. However, by film thicknesses of 50 nm, the films were mostly relaxed, with their in-plane lattice parameters approaching bulk lattice parameter values.

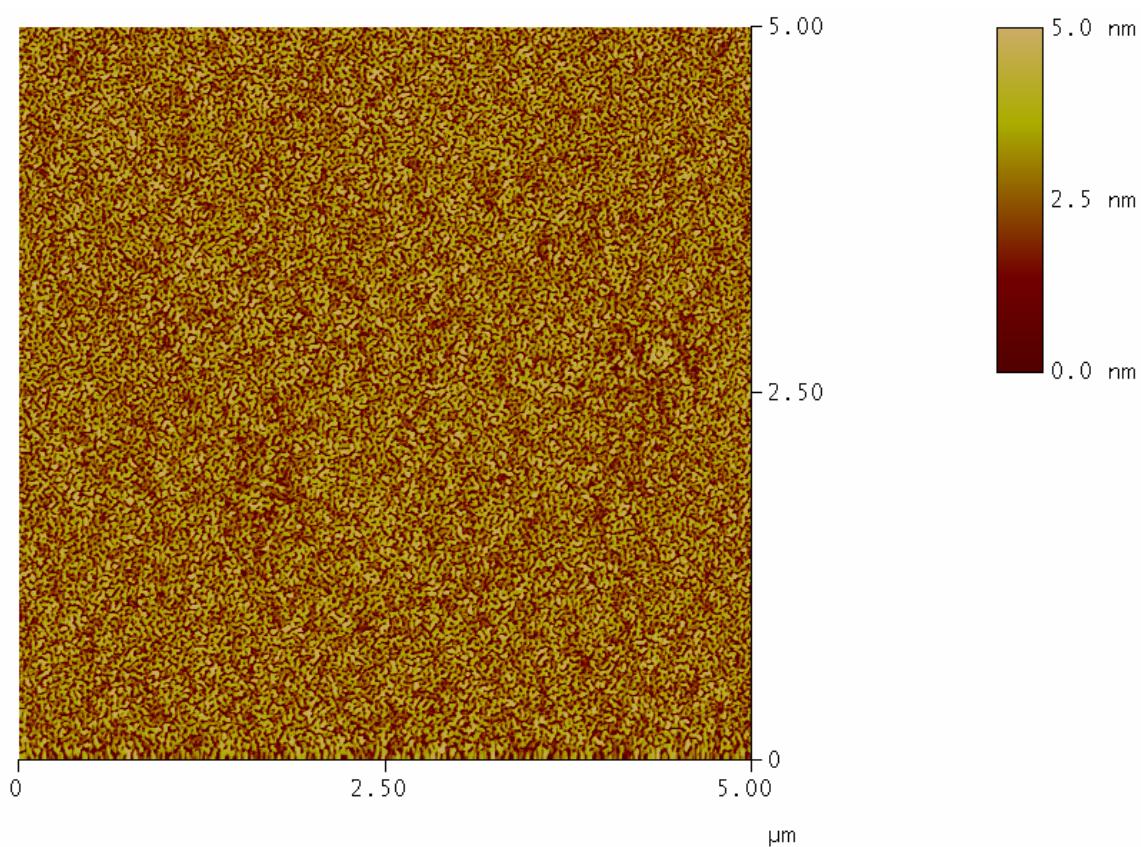


Figure 4.10: Atomic force micrograph of a PrCoO_3 thin film. The roughness is quite low, less than 1 nm RMS, but shows some sort of shallow surface structuring.

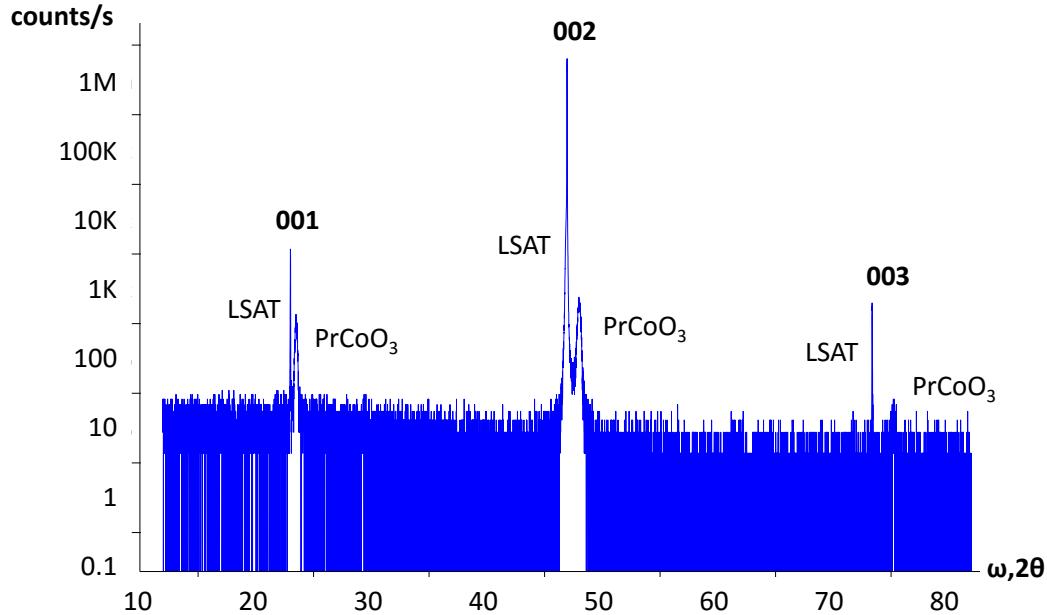


Figure 4.11: A wide-angle θ - 2θ X-ray diffraction scan of a thin PrCoO_3 film reveals good crystallinity with no other detectable crystal phases.

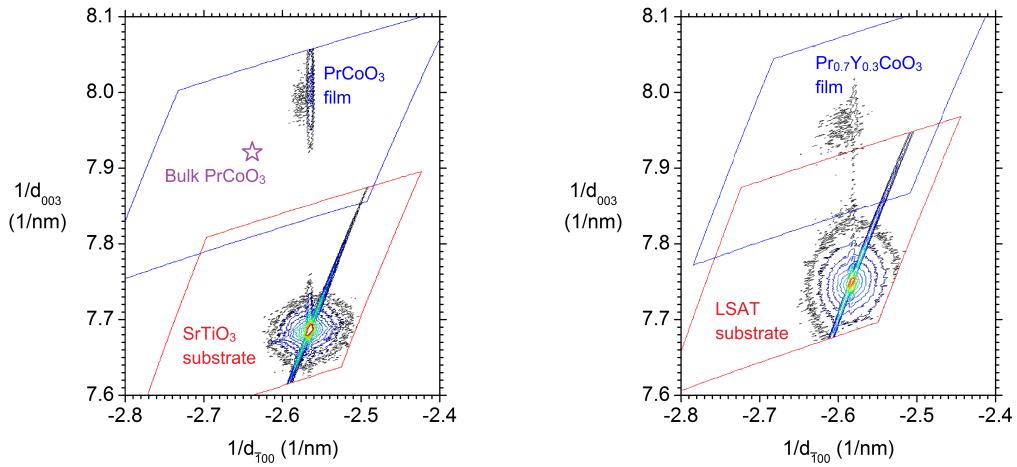


Figure 4.12: Reciprocal space maps of the $\bar{1}03$ peaks of a 9-nm PrCoO_3 film on SrTiO_3 and a 14-nm $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ film on LSAT show that the thin films are epitaxially strained to their substrates. Scans like these were used to calculate the lattice parameters of all the films in Figure 4.13 and Table 4.3. The colored contours of X-ray intensity are spaced evenly on a logarithmic scale. The large diagonal lines through the substrate peaks are an experimental artifact from using a line detector. The blue and red quadrilaterals are the areas covered by two separate scans.

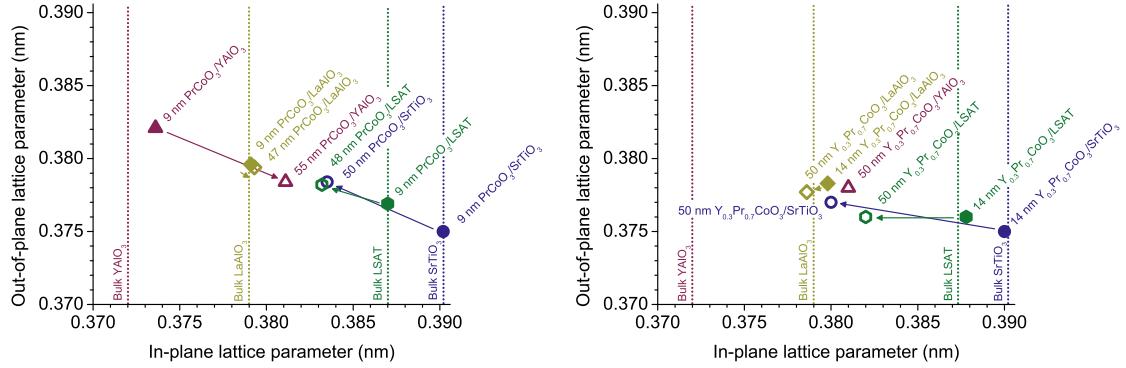


Figure 4.13: In-plane and out-of-plane lattice parameters for a set of PrCoO_3 films (left) and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films (right), as measured by X-ray reciprocal space maps (such as those in Figure 4.12). The thinnest films (solid points) are epitaxially strained, with their in-plane lattice parameters matching those of their crystal substrates. As their thicknesses grow to 50 nm (hollow points), the films relax toward a common structure, as shown by the arrows.

Scanning transmission electron microscopy

STEM images confirmed that the films were epitaxial, had atomically abrupt interfaces, and had good crystallinity in general. Figure 4.14 shows the microstructure of a 14-nm-thick PrCoO_3 film on a SrTiO_3 substrate. Close to the substrate-film interface, the films exhibited excellent crystal quality with minimal defects, but beyond about 5 nm, more defects appear.

Electron energy loss spectroscopy and high-energy ion scattering spectrometry

EELS on the same samples indicated that the films were stoichiometric near the film-substrate interface, but occasionally contained cobalt-deficient regions near the surface, as shown in the dashed red rectangle of Figure 4.14. This cobalt deficiency is consistent with results from high-energy ion scattering spectrometry, which indicated the films had around 0%–10% Co deficiency. These likely Pr_2O_3 -rich regions were too rare to show up in X-ray diffraction and did not contribute any ferromagnetic signal. Oxygen vacancy planes were occasionally observed in some samples, but were not universal.

4.6.5 The magnetism of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ thin films

Magnetic properties of the films were investigated with two techniques: superconducting quantum interference device (SQUID) magnetometry, which measures the aggregate magnetic moment of each sample, and X-ray magnetic circular dichroism (XMCD) spectroscopy in total electron yield mode, which measures the magnetic moment of specific elements near the surface of the film. By studying strained and relaxed films of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ deposited on four different substrates, we

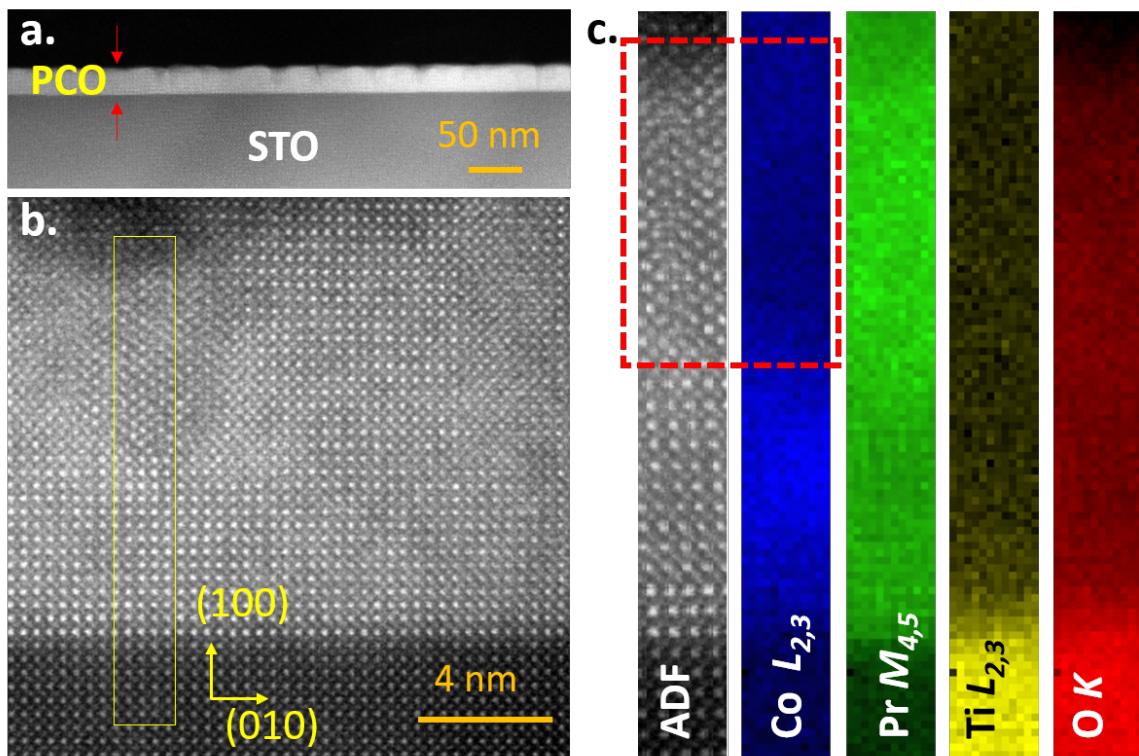


Figure 4.14: (a) Low magnification high angle annular dark field (HAADF) image of a PrCoO_3 thin film grown on (100) SrTiO_3 . (b) High resolution HAADF image showing the film/substrate interface. The yellow rectangle marks the approximate area where an EEL spectrum image was acquired. (c) EEL spectrum imaging analysis. From left to right: Simultaneously acquired ADF signal along with EELS chemical maps of Co (blue), Pr (green), Ti (yellow) and O (red) edges. The dashed red square highlights a region where the crystal structure is different from the rest of the film. Here, the relative Co concentration increases while the Pr signal increases. Some spatial drift is present.

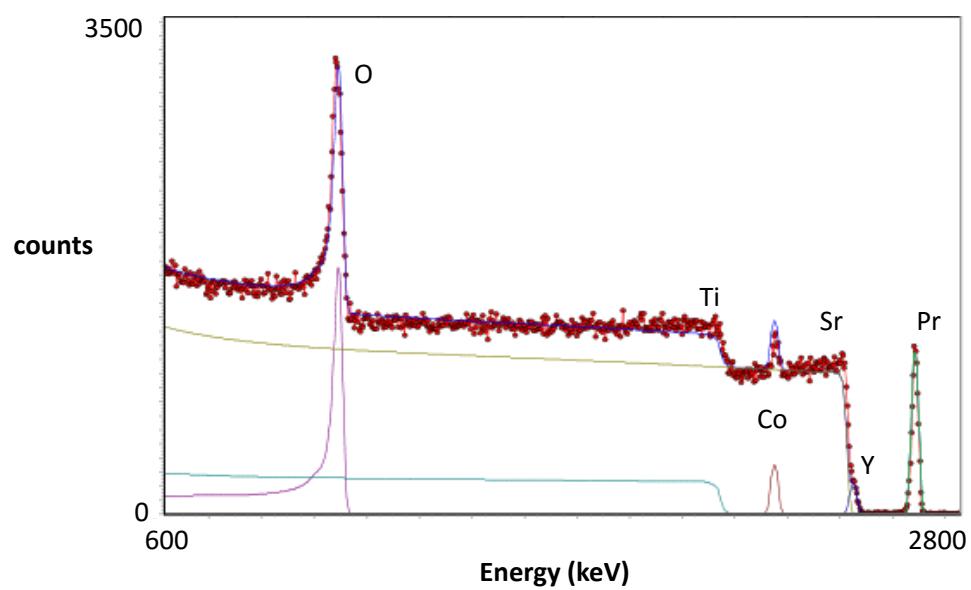


Figure 4.15: High-energy ion scattering spectrometry measures the elemental composition of a material.

Substrate	Thickness	T_c	In-plane lattice parameter	Out-of-plane lattice parameter
Relaxed PrCoO₃ on SrTiO ₃ LSAT LaAlO ₃ YAlO ₃	50 nm	65 K	0.384 nm	0.378 nm
	48 nm	65 K	0.383 nm	0.378 nm
	47 nm	x	0.379 nm	0.379 nm
	54 nm	x	0.381 nm*	0.378 nm
Strained PrCoO₃ on SrTiO ₃ LSAT LaAlO ₃ YAlO ₃	9 nm	58 K	0.390 nm	0.375 nm
	9 nm	x	0.387 nm	0.377 nm
	9 nm	x	0.379 nm	0.380 nm
	9 nm	x	0.374 nm*	0.382 nm
Relaxed Pr_{0.7}Y_{0.3}CoO₃ on SrTiO ₃ LSAT LaAlO ₃ YAlO ₃	50 nm	x	0.380 nm	0.377 nm
	50 nm	x	0.382 nm	0.376 nm
	50 nm	x	0.379 nm	0.378 nm
	50 nm	x	0.381 nm*	0.378 nm
Strained Pr_{0.7}Y_{0.3}CoO₃ on SrTiO ₃ LSAT LaAlO ₃	14 nm	x	0.390 nm	0.375 nm
	14 nm	x	0.388 nm	0.376 nm
	14 nm	x	0.380 nm	0.378 nm

Table 4.3: Four batches of PrCoO₃ and Pr_{0.7}Y_{0.3}CoO₃ films, extensively characterized with X-ray reflectivity (for thickness), SQUID magnetometry (for T_c), and X-ray reciprocal space maps (for the lattice parameters). To reduce sample variability, each batch was deposited simultaneously, and substrates across batches were cut from the same crystal. The italicized thicknesses were not directly measured, but were assumed to be close to other thicknesses in the batch. *YAlO₃ crystals have significantly different lattice parameters along the [100] and [010] directions, so to be consistent, all in-plane measurements of films on YAlO₃ were performed along the direction in which the substrate's lattice parameter is about 0.372 nm.

may infer the magnetic response to epitaxial strain and chemical pressure.

Superconducting quantum interference device (SQUID) magnetometry

The temperature dependence of magnetization was measured with SQUID magnetometry for all samples, as plotted in Figure 4.16. Long-range magnetic ordering was measured in all films of PrCoO_3 on SrTiO_3 , which nominally applies 3.1% tensile strain to PrCoO_3 . In particular, Figure 4.16(a) shows that the relaxed, 50-nm-thick PrCoO_3 film exhibits a Curie temperature T_c of 65 K, the highest T_c ever measured in PrCoO_3 to date.[330] Although this relaxed film on SrTiO_3 has a higher T_c , the strained film in panel (c) is more strongly magnetized at low temperature. This trend of higher magnetization for thinner PrCoO_3 is in qualitative agreement with prior work by Mehta et al.,[330] and suggests that epitaxial strain promotes long-range magnetic order in PrCoO_3 films. The triangular shape of the magnetization versus temperature scans suggests that there may be a distribution of Curie temperatures, where more and more of the material becomes ferromagnetic as the temperature is lowered.

Magnetization versus applied field measurements of PrCoO_3 films on SrTiO_3 at 5 K confirm that the long-range magnetic order is hysteretic, with coercive fields around ± 0.5 T (see Figure 4.17). The relatively low saturation magnetization values, on the order of 0.2 Bohr magnetons per unit cell, suggest that only a small fraction of the material is magnetized (or else the magnetization is weakly canted).

On LSAT substrates, which nominally apply 2.1% tensile strain to PrCoO_3 , most of the PrCoO_3 films were paramagnetic. However, two of the seven films we deposited did exhibit ferromagnetism. One of these ferromagnetic films is the relaxed PrCoO_3 /LSAT sample seen in Figure 4.16(a). And although its strained counterpart in panel (c) also appears to possess a large magnetic response, suggesting ferromagnetism, it exhibited no magnetic hysteresis and is well fit by Curie's law. The variability in the magnetic response of PrCoO_3 films on LSAT suggests that, for intermediate values of tensile strain, the ferromagnetic order is sensitive to small variations in material quality.

On LaAlO_3 , which is nearly lattice matched to PrCoO_3 , and on YAlO_3 , which applies compressive strain, PrCoO_3 films showed no signatures of long-range magnetic order in either their temperature dependence or field dependence of magnetization.

In contrast to the PrCoO_3 films, none of the $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films showed any sign of long-range magnetic ordering in their temperature dependence of magnetization, as shown in Figure 4.16. Nor did any $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films show any magnetic hysteresis at 5 K.

Together, these SQUID measurements demonstrate that while tensile strain from SrTiO_3 or LSAT is enough to induce ferromagnetism in LaCoO_3 and PrCoO_3 , it is not enough to induce ferromagnetism in $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$, which has a smaller unit cell and smaller Co-O-Co bond angles.

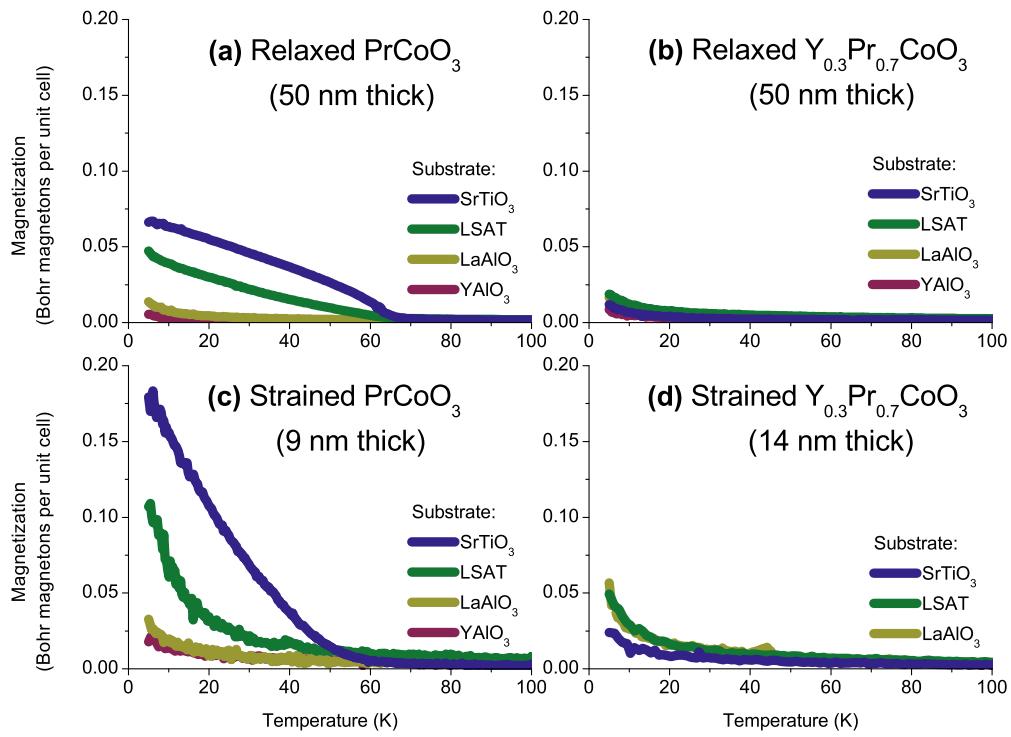


Figure 4.16: Magnetization versus temperature of the four batches of PrCoO_3 thin films, half of which were epitaxially strained or not, and half of which were 30%-Y-doped or not. The samples were measured while warming in 0.03 T, after first being field-cooled in 7 T. The applied magnetic field was applied in-plane, in the (pseudocubic) [100] direction. Diamagnetic backgrounds were subtracted by shifting the room-temperature magnetizations to 0. Scans taken with different warming fields were similar to those at 0.03 T, as were scans taken months after deposition. The small bumps near 40 K (visible in strained $\text{PrCoO}_3/\text{LSAT}$ and strained $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3/\text{LaAlO}_3$) are a known experimental artifact from melting oxygen.

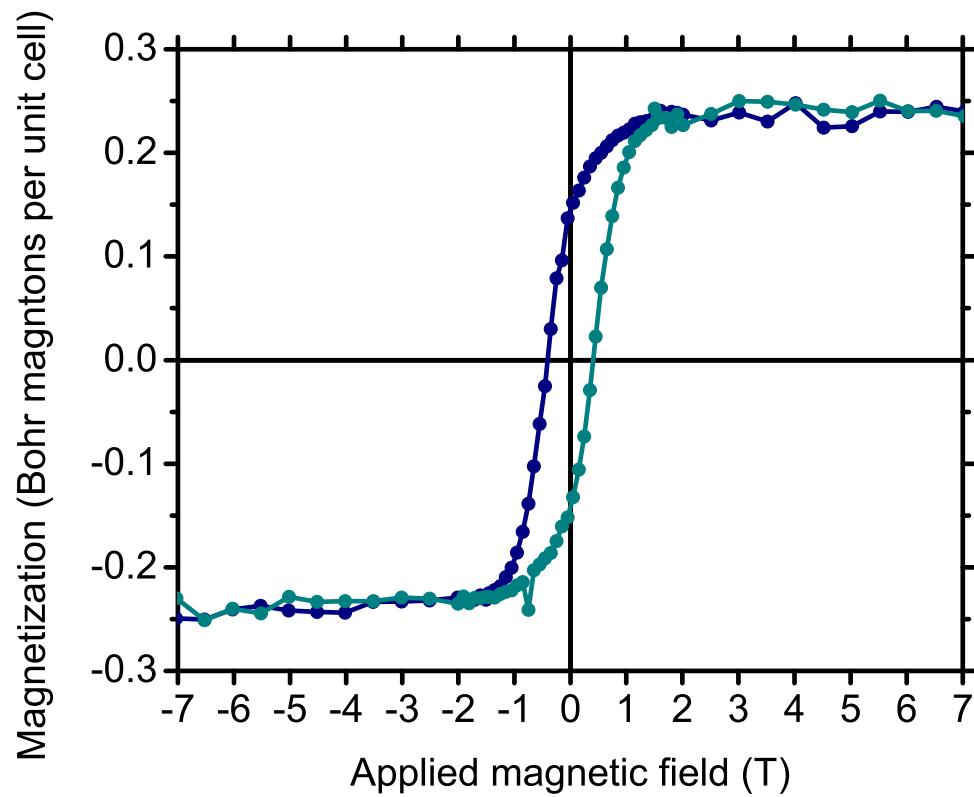


Figure 4.17: A magnetic hysteresis loop of 9-nm-thick PrCoO_3 film on (001) SrTiO_3 , measured at 5 K with the magnetic field applied along the in-plane [100] direction, after being field-cooled in 7 T. Diamagnetic and paramagnetic backgrounds were subtracted after fitting a linear term for the diamagnetism and the Brillouin function with $J=2$ and $g=2$ for the paramagnetism.

X-ray magnetic circular dichroism (XMCD) spectroscopy

X-ray magnetic circular dichroism (XMCD) was used to measure the individual magnetic contributions of Pr and Co cations in PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films. Because PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ are semiconductors with low conductivity, sample charging can be problematic when performing XMCD measurements in total electron yield mode. To reduce sample charging effects, PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films were deposited on electrically conductive (001) Nb-doped SrTiO_3 substrates.

XMCD of the Co L_{2,3} edges of PrCoO_3 films in Figure 4.18(a) shows that the Co magnetic moments are aligned parallel to the applied magnetic field of 1.8 T at 25 K.[319] XMCD of the Pr M_{4,5} edges of PrCoO_3 films shows that the Pr magnetic moments are also aligned parallel to the applied magnetic field.[336, 337] Because we did not see magnetic hysteresis with XMCD at either the Co L₃ or the Pr M₄ edges in these PrCoO_3 films, it remains possible that this XMCD signal comes from paramagnetic polarization near the surface of the film while the long-range magnetic order exists in some undetected form below. However, Mehta et al.'s observation of XMCD hysteresis in similar PrCoO_3 films suggests that the magnetic order in PrCoO_3 films is indeed ferromagnetic. Mehta et al. interpreted their XMCD to indicate *ferrimagnetic* ordering, but we believe this was an error caused by a non-standard sign convention in one of their Pr XMCD references.

$\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$, despite its lack of ferromagnetism, still exhibits some XMCD at both the Co L_{3,2} and Pr M_{5,4} edges, presumably from paramagnetic polarization. Notably, the fact that Co can be polarized means that at least some of the Co ions are in a non-zero spin state at 25 K, in contrast to bulk PrCoO_3 , where Co^{3+} ions are in a low spin ($S=0$) state at low temperatures. This means that the lack of ferromagnetism in $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ is likely due to a lack of ferromagnetic exchange interaction rather than a lack of magnetic moment on the Co ions.

Together, the ferromagnetism in films of PrCoO_3 on SrTiO_3 substrates and the lack thereof in the corresponding $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films on SrTiO_3 indicate that lattice modifications induced by Y substitution (simulating hydrostatic pressure) and epitaxial strain modulate the Co-O-Co exchange interactions in different ways. The observation of ferromagnetism has been attributed to superexchange interactions among low-spin and high-spin Co^{3+} ions mediated by a correlated hopping as in epitaxial LaCoO_3 films on SrTiO_3 substrates.[304, 329] However, the substitution of Y for Pr may disrupt this interaction by further rotating the CoO_6 octahedra. The fact that $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ films exhibit no long-range magnetic order on any substrate is a strong indication that the CoO_6 octahedra rotation and tilting as a result of chemical pressure disrupts the ferromagnetic superexchange interactions among Co ions. However, in the absence of this chemical pressure, epitaxial tensile strain helps to stabilize a ferromagnetic ground state.

4.6.6 Conclusion

In conclusion, both epitaxial strain and chemical pressure affect the magnetic order of PrCoO_3 thin films. PrCoO_3 thin films exhibit ferromagnetic order when deposited on SrTiO_3 or (sometimes)

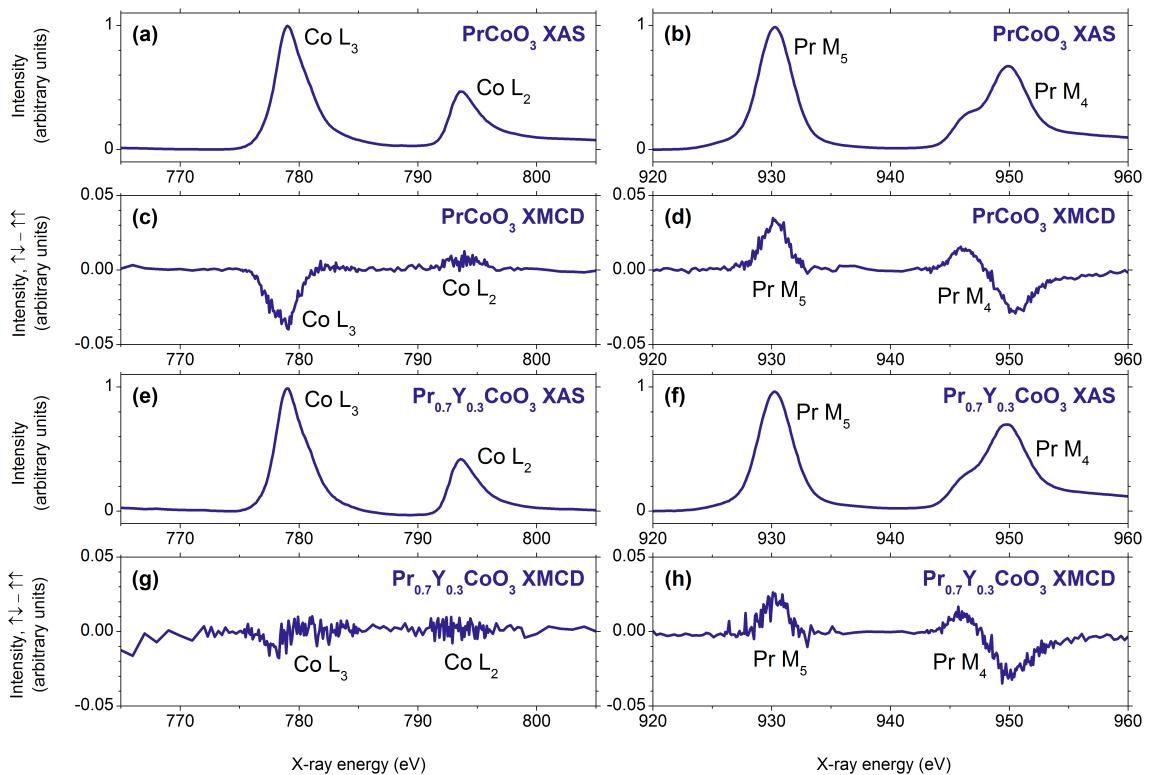


Figure 4.18: X-ray absorption spectra and XMCD spectra of the $\text{Co L}_{3,2}$ edges and $\text{Pr M}_{5,4}$ edges of 15-nm-thick films of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ on (001) Nb-doped SrTiO_3 . The scans were taken at 25 K in total-electron-yield mode at 30-degree grazing incidence with an alternating magnetic field reaching up to ± 1.8 T. X-ray absorption curves were normalized by subtracting the pre-edge to 0 and then scaling the maximum to 1. Four scans were averaged for the PrCoO_3 plots and two scans were averaged for the $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ plots (this is partly why the $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$ data are noisier).

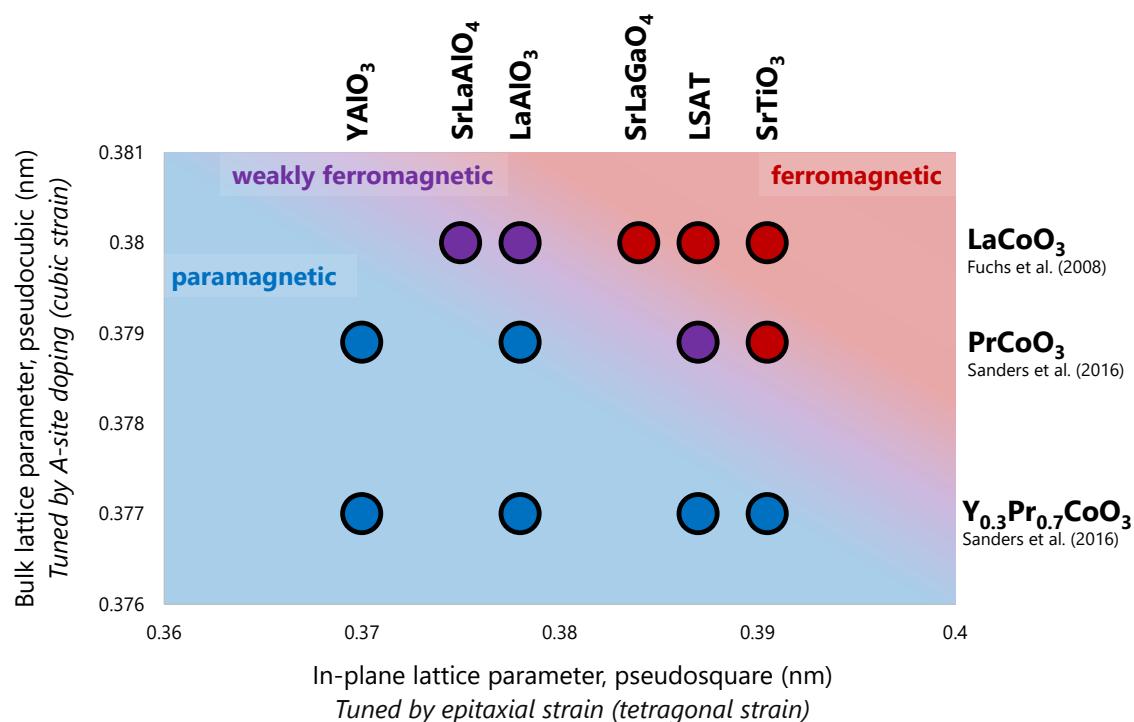


Figure 4.19: A structural phase diagram of magnetism in cobalt perovskite thin films. My work reveals that ferromagnetism is promoted by larger A-site cations and more tensile strain.

LSAT, two substrates that apply tensile epitaxial strain. However, for $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$, which has Co-O octahedra more distorted from cubic, this tensile strain is not sufficient to stabilize ferromagnetic order. This work extends the magnetic phase diagram of cobalt perovskites and demonstrates how chemical pressure and epitaxial strain provide two distinct routes to modulating magnetism through lattice distortions.

4.7 Technological applications

Although far off, one dream of this line of research is to make materials whose magnetism can be controlled electronically. This would make it easier to interface electronic and magnetic technology, as well as make it easier to build hybrid technology that draws strengths from both platforms.

One small step in this direction was published by Chengqing Hu et al. in 2013.[\[298\]](#) They were able to use the piezoelectric effect in SrTiO_3 to tune the strain state of an epitaxial LaCoO_3 film grown on top. When strained, this LaCoO_3 film exhibited strongly enhanced magnetoresistance and resistance. This enhancement only occurred below the T_c of 85 K, bolstering the notion that it arises by altering the material's magnetic state. One complication of their experiment is that the applied voltage comes from a top-gate, so the semiconducting LaCoO_3 and SrTiO_3 are concomitantly electrostatically gated at the same time as they are strained by the piezoelectric effect. Nonetheless, this experiment is a promising early demonstration of electric control of magnetism.

Chapter 5

Conclusions

In this dissertation, I have tried to frame the technological opportunities that still lay before humankind, and explain why complex oxides and their correlated electron behavior possess potential for future information technology. In particular, I have sought to describe my small steps over the past six years toward that future, a future where humankind has harnessed the complexity of complex oxides.

My two major projects in graduate school concerned two different aspects of correlated $3d$ transition-metal electrons. On the delocalized side of the spectrum, I studied how to control the conduction of titanium electrons at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. And on the localized side of the spectrum, I studied how to control the magnetism of cobalt electrons in thin films of PrCoO_3 and $\text{Pr}_{0.7}\text{Y}_{0.3}\text{CoO}_3$.

In my $\text{LaAlO}_3/\text{SrTiO}_3$ project, I highlighted the steep anticorrelation between carrier mobility and carrier concentration, exploring why that relationship might come about and how it restricts the space of possible models for this system.^[248] In addition, I tested how rare-earth dopants affected the carrier concentration, mobility, and magnetoresistance of the interface, ultimately finding that the interface's electronic transport was robust to their presence.

In my cobalt perovskite magnetism project, I expanded the magnetic phase diagram of cobalt perovskites in two directions: first, by chemical pressure, where I substituted Pr and $\text{Pr}_{0.7}\text{Y}_{0.3}$ for La in LaCoO_3 , and second, by epitaxial strain, where I deposited films on a range of substrates that applied both compressive and tensile strain. My main result was that a ferromagnetic ground state is stabilized at low temperatures by larger A-site cations (which promote less orbital overlap and larger bond angles) as well as tensile strain.

For information technology to break past the barriers of the semiconductor transistor, we need a new materials platform with more functionality. The correlated-electron behavior of complex oxides makes them difficult to understand, but also gives them great potential. The work in my dissertation is a small step forward to harnessing that potential.

Appendix A

Who pays for technological innovation?

Today we take it for granted that science is funded by the government and performed at national labs and universities. However, historically speaking, this model of science funding is a relatively recent development. For most of human history, advances in science usually came from self-funded curiosity, practical investigation with short-term payouts, or from scientists working for benevolent patrons. It wasn't until the 1900s that national level science spending really began to blossom. World Wars I and II spurred huge increases in military spending, which included military R&D spending. The United States's Manhattan Project alone cost about \$25 billion in today's dollars.

Following World War II, Truman science advisor Vannevar Bush laid the foundation of modern science policy in his report *Science, The Endless Frontier*, which called for the creation of the National Science Foundation.^[338] A few years later Vannevar Bush's vision was realized and the National Science Foundation was founded. With time, the United States added more science agencies to its portfolio (never proactively, of course, but always as a response to some crisis). NASA was created in 1958, a year after the launch of Sputnik. Later, the oil shocks of the 1970s led to the creation of the Department of Energy (and its head, the cabinet-level Secretary of Energy).¹

The NSF is unique among US science agencies in that it operates no facilities of its own. So while its budget is smaller than its peer agencies, it is a large force in science funding at universities,

¹Although the words ‘founded’ and ‘created’ conjure up images of agencies being built and staffed from scratch, often these new government agencies were just old agencies being reorganized or reprioritized. NASA, for example, began as a rebranding of NACA, the National Advisory Committee on Aeronautics, which had existed since 1915. And the Department of Energy began as a consolidation of the Federal Energy Administration, the Federal Power Commission, the Energy Research and Development Administration, and some smaller agencies.

where progress is made by professors and their teams.²

The US government is the largest funder of science in the world. It spends about \$150 billion each year on R&D, broken down as follows:

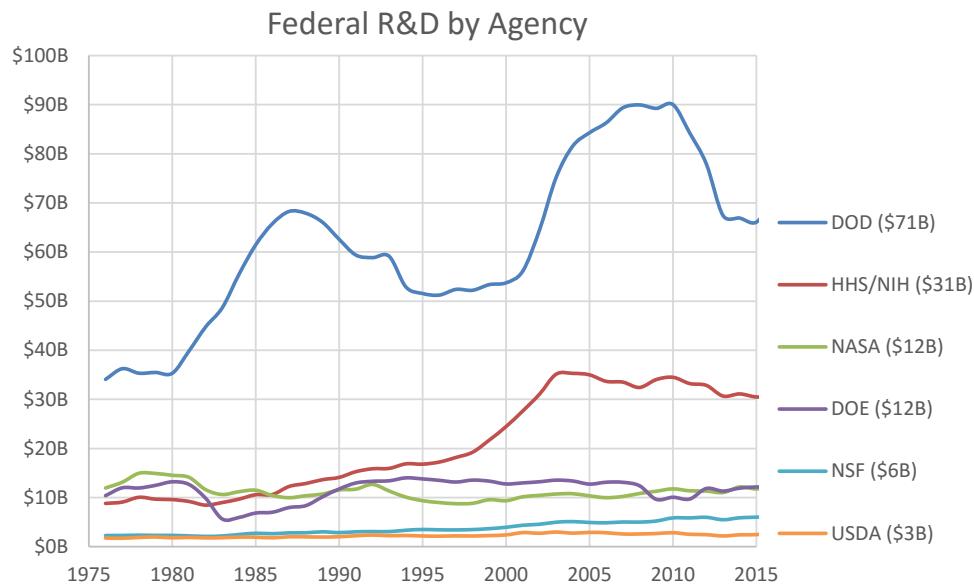


Figure A.1: Note that these are not the total budgets of the agencies, only the portions of their budgets classified as R&D spending.

Defense is about half the pie. After that, the NIH is largest. A cynic might argue that the NIH has had more success in securing congressional funding because cancer is more relevant to 60-year-old senators than the issue of developing energy sources for the next generation (however, I'm not a cynic so I wouldn't know). Following the NIH are NASA, the DOE, and the NSF.

²Fun fact: the annual R&D budget of the NSF is only about two submarines. (Then again, an annual budget and a capital good don't have the same units, so let's do some proper dimensional analysis. A military submarine lasts around 30 years, so buying two submarines a year would sustain a fleet of around 60 submarines. Coincidentally, that's about the size of the US submarine fleet, implying that the US values submarines and the NSF about equally).

Most countries have a single ministry of science, but the United States, due to its idiosyncratic history has a rather fragmented system of science funding. Although this might seem needlessly disorganized or inefficient, some have argued that this has actually helped the cause of US science funding, since it's more difficult to cut from five agencies (and consequently fight five times as many political battles) than it would be to cut the budget of a single agency. Regardless, that's how it stands.

In my lab, which straddles physics and materials science and basic research, the three most important funding agencies tend to be the DOD, DOE, and NSF (we don't get funding from the NIH or NASA, because they study biology and space. We also don't get funding from commercial sources because our research is relatively fundamental). In my own case, I was supported by all three agencies. The NSF supported me directly for three years through an NSF Graduate Research Fellowship, the DOD supported my $\text{LaAlO}_3/\text{SrTiO}_3$ research, and the DOE supported my cobalt perovskite research. Given the difficulty of measuring return on research investment,[339, 340] it takes real faith to fund basic science research. I am immensely grateful to these agencies as well as the taxpayers and voters who fund them.

Appendix B

Noether's theorem

Noether's theorem[38] is one of the deepest insights in physics, relating the symmetry of physical laws to conserved quantities such as energy and momentum. Although its first formulation and proof in 1915 applied only to classical Langrangian physics, Noether's theorem has been extended to many other non-classical descriptions, including field theories, quantum field theories (refer to the Ward-Takahasi identity, derived in 1950[341] and extended in 1957[342]), manifolds/fiber bundles, and even Lie algebras. I admit that these generalizations of Noether's theorem lie beyond my ken, but the derivation of Noether's theorem for a Langragian of a single independent variable still communicates the essence of the idea in a relatively simple and concrete fashion. Here it is.

First, the action, I , is defined as the integral over time of the Lagrangian, L . L is a function of time, t , as well as the system's coordinates, \mathbf{q} , and their time derivative, $\dot{\mathbf{q}}$.

$$I = \int_{t_1}^{t_2} L[\mathbf{q}[t], \dot{\mathbf{q}}[t], t] dt \quad (\text{B.1})$$

This definition plus Hamilton's principle, which states that \mathbf{q} will follow a path that extremizes the action, leads to the Euler-Lagrange equation(s):

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\mathbf{q}}}[t] = \frac{\partial L}{\partial \mathbf{q}}[t] \quad (\text{B.2})$$

If the Lagrangian does not depend on \mathbf{q} , then the right hand side of equation B.2 is 0. This means that the right hand side after the derivative is constant, or conserved. This suggests that some quantities can be conserved, although it does not say what they are or how many there can be. However, those questions can be answered by perturbation theory.

If the Lagrangian has a symmetry, that means that the Lagrangian is unchanged by infinitesimal perturbations that obey that symmetry. Therefore, the Euler-Lagrange equations still hold even if we change t by an infinitesimal amount, ϵT , or we change \mathbf{q} by an infinitesimal amount, denoted by

$\phi[\epsilon]$ (assuming these obey the symmetry of the Lagrangian).¹

$$t \rightarrow t' = t + \varepsilon T \quad (\text{B.3})$$

$$\mathbf{q}[t] \rightarrow \mathbf{q}'[t'] = \phi[\mathbf{q}[t], \varepsilon] = \phi[\mathbf{q}[t' - \varepsilon T], \varepsilon] \quad (\text{B.4})$$

$$\dot{\mathbf{q}}[t] \rightarrow \dot{\mathbf{q}}'[t'] = \frac{d}{dt} \phi[\mathbf{q}[t], \varepsilon] = \frac{\partial \phi}{\partial \mathbf{q}}[\mathbf{q}[t' - \varepsilon T], \varepsilon] \dot{\mathbf{q}}[t' - \varepsilon T] \quad (\text{B.5})$$

Substituting these into the Euler-Lagrange equations and doing some more math, Noether showed that the following expression is constant for each ϕ and T :

$$\left(\frac{\partial L}{\partial \dot{\mathbf{q}}} \frac{\partial \phi}{\partial \mathbf{q}} \dot{\mathbf{q}} - L \right) T - \frac{\partial L}{\partial \dot{\mathbf{q}}} \frac{\partial \phi}{\partial \varepsilon} \quad (\text{B.6})$$

which simplifies to

$$\left(\frac{\partial L}{\partial \dot{\mathbf{q}}} \dot{\mathbf{q}} - L \right) T - \frac{\partial L}{\partial \dot{\mathbf{q}}} \frac{\partial \phi}{\partial \varepsilon} \quad (\text{B.7})$$

Although this expression is still rather abstract (which it has to be, to handle any possible symmetry), we can look at a more concrete example. For instance, suppose the Langrangian does not depend on time. Then the rightmost term goes to zero, leaving

$$\left(\frac{\partial L}{\partial \dot{\mathbf{q}}} \dot{\mathbf{q}} - L \right) T \quad (\text{B.8})$$

And if this whole expression is constant, and T is by definition constant, then the expression in parentheses must be constant too.

$$\frac{\partial L}{\partial \dot{\mathbf{q}}} \dot{\mathbf{q}} - L \quad (\text{B.9})$$

You may recognize this expression as the total energy of the system. In this particular case, Noether's theorem shows that if the laws of physics are independent of time (symmetric under infinitesimal time translations), then energy is conserved as a consequence. And in way, this is definitional. Energy is that which is conserved under time translations.

¹I think this assumes that the symmetries are not themselves functions of time. There is likely a more general proof that handles this case.

Appendix C

Biology is constrained by physics

Biological life is stunningly diverse. From tardigrades to mantis shrimp to pterodactyls to chemosynthetic bacteria, life has evolved into bizarre forms and ecological niches.

In some ways, the evolution of life has been random and ideosyncratic. But in other ways, the evolution of life has been surprisingly predictable. The surprising predictability of life is the focus of this appendix.

C.1 Why aren't the best sprinters 8 feet tall?

When I was a kid, I used to imagine that the best sprinters in the world would simply be the biggest people in the world. I reasoned that if someone was twice as big as everyone else, then from their perspective the world would effectively feel twice as small. So to a giant, a 100 m sprint would feel as easy as a 50 m sprint feels to a normal-sized person.

However, it turns out that scaling is not so simple.

[1](#) [2](#)

¹Even if kid me had been correct about the advantage of tallness, this still would not imply that the best sprinters would be the tallest people. For instance, in the NBA, where tallness is clearly an advantage, there are still more 6'1" players than 7'1" players, simply because there are so many more 6'1" humans than 7'1" humans. Roughly, a random 7'1" man is about 10,000 times more likely to play in the NBA than a random 6'1" man, but this is more than outweighed by the fact that there are about 100,000 6'1" men for each 7'1" man.[\[343, 344\]](#)

²Actually, when it comes to sprinting, tall runners like Usain Bolt *do* seem to have a small advantage over their shorter brethren.[\[345, 346\]](#) However, for long distance running the opposite is true: it helps to be short and slender for better heat dissipation.[\[347\]](#)

C.2 Biological scaling laws

asdf[348, 349, 350]

Appendix D

The Moore's Law of Moore's Laws

Published in the November 2015 issue of MRS Bulletin and reprinted here with permission.[351] (The published version has much better graphic design than this L^AT_EXversion.)

50 years ago, a mild-mannered, 36-year-old chemist named Gordon Moore penned an innocuous article in the trade magazine Electronics.[73, 74] In the article, Moore, the director of R&D at Fairchild Semiconductor, put forth a prediction about the nascent semiconductor industry. After seeing transistor counts jump year-to-year from roughly 8 to 16 to 32 to 64, Moore forecast that this exponential progress in integrated circuits would continue unabated until at least 1975, and perhaps even beyond.

Well, half a century hence, I'm typing out this article on a computer packing around 1,400,000,000 transistors (for those keeping score at home, that's about 30 doublings). To call Moore's prediction a success would be like calling Serena Williams a semi-decent tennis player. Usually, a prediction is fortunate if it correctly predicts the future just once. If a prediction is right again and again, decade after decade, it's practically a miracle.

And when I say Moore's law is practically a miracle, I don't mean to be hyperbolic. The exponential rise in computing power is the engine powering the digital revolution. It's lifting living standards around the world and forever changing the way humans work and play (and even how they watch British babies bite fingers. Bad Charlie!).

Given the tremendous success and fame of Moore's law, it's no surprise that, just like a rock star, it would attract groupies and posers and copycats and coattail-riders.

Suppose you're a materials scientist trying to publicize your research but failing to get any traction. Every year, you improve your material, but beyond some rote applause at a conference and a citation or two, no one seems to really care about your life's work. How can you ever hope to attain some hype?

These days, I see more and more scientists resorting to the same simple strategy. Do you

research batteries? Then talk about the Moore's law of batteries! Do you research materials for nuclear fusion? Talk about the Moore's law for fusion! Do you research how paint dries? Talk about the Moore's law of drying paint!

Comparing your research to Moore's law is an instant recipe for getting your audience to imagine how your work might one day spawn entire industries and radically transform the world. And the best part about exponential growth is that it starts small. If anyone ever questions whether your work actually is world-changing, you can just rebut that while your first steps are admittedly small on an absolute scale, that's how exponential curves always start. Only after growing exponentially for decades will they become obviously huge.

Riding coattails is a time-tested strategy, and in the world of materials science and technology, there may be no bigger coattails than those of Moore's law. So it's hardly a surprise to see more and more scientists calling their research subject's progress the "Moore's law of ____." In the past few years I've heard scientists reference the Moore's law of solar power, the Moore's law of mass spectroscopy, and the Moore's law of batteries, just to name a few.

Seeing this explosion of references to Moore's law got me thinking along the same lines as Gordon Moore 50 years ago. How fast are these pseudo Moore's laws being invented? Are they following any sort of predictable trend that would invite us to cautiously extrapolate? And if so, is this merely a short-term fad or the beginning of a tectonic shift in science salesmanship?

Well, my dear reader, you are in for a treat. On your behalf, I have humbly performed some original scholarly research, scouring the web for every reference I could find to the "Moore's law of X" or "Moore's law for Y" and then tracing each back to its earliest mention. As I compiled these data, I made a shocking discovery:

There is a Moore's law of Moore's laws! (See Figure D.1!)

For decades now, the number of Moore's laws coined has been roughly doubling every five years. Early Moore's laws were technical in nature (e.g., the Moore's law of software or the Moore's law of bandwidth), but as time passed Moore's laws were coined for topics far afield of computers (e.g., the Moore's law of corn or the Moore's law for NFL field goals).

Let's extrapolate this exponential growth forward. If the number of Moore's laws continues to double every five years, then, by the year 2080, there will exist a Moore's law for every single word in the English language (which number a few hundred thousand to a million, depending on your degree of vocabulistic conservatism). We'll have a Moore's law of zebras, a Moore's law of love, and even a Moore's law of absquatulating. At that point, for the Moore's law of Moore's laws to continue, we may need to start inventing new words. Are you ready for a Moore's law of zakalaxing?

Of course, the other possibility is that at some point this exponential growth will decelerate. As the poet Chaucer cautioned back in 1374, "All good things must come to an end."^[77] Perhaps what so far looks like an exponential curve is really just the first half of its calmer cousin, the S-curve.

When it comes to the original Moore's law of integrated circuits, the writing may already be on

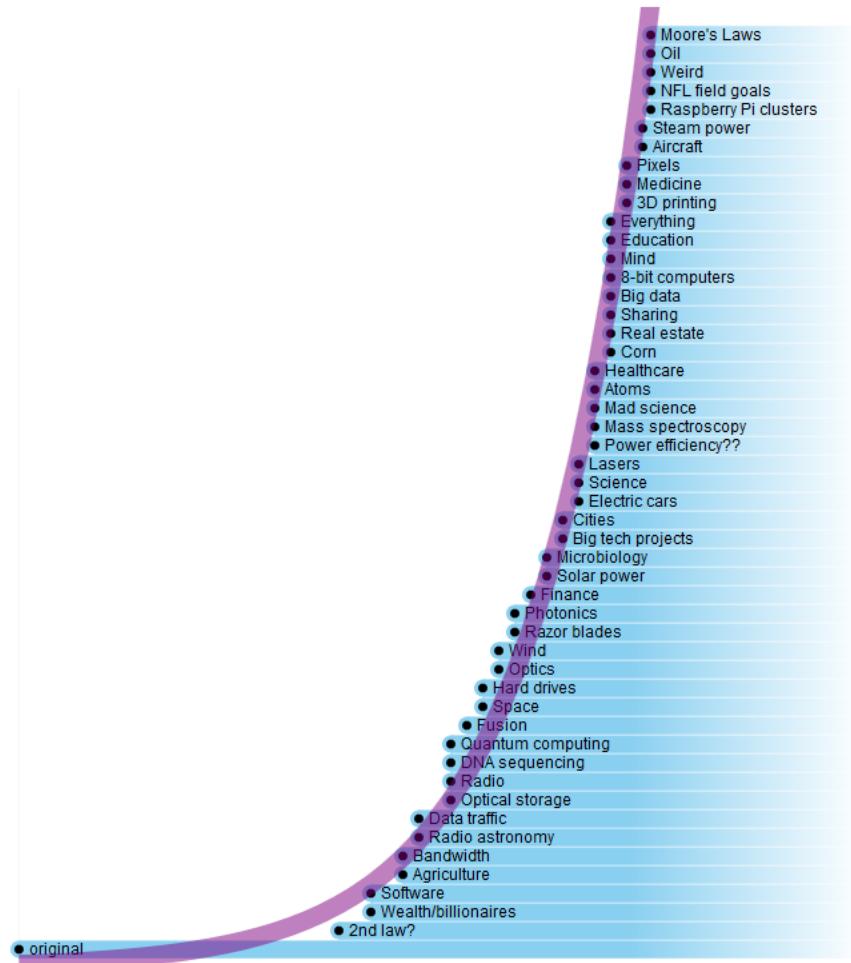


Figure D.1: The Moore's Law of Moore's Laws: the number of Moore's Laws doubles every five years. (I wanted to put the citations on the plot, but it would have been a hassle because they change each time I edited earlier parts of the document. The citation order here is from bottom to top.)[352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421]

the wall (and I'm not talking about the Moore's law poster in my hallway). A constellation of facts suggest that the era of rapidly shrinking transistors is at last ending. Next-gen EUV lithography is years behind schedule. Graphics chips from AMD and NVIDIA have been stuck at the 28-nm node since 2011.^[422] And the industry's most successful transistor shrinker, Intel, recently delayed its Cannonlake processor indefinitely, breaking the company's famous tick-tock pattern of CPU releases.^[423] Ultimately, as transistors approach the atomic scale, it's becoming harder to make them cheaply and reliably.

If Moore's law is ending, what does that bode for the Moore's law of Moore's laws? Well, just as Gordon Moore made a bold prediction at the end of his famous 1965 article in Electronics magazine, I'll end this article with a bold prediction of my own:

50 years from today, I, like Gordon Moore before me, will be a CEO billionaire, famous around the world for first recognizing the Moore's Law of Moore's Laws. And you, dear reader, will be able to brag at dinner parties that you were among the first to read about it, in your very own issue of MRS bulletin now framed on your living room wall.

Appendix E

Predicting innovation

“It’s difficult to make predictions, especially about the future.”

— Unknown Dane[424] (commonly misattributed to Yogi Berra, Niels Bohr, and at least 27 others[425, 426])

In the introduction, I argued that physics is worth knowing partly because it tells you whether a technology is possible or impossible. This is important, because once a hardworking physicist has accomplished the difficult step of identifying that a technology is indeed possible, all that remains is for a lazy engineer to get around to inventing it!

Obviously, the question of physical impossibility is just the first baby step in answering our ultimate question of where to invest our research dollars. Certainly, before trying to invent a new technology, it’s a good idea to make sure that it’s possible (or at the very least possibly possible). But once you’ve checked that initial box, there may still be a tremendous gulf between ‘possible in principle’ and ‘probable in practice.’

For example, consider the goal of colonizing the galaxy.[427] As far as we know, this is possible. But we’re still a long ways from colonizing the moon or Mars, let alone a solar system many light-years away. So while physics can tell us that this goal is possible, it remains difficult to know exactly how to achieve this goal and how likely we are to achieve it.

Or consider the goal of using a computer to emulate a human brain.[428, 429] Again, as far as we know, emulating a brain with a computer is possible. But it’s still not at all clear what technological path we should take to achieve this goal, or how long these paths might take.

In general, there are many technological goals that we’d like to achieve but only a limited amount of resources to invest toward achieving them. So we must ask: which technological investments will give us the most bang for our buck? Although this is a question that depends on the specific details of each goal, it turns out that there are some general principles and tools that can help us answer the critical question of where to invest our research dollars.

In this appendix, I will explore this issue further. I'll talk about why predicting innovation matters, why it's so hard, why it's not impossible, and recent ideas about how to do it well. I'll then tie it all up by sharing my experience in the SciCast Science & Technology Forecasting Tournament (which itself was a participant in a tournament of forecasting tournaments, put on by IARPA, the Intelligence Advanced Research Projects Activity).[430]

E.1 Why predicting innovation matters

In his recent book *Superforecasting: The Art and Science of Prediction*, political scientist Philip Tetlock writes, “We are all forecasters. When we think about changing jobs, getting married, buying a home, making an investment, launching a product, or retiring, we decide based on how we expect the future to unfold.”[431]

Nate Silver, the statistician of FiveThirtyEight fame, agrees: “Prediction is indispensable to our lives. Every time we choose a route to work, decide whether to go on a second date, or set money aside for a rainy day, we are making a forecast about how the future will proceed.”[432]

Planning investment in innovation similarly depends on how we expect the future to proceed. Every investment in a new technology is a bet on that technology’s future success, and when making bets it’s essential to estimate the odds. Better knowledge of the odds allows us to avoid bad bets and instead allocate our efforts into smarter, more profitable bets.

E.1.1 An example: the PfSPZ malaria vaccine

One high-stakes example of technological forecasting is the fight against malaria, which kills about a million people a year (particularly young children in tropical Africa).

Suppose you have \$1 billion and your goal is reduce the number of children dying from malaria each year. Your advisers tell you that you have two main options for spending your money. Option 1 is distributing 100 million insecticide-treated bed nets to prevent mosquitoes from biting children at night.¹ Option 2 is to invest your money into speeding development and distribution of the PfSPZ malaria vaccine. Which option should you choose to save the most lives? Remember, making the wrong choice will result in the avoidable deaths of hundreds of thousands of innocent children.

Clearly, there’s not enough information to answer either way with confidence—the answer depends on the expected benefits of each intervention. Bed nets have been well studied through

¹According to Noor et. al. in 2009,[433] about 20 million African children have bed nets, while 90 million remain unprotected. A bed net costs less than \$10 and is one of the most cost-effective ways to save a life. If you wish to help fight malaria, please donate to Against Malaria Foundation, an outstanding charity that has been thoroughly vetted and recommended by GiveWell, a charity evaluator.

randomized controlled trials[434, 435] and we know that roughly one life is saved for every \$3,000 worth of bed nets distributed. As for the PfSPZ malaria vaccine, no one really knows exactly how many lives it can save or at what cost. Experts have a wide range of estimates and differing opinions on how effective this vaccine might be. This uncertainty means that would-be policy-makers and philanthropists are stuck having to make their best guess whether it's better to spend money on bed nets or vaccine development.

But imagine if you had a crystal ball that would divine the effectiveness and cost of the future PfSPZ malaria vaccine. You would immediately know whether to invest your billion dollars into the safe-but-sure bed nets or the high-risk vaccine development. Here, an accurate technology forecast would save millions of lives and millions of dollars.

Questions like these are everywhere. Research into new technology always has uncertainty about its likelihood and payoff, which makes it hard to know which new technologies we should fund. Earth's annual R&D budget is roughly \$1 trillion, and much of it ends up being 'wasted' on bets that don't pay off. Imagine how tremendously more effective that trillion dollars could be if we had a better idea of which bets would pay off and which bets wouldn't. Better technological forecasting would change the world.

E.2 Predicting innovation is hard

Of course, predicting innovation is a hard problem. No one can fault a farmer in 1700 for not anticipating electrification or spaceflight or other fruits of the Industrial Revolution(s). Paradigm-shifting advances in science and technology are by their nature difficult to foresee.

Many companies and government agencies work hard to predict future technology trends, hiring expert analysts to do the best they can. These organizations are often humble about their ability to foresee the future, explicitly diversifying their bets among many possibilities.

E.3 Predicting innovation is not impossible

Despite its difficulty, accurately predicting innovation is not impossible. Moore's Law stands as one of the most famous examples of future innovation being predictable by mere extrapolation. For fifty years now, Moore's Law has more or less followed a simple exponential curve.

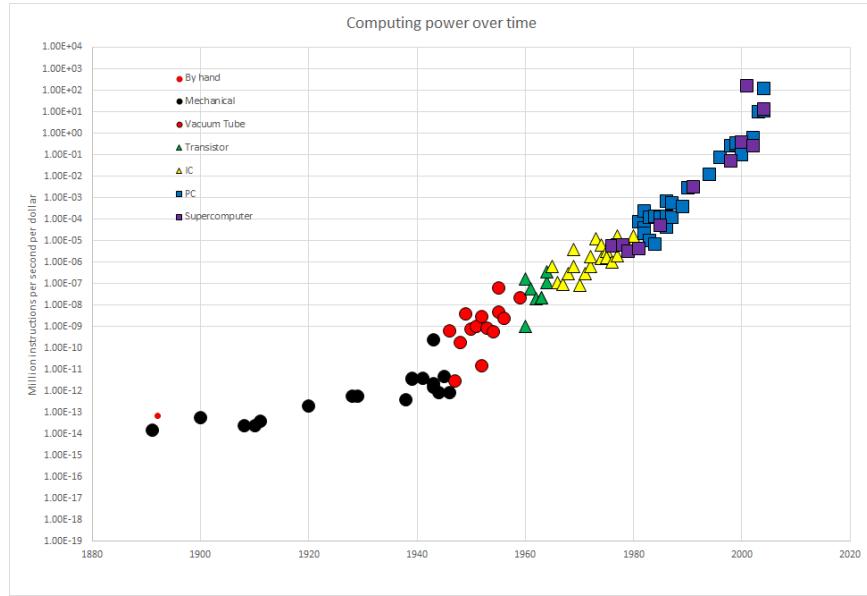


Figure E.1: Moore’s Law is an example of predictable technological innovation. (Data are from Koh[42] and Moravec[72].)

An important question for society is how can we do better at predicting technological innovation? And what are the limits to such prediction?

E.4 Ways to predict innovation

In the game show *Who Wants to be a Millionaire*, a contestant is tasked with answering a series of questions in order to win up to a million dollars in prize money. Questions start out easy, but as the show progresses they become increasingly difficult. Eventually, the contestant reaches the limit of their knowledge and, to continue, must guess in the face of uncertainty. To help overcome this uncertainty, the game show grants contestants three lifelines: the 50:50 (which randomly removes two wrong answers), phone a friend (which dials a friend for advice), and ask the audience (which polls the studio audience for their opinions).²

²Although these three lifelines were offered by the original version of the game show, later versions of the show modified the lifelines offered. Phone a friend, for instance, was removed in 2010 due to the ease with which a friend could quickly Google information over the internet.[436]



Figure E.2: The three lifelines in the TV game show 'Who Wants to be a Millionaire?'

In a sense, the situation faced by a contestant on *Who Wants to be a Millionaire* is not too dissimilar from the situation faced by a government official trying to predict the future path of innovation. In both cases, an uncertain decision maker must guess at the right answer to a high-stakes question, as well as choose how to spend their limited resources on reducing the odds of a mistake.

In the next few subsections, I'll explore this analogy, illustrating the (likely coincidental) correspondence between the three *Millionaire* lifelines and three approaches to predicting future innovation.

E.4.1 Guess at random

Guess randomly (the base case) 50% (assuming no knowledge)

E.4.2 Phone a friend (or a friendly expert)

Phone a friend (ly expert) 65%[\[437\]](#)

E.4.3 Ask the audience (the wisdom of the crowds)

Ask the audience (wisdom of the crowds) 91%[\[437\]](#)

E.4.4 Delphi method

Delphi method Prediction markets Expert political judgment[\[438\]](#)

E.4.5 The Good Judgment Project

E.4.6 Prediction markets

E.5 My experience in the SciCast Science & Technology Forecasting Tournament

For the past few years, I have been one of the world's top traders on SciCast.org, prediction market for technology, earning thousands of dollars for making well-calibrated guesses about future technology (and especially about perovskite solar cells, one of my specialties). Because of my success, I was invited to speak to 500 ACS chemists about predicting future scientific developments.

Appendix F

The parable of the salad

(If you are an expert, feel free to skip this section. If you are not an expert, then the following section was written for you!)

Imagine that one day you decide to make yourself a salad. First, you toss a handful of spinach into the left half of your bowl. Next, you toss a handful lettuce into the right half of your bowl. Then, suddenly and without warning—*POOF*—a strip of bacon magically appears down the middle, right at the interface between the spinach and lettuce.¹ You'd be pretty surprised, right?

This story, though fictional, is essentially what happened a decade ago² in the lab of scientists Akira Ohtomo and Harold Hwang in Japan.[184] However, instead of trying to build a salad from spinach and lettuce, they were trying to build a transistor out of two minerals, strontium titanum oxide and lanthanum aluminum oxide.³ Ohtomo and Hwang found that when they put these two electrically insulating materials in contact with one another, *POOF* electrical conductivity appeared at their interface!⁴

¹For those of you unfamiliar with bacon, it is a substance quite dissimilar from spinach and lettuce.

²2004 was the year they published their discovery, for those of you in the far future who don't want to look up when this dissertation was written and then subtract 10ish.

³Incidentally, strontium titanate is a cheap alternative to diamond if you're in the market for a wedding ring. It has over four times the 'fire' of diamond, but because it's easier to scratch, I only recommend it for marriages unlikely to endure.

⁴...under the right conditions. In truth, it is a bit more complicated than simply putting these two minerals in contact with one another. To get conductivity, the lanthanum aluminum oxide crystal has to grow atop the strontium titanum oxide in a certain crystal direction with a certain crystal termination in a certain oxygen pressure and with a certain thickness. So don't grab two rocks from the ground and expect to see a spark between them.



Figure F.1: Yum.

And this electrical conductivity wasn't just any old boring conductivity. Measurements showed that it was two-dimensional⁵ and possibly even magnetic.

This discovery sparked a flurry of research, as governments began spending millions of dollars on experiments to try and settle the questions of what causes the conductivity and possible magnetism. It's not every day that scientists run across magical new properties of minerals, so they wanted to know more.

For the past few years, I was part of this debate, performing experiments to better understand this magical bacon. Where does it come from? Why does it taste the way it does? The main experiment I performed was to see whether adding some raisins and croutons⁶ into the lettuce

⁵When physicists say that a bunch of conducting electrons are two-dimensional, they don't mean that the region of conductivity has zero thickness. They just mean that the electrons are free to move in two directions but constrained in the third direction. So in this sense, we human beings, despite having height, are nevertheless two-dimensional because we cannot fly. We're constrained to move in only two dimensions along the ground. And when it comes to electrons, it turns out they act quite differently when constrained to two-dimensions, sometimes in very interesting and Nobel prize-winning ways.

⁶Also known as the rare-earth ions thulium (4f12) and lutetium (4f14). You know, those ones? No? Well, then let's just call them raisins and croutons.

side of the salad would affect the taste of the bacon (translation: I chemically doped rare-earth impurities into the lanthanum aluminum oxide film to see whether increased spin-orbit scattering affected the magnetoresistance of the 2D electron gas at the interface). After many months of carefully assembling salads and then tasting their bacon—by which I mean assessing the electrical properties of the resulting minerals—I concluded that no, the raisins and croutons did not really change the flavor of the bacon.

Sadly, this is somewhat boring result and it's hard to say very much with confidence. Although it seems like the raisins and croutons didn't affect the bacon, maybe raisins and croutons **do** affect bacon, but I just didn't add enough of them. Or maybe raisins and croutons do affect bacon, but I was tasting the wrong parts of the bacon. Or maybe they do affect bacon but I wasn't sprinkling them in well and they landed far away from the bacon. And since no one was really expecting that the raisins or croutons would affect the bacon, the results are not surprising or interesting.

However, while I failed to solve the puzzle of the magic bacon, I like to think that I succeeded along other dimensions. I learned how to make salads and how to taste things, kitchen skills that I still regularly use today. I learned how to ask good questions and generate good hypotheses. And I learned how to write amusing science parables!

Appendix G

SketchFET Press Release

Sharing government-funded science with the public is important, especially when you consider that one, science is performed on behalf of the public, and two, science is paid for out of the public's pockets.

Those who write scientific press releases face many difficult balancing acts. They need to make the research sound interesting and impactful, but without overselling it. They need to get the main idea across, but without dumping pages of background on innocent readers. And they need to keep their article short and simple, but without missing the key details that distinguish this research from its predecessors.

Below is an example press release that I wrote about a project that I worked on in collaboration with the Levy Lab from the University of Pittsburgh.

G.1 Scientists invent ‘fingerpainted’ transistor

Fingerpainting may no longer be just for kids. Scientists at University of Pittsburgh and Stanford University have developed a new method for ‘fingerpainting’ nanoscale electronic circuits using a tiny metal ‘finger’ that is only a few atoms wide at its tip.

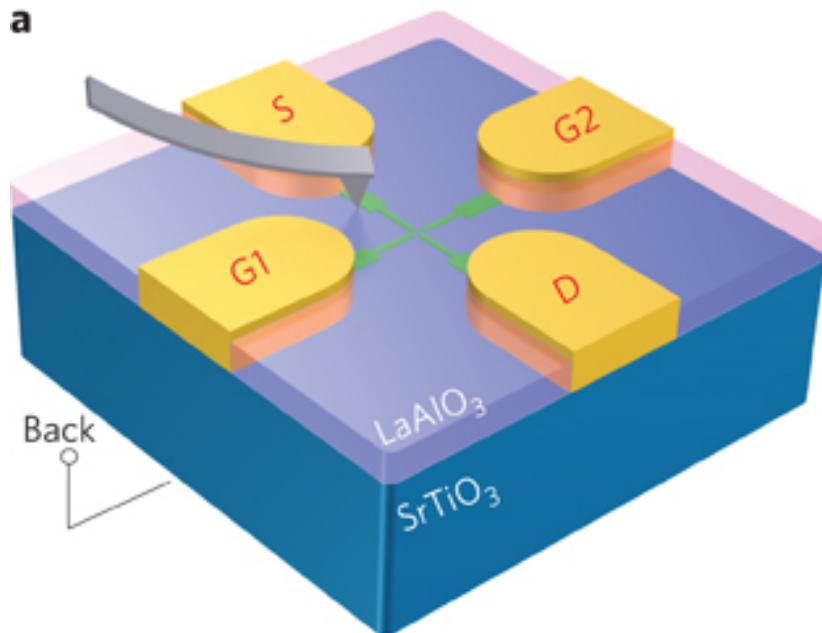


Figure G.1: Named SketchFET, it is the world's first nanometer-scale gigahertz-speed transistor that can be 'drawn' onto a circuit by a tiny metal finger. Reprinted from P. Irvin, M. Huang, F. J. Wong, T. D. Sanders, Y. Suzuki, and J. Levy, *Appl. Phys. Lett.* **102**, 103113 (2013) with the permission of AIP Publishing under license number 3871200208210.

To make their 'fingerpainted' circuits, the scientists started with a 'canvas' made of two minerals, LaAlO₃ and SrTiO₃. Then, using precision laser tracking, the scientists carefully lower a tiny, finger-like metal cantilever, which at its tip is only a few atoms across. When the scientists electrically charge this tiny metal finger and drag it along the canvas material, the finger leaves an electrically conductive path in its wake—in essence, a wire. By dragging the metal finger around the mineral canvas in this fingerpainting-esque way, scientists are able to 'draw' wires as well as more complicated circuits.

The scientists hope that their invention could be used to better measure the electrical properties of molecules. Currently, it's very difficult to move an individual molecule into a pre-built measurement circuit—but with this new invention, scientists may be able to simply draw the circuit around the molecule, with no need to move molecules themselves.

Key to these 'fingerpainted' circuits is the special canvas material, a sandwich of the two minerals LaAlO₃ and SrTiO₃. A decade ago, researchers Akira Ohtomo and Harold Hwang discovered that these two minerals, though each insulating by themselves, could conduct electricity when sandwiched together under certain conditions. One of the important conditions required is that the top layer of the mineral sandwich, made of LaAlO₃, needs to be at least eight atoms thick.

Though some might see this minimum required thickness as a limitation, a few scientists saw

it as an opportunity. They created a layer of LaAlO₃ thin enough to be just shy of turning the sandwich electrically conductive. Then, with this mineral sandwich on the verge of conductivity, the scientists discovered that a small electrical prod from a metal finger was enough to turn the prodded location conductive, like a wire. Continuing to drag this metal finger along the surface left behind a trail of conductivity, similar to how a fingerpainting finger would leave behind a trail of paint.

However, wires by themselves are not enough to make a complex circuit. This week, in the journal Applied Physics Letters, these scientists have shown that not only can they draw wires, but they can draw transistors too.

One of the paper's authors, physicist Ted Sanders, said "Being able to draw wires that act like a transistor is a big step forward, because transistors are the building block of modern electronics."

The transistor they drew was mere nanometers across and able to operate up to a frequency of 2.4 GHz, making it competitive with transistors in today's computers and phones. However, Sanders cautioned, "These transistors are worse than commercial transistors in many ways: they're hard to mass produce, less energy efficient, and not as stable. But the advantage of our invention is that now we can draw custom circuits quickly."

Though the scientists have no plans to commercialize their invention, they suggest that someday it could be used to draw circuits to measure tiny molecules or nanostructures, helping to expand the frontiers of nanoscale science and technology.

Referenced article: P. Irvin, M. Huang, F. J. Wong, T. D. Sanders, Y. Suzuki, and J. Levy, *Appl. Phys. Lett.* **102**, 103113 (2013).[\[439\]](#)

Appendix H

Wikipedia and scientific publishing

H.1 Why it makes sense to publish on Wikipedia

More scientists should publish on Wikipedia, in my opinion. Wikipedia is an outlet that's open access, highly read, and highly ranked (by Google). Authoring a review-like encyclopedia article for Wikipedia is a great way to disseminate specialized knowledge to a broader audience. This broader audience is not just the lay public, but includes new graduate students, senior scientists in adjacent fields, and even senior scientists in the same field.

H.2 When it doesn't make sense to publish on Wikipedia

Of course, not every topic is appropriate for Wikipedia. Wikipedia only wants articles that put forth a neutral, consensus view. When science is very new, and no consensus exists, then it may be premature to include it on Wikipedia.

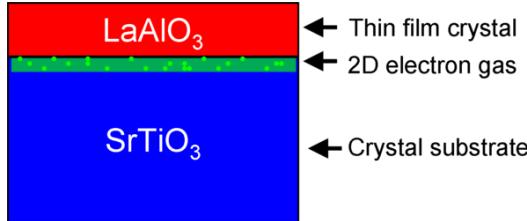
Also, Wikipedia is no substitute for traditional publishing. Original scientific research is not allowed on Wikipedia. Wikipedia ideally only publishes facts that have been accepted through many layers of literature. First (and even secondary) sources are discouraged, with tertiary sources being preferred.

H.3 My major Wikipedia contributions

Although I regret not contributing more, I am proud of the scientific contributions I did make while in graduate school. In addition to numerous small edits, I authored two original articles. One was on the topic of the LaAlO₃/SrTiO₃ interface[440] and the other was on the broader topic of complex oxides[103]. They are reproduced below (possibly not quite up to date):

H.3.1 LAO/STO article

Lanthanum aluminate-strontium titanate interface



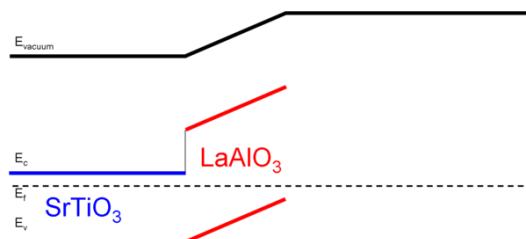
- The SrTiO₃ side of the interface is TiO₂-terminated (causing the LaAlO₃ side of the interface to be LaO-terminated)^[1]
- The LaAlO₃ layer is at least 4 unit cells thick^[8]

Conductivity can also be achieved when the SrTiO₃ is doped with oxygen vacancies; however, in that case, the interface is technically LaAlO₃/SrTiO_{3-x} instead of LaAlO₃/SrTiO₃.

1.1.2 Hypotheses for conductivity

The source of conductivity at the LaAlO₃/SrTiO₃ interface has been debated for years. SrTiO₃ is a wide-band gap semiconductor that can be **doped n-type** in a variety of ways. Clarifying the mechanism behind the conductivity is a major goal of current research. Four leading hypotheses are:

- Polar gating
- Oxygen vacancies
- Intermixing
- Structural distortions



Below the critical thickness: Further from the interface, the energy of electrons in the LaAlO₃ rises, due to the LaAlO₃'s built-in electric field. (Not to scale)

1 Emergent properties

1.1 Conductivity

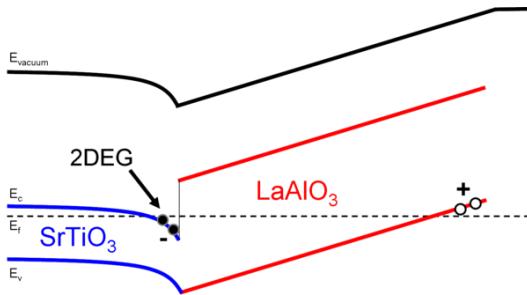
Under the right conditions, the LaAlO₃/SrTiO₃ interface is electrically conductive, like a metal. The angular dependence of Shubnikov-de Haas oscillations indicates that the conductivity is two-dimensional,^[6] leading many researchers to refer to it as a two-dimensional electron gas (2DEG). Two-dimensional does not mean that the conductivity has zero thickness, but rather than the electrons are confined to only move in two directions. It is also sometimes called a two-dimensional electron liquid (2DEL) to emphasize the importance of inter-electron interactions.^[7]

1.1.1 Conditions necessary for conductivity

Not all LaAlO₃/SrTiO₃ interfaces are conductive. Typically, conductivity is achieved only when:

- The LaAlO₃/SrTiO₃ interface is along the 001 crystallographic direction
- The LaAlO₃ and SrTiO₃ are crystalline and epitaxial

Polar gating Polar gating was the first mechanism used to explain the conductivity at LaAlO₃/SrTiO₃ interfaces.^[1] It postulates that the LaAlO₃, which is polar in the 001 direction (with alternating sheets of positive and negative charge), acts as an electrostatic gate on the semiconducting SrTiO₃.^[1] When the LaAlO₃ layer



Above the critical thickness: As the LaAlO_3 grows thicker, the energy of electrons on the surface rises so high that they leave, leaving holes (or oxygen vacancies) behind. The positively charged holes (or oxygen vacancies) attract electrons to the lowest-energy empty states, located in the conduction band of the SrTiO_3 . (Not to scale)

grows thicker than three unit cells, its valence band energy rises above the Fermi level, causing holes (or positively charged oxygen vacancies^[9]) to form on the outer surface of the LaAlO_3 . The positive charge on the surface of the LaAlO_3 attracts negative charge to nearby available states. In the case of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, this means electrons accumulate in the surface of the SrTiO_3 , in the Ti d bands.

The strengths of the polar gating hypothesis are that it explains why conductivity requires a critical thickness of four unit cells of LaAlO_3 and that it explains why conductivity requires the SrTiO_3 to be TiO_2 -terminated. The polar gating hypothesis also explains why alloying the LaAlO_3 increases the critical thickness for conductivity.^[10]

One weakness of the hypothesis is that it predicts that the LaAlO_3 films should exhibit a built-in electric field; so far, x-ray photoemission experiments^{[11][12][13][14]} and other experiments^{[15][16][17]} have shown little to no built-in field in the LaAlO_3 films. The polar gating hypothesis also cannot explain why Ti^{3+} is detected when the LaAlO_3 films are thinner than the critical thickness for conductivity.^[12]

The polar gating hypothesis is sometimes called the polar catastrophe hypothesis,^[18] alluding to the counterfactual scenario where electrons don't accumulate at the interface and instead voltage in the LaAlO_3 builds up forever. The hypothesis has also been called the electronic reconstruction hypothesis,^[18] highlighting the fact that electrons, not ions, move to compensate the building voltage.

Oxygen vacancies Another hypothesis is that the conductivity comes from free electrons left by oxygen vacancies in the SrTiO_3 .^[19] SrTiO_3 is known to be easily doped by oxygen vacancies, so this was initially considered a promising hypothesis. However, electron energy loss spectroscopy measurements have bounded the density of oxygen vacancies well below the density necessary to supply the measured free electron densities.^[20]

Another proposed possibility is that oxygen vacancies in the surface of the LaAlO_3 are remotely doping the SrTiO_3 .^[12] Under generic growth conditions, multiple mechanisms can coexist. A systematic study^[21] across a wide growth parameter space demonstrated different roles played by oxygen vacancy formation and the polar gating at different interfaces. An obvious difference between oxygen vacancies and polar gating in creating the interface conductivity is that the carriers from oxygen vacancies are thermally activated as the donor level of oxygen vacancies is usually separated from the SrTiO_3 conduction band, consequently exhibiting the carrier freeze-out effect^[22] at low temperatures; in contrast, the carriers originating from the polar gating are transferred into the SrTiO_3 conduction band (Ti 3d orbitals) and are therefore degenerate.^[21]

Intermixing Lanthanum is a known dopant in SrTiO_3 ,^[23] so it has been suggested that La from the LaAlO_3 mixes into the SrTiO_3 and dopes it n-type. Multiple studies have shown that intermixing takes place at the interface;^[24] however, it is not clear whether there is enough intermixing to provide all of the free carriers. For example, a flipped interface between a SrTiO_3 film and a LaAlO_3 substrate is insulating.^[25]

Structural distortions A fourth hypothesis is that the LaAlO_3 crystal structure undergoes octahedral rotations in response to the strain from the SrTiO_3 . These octahedral rotations in the LaAlO_3 induce octahedral rotations in the SrTiO_3 , increasing the Ti d-band width enough so that electrons are no longer localized.^[26]

1.2 Superconductivity

Superconductivity was first observed in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces in 2007, with a critical temperature of ~ 200 mK.^[27] Like the conductivity, the superconductivity appears to be two-dimensional.^[2]

1.3 Ferromagnetism

Hints of ferromagnetism in $\text{LaAlO}_3/\text{SrTiO}_3$ were first seen in 2007, when Dutch researchers observed hysteresis in the magnetoresistance of $\text{LaAlO}_3/\text{SrTiO}_3$.^[28] Follow up measurements with torque magnetometry indicated that the magnetism in $\text{LaAlO}_3/\text{SrTiO}_3$ persisted all the way to room temperature.^[29] In 2011, researchers at Stanford University used a scanning SQUID to directly image the ferromagnetism, and found that it occurred in heterogeneous patches.^[3] Like the conductivity in $\text{LaAlO}_3/\text{SrTiO}_3$, the magnetism only appeared when the LaAlO_3 films were thicker than a few unit cells.^[30] However, unlike conductivity, magnetism was seen at SrO -terminated surfaces as well as TiO_2 -terminated surfaces.^[30]

The discovery of ferromagnetism in a materials system that also superconducts spurred a flurry of research and debate, because ferromagnetism and superconductivity almost never coexist together.^[3] Ferromagnetism requires electron spins to align, while superconductivity typically requires electron spins to anti-align.

1.4 Magnetoresistance

Magnetoresistance measurements are a major experimental tool used to understand the electronic properties of materials. The magnetoresistance of LaAlO₃/SrTiO₃ interfaces has been used to reveal the 2D nature of conduction, carrier concentrations (through the hall effect), electron mobilities, and more.^[6]

1.4.1 Field applied out-of-plane

At low magnetic field, the magnetoresistance of LaAlO₃/SrTiO₃ is parabolic versus field, as expected for an ordinary metal.^[31] However, at higher fields, the magnetoresistance appears to becomes linear versus field.^[31] Linear magnetoresistance can have many causes, but so far there is no scientific consensus on the cause of linear magnetoresistance in LaAlO₃/SrTiO₃ interfaces.^[31] Linear magnetoresistance has also been measured in pure SrTiO₃ crystals,^[32] so it may be unrelated to the emergent properties of the interface.

1.4.2 Field applied in-plane

At low temperature ($T < 30$ K), the LaAlO₃/SrTiO₃ interface exhibits negative in-plane magnetoresistance,^[31] sometimes as large as -90% .^[4] The large negative in-plane magnetoresistance has been ascribed to the interface's enhanced spin-orbit interaction.^{[4][33]}

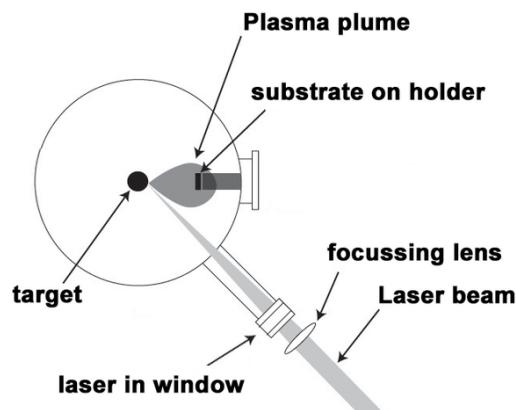
1.5 Electron gas distribution at the LaAlO₃/SrTiO₃ interface

Experimentally, the charge density profile of the electron gas at the LaAlO₃/SrTiO₃ interface has a strongly asymmetric shape with a rapid initial decay over the first 2 nm and a pronounced tail that extends to about 11 nm.^{[34][35]} A wide variety of theoretical calculations support this result. Importantly, to get electron distribution one have to take into account field-dependent dielectric constant of SrTiO₃.^{[36][37][38]}

2 Comparison to other 2D electron gases

The 2D electron gas that arises at the LaAlO₃/SrTiO₃ interface is notable for two main reasons. First, it has very high carrier concentration, on the order of 10^{13} cm⁻². Second, if the polar gating hypothesis is true, the 2D electron gas has the potential to be totally free of disorder, unlike other 2D electron gases that require doping or gating to form. However, so far researchers have been unable to synthesize interfaces that realize the promise of low disorder.

3 Synthesis methods



Interfaces are synthesized by shooting a laser at a LaAlO₃ target. Ablated material flies off the target and lands onto a heated SrTiO₃ crystal.

Most LaAlO₃/SrTiO₃ interfaces are synthesized using pulsed laser deposition. A high-power laser ablates a LaAlO₃ target, and the plume of ejected material is deposited onto a heated SrTiO₃ substrate. Typical conditions used are:

- Laser wavelength of 248 nm
- Laser fluence of 0.5 J/cm² to 2 J/cm²^[39]
- Substrate temperature of 600 °C to 850 °C^[28]
- Background oxygen pressure of 10^{-5} Torr to 10^{-3} Torr^[28]

Some LaAlO₃/SrTiO₃ interfaces have also been synthesized by molecular beam epitaxy, sputtering, and atomic layer deposition.^[40]

4 Similar interfaces

To better understand in the LaAlO₃/SrTiO₃ interface, researchers have synthesized a number of analogous interfaces between other polar perovskite films and SrTiO₃. Some of these analogues have properties similar to LaAlO₃/SrTiO₃, but some do not.

4.1 Conductive interfaces

- GdTiO₃/SrTiO₃^[41]
- LaTiO₃/SrTiO₃^[42]
- LaVO₃/SrTiO₃^[42]
- LaGaO₃/SrTiO₃^[43]
- PrAlO₃/SrTiO₃^[44]
- NdAlO₃/SrTiO₃^[44]
- NdGaO₃/SrTiO₃^[44]
- GdAlO₃/SrTiO₃^[45]
- Nd_{0.35}Sr_{0.65}MnO₃/SrTiO₃^[46]
- Al₂O₃/SrTiO₃^[47]
- amorphous-YAlO₃/SrTiO₃^[40]
- La_{0.5}Al_{0.5}Sr_{0.5}Ti_{0.5}O₃/SrTiO₃^[10]
- DyScO₃/SrTiO₃^[48]
- KTaO₃/SrTiO₃^[49]
- CaZrO₃/SrTiO₃^[50]

4.2 Insulating interfaces

- LaCrO₃/SrTiO₃^[51]
- LaMnO₃/SrTiO₃^[43]
- La₂O₃/SrTiO₃^[40]
- Y₂O₃/SrTiO₃^[40]
- LaYO₃/SrTiO₃^[40]
- EuAlO₃/SrTiO₃^[45]
- BiMnO₃/SrTiO₃^[52]

5 Applications

As of 2015, there are no commercial applications of the LaAlO₃/SrTiO₃ interface. However, speculative applications have been suggested, including field-effect devices, sensors, photodetectors, thermoelectrics, and solar cells.^[53]

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7 External links

- Materials science: Enter the oxides

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H.3.2 Complex oxides article

Complex oxide

A **complex oxide** is a chemical compound that contains oxygen and at least two other elements (or oxygen and just one other element that's in at least two **oxidation states**).^[1] Complex oxide materials are notable for their wide range of magnetic and electronic properties, such as ferromagnetism, ferroelectricity, and **high-temperature superconductivity**. These properties often come from their strongly correlated electrons in d or f orbitals.

1 Natural occurrence

Many minerals found in the ground are complex oxides. Commonly studied mineral crystal families include spinels and perovskites.

2 Applications

Complex oxide materials are used in a variety of commercial applications.

2.1 Magnets

Magnets made of the complex oxide ferrite are commonly used in transformer cores and in inductors.^[2] Ferrites are ideal for these applications because they are magnetic, electrically insulating, and inexpensive.

2.2 Transducers and actuators

Piezoelectric transducers and actuators are often made of the complex oxide PZT (lead zirconate titanate).^[3] These transducers are used in applications such ultrasound imaging and some microphones. PZT is also sometimes used for piezo ignition in lighters and gas grills.

2.3 Capacitors

Complex oxide materials are the dominant dielectric material in ceramic capacitors.^[4] About one trillion ceramic capacitors are produced each year to be used in electronic equipment.

2.4 Fuel cells

Solid oxide fuel cells often use complex oxide materials as their electrolytes, anodes, and cathodes.^[5]

2.5 Gemstone jewelry

Many precious gemstones, such as emerald and topaz, are complex oxide crystals. Historically, some complex oxide materials (such as strontium titanate, yttrium aluminium garnet, and gadolinium gallium garnet) were also synthesized as inexpensive diamond simulants, though after 1976 they were mostly eclipsed by cubic zirconia.

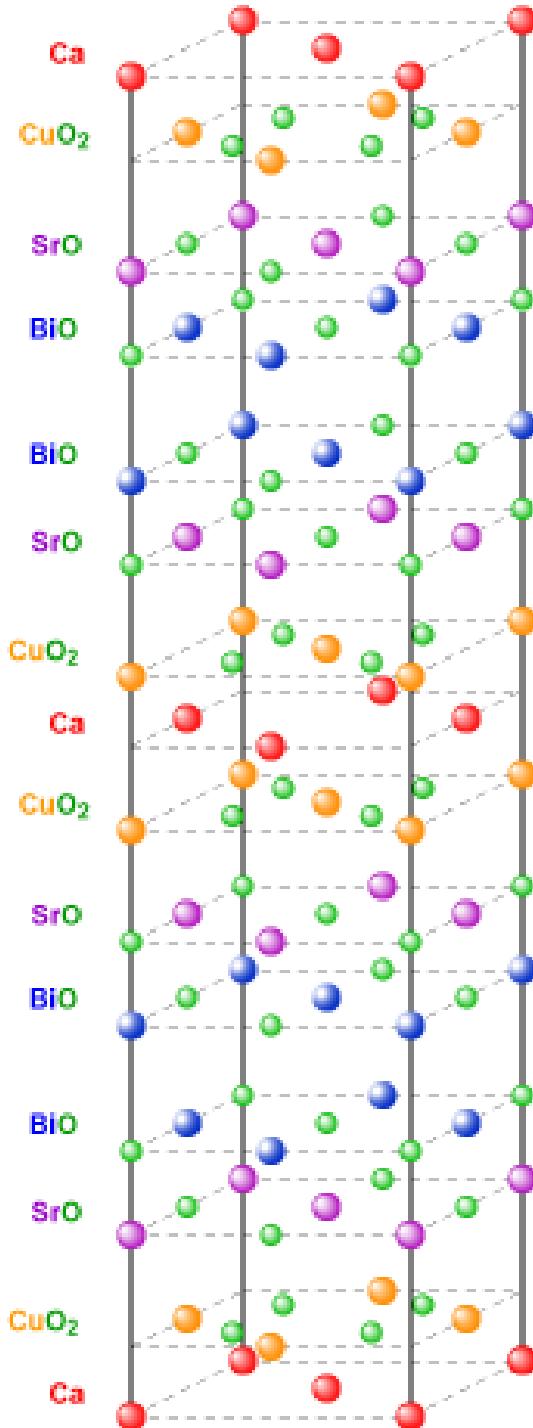
2.6 New electronic devices

As of 2015, there is research underway to commercialize complex oxides in new kinds of electronic devices, such as ReRAM, FeRAM, and memristors. Complex oxide materials are also being researched for their use in spintronics.

Another potential application of complex oxide materials is superconducting power lines.^[7] A few companies have invested in pilot projects, but the technology is not widespread.

3 Commonly studied complex oxides

- Lead zirconate titanate (a piezoelectric material)
- Lanthanum aluminate (a high-dielectric insulator)
- Strontium titanate (a high-dielectric semiconductor)
- Lanthanum strontium manganite (a material exhibiting colossal magnetoresistance)
- Barium titanate (a multiferroic material)
- Bismuth ferrite (a multiferroic material)
- Yttrium barium copper oxide (a high-temperature superconductor)
- Bismuth strontium calcium copper oxide (a high-temperature superconductor)



The crystal structure of bismuth strontium calcium copper oxide, a high-temperature superconductor and complex oxide.

4 See also

- Multiferroics
- Mott insulator
- Colossal magnetoresistance



A ferrite bead near the end of a Mini USB cable helps suppress high-frequency noise.



Spanish-made emerald and gold pendant exhibited at Victoria and Albert Museum.^[6]

- Half metal
- Lanthanum aluminate-strontium titanate interface

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6 External links

- Materials science: Enter the oxides
- Condensed-matter physics: Complex oxides on fire
- Complex oxides: A tale of two enemies
- Oxide interfaces

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H.4 My minor Wikipedia contributions

In addition to authoring these prior articles, I also contributed to pre-existing scientific articles on subjects such as pulsed laser deposition, compressed sensing (a statistical technique based on sparse matrices and the L^1 norm), flight airspeed records, combinatorial prediction markets, Moore’s law, the three-sector theory, Maxwell’s demon, and Landauer’s principle (which asserts there is a minimum average energy cost of $k_B T \ln 2$ to erase one bit of information).

H.5 A selfish reason for contributing to Wikipedia: Networking

Donating your time and expertise to Wikipedia may appear to be a thankless job done in service to science rather than to advance your career. However, to my surprise I’ve seen my contributions recognized far more frequently than I expected.¹ While editing Wikipedia may not be the best way to get ahead in life, it still can be a good way to network with interesting and impactful people and to get attention for your expertise.

For example, shortly after expanding the Wikipedia article on prediction markets to include a section about combinatorial prediction markets, Rob Bernstein, the CEO of InTrade (which is the world’s most well-known prediction market), connected with me on LinkedIn and sent me a message telling me that he had noticed my contributions. It’s not every day that a CEO tries to network with you, rather than the other way around.

Another time, I was quoted speaking about my Wikipedia editing in a long Vox article on problems facing science, which ended up being shared over 50,000 times on Facebook.[441] After the story was published, I was contacted by a number of interested folks to say thanks or make connections, including NPR’s very own Science Correspondent Joe Palca (the one time I was glad to pick up a call from an unknown number!).

And a third time, I was once contacted by a famous tenured physics professor at a top university who emailed me to say:

“So I just looked at the LAO/STO wikipedia page and thought ‘Wow! This is awesome! What a professional job! Who wrote this??’

From the History page, I gather it was mostly you. Nice job.”

¹ And it’s not just the broader world who benefits. Surprisingly to me, even people I know personally have found my contributions useful. A friend who’s a research fellow at the MIT Media Lab and Singapore University of Technology and Design once contacted me to thank me for plots on airplane speed records, a plot that he was about to use in a presentation at Oxford University.

That compliment made my day.² :)

²Besides networking, the occasional heartfelt compliment is another selfish reason to contribute to Wikipedia.

Appendix I

Quantum misconceptions

“I think I can safely say that nobody understands quantum mechanics.”

— Richard Feynman, *The Character of Physical Law*[442]

“Quantum mechanics is well understood.”

— Charles Bennett, *Quantum Summit*[443]

“Uh...”

— Ted Sanders, *here*

Not only is quantum mechanics central to my dissertation, but quantum mechanics is also central to how the world works. Yet despite the centrality of quantum mechanics, many people still hold fundamental misconceptions about what quantum mechanics actually means. To help defeat these persistent misconceptions, this appendix identifies the errors behind some common myths.

(And even if you yourself fall victim to none of these myths, I still hope this appendix adds real value by familiarizing you with others’ mistaken perspectives. Whether in the form of one-way teaching or two-way discussion, communication is an inherently empathetic process, requiring some implicit model of your audience’s beliefs.)

I.1 Misconceptions about quantum mechanics

I.1.1 MYTH: Quantum mechanics is inherently random.

Although the Copenhagen interpretation of quantum mechanics addresses the measurement problem of quantum mechanics by invoking random wavefunction collapse, there are nevertheless mainstream

interpretations of quantum mechanics that remain compatible with determinism. For example, the many-worlds interpretation (also called the relative state formulation)[444, 445] addresses the measurement problem by suggesting (roughly) that each a time a quantum measurement is performed,¹ the universe splits into non-interacting branches, with each branch corresponding to a different outcome of the measurement. When this branching occurs, each copy of ourselves may subjectively experience a ‘random’ outcome, but the universe itself will have followed completely deterministic and reversible rules in which all outcomes are realized simultaneously.[446, 447]

I.1.2 MYTH: Quantum entanglement goes faster than the speed of light

Related to the previous myth, some people believe that because the Copenhagen interpretation relies on instantaneous wavefunction collapse, that so too does quantum mechanics. But in fact, there are interpretations that preserve locality, such as the many-worlds interpretation.²

I.1.3 MYTH: Quantum theory might easily be wrong in small ways

Of course, any theory has the potential to be wrong. However, quantum theory is relatively special in the sense that if it were wrong, it would perversely disagree with fundamental principles we currently believe to be true. Scott Aaronson wrote an interesting paper in 2004 titled *Is Quantum Mechanics An Island In Theoreyspace* in which he briefly explores the perverse consequences of modifications to the theory. In particular, he goes over the perverse consequences of replacing the 2-norm by some other p-norm, of relaxing the condition that norm be preserved, of restricting amplitudes to the real numbers, and of making the Schrödinger equation nonlinear.[448]

I.1.4 MYTH: The wavefunction is a function of space

Because students are first taught quantum mechanics in its simplest form, with just a single particle, they often come away with the impression that wavefunctions are functions over space. For example, in the classic problem of a (spinless) particle in a three dimensional box, the wavefunction is a function of three dimensions. However, the dimensions of this wavefunction are not the dimensions

¹To be fair, this is a somewhat circular definition, since a quantum measurement is taken to be anything that splits the universe into non-interacting branches. But one person’s circularity is another person’s self-consistency.

²I believe a major factor in the success of the many-worlds interpretation is that it preserves determinism and locality, two features of classical physics that conservative physicists are loathe to give up unnecessarily. Of course the tradeoff is that you start to sound a bit crazy when you talk about the gazillions of unmeasurable parallel universes existing alongside us in a quantum superposition.

of real space! They are the coordinates of the particle in real space. The importance of this distinction becomes clear as the number of particles grows. In a two-particle system in three spatial dimensions, the wavefunction no longer has three dimensions; now it has six. These six dimensions correspond to the possible configurations of the two particles. Hence, the space is called configuration space. It is important to remember that wavefunctions are functions over configuration space, not real space.

I.1.5 MYTH: Quantum states jump from one state to another

In 2014, Edge magazine asked a couple hundred intellectuals the following question: What Scientific Idea is Ready for Retirement?^[449] One of these intellectuals was physicist David Deutsch, and his candidate for retirement was the idea of quantum jumps. The notion that a quantum system instantaneously jumps from one state to another has been around as long as quantum theory itself^[450, 451, 452] and is practically embodied in its name: quantum has come to mean a thing that is discrete rather than continuous. Yet, whether quantum jumps exist at all is an open question at best. By now, it is well accepted that time evolution of the wavefunction is smooth and continuous, outside of collapse. The many worlds interpretation, supported by Deutsch, argues that the phenomenon of collapse is simply an apparent illusion, and as a consequence *all* time evolution is smooth and continuous.^[453] Even under other interpretations, the existence of quantum jumps remains unclear,^[454] though experiments have been proposed to test the existence of quantum jumps.^[455]

I.1.6 MYTH: Einstein hated quantum physics

Einstein is a magnet for misconceptions.^[456] One of the larger misconceptions regarding Einstein is that he hated or disliked quantum theory. In fact, although he wrestled with parts of it over his career, his letters show that he very much respected the theory and those who created it. All of his (confidential and therefore revealing) Nobel prize recommendations after 1927 were for quantum physicists.^[457]

I.2 Misconceptions about quantum computers

Misconceptions regarding quantum computers are so pervasive that I have broken them out into their own section.

I.2.1 MYTH: Quantum computers are faster than classical computers.

Although this myth might actually be true, mathematically, it is still an open question. No one knows whether $P = PSPACE$. It might be true that quantum computers are faster than classical computers, but it might also be false. As of today, there is no proof that quantum computers are faster than classical computers.^[458]

I.2.2 MYTH: Quantum computers might be faster than classical computers at most tasks.

No.[459]

I.2.3 MYTH: Quantum computers can solve NP-hard problems, like integer factoring, in polynomial time

Actually, integer factoring is not an NP-hard problem. As far as anyone knows, it's still possible that sometime somewhere someone will devise a clever classical algorithm capable of factoring integers in polynomial time. So although a quantum computer can use Shor's algorithm to factor integers in polynomial time, there's no guarantee that classical computers won't one day catch up. All we know is that quantum algorithms are faster than *today's best known* classical algorithm for factoring integers.

Putting aside integer factoring, let's return to the notion that quantum computers can solve NP-hard problems in polynomial time. In fact, that is also a myth. Quantum computers cannot solve NP-hard problems in polynomial time.

I.2.4 MYTH: Quantum computers are fast because instead of encoding 0 or 1, they can encode a range between 0 and 1

Although it's true that quantum computers encode information in the continuum of states between 0 and 1, this is not where their power comes from. Analog computers can similarly store numbers in a range,³ but they lack the magic of quantum algorithms.

I.2.5 MYTH: Quantum computers are fast because they compute every solution in parallel

Like many myths, this one has a kernel of truth behind it. From one point of view, quantum computers *do* compute every solution to a problem in parallel. Unfortunately, this isn't helpful in general, because all the wrong answers are still mixed in with the correct answer. However, for a few mathematical problems with special structure, such as integer factoring, there are ways to get the wrong answers to cancel out, leaving only the correct answer behind.⁴ However, in general quantum computers cannot use "quantum brute force" to solve NP-hard problems in polynomial time by

³As an aside, the fact that today's silicon computers store information as 0s and 1s is a feature, not a bug. Fewer states mean fewer errors.

⁴In fact, clever ways of getting the wrong answers to cancel out in problems with special structure is the big idea behind quantum speedups.

trying every solution in parallel. So in that sense, it's a myth that quantum computers compute every solution in parallel.

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Although hyperlinking has made it easier than ever to access works of scholarship, hyperlinks rot at an astonishingly high rate.[\[460, 461\]](#) In light of this problem, I have taken care to hyperlink to DOIs (Digital Object Identifiers) or the Internet Archive whenever possible. These hyperlinks should remain functional as long as the the DOI system, the Internet Archive, and the internet itself stay funded.

Also, to assist you in deciding whether to check a reference, I have annotated some of the better references with brief descriptions of their contents and their intended audience.

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