Physics in Perspective



Superconducting Niobium-Titanium: Enabler for Affordable MRI and the Search for the Higgs Boson

T. G. Berlincourt*

In 1961, Bell Telephone Laboratories researchers startled the world of physics by reporting that, at temperatures near absolute zero, a superconducting niobium-tin compound could support enormous electric current densities without resistance in the presence of very high magnetic fields. Suddenly, it became possible to fabricate supermagnets that generate high magnetic fields with unprecedented efficiency and economy. Scientists raced to find additional such materials and also to account theoretically for their behavior. Disregarded early on as unpromising, niobium-titanium alloys eventually emerged from among thousands of superconductors to become the most widely used, finding application in many thousands of MRI medical imaging systems and in huge particle accelerator magnets. In 1962, at Atomics International, experiments that revealed the supermagnet promise of niobium-titanium alloys also made essential contributions to the confirmation of the initially overlooked superconductivity theories of Soviet scientists Ginzburg, Landau, Abrikosov, and Gor'kov as the appropriate framework for understanding the physics of high magnetic field superconductivity.

Key words: Cryogenics; Higgs boson; MRI; superconductivity.

Much excitement attended the epic and successful search for the Higgs boson at the European Center for Particle Physics (CERN). Far less noted was the type II superconducting niobium-titanium alloy that enabled that search. Cooled with superfluid helium to 1.9 K (i.e., 456.25 degrees below zero Fahrenheit), niobium-titanium comprises the current-carrying windings of 1232 enormous dipole supermagnets (Fig. 1), which bend opposing highly energetic proton beams around the twenty-seven kilometer circumference of the Large Hadron Collider (LHC), causing proton–proton collisions that produce the elusive Higgs. Each dipole bending magnet is fifteen meters in length, weighs approximately thirty-five tons, and generates a magnetic field of 8 tesla, or about 160,000 times the average magnetic field at the surface of Earth. Many thousands of additional dipole, quadrupole, sextupole, octupole, decupole, and duodecupole niobium-titanium supermagnets perform a variety of other proton-beam-manipulating functions in

^{*} T. G. Berlincourt's past affiliations include the Naval Research Laboratory, Atomics International, Colorado State University, the Office of Naval Research, and the Office of the Secretary of Defense.



Published online: 14 December 2015



Fig. 1. At CERN, niobium-titanium dipole supermagnets guide high-energy proton beams around the circumference of the Large Hadron Collider. Credit: CERN.

the LHC. Embedded within one of the LHC's enormous particle detectors is a gigantic niobium-titanium supermagnet, the world's largest solenoid supermagnet, with a 220-ton cold mass and a 12,000-ton iron yoke. As LHC Project Leader Lyndon Evans stated, "superconductivity and superfluidity have been brought together as the two pillars on which the design of the largest and most complex scientific instrument ever built rests."

Particle physics research is merely one of niobium-titanium's myriad applications. Closer to the public at large is its use in the windings of tens of thousands of large supermagnets in which millions have undergone life-saving magnetic resonance imaging (MRI) medical diagnoses (Fig. 2). Conectus (the Consortium of European Companies Determined to Use Superconductivity) estimates that global economic activity for which superconductivity was indispensable in 2014 amounted to €5.4 billion.² MRI systems accounted for about 78% of that total, and almost all utilized niobium-titanium. Yet the virtues of niobium-titanium alloys might very well have been missed had it not been for experiments designed primarily to test theories with possible relevance to high magnetic field superconductivity.

Together with my colleagues Richard R. Hake and Donald H. Leslie at the Atomics International (AI) Division of North American Aviation, Inc., I was fortunate to participate in the discovery of the desirable supermagnet properties of niobium-titanium alloys and also to make essential contributions to the experimental confirmation of the elegant, but initially overlooked theories that provide

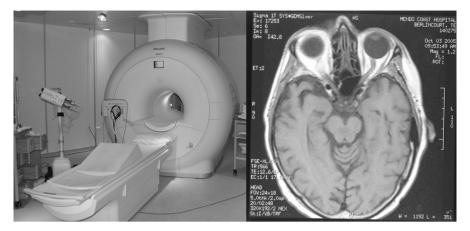


Fig. 2. a In a typical MRI system such as this, the patient being scanned is situated in a magnetic field generated (and made affordable) by a large electromagnet with superconducting niobium-titanium windings maintained at 4.2 K. **b** MRI scan of the author's brain. Such scans provide remarkable detail, enabling accurate medical diagnoses. Credit: Jan Ainali, Wikimedia Commons; Mendocino Coast District Hospital.

the appropriate framework for understanding high magnetic field superconductivity. Those theories are collectively known as "GLAG," after the initials of the quartet of ingenious Soviet physicists who set them forth—Vitaly L. Ginzburg, Lev D. Landau, Alexei A. Abrikosov, and Lev P. Gor'kov.

The niobium-titanium story is a classic example of scientific research leading to revolutionary applications that benefit society, while at the same time enabling progress in a variety of other scientific and technical arenas. It is also a classic example of how elegant (though abstruse) mathematical equations are capable of accounting in detail for the intricate and diverse properties of complex physical systems. In what follows, I will characterize superconductivity, explore its theoretical underpinnings, explain why superconductivity is so important in the generation of magnetic fields, and recount how niobium-titanium became the superconducting alloy of choice in so many revolutionary applications.

As a basis for understanding the operation of a supermagnet, a brief review of an ordinary electromagnet with normal-metal windings is in order. In an electromagnet, an electric current is sent through a coil of wire in order to produce a magnetic field. The larger the current, the higher the magnetic field generated. In many applications, magnetic field strength is boosted modestly by winding the coil on a ferromagnetic (e.g., iron) yoke. Complicating matters, an electric current flowing through a normal-metal (e.g., copper) coil encounters resistance and generates heat. As a consequence, a large electromagnet with normal-metal windings requires a large power supply to overcome the resistance and force current through the electromagnet's windings, and also a cumbersome cooling

system to remove the heat generated in the windings. But, remarkably and most fortunately, when many metals (copper and some others excepted) are cooled to temperatures approaching absolute zero, their resistance to *steady* current flow vanishes abruptly at a so-called "critical temperature" (T_c) characteristic of each metal, and they become superconducting: they present no resistance whatsoever to a steady flow of electric current. Moreover, no heat is generated. As a consequence, a relatively modest power supply is adequate to supply current to a supermagnet (an electromagnet with superconducting windings), and modest refrigeration power is sufficient to keep the supermagnet below its superconducting transition temperature.

Once a steady current flow has been established in a supermagnet, a superconducting shunt can be placed across the supermagnet terminals and the power supply can be disconnected, placing the supermagnet in a constant-current, constant-magnetic-field mode, known as the persistent-current mode. In that mode, the only energy required to maintain the magnetic field is the energy needed to keep the supermagnet refrigerated. MRI supermagnets are most often operated in the persistent mode. On the other hand, many high-energy particle accelerator supermagnets, such as those used in the LHC, are operated with time varying current and magnetic field levels and so must remain connected to their power supplies. Whenever current and magnetic field are varied in a supermagnet, small amounts of resistance and heating arise from redistribution of magnetic flux in the windings. If that heat is not efficiently removed, it can cause a temperature increase sufficient to drive the winding into its highly resistive normal state. Early on, it was recognized that this problem could be mitigated to a considerable extent by embedding superconducting windings in normal metal with high electrical conductivity and high thermal conductivity, such as copper, silver, or aluminum.

For both steady-current and varying-current modes of operation, supermagnets consume orders of magnitude less energy than required for operation of normal-metal electromagnets. Attaining magnetic fields ranging up to fifteen tesla with supermagnets is convenient, relatively inexpensive, and commonplace. In contrast, attaining magnetic fields above a mere 3 tesla with normal-metal electromagnets is cumbersome, energetically inefficient, expensive, and hence rare. According to Laurent Tavian, Chief Engineer for Cryogenics at CERN, "If we used normal conducting magnets, the LHC would have to have a circumference of 120 km and would use 30 times as much energy." Such a normal-magnet accelerator would of course be prohibitively expensive to build and operate.

The discovery of superconductivity took place in 1911, when Kamerlingh Onnes, the Dutch physicist who had been the first to liquefy helium, cooled a frozen solid mercury specimen to approximately 4 K. There, the resistance dropped precipitously to zero. Early on, Onnes recognized the possible advantages of using superconductivity in the generation of magnetic fields. But his attempts to make a useful supermagnet were frustrated. To his great disappointment, he found that a modest electric current, or a modest magnetic field, or a combination



Fig. 3. Bell Telephone Laboratories research scientists B. T. Matthias (left) and J. E. Kunzler ponder the periodic chart of the elements. Credit: Bell Telephone Laboratories.

thereof, destroyed superconductivity in the metals he studied. Stated another way, a supermagnet is limited not only by the necessary low temperature of operation, but also by the magnitude of the current flowing through it and by the strength of the magnetic field the supermagnet itself generates. What was needed, which Onnes did not possess, was a metal that would (a) remain superconducting at temperatures high enough for refrigeration to be convenient and economical, (b) support large electric current densities without dissipation in the presence of a high magnetic field, (c) be ductile and easily fabricated, and (d) be affordable. Discouraged by Onnes's disappointing findings, few researchers engaged in supermagnet-related research over the next fifty years. Those who did achieved only modest progress. Then, on January 9, 1961, Physical Review Letters received a manuscript from Bell Telephone Laboratories (BTL) researchers John E. Kunzler, Ernest Buehler, F. S. L. Hsu, and Jack H. Wernick (Fig. 3). They reported that at 4.2 K the compound Nb₃Sn (a combination of the elements niobium and tin in a three to one ratio) was able to pass electric current densities greater than 100,000 amperes/cm² without resistance in the presence of the very high magnetic field of 8.8 tesla.

Not yet aware of that spectacular BTL discovery, Hake, Leslie, and I at AI (Fig. 4) were also experimenting with superconductors of possible interest for application to supermagnets. Earlier, in 1957, I had observed superconducting



Fig. 4. Atomics International research scientists T. G. Berlincourt (*left*), D. H. Leslie (*center*), and R. R. Hake (holding a small, early niobium-zirconium supermagnet). Credit: Atomics International.

critical fields in uranium-molybdenum alloys high enough to eclipse a record that had stood for twenty-seven years. Within two years, Hake, Leslie, and I topped that record in an investigation of titanium-molybdenum alloys. Then, on January 12 and 13, 1961, we carried out critical supercurrent density measurements on a number of superconductors in magnetic fields up to 3 tesla. Included were the compound Nb₃Sn and the alloys tantalum-titanium and vanadium-titanium. The observed critical supercurrent densities ranged up to 560 amperes/cm² at 3 tesla. Because current densities of that magnitude are typical in copper-wire (normalmetal) electromagnets and, because we knew nothing of the BTL observations, we viewed our findings as only mildly encouraging. But, curiously, the critical supercurrent densities we measured did not vary greatly from specimen to specimen, nor did they increase appreciably with decreasing temperature. That suggested that the contacts between the specimens and the copper wires supplying current to them were inadequate. Not having anticipated enormous critical supercurrent densities, we had not made suitable provisions for measuring them. While we were rectifying that deficiency, the February 1, 1961, issue of *Physical* Review Letters arrived at AI with news of the astonishing BTL advance. We had been too late with too little.

The BTL breakthrough revealed that Nb₃Sn fulfills many of the ideal requirements listed above, but unfortunately it is brittle and difficult to fabricate. No matter; it ushered in the supermagnet era, and, despite the brittle nature of Nb₃Sn, ingenious developments have since enabled its implementation in a multitude of revolutionary high magnetic field supermagnets. Although the BTL discovery appeared to many to be a bolt from the blue, there had been many tantalizing hints of what was to come and others besides us had also been close on BTL's heels. The race was on to find additional useful supermagnet materials.

On April 24, 1961, BTL filed applications for patents on two alloy superconductors based on critical supercurrent density measurements in magnetic fields up to 8.8 tesla. Kunzler and Bernd T. Matthias together filed for niobium-zirconium alloys, which supported very large critical supercurrent densities. Matthias filed for niobium-titanium alloys, despite the fact that the observed critical supercurrent densities were orders of magnitude smaller than for niobium-zirconium. Again unaware of the BTL developments, we had independently made critical supercurrent density measurements at AI on the very same alloys (as well as numerous others) in magnetic fields up to 3 tesla. With our current-contact problem far behind us, we measured niobium-titanium alloys on April 17, 1961, and niobium-zirconium alloys on April 19, 1961.

Like Kunzler and Matthias, we observed very large critical supercurrent densities for the tough, and difficult to fabricate, niobium-zirconium alloys and discouragingly small critical supercurrent densities for the ductile, and easy to fabricate, niobium-titanium alloys. In light of those results, AI filed a patent application for the niobium-zirconium alloys but chose not to do so for the niobium-titanium alloys. A contentious patent interference battle ensued over niobium-zirconium. Ultimately, AI settled for a non-exclusive, royalty-free license, and in 1966 the patent was awarded to BTL. Immediately, small Nb₃Sn and niobium-zirconium supermagnets began appearing in research applications, and they soon became commonplace. Eclipsed by Nb₃Sn and niobium-zirconium, niobium-titanium faded into the background, seemingly destined for obscurity.

How did it happen that investigators at both BTL and AI had been independently investigating the same compounds and alloys? As noted earlier, temperature, current, and magnetic field are enemies of superconductivity. Should the compounds and alloys with the highest superconducting transition temperatures (i.e., the greatest tendency to be superconducting) not also have the highest critical magnetic fields and support the largest critical supercurrent densities? This suggested a focus on the high transition temperature compounds and alloys composed of elements from the fourth and fifth columns of the periodic table. In the absence of any reliable theoretical guiding principle, this was an obvious starting point at that time, though we now know that much higher superconducting transition temperatures occur in more complex and exotic materials composed of elements that lie in completely different regions of the periodic chart.

Years prior to the Nb₃Sn breakthrough at BTL, fundamental theories capable of accounting for that remarkable class of superconductors had already been developed by Ginzburg, Landau, Abrikosov, and Gor'kov, whose approach became known as the GLAG theory. Yet neither they nor apparently anyone else at that time realized that those theories might account for the extremes of critical magnetic field and critical supercurrent density that were later observed in Nb₃Sn. In fact, for several months after the discovery of the remarkable properties of Nb₃Sn, GLAG was almost universally ignored in favor of the now-superceded, "sponge" model. 13

Ginzburg and Landau (GL) developed the foundation for GLAG in 1950.¹⁴ At that time, both were fulfilling key roles in the Soviet nuclear weapons program. That they would be participants in such a high-security program is surprising in view of their past precarious relationships with the KGB. Landau had been imprisoned on political charges from 1938 to 1939.¹⁵ For many years, Ginzburg was under KGB suspicion and subject to restrictions, a consequence of having chosen for his second wife Nina Ermakova, who had earlier been imprisoned on unsubstantiated charges of plotting to assassinate Stalin.¹⁶ It would appear that Ginzburg and Landau were spared during the Stalin purges because of their extraordinary scientific prowess. Indeed, in Ginzburg's Nobel autobiography, he remarked, ever so ironically, "I was saved by the hydrogen bomb." 17

In their superconductivity theory, Ginzburg and Landau devised elegant mathematical equations designed to account for the macroscopic behavior of what we now refer to as type I superconductivity. Unbeknownst to them at that time, their remarkable equations would ultimately account as well for a multitude of other exotic superconducting phenomena, including what we now know as type II superconductivity. When a type I superconductor is cooled below its superconducting transition temperature, it presents no resistance to steady electric current flow and that current flow is confined to a thin layer—up to the penetration depth at the surface of the type I superconductor. If a magnetic field is applied to it, currents arise spontaneously within that penetration depth and shield the interior from the applied magnetic field. However, establishing and maintaining those currents, i.e., resisting penetration of the magnetic field, is a burden for the type I superconductor. As a consequence, when the applied magnetic field is increased to a threshold magnetic field (the so-called critical magnetic field H_c), the burden of supporting those surface currents becomes overwhelming, the shielding currents collapse, the magnetic field penetrates precipitously into the interior, and the type I superconductor reverts to the normal state. Critical magnetic fields for type I superconductors fall well below 0.1 tesla, and so type I superconductors are not capable of generating high magnetic fields.

Built into the GL equations is a parameter "kappa," whose value is different for different materials depending on their individual electronic structures. For kappa *less* than one divided by the square root of two (i.e., kappa less than 0.707), Ginzburg and Landau found solutions to their equations that describe type I

superconductivity very successfully. However, they chose not to explore solutions to their equations for kappa greater than 0.707, because they believed kappa to be less than 0.707 for all real superconductors; that is, they mistakenly assumed that the case of kappa *greater* than 0.707 was merely a mathematical abstraction with no physical manifestation.

That is curious, because a wealth of experimental evidence supported the existence of superconductors of a second type, a type that exhibits more complex behavior and is now known as type II. Most were alloys and compounds rather than pure elements. In the physics literature, these were often referred to as "nonideal," or "dirty." In 1937, Lev V. Shubnikov, V. I. Khomkevich, Yu. D. Shepeley, and Yu. N. Rjabinin, also in the USSR, published a paper on their investigations of the magnetic behavior of numerous alloy superconductors, which they had characterized in considerable detail in magnetic fields up to 0.45 tesla. They found that, in low applied magnetic fields, a well annealed, highly homogeneous, monocrystalline alloy superconductor behaved just like a type I superconductor, setting up surface currents that shielded its interior from an applied magnetic field. However, at higher magnetic fields, the nature of magnetic field penetration was very different in the alloy superconductor. Instead of taking place precipitously to completion as it did in a type I superconductor, magnetic field penetration took place gradually over a large range of applied magnetic field strengths, commencing at a "lower critical magnetic field," which Shubnikov et al. labeled H_{cI} , and reached completion with restoration of the normal state at a much-higher "upper critical magnetic field," which they labeled H_{c2} . Typical observed values for H_{c2} were ten to twenty times larger than the observed values for H_{cl} . ¹⁹

For well-annealed, highly homogeneous monocrystalline specimens, they observed nearly the same behavior whether the applied measuring magnetic fields were increasing or decreasing. In contrast, for unannealed polycrystalline alloy specimens, they obtained different results when measurements were made in increasing or decreasing applied magnetic fields; that is, they observed hysteresis. Significantly, when the applied magnetic field was decreased from $H_{\rm c2}$ to zero, a considerable amount of magnetic flux remained trapped in the unannealed polycrystalline specimens, causing them to act like permanent magnets. That implied that persistent supercurrents were trapped within them. We now attribute such magnetic flux trapping to the presence of inhomogeneities in the hysteretic specimens.

Fifteen years later, also in the USSR, N. N. Zavaritskii created amorphous (noncrystalline) elemental superconducting films by depositing them at low temperatures and showed that they exhibited alloy-like superconducting behavior. In an effort to account for Zavaritskii's observations, his colleague, Abrikosov, sought solutions to the GL equations for kappa *greater* than 0.707. His solutions, published in 1952, proved to be consistent with Zavaritskii's observations. That led Abrikosov to conclude that there are indeed two types of superconductors, which he labeled type I (kappa *less* than 0.707) and type II (kappa *greater* than 0.707).

Curiously, Abrikosov's paper made no mention of any comparison between his type II GL solutions and the extensive experimental results published earlier by Shubnikov et al.

Five years later, in 1957, Abrikosov¹⁶ published another paper in which he explored type II solutions to the GL equations in greater detail.²² Abrikosov's more in-depth solutions predicted that, between the lower critical field H_{cl} and the upper critical field H_{c2} , the gradual penetration of magnetic field into the alloy superconductor takes place via single-quantum "fluxoids," tiny quantized supercurrent vortices or discrete magnetic-flux bundles. He called the fluxoid-permeated state the "mixed state." He further concluded that just above the lower critical field there would be a low density of independent fluxoids, but that with increasing penetration the fluxoids would interact with one another and form a regular lattice array. Abrikosov suggested that inhomogeneities would tend to compromise the perfection of the lattice array. The implication was that fluxoids would be attracted to and pinned by minute regions where superconductivity was weaker and would be repelled by regions where superconductivity was stronger.

Thus, Abikosov recognized that inhomogeneities could lead to hysteresis and to trapped persistent supercurrents. Significantly, in his 1957 paper, Abrikosov demonstrated good agreement between his type II GL solutions and the experimental data that Shubnikov et al. had reported twenty years earlier. Why the belated comparison with those experimental data? The answer is not known for certain, but it is known that Shubnikov, being less fortunate than Ginzburg and Landau, was arrested in 1937 during the Stalin purges, sent to prison, and executed.²³ Twenty years later, in 1957, he was posthumously exonerated of all charges by the USSR Military Board of the Supreme Court. British physicist Kurt Mendelssohn speculated that that exoneration "made it possible for Abrikosov to refer to Shubnikov's papers, since up to then Soviet etiquette required that anyone who disappeared in the purges had never lived."²⁴

At this point, the GLA theory (with the A added for Abrikosov) could account for much of the general behavior of types I and II superconductors, but it was not fully quantitative. For example, it was incapable of predicting the value of kappa (and hence the upper critical magnetic field) for a particular metal. Then, in 1959, Gor'kov²⁵ put the icing on the GLAG (with the G added for Gor'kov) cake by demonstrating that the macroscopic GL equations were consistent with the Bardeen-Cooper-Schrieffer (BCS) microscopic theory of superconductivity.²⁶ That advance made possible theoretical predictions of a number of the properties of a type II superconductor with no adjustable parameters. For example, in order to obtain theoretical predictions for the superconductor's upper critical magnetic field, H_{c2} , one need only insert into Gor'kov's equations experimentally determined values for the superconductor's transition temperature (T_c), its *normal-state* electrical resistivity, and its *normal-state* electronic-specific heat coefficient. The resulting predicted values could then be compared with the experimentally determined values for H_{c2} .

Even though this rigorous, testable theoretical structure was already in existence, GLAG theory was not immediately seized upon as relevant to the BTL breakthrough on Nb₃Sn because most superconductivity researchers were captivated by the sponge model, which hypothesized the existence of a high-criticalmagnetic-field sponge embedded in a low-critical-magnetic-field matrix.²⁷ The sponge model was twenty years old, consistent with much of the behavior of alloy superconductors, and beguilingly easy to understand. Moreover, it was even possible to manufacture real sponge-like superconductors. Nevertheless, the sponge model was not quantitative. Any supposition could be made regarding the structure of the phantom sponge, and there was no quantitative means to dispute it. The GLAG formalism was another matter. It was rigidly quantitative and more than a little complex, indeed, so complex as to discourage efforts to understand it and determine how to make meaningful comparisons with experiment. Nevertheless, Bruce B. Goodman in France broke through the complexity. ²⁸ At the June 1961 IBM Conference on Fundamental Research on Superconductivity, four months after the publication of the BTL breakthrough, he reported "surprisingly" good agreement between a GLAG-theory prediction and the upper critical magnetic field I had reported years earlier for a uranium-molybdenum alloy. Might this one instance have been simply a coincidence? That was a very real possibility, for the magnetic field-induced resistive transitions I had observed were functions of measuring current density. Further, I suspected that for different magnetic field and current orientations, and for different mechanical and metallurgical treatments, I might have observed significantly different transition fields. I discussed these possibilities with Goodman, who agreed that the matter was not vet settled. In any event, Goodman's observation was simply ignored by most superconductivity researchers. But at AI, we regarded it seriously enough to undertake a series of measurements aimed at testing GLAG theory for a multitude of transition-metal alloys. In this round of investigations, we were equipped with a pulsed, liquid-nitrogen cooled, copper-coil electromagnet that I had developed for an entirely different experiment. It allowed experimentation in transient magnetic fields up to 16 tesla, nearly twice the magnetic field strength available at BTL. This was a fortunate escalation because the critical magnetic fields of most of the alloys we studied rose well above 10 tesla.

In our new investigations we found that, as long as measuring current densities were maintained at or below about 10 amperes/cm², the measured magnetic-field-induced resistive transition fields for concentrated alloys were independent of current and magnetic field orientations and were also independent of the degree of cold working.²⁹ This suggested that the low current density, magnetic field induced resistive transition field was related to fundamental bulk electronic properties, rather than to the more capricious inhomogeneities of an imagined sponge structure. Thus, in hindsight, Goodman's application of GLAG theory to my uranium-molybdenum data appeared to be fully justified, and indeed our new, wide-ranging measurements revealed remarkably good agreement with GLAG

theory predictions for measured upper critical magnetic fields up to about 5 tesla. For higher upper critical magnetic fields, however, there were discrepancies between theory and experiment. For example, for a vanadium-titanium alloy with a measured upper critical field of 10 tesla, the GLAG prediction was 20 tesla. Something was clearly amiss.

Again, the scientific literature already contained a basis for explaining the discrepancy. In addition to having charge, electrons have spin and act like tiny magnets, which, like the magnetized needle of a compass, tend to align with applied magnetic fields. According to BCS theory, interactions of electrons with vibrations of the crystal lattice cause electrons of opposite spin and opposite momentum to pair up. Below the superconducting transition temperature, thermal excitations are weak enough that such electron pairing can take place and give rise to superconductivity, whereas above the superconducting transition temperature thermal excitations are so strong that they inhibit electron pairing. But electron pairing can also be inhibited by the action of a magnetic field on electron spins. In fact, in 1958, before anyone imagined that very high superconducting critical magnetic fields might be possible, Volker Heine and Alfred Brian Pippard had noted that very high magnetic fields would inhibit the electron pairing necessary for the existence of superconductivity by causing electron spins that are antiparallel to the applied magnetic field to decouple from their parallel-to-the-magnetic-field partners and themselves align with the applied magnetic field. 30 This possibility of magnetic field-induced, opposite-spin depairing had not been included in the formulation of the BCS and GLAG theories because, when those theories were under development, it was not known that superconductivity might persist to magnetic fields sufficiently high that such magnetic depairing could become a significant factor. Taking account of this factor using an approximate criterion proposed by Albert M. Clogston, we found remarkable agreement between our measured and theoretically predicted upper critical magnetic fields over the entire magnetic field range of our investigations.³¹

All factors considered, our findings provided compelling evidence that, with appropriate modification, GLAG comprised the appropriate theory for high magnetic field superconductivity. Even so, publication of our findings was delayed for a month by a referee still enamored of the sponge model.³² But such objections soon dissipated as additional evidence accumulated in support of GLAG. For example, while making magnetic measurements on thick alloy films with modest upper critical magnetic fields (a few tenths of a tesla), my AI colleagues Walter J. Tomasch and Alfred S. Joseph happened upon a conundrum.³³ For the magnetic field perpendicular to the planes of the films, evidence of superconductivity vanished at magnetic field values in good accord with earlier upper critical magnetic field (H_{c2}) results for bulk specimens. However, for the magnetic field parallel to the planes of the films, evidence of superconductivity persisted up to magnetic fields greater by a factor of 1.69. The same day Tomasch and Joseph encountered this conundrum, I received a preprint from D. Saint-James and Pierre G. de-

Gennes in France containing just such a theoretical prediction!³⁴ Whereas Abrikosov had solved the GL equations for the case of a superconductor filling all space (i.e., having no surfaces) Saint-James and de Gennes solved the GL equations for the case of the magnetic field parallel to the surface of a superconductor. That yielded the prediction that superconductivity would survive in a thin surface layer or sheath above H_{c2} all the way to a field H_{c3} , that is, 1.692 times greater than H_{c2} . Stated another way, in a magnetic field applied parallel to its surface, a type II superconductor has a magnetically tough surface layer.

Such striking agreement between experiment and a solution to the GL equations for a different geometry inspired confidence in the physical reality of Abrikosov's mathematically predicted fluxoid lattice as well. After all, the fluxoid lattice and the sheath are both simply physical manifestations of different and purely mathematical solutions of the GL equations for different geometries. Hence, it was inevitable that efforts would soon be made to observe the fluxoid lattice experimentally. Indeed, just a few months later, D. Cribier, B. Farnoux, B. Jacrot, L. Madhav Rao, B. Vivet, and M. Antonini, also in France, confirmed the existence of the fluxoid lattice via neutron scattering experiments.³⁵ Just as X-rays scatter from atoms in crystals in a way that indirectly reveals the periodic arrangement of the atoms in crystals, neutrons (themselves minute, wavelike magnets) scatter from the spatially periodic magnetic field of the fluxoid lattice in a way that indirectly reveals the structure of the fluxoid lattice. As if that were not enough to convince the harshest of skeptics, three years later, U. Essmann and H. Trauble of West Germany reported a more direct and graphic confirmation of the fluxoid lattice using a decoration technique.³⁶ They evaporated cobalt atoms onto a superconducting lead-indium alloy in the mixed state. Being magnetic, the cobalt atoms congregated at the centers of the fluxoids, where the magnetic field is a maximum. An electron microscope then revealed the locations of the decorated fluxoids (Fig. 5). This elegant demonstration was almost anticlimactic, however, for by then we knew that the fluxoid lattice just had to be there. Thus, all of the pieces of the high magnetic field jigsaw puzzle that had confounded superconductivity researchers for fifty years finally fell neatly into place. Much later, in 2003, Ginzburg and Abrikosov were awarded Nobel Prizes for their contributions to the GLAG theory.

Significantly, in the experiments we conducted at AI to test the GLAG theory, niobium-titanium alloys exhibited the highest critical magnetic fields (followed ever so closely by tantalum-titanium alloys and trailed by niobium-zirconium alloys). The highest critical magnetic field for the niobium-titanium alloys, 14.5 tesla, was a clue that they might after all be useful for supermagnet windings despite the discouragingly low critical supercurrent density results obtained earlier at both BTL and AI. Accordingly, armed with greater basic understanding provided by GLAG, encouraged by knowledge of the high critical magnetic fields of niobium-titanium alloys, and tantalized by their highly ductile, easy-to-fabricate nature, we reasoned that with appropriate metallurgical treatment niobium-

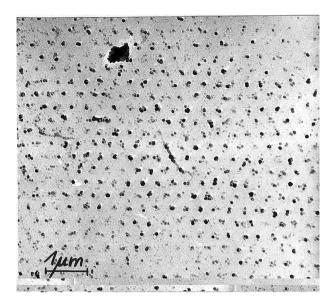


Fig. 5. Abrikosov's mixed-state fluxoid lattice, as revealed by Essmann and Traubel using an electron microscope decoration technique. The fluxoid spacing is evident from the one-micrometer (i.e., 0.0001 cm) scale marker at lower left. Credit: Essmann and Traubel preprint.

titanium alloys might be made to support large critical supercurrent densities of practical interest. We soon found that extremely severe cold working was highly effective and resulted in critical supercurrent densities approximately thirty times greater than had been observed in the earlier studies at BTL and AI. Significantly, our new data revealed conclusively the utility of niobium-titanium windings for supermagnets capable of generating magnetic fields greater than 10 tesla. We immediately sought patent coverage—only to learn of the pending Matthias patent on niobium-titanium. Needless to say, that tempered the celebration of our niobium-titanium findings, for, instead of being patentable, our findings had simply rendered highly valuable a BTL patent that had previously been worthless.

We described our encouraging results on the supermagnet potential of nio-bium-titanium and on the utility of GLAG in accounting for high-magnetic-field superconductivity in a post-deadline paper at the April 1962 Washington, DC, meeting of the American Physical Society and at two additional scientific conclaves. Subsequently, AI researchers James B. Vetrano and Roger W. Boom achieved significant additional supercurrent-density enhancement in niobium-titanium alloys through introduction of inhomogeneities by appropriate heat treatment.

With proof of principle established at AI, niobium-titanium quickly displaced niobium-zirconium as the most widely used superconducting alloy. In 1966, construction began on the enormous 1.8-tesla, 80-megajoule, 4.8-meter inside-

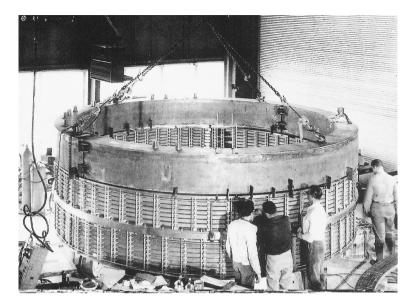


Fig. 6. One of the two coil halves of Argonne National Laboratory's niobium-titanium bubble chamber magnet prior to its installation in its cryogenic enclosure. Credit: Argonne National Laboratory.

diameter superconducting bubble-chamber magnet at Argonne National Laboratory (Fig. 6). The windings for that audacious demonstration consisted of six small cross-section niobium-titanium strips embedded in a massive copper-strip matrix (0.25 cm \times 5 cm in cross section). That amounted to a very cautious copper-to-superconductor ratio of twenty-four, whereas in current practice ratios of one to two are typical. Apparently, the designers of that first very large supermagnet were reluctant to place their full confidence in superconductivity.

The factors that determine the critical supercurrent densities in type II superconductors require further discussion. Early on, it was understood that sending a current through a perfectly homogeneous type II superconductor in the mixed state forces the fluxoid lattice to flow through the superconductor (akin to the way the Lorentz force drives an electric motor). That is an undesirable dissipative process even for steady current and steady magnetic field strength; indeed, observed critical supercurrent densities for highly homogeneous type II superconductors are much too low to be of practical use. But as Abrikosov noted in his 1957 paper, inhomogeneities can distort the fluxoid lattice and result in hysteretic behavior. That implies that inhomogeneities are capable of trapping fluxoids and stabilizing fluxoid-lattice configurations that correspond to significant critical supercurrent flow. Suitable inhomogeneities can be introduced in a number of ways, for example by cold working, by heat treatment, or by inserting minute inclusions of other materials or even voids. For steady supermagnet current and steady magnetic field strength, the pinned

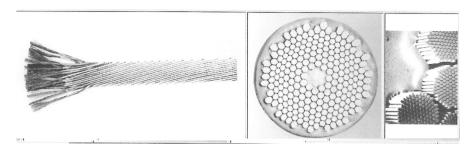


Fig. 7. Typical embodiment of the Rutherford superconducting niobium-titanium cable used in CERN's Large Hadron Collider. The cable (*left*) is composed of 36 strands, one of which is shown in cross section at center. Each strand contains 6300 fine niobium-titanium wires about 0.0006 cm in diameter, embedded in a copper matrix. In the microscopic view at right, individual niobium-titanium wires are revealed. Credit: CERN.

fluxoid lattice configuration is stable and dissipationless. But, with each *change* of current and magnetic field, the fluxoid lattice must readjust to a new pinned configuration, and that readjustment is a dissipative process. Fortunately, the amount of heat generated is small when the current and magnetic field are well below their limits, and adverse effects from that heating can be mitigated by embedding superconducting windings in a high electrical conductivity, high thermal conductivity normal metal such as copper. In that case, if a local warm spot arises from a flux lattice readjustment, some current can be transferred from the superconductor to the copper temporarily while the heat is carried away and the superconductor recovers. Nevertheless, when the supermagnet current and magnetic field reach their ultimate limits, the copper matrix is unable to prevent runaway heating, and the magnet quenches; the copper matrix is not a panacea.

With the successful completion of the Argonne bubble-chamber supermagnet, niobium-titanium became the choice for a multitude of large-scale applications in high energy physics research, MRI medical imaging systems, magnetic confinement controlled thermonuclear fusion research, magnetic energy storage, electric power systems, motors, generators, levitated trains, and ship propulsion systems, to name but a few. Developers with those interests were quick to seize the opportunities offered by supermagnets and have since figured prominently in the highly sophisticated optimization and engineering that followed. Today's MRI imagers, the Tevatron, and the LHC are among the many monuments to their accomplishments. Particularly noteworthy is the development of the so-called "Rutherford" cable (Fig. 7), which emerged from a collaboration of the Central Electricity Generating Board, the Rutherford Laboratory, and Imperial Metal Industries in the United Kingdom. 40 In its many embodiments in the LHC, the Rutherford cable typically consists of up to 200,000 or so fine niobium-titanium wires (each about 0.0006 cm in diameter, or about ten times smaller than the diameter of a human hair) embedded in a copper matrix. In that configuration, the

copper-to-superconductor ratio is much reduced, typically ranging between one and two, yet that relatively meager amount of copper is sufficient to circumvent instabilities and carry away heat under the LHC's stringent operating conditions. It is noteworthy that at the LHC's maximum operating field of eight tesla, the fluxoid lattice spacing is 0.0000016 cm, or approximately 375 times smaller than the diameter of the tiny niobium-titanium wires in the Rutherford cable.

It should be emphasized that the great utility of niobium-titanium is to a considerable extent a consequence of its ductility and ease of fabrication. Numerous uncooperatively brittle materials have much superior superconducting properties. For example, Nb₃Sn has a superconducting transition temperature twice as high (18 versus 9 K, easing refrigeration requirements), has a critical magnetic field twice as high (30 tesla versus 15 tesla for niobium-titanium, enabling fabrication of higher magnetic field supermagnets), and is capable of supporting higher critical-supercurrent densities (facilitating more compact supermagnet windings). Still to be developed to its full potential is the spectacular class of brittle ceramic high-temperature superconductors (HTS) discovered in 1986 by Johannes Georg Bednorz and Karl Alex Muller of Switzerland. 41 Materials of that class have since been shown to have superconducting transition temperatures as high as 133 K and critical magnetic fields many times those of niobium-titanium alloys. Unfortunately, they are extremely difficult to prepare and fabricate into supermagnets. To date, that has limited their use to applications requiring the most extreme superconducting capabilities. Although rapid growth is anticipated for HTS applications, Conectus has estimated that they accounted for less than two percent of the total superconductivity market activity in 2014.⁴² Thus, despite niobium-titanium's much more limited superconducting capabilities, it remains today the most widely used superconductor.

All told, more than fifty years passed from the discovery of superconductivity to the understanding of its theoretical underpinnings and the achievement of its widespread application. Progress was often agonizingly slow, with numerous wrong turns and missed opportunities. Clues that appear obvious now in hindsight were somehow overlooked. The critical investigations by Shubnikov et al. that first accurately characterized type II superconductivity experimentally were simply ignored for twenty years. The GL theory was created to account for type I superconductivity, but, unbeknownst to its creators, was capable of accounting for type II superconductivity as well, as Abrikosov so aptly demonstrated. Gor'kov's subsequent linkage of the GL theory with the BCS microscopic theory enabled direct quantitative comparison of GLAG theory predictions with experiment. Nevertheless, when Kunzler et al. reported their historic, high critical magnetic field, high critical supercurrent density breakthrough, GLAG theory was almost universally ignored in favor of the simple, non-quantitative sponge model. Eventually, four months after publication of the BTL advance, Goodman reported "surprisingly" good agreement between a GLAG theory prediction and the upper critical magnetic field that I had measured years earlier for a uranium-

molybdenum alloy. That led us at AI to make comparisons between measured upper critical fields and GLAG predictions for a wide range of high critical magnetic field alloy superconductors. Those experiments provided compelling confirmation of GLAG theory and, at the same time, revealed the supermagnet promise of niobium-titanium alloys, which had appeared unpromising in earlier lower magnetic field measurements at both BTL and AI.

In the final analysis, the achievement of theoretical understanding and the practical application of high magnetic field superconductivity depended critically on interactions between experiment and theory, but, as is evident from this saga, superconductivity experimenters and theorists all too often paid too little heed to each other, and so the path to enlightenment was both long and tortuous. As Pippard stated so pungently with regard to a different aspect of superconductivity: "If we wish to boast of our achievements, let us not point to the unerring pursuit of truth by a logically faultless thinking machine, but to the more astonishing way in which truth can be caused to emerge from the toils of error and stupidity." 43

References

- ^{1.} Lyndon Evans, ed., "The Large Hadron Collider: Marvel of Technology" (Lausanne: CERN and EPFL Press, 2009), 4.
- ^{2.} "Market," Conectus, accessed September 24, 2015, http://www.conectus.org/market.html.
- ^{3.} Bernd Müller, "Refrigerator for the Big Bang," Linde Technology 2(8) (2008), 13-15.
- ^{4.} John E. Kunzler, Ernest Buehler, F. S. L. Hsu, and Jack H. Wernick, "Superconductivity in Nb₃Sn at High Current Density in a Magnetic Field of 88 kgauss," *Physical Review Letters* **6** (1961), 89–91.
- ^{5.} Ted G. Berlincourt, "Size Effect in the Hall Effect of Cu, and Superconductivity of Metastable U Base Mo Alloys," in *Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry* (Madison: University of Wisconsin Press, 1958) 492–96; "Hall Effect, Resistivity and Superconductivity of Some Metastable Uranium-Rich Alloys," *Journal of the Physics and Chemistry of Solids* 11 (1959), 12–17.
- ^{6.} Richard R. Hake, Donald H. Leslie, and Ted G. Berlincourt, "Resistivity, Hall Effect, Electronic Specific Heat, and Superconductivity of Binary bcc Ti alloys," *Bulletin of the American Physical Society* **4** (1959), 362.
- ^{7.} Ted G. Berlincourt, Richard R. Hake, and Donald H. Leslie, Atomics International Laboratory Notebook A121484–A121492 (1961).
- ^{8.} Ted G. Berlincourt, "Type II Superconductivity: Quest for Understanding," *Institute of Electrical and Electronics Engineers Transactions on Magnetics* **20** (1987), 403–12.
- ^{9.} John E. Kunzler and Bernd T. Matthias, Superconducting Device Consisting of a Niobium-Zirconium Composition, US Patent 3,281,736, filed April 24, 1961, and issued October 25, 1966.
- ^{10.} Bernd T. Matthias, Superconducting Device Consisting of a Niobium-Titanium Composition, US Patent 3,167,692, filed April 24, 1961, and issued January 26, 1965.
- ^{11.} Ted G. Berlincourt, Richard R. Hake, and Donald H. Leslie, Atomics International Laboratory Notebook B063551–B063562 (1961).

Superconducting Niobium-Titanium

- 12. Vitaly L. Ginzburg and Lev D. Landau, "On the Theory of Superconductivity," *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 20 (1950), 1064–82; Vitaly L. Ginzburg, "On the Theory of Superconductivity," *Nuovo Cimento* 2 (1955), 1234–50; Alexei A. Abrikosov, "Influence of Size on Critical Field of Superconductors of Second Group," *Doklady Akademii Nauk SSSR* 86 (1952), 489–92; Alexei A. Abrikosov, "On the Magnetic Properties of Superconductors of the Second Group," *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 32 (1957), 1442–52 [English Translation: *Soviet Physics—JETP* 5 (1957), 1174–82]; Lev P. Gor'kov "Microscopic Derivation of the Ginzburg-Landau Equations in the Theory of Superconductivity," *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 36 (1959), 1918–23 [English Translation: *Soviet Physics—JETP* 36 (1959), 1364–67]; Lev P. Gor'kov "Theory of Superconducting Alloys in a Strong Magnetic Field Near the Critical Temperature," *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 37 (1959), 1407–16 [English Translation: *Soviet Physics—JETP* 10 (1960), 998–1004].
- ^{13.} Kurt Mendelssohn and J. R. Moore, "Specific Heat of a Superconducting Alloy," *Proceedings of the Royal Society of London* **A151** (1935), 334–41; "Supra-Conducting Alloys," *Nature* **135** (1935), 826–27.
- ^{14.} Ginzburg and Landau, "Theory of Superconductivity" (ref. 12); Ginzburg, "Theory of Superconductivity" (ref. 12).
- ^{15.} Gennady Gorelik, "The Top-Secret Life of Lev Landau," Scientific American 277 (1997) 72–77.
- ^{16.} "Vitaly L. Ginzburg-Biographical," accessed September, 24, 2015, http://www.nobelprize.org/nobel_prizes/physics/laureates/2003/ginzburg-bio.html.
- ^{17.} Ibid.
- ^{18.} Lev V. Shubnikov, V. I. Khomkevich, Yu. D. Shepelev, and Yu. N. Rjabinin, "Magnetic Properties of Superconducting Metals and Alloys," *Zhurnal Eksperimental noi i Teoreticheskoi Fiziki* 7 (1937), 221–37.
- ^{19.} Ibid.
- ^{20.} N. V. Zavaritskii, "Investigation of Superconducting Properties of Films of Thallium and Tin Deposited at Low Temperatures," *Doklady Akademii Nauk SSSR* **86** (1952), 501–4.
- ^{21.} Abrikosov, "Influence of Size on Critical Field" (ref. 12).
- ^{22.} Abrikosov, "Magnetic Properties of Superconductors" (ref. 12). In this paper, he attributed to Landau the first suggestion that kappa might be greater than 0.707 for alloys.
- ^{23.} A. G. Shepelev, "The Discovery of Type II Superconductors (Shubnikov Phase)," in *Superconductor*, ed. Adir Moyses Luiz, (Rijeka, Croatia: InTech, 2010), 17–46, doi: 10.5772/10117.
- ^{24.} Kurt Mendelsohn, letter to the author, September 27, 1963.
- ^{25.} Gor'kov "Microscopic Derivation: (ref. 12): "Theory of Superconducting Alloys" (ref. 12).
- ^{26.} John Bardeen, Leon N. Cooper, and John R. Schrieffer, "Theory of Superconductivity," *Physical Review* **108** (1957), 1175–204.
- ^{27.} Mendelssohn and Moore, "Specific Heat" (ref. 13); "Supra-Conducting Alloys" (ref. 13).
- ^{28.} Bruce B. Goodman, "The Magnetic Behavior of Superconductors of Negative Surface Energy," IBM Journal of Research and Development 6 (1962) 63–67.
- ^{29.} Ted G. Berlincourt and Richard R. Hake, "Upper Critical Fields of Transition Metal Alloy Superconductors," *Physical Review Letters* **9** (1962), 293–95; "Pulsed-Magnetic-Field Studies of Superconducting Transition Metal Alloys at High and Low Current Densities," *Bulletin of the American Physical Society* **7** (1962), 408; "Superconductivity at High Magnetic Fields," *Physical Review* **131** (1963), 140–57; Ted G. Berlincourt, "Pulsed Magnetic Field Studies of Superconducting Transition Metal Alloys at High and Low Current Densities," in *Proceedings of the Eighth International Conference on Low Temperature Physics* (London: Butterworth & Co. 1964) 338–41.

^{30.} Volker Heine and Alfred B. Pippard, "The Knight Shift in Superconductors," *Philosophical Magazine* **3** (1958), 1046–50.

- ^{31.} Albert M. Clogston, "Upper Limit for the Critical Field in Hard Superconductors," *Physical Review Letters* **9** (1962), 266–67.
- ^{32.} Berlincourt and Hake, "Upper Critical Fields" (ref. 29).
- ^{33.} Walter J. Tomasch and Alfred S. Joseph, "Experimental Evidence for a New Superconducting Phase Nucleation Field in Type-II Superconductors," *Physical Review Letters* **12** (1964), 148–50.
- ^{34.} D. Saint-James and Pierre G. de Gennes, "Onset of Superconductivity in Decreasing Fields," *Physics Letters* **7** (1963), 306–8.
- ^{35.} D. Cribier, B. Farnoux, B. Jacrot, L. Madhav Rao, B. Vivet, and M. Antonini, "Neutron Diffraction by Vortex Lines in Superconducting Niobium," in *Proceedings of the International Conference on Magnetism, Nottingham September 1964* (London, The Institute of Physics and The Physical Society, 1964), 285–87.
- ^{36.} U. Essmann and H. Trauble, "The Direct Observation of Individual Flux Lines in Type II Superconductors," *Physics Letters* **24A** (1967), 526–27.
- ^{37.} Berlincourt and Hake, "Pulsed-Magnetic-Field Studies" (ref. 29); "Superconductivity at High Magnetic Fields" (ref. 29).
- ^{38.} James B. Vetrano and Roger W. Boom, "High Critical Current Superconducting Titanium-Niobium Alloy," *Journal of Applied Physics* **36** (1965), 1179–80.
- ^{39.} John R. Purcell, "The 1.8 Tesla, 4.8 M I.D. Bubble Chamber Magnet," in *Proceedings of the 1968 Summer Study on Superconducting Devices and Accelerators, Brookhaven National Laboratory* (Brookhaven: Brookhaven National Laboratory, 1968) 765–85.
- ^{40.} Horst Rogalla and Peter H. Kes, eds., *100 Years of Superconductivity* (Boca Raton: CRC Press, Taylor and Francis Group, 2012), 648–49.
- ^{41.} Johannes Georg Bednorz and Karl Alex Muller, "Possible High T_c Superconductivity in the Ba-La-Cu-O System," *Zeitschrift fur Physik-Condensed Matter* **B64** (1986), 189–93.
- 42. "Market" (ref. 2).
- ^{43.} Alfred B. Pippard, "The Historical Context of Josephson's Discovery," in *Superconductor Applications: SQUIDS and Machines*, B. B. Schwartz and S. Foner, eds. (New York: Plenum Press, 1977), 1–20, on 20.

5555 Montgomery Drive #97 Santa Rosa, CA 95409, USA e-mail: tgberlincourt@aol.com