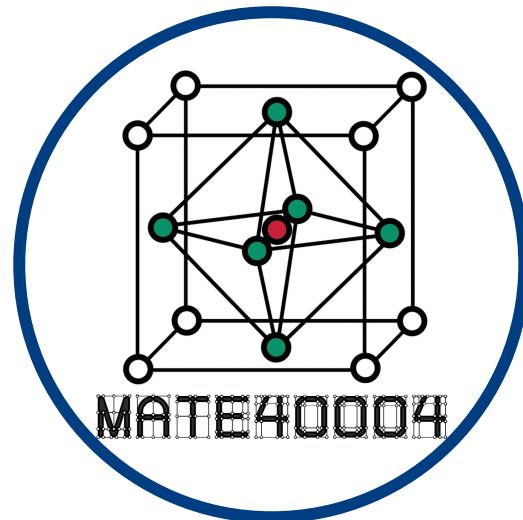


MATE40004 – Structure 1

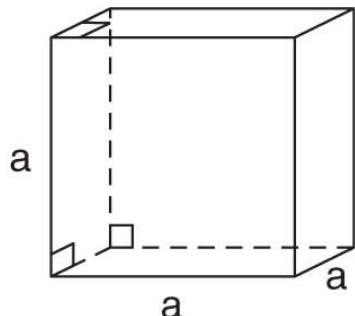
**Crystallography**  
**E. Crystals 1**

**Professor Aron Walsh**  
Department of Materials  
Imperial College London

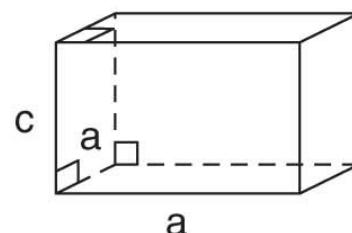


<http://www.imperial.ac.uk/people/a.walsh>

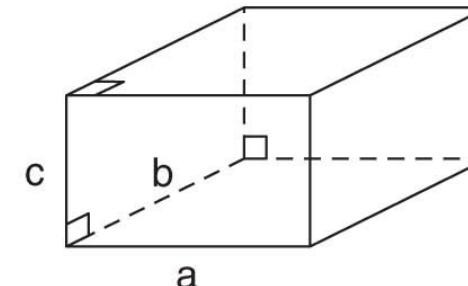
# A: 7 Crystal Systems in 3D



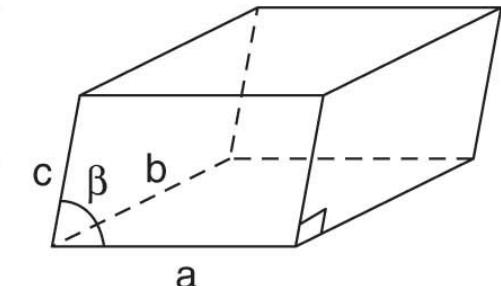
Cubic



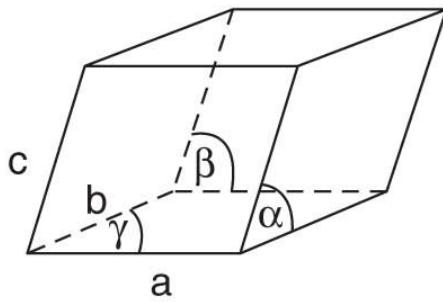
Tetragonal



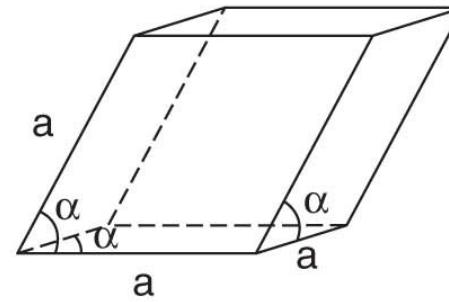
Orthorhombic



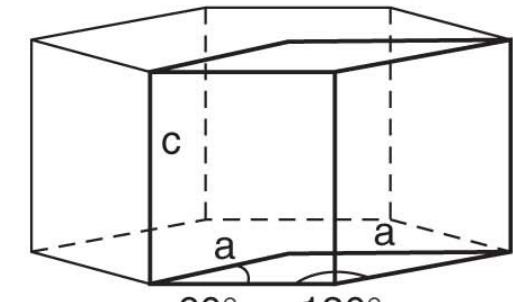
Monoclinic



Triclinic



Rhombohedral  
(or Trigonal)



Hexagonal

Remember the constraints on lengths ( $a, b, c$ ) and angles ( $\alpha, \beta, \gamma$ )

## B: 5 Symmetry Operations

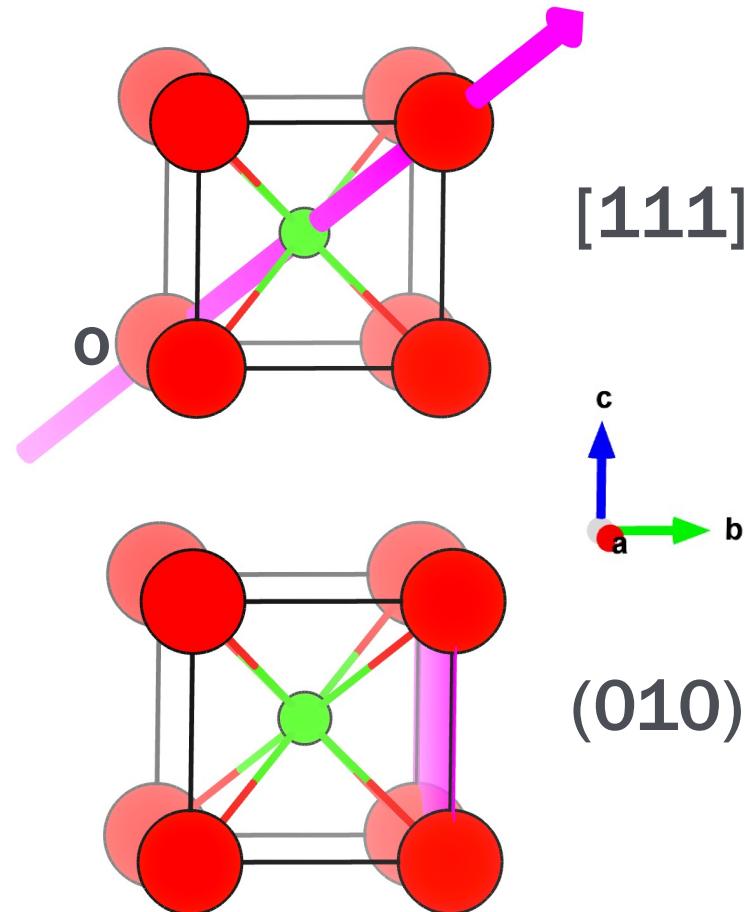
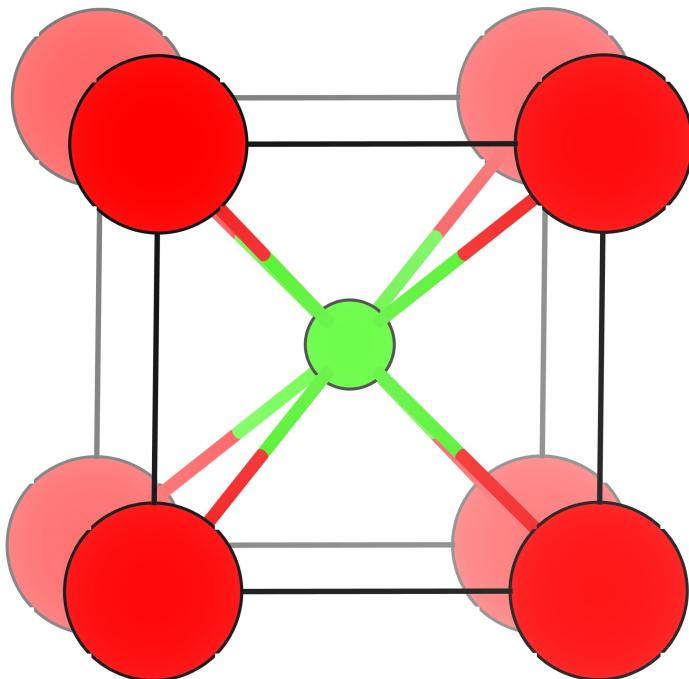
Operation	Element	Symbol
Identity	'whole of space'	E
Rotation by $360^\circ/n$	n-fold rotation axis	$C_n$
Reflection	mirror plane	$\sigma$
Inversion	centre of inversion	i
Rotation by $360^\circ/n$ followed by reflection in a perpendicular plane	n-fold improper rotation axis	$S_n$

## C: Crystal Coordinates

Cubic crystal system

Cs ( $0,0,0$ )

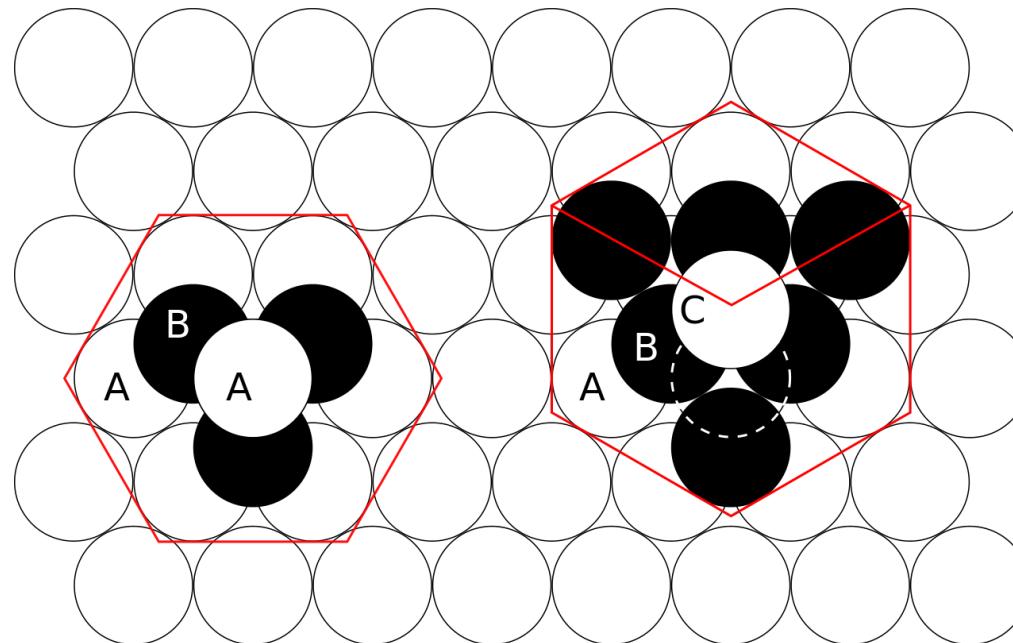
Cl ( $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ )



Lattice points ( $h,k,l$ ), directions [ $hkl$ ], and planes ( $hkl$ )

## D: Close Packing

Packing type	Stacking sequence	Packing fraction	Packing direction	Coordination number
ccp	ABC	0.74	[111]	12
hcp	AB	0.74	[0001]	12



# Outline of Crystallography

## Mix of lectures & activities

- A. Lattices
- B. Symmetry
- C. Geometry
- D. Packing



Core concepts

### Test 1 with feedback

- E. Crystals 1
- F. Crystals 2
- G. Diffraction

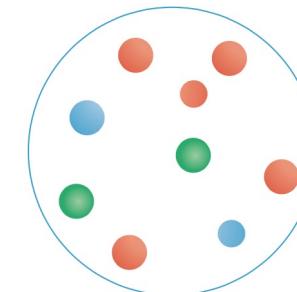


Real materials

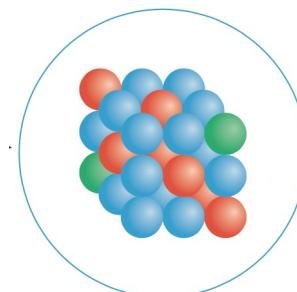
### Test 2 with feedback

# What Defines a Material?

**Chemical Composition**



**Crystal Structure**

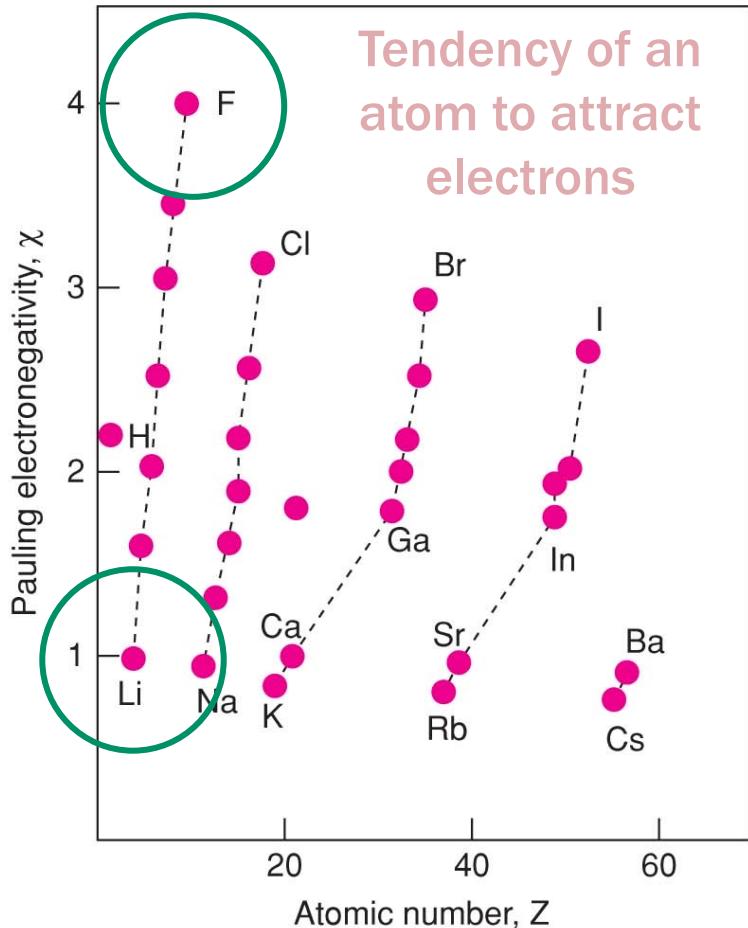


# Bonding in Crystalline Solids

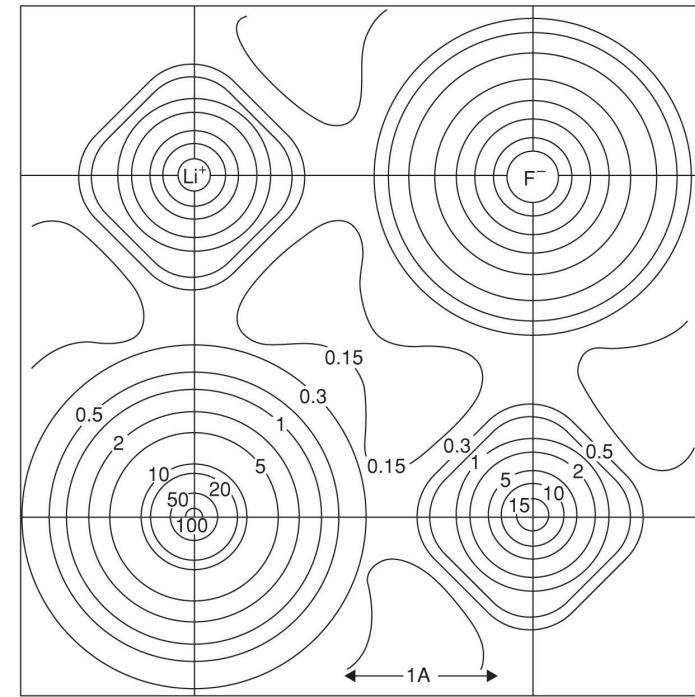
Classification	Example	Key Interaction
Molecular solids	Xe, N <sub>2</sub>	van der Waals forces
Ionic solids	NaCl, MgO	Electrostatic (Coulomb's law)
Covalent solids	C, Si	Directional hybrid orbitals
Metallic solids	Fe, Cu	Delocalised electrons

Covered in other course. These are extreme classifications: real systems are complex (combinations of interactions)

# Ionic (Heteropolar) Bond Formation



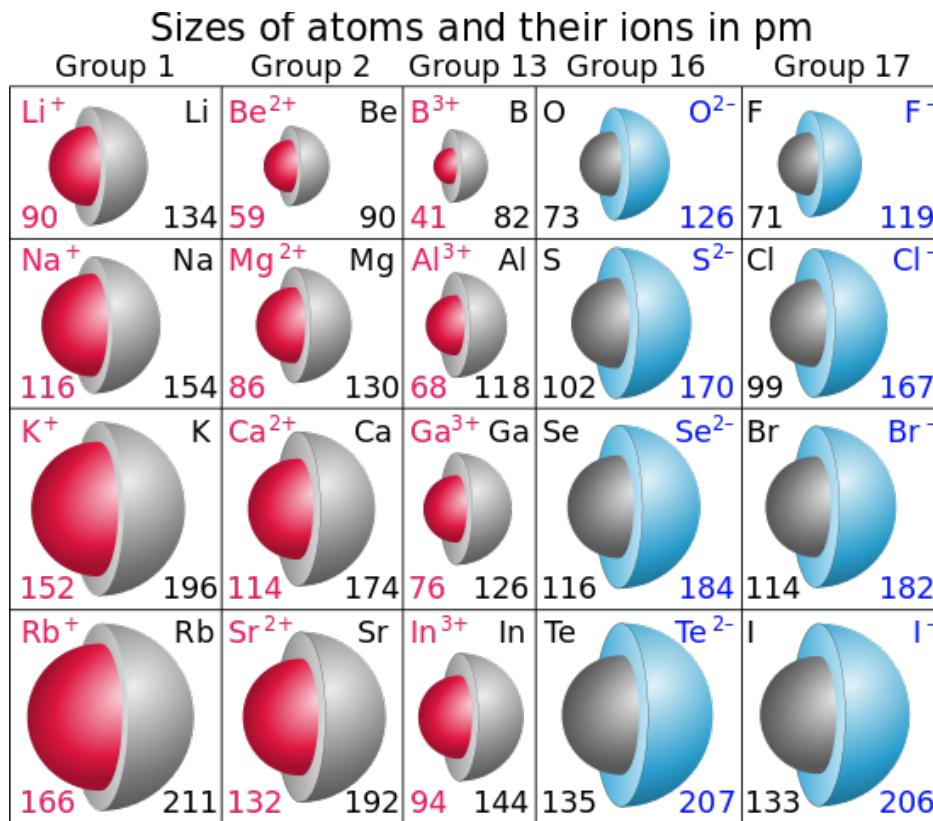
Tendency of an atom to attract electrons



Electron density of LiF  
(unequally shared)

# Atomic and Ionic Radii

Many structures can be explained by a close-packed arrangement of the larger element

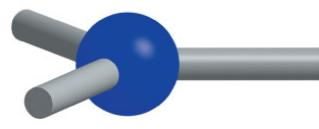


Effective radius of an element depends on its charge and environment:

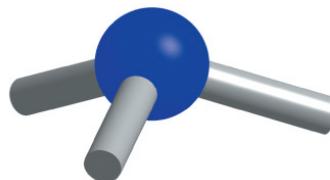
- Number of electrons
- How tightly they are bound to the nucleus

# Atomic Coordination Environments

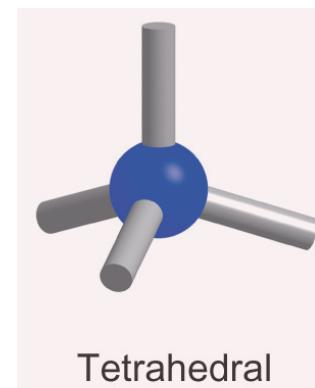
1



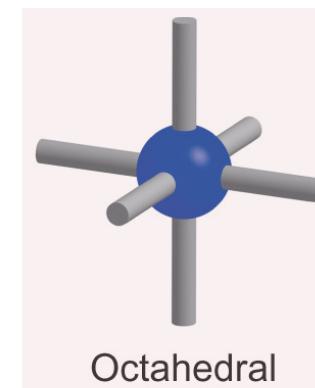
Trigonal planar



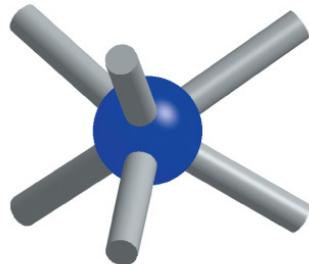
Trigonal pyramidal



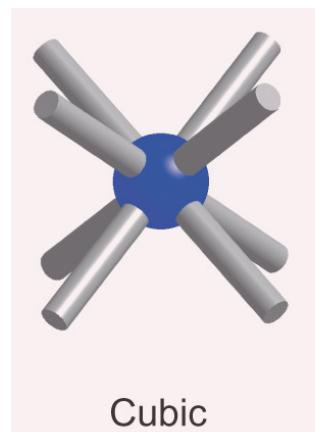
Tetrahedral



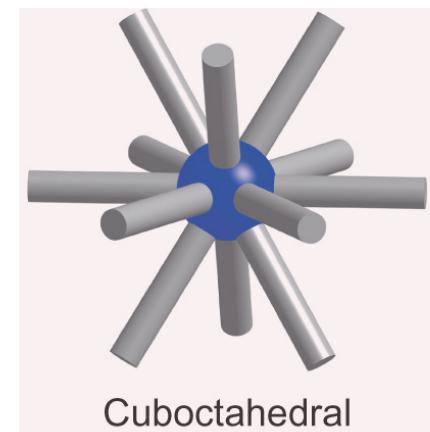
Octahedral



Trigonal prismatic



Cubic



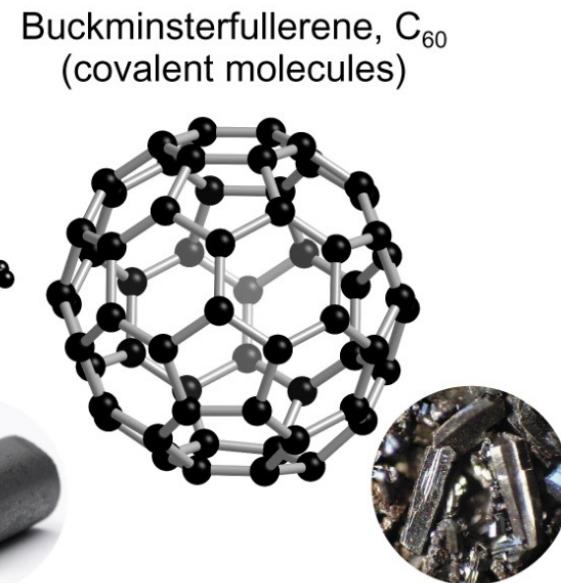
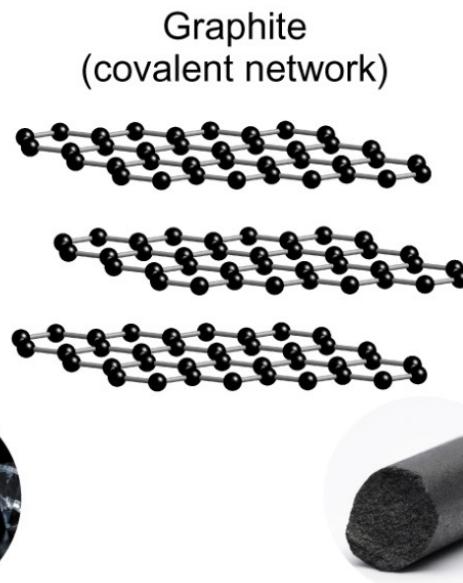
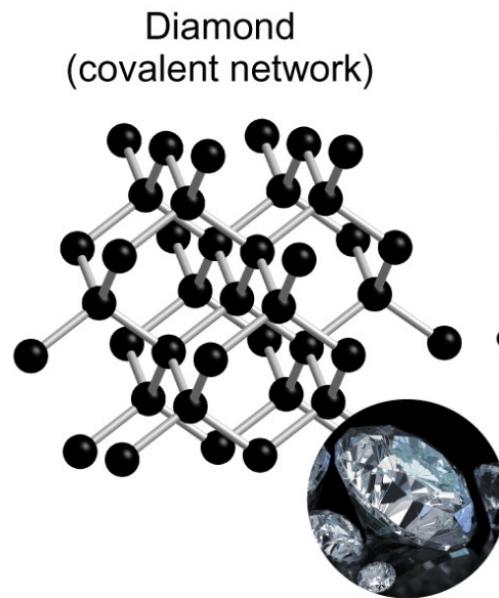
Cubooctahedral

The four shaded pink are common in crystals

A wider range of environments described by VSEPR theory (popular with chemists): [https://en.wikipedia.org/wiki/VSEPR\\_theory](https://en.wikipedia.org/wiki/VSEPR_theory)

# Allotropes of Carbon

Some elements form more than one structure.  
Diamond, graphite, and fullerene ( $C_{60}$ ) are all carbon



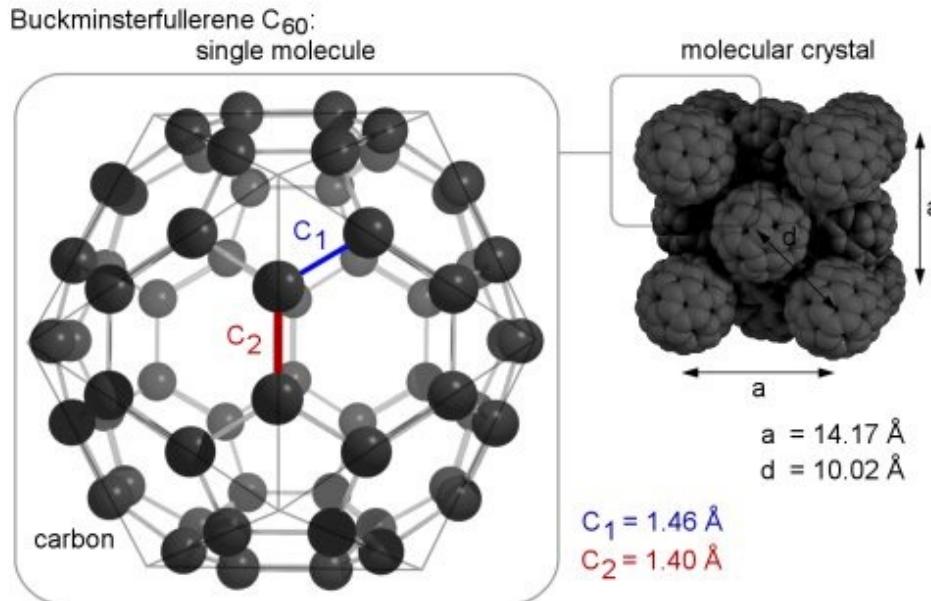
Diamond has a  
three-dimensional  
structure

Graphite has a layer  
structure, with only  
weak interactions  
between the layers

Buckminsterfullerene  
consists of  $C_{60}$   
molecules  
(‘buckyballs’)

# Crystals with Larger Building Blocks

Discovery of  $C_{60}$  (fullerene) led to 1996 Nobel prize in chemistry.  $C_{60}$  also adopts an fcc lattice. Add  $Na^+$  and it becomes a superconductor!



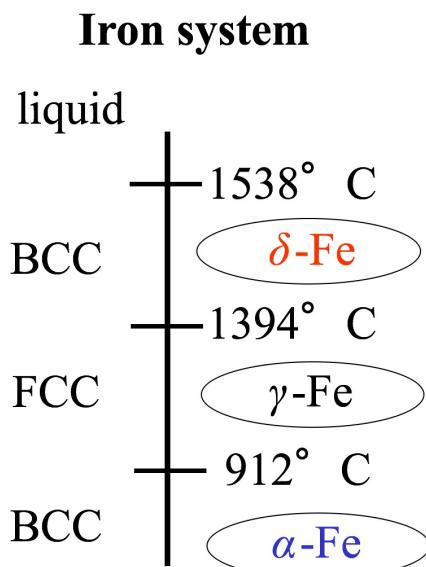
Molecular crystals form a rich and vibrant branch of crystallography

Over 1 million entries in  
<https://www.ccdc.cam.ac.uk>

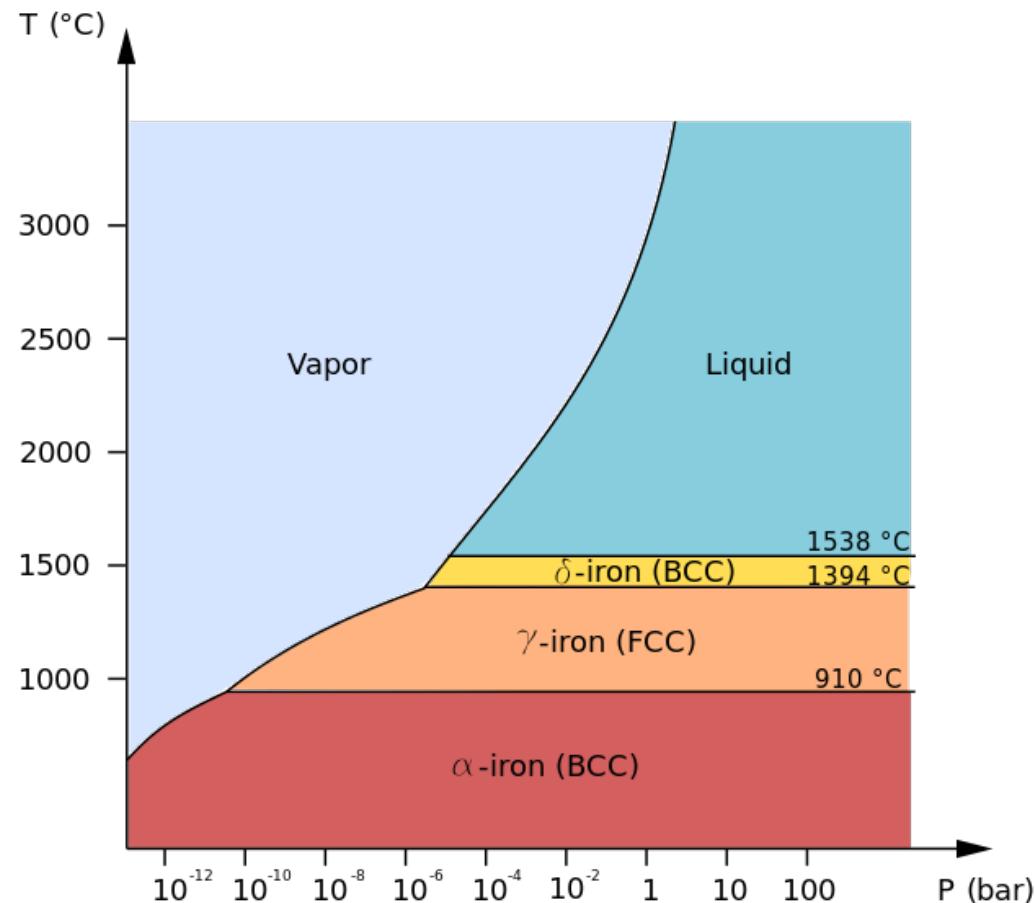
Image from: <http://www.ieap.uni-kiel.de>

# Allotropes of Iron

Alternative structures accessed by crystal growth engineering or by external stimuli (e.g. T and P)



See phase diagram lectures  
by Milo Shaffer



# AB Binary Solids

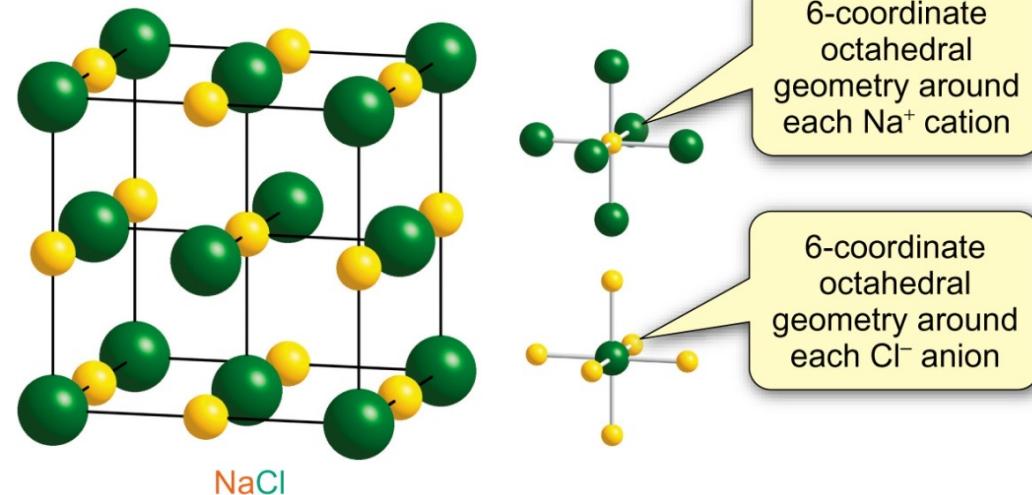
Strukturbericht (1913-1928) is a classification system for crystal structures. We will cover the most popular structures adopted by 1:1 compounds

Type	Prototype	Mineral Name
B1	NaCl	Rocksalt
B2	CsCl	None (secondary phase)
B3	ZnS	Sphalerite or Zincblende
B4	ZnS	Wurtzite

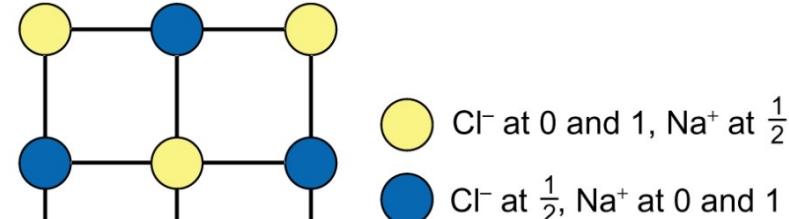
## (B1) Rocksalt – NaCl

In ionic solids, the anion is usually larger and determines the packing. NaCl described as close-packed Cl<sup>-</sup> with Na<sup>+</sup> occupying octahedral holes

(a) Unit cell for NaCl



(b) Cell projection diagram for NaCl



## (B1) Rocksalt – NaCl

Other compounds with the rocksalt structure include:

MgO (catalytic support)

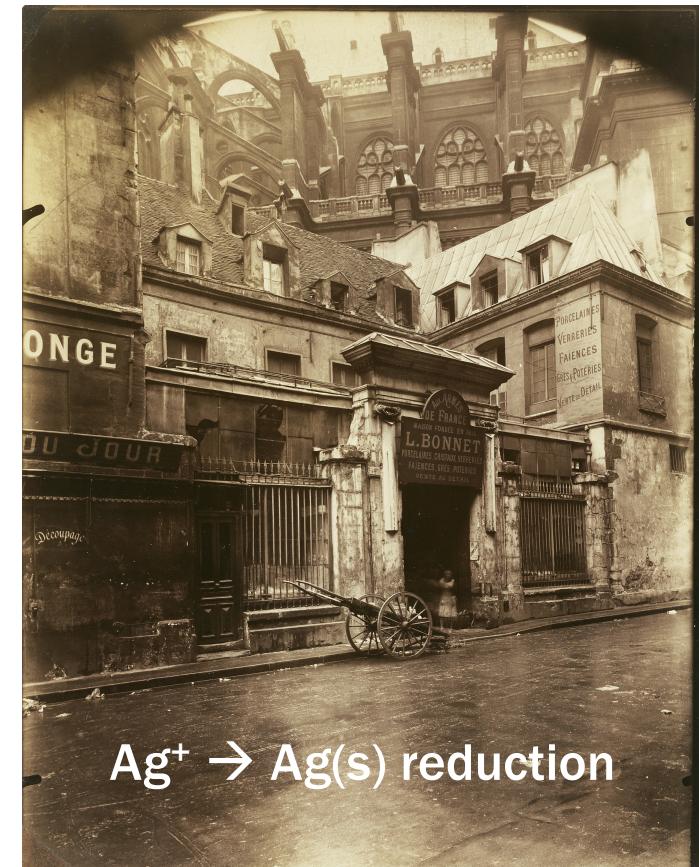
LiF (UV optics)

AgCl (photographic paper)

PbTe (thermoelectric devices)

GeTe (phase change memory)

SnTe (topological insulator)

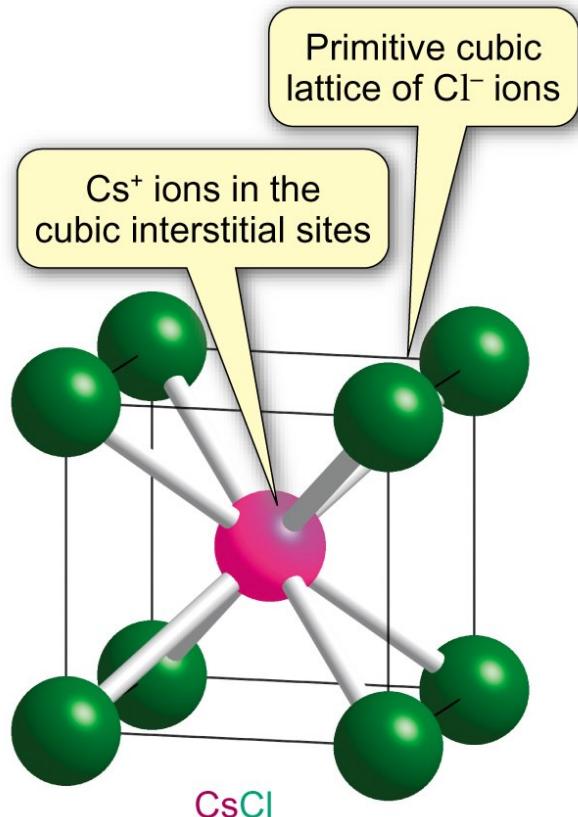


$\text{Ag}^+ \rightarrow \text{Ag(s)}$  reduction

4 Rue du Jour, Paris (1898)

## (B2) CsCl

Structure type not based on close packing.  
No octahedral or tetrahedral sites to occupy



Is the lattice type:

- (a) primitive
- (b) body-centred
- (c) face-centred

## (B2) CsCl

Other compounds with the CsCl structure include:

CsBr (optics)

CsI (phosphor)

Many metal alloys, e.g.

ScZn, TiFe, AgCd

CoCu, TcAg, CrNi

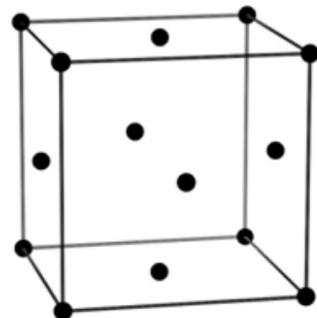
FeZn, MoAg, NbRu



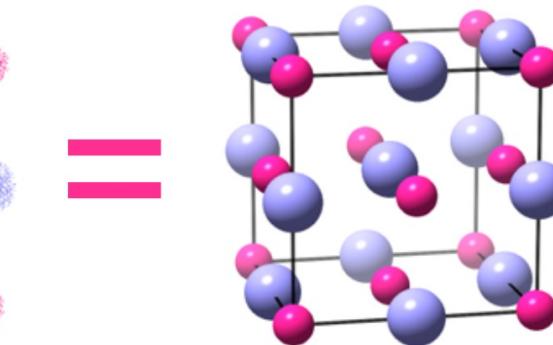
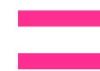
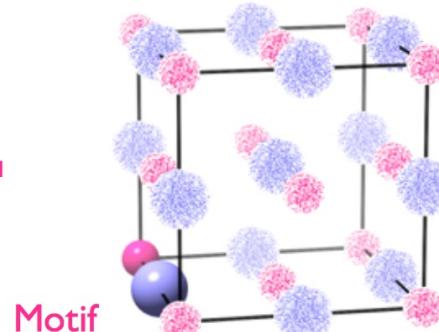
Blue LED with phosphor  
coating to make white light

# Reminder of Lattice and Motif (Basis)

**NaCl**

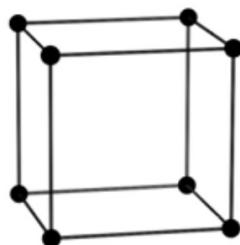


Lattice

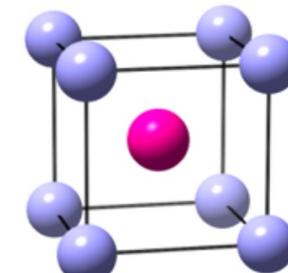
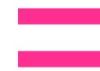
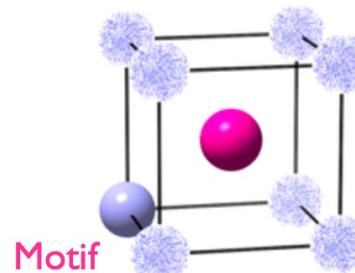


FCC Bravais Lattice with a basis of:  
 $\text{Na}^+$  at  $(0,0,0)$  and  $\text{Cl}^-$  at  $(\frac{1}{2},0,0)$

**CsCl**



Lattice



Simple Cubic Bravais Lattice  
with a basis of:  
 $\text{Cs}^+$  at  $(0,0,0)$  and  $\text{Cl}^-$  at  $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

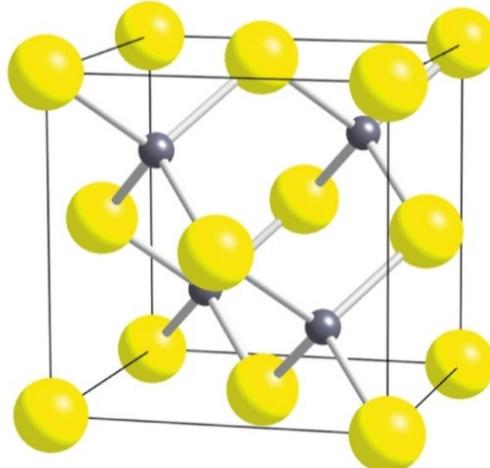
## (B3) Zincblende and (B4) Wurtzite

ZnS can adopt cubic and hexagonal polymorphs. Zincblende (sphalerite) and wurtzite can be viewed as close-packed S with Zn occupying tetrahedral holes

A cubic close-packed arrangement of  $S^{2-}$  ions with  $Zn^{2+}$  ions in half of the tetrahedral sites

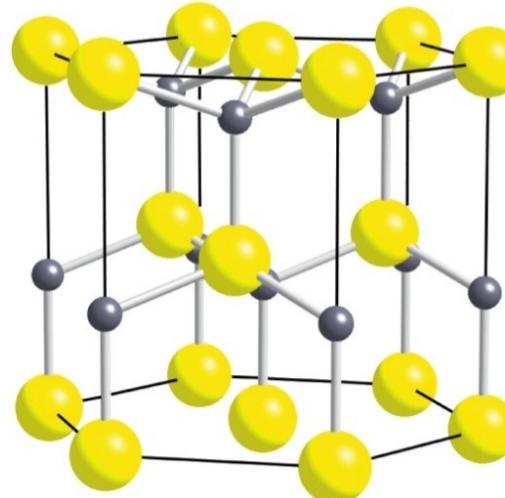
A hexagonal close-packed arrangement of  $S^{2-}$  ions with  $Zn^{2+}$  ions in half of the tetrahedral sites

Derived from fcc



(a) Sphalerite ( $ZnS$ )

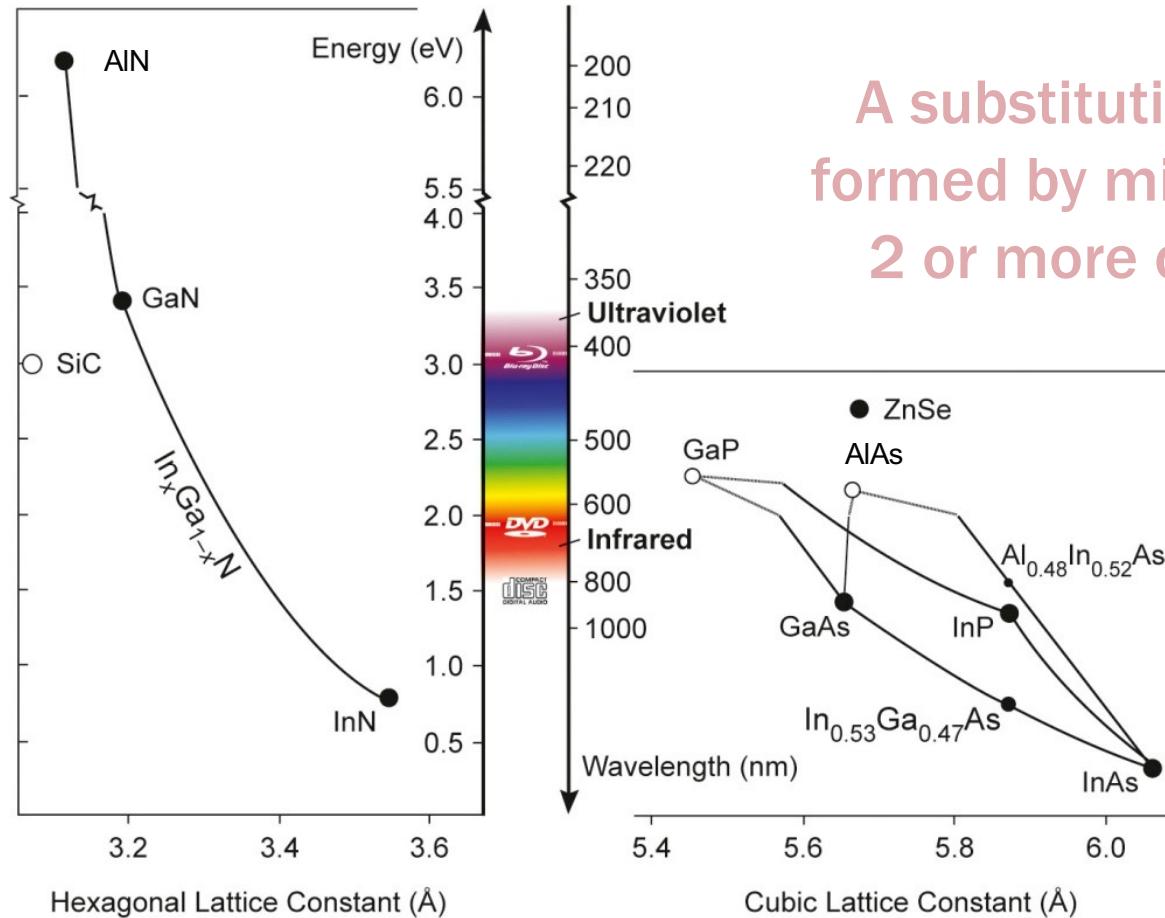
Derived from hcp



(b) Wurtzite ( $ZnS$ )

# Zincblende and Wurtzite Compounds

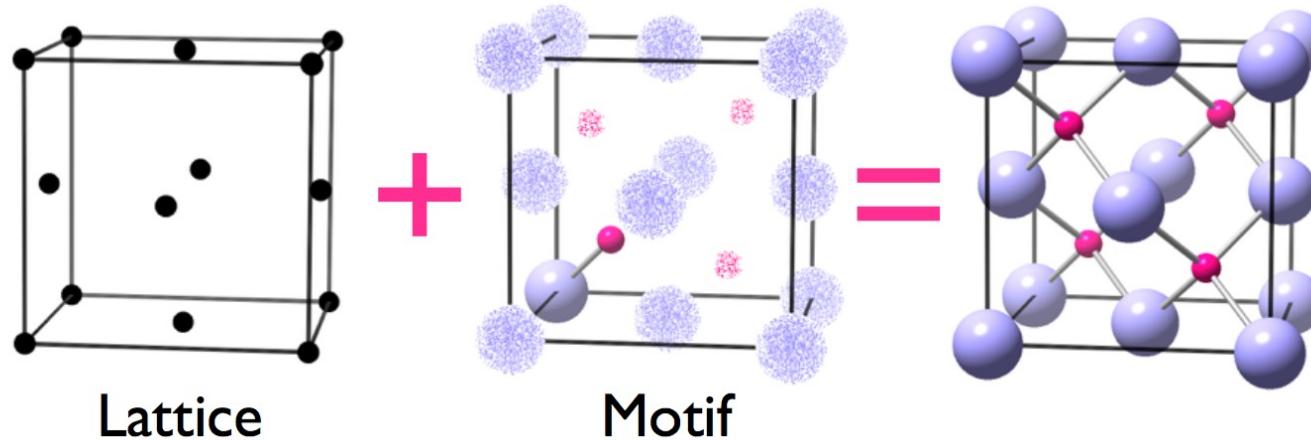
Most important structures in semiconductor physics,  
including GaN LEDs; GaAs solar cells; ZnO electronics



A substitutional alloy is  
formed by mixing together  
2 or more compounds

# Zincblende Related Structures

	Structure Type	Examples
Elemental (A)	Diamond	C, Si
Binary (AX)	Zincblende	ZnS, GaAs
Ternary ( $ABX_2$ )	Chalcopyrite	$\text{CuGaS}_2$
Quaternary ( $A_2BCX_4$ )	Kesterite	$\text{Cu}_2\text{ZnSnS}_4$



# Which Structure will be Adopted?

One challenge in materials science is to predict the structure a combination of elements will adopt

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 192]

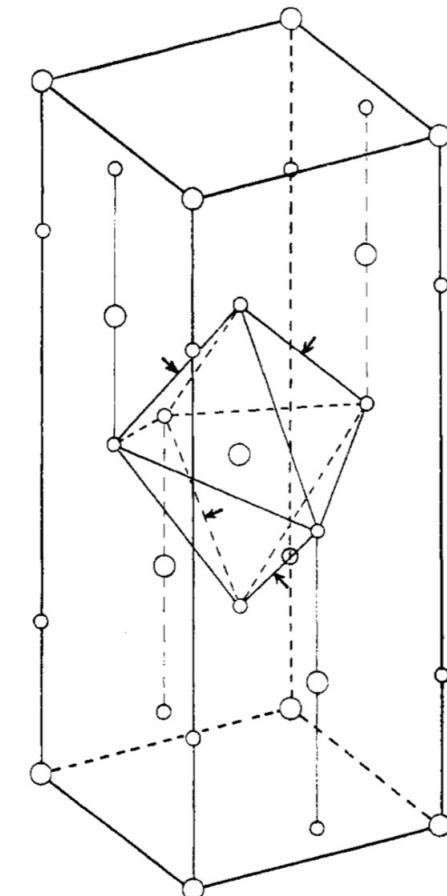
## THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

BY LINUS PAULING

RECEIVED SEPTEMBER 5, 1928

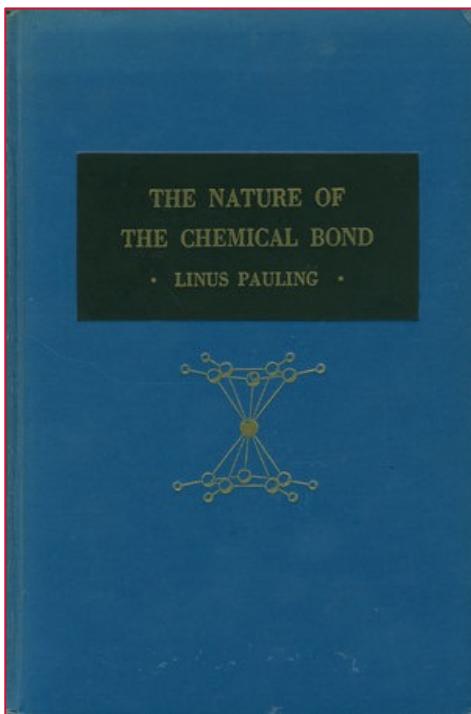
PUBLISHED APRIL 5, 1929

1. The Relative Stability of Alternative Structures of Ionic Crystals.—The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state. Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure? Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase? Why does aluminum fluosilicate,  $\text{Al}_2\text{SiO}_4\text{-F}_2$ , crystallize with the structure of topaz and not with some other structure? These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable. This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy



# Linus Pauling (1901-1994)

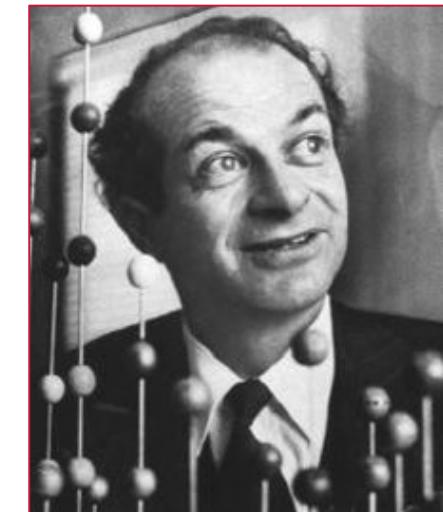
Born in USA. Chemist and Pacifist (two Nobel prizes!)



Applied quantum  
mechanics to chemical  
problems

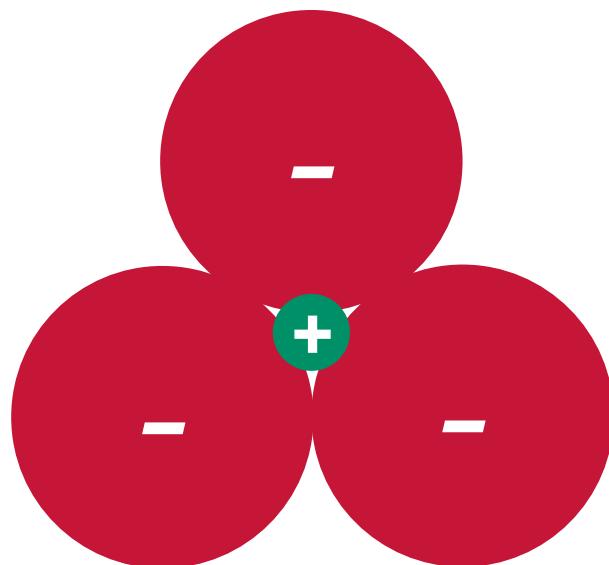
Early structure-property  
relationships for solids

Developed rules for  
predicting crystal structures

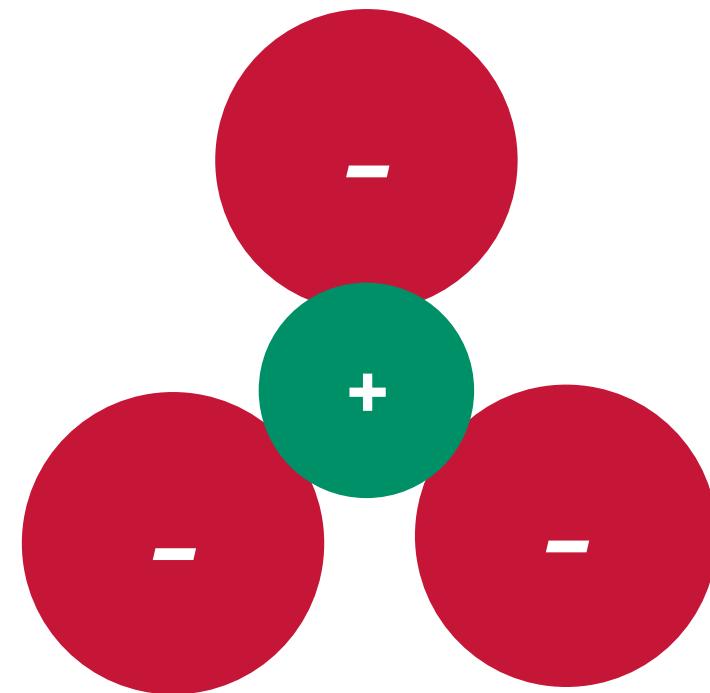


# Quiz

Which combination of ions do you think is more stable?



A

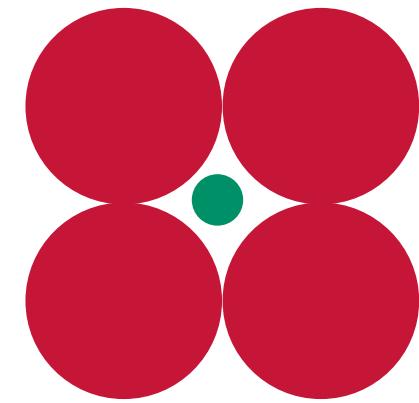


B

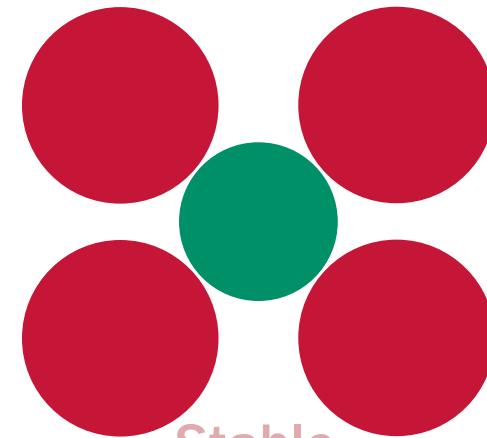
# Geometric Model: Radius Ratio Rules

## Assumptions for Radius Ratio Rules:

1. Ions are charged, incompressible, spheres
2. Arrangement of anions ( $r^-$ ) about a cation ( $r^+$ ) is stable only if anions avoid contact: **radius ratio limit**
3. The coordination number is as large as possible (subject to point 2)
4. Arrangement of anions minimises the charge repulsion between them



Unstable



Stable

# Limiting Radius Ratio ( $r_{\text{Cation}}/r_{\text{Anion}}$ )

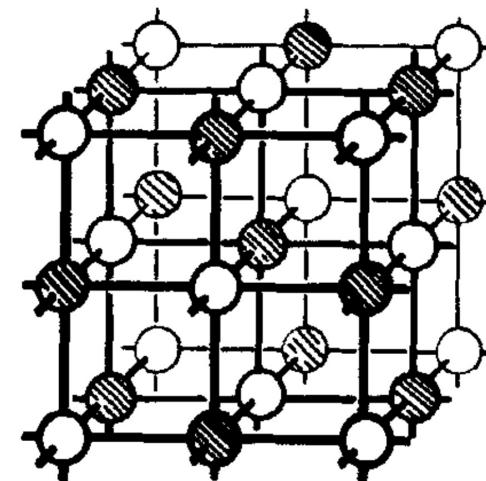
Interstitial Site	Cation Coordination	Radius Ratio
Linear	2	$0.000 \rightarrow 0.155$
Triangular	3	$0.155 \rightarrow 0.225$
Tetrahedral	4	$0.225 \rightarrow 0.414$
Octahedral (anions touch along [110], anion-cation-anion along [100])	6	$0.414 \rightarrow 0.732$
Cubic	8	$0.732 \rightarrow 1.000$

# Radius Test: Rocksalt Structure

SOME IONIC CRYSTALS WITH THE ROCKSALT STRUCTURE (150)

Compound	M-X (Å)	Ionic radius sum $r_M/r_X$ (Å)	Compound	M-X (Å)	Ionic radius sum $r_M/r_X$ (Å)		
LiF	2.01	1.96	0.44	MgO	2.10	2.05	0.46
LiCl	2.57	2.41	0.33	CaO	2.41	2.39	0.71
LiBr	2.75	2.55	0.31	SrO	2.57	2.53	0.81
LiI	3.00	2.76	0.28	BaO	2.76	2.75	0.96
NaF	2.31	2.31	0.70	TiO	2.12	—	—
NaCl	2.81	2.76	0.52	VO	2.04	—	—
NaBr	2.98	2.90	0.49	MnO	2.22	2.20	0.57
NaI	3.23	3.11	0.44	FeO	2.16	2.15	0.53
KF	2.67	2.69	0.98	CoO	2.13	2.12	0.51
KCl	3.14	3.14	0.73	NiO	2.10	2.10	0.50
KBr	3.29	3.28	0.68	CdO	2.35	2.37	0.69
KI	3.52	3.49	0.62	TaO	2.21	—	—
RbF	2.82	2.84	1.09	MnS	2.61	2.64	0.43
RbCl	3.27	3.29	0.82	PbS	2.96	—	—
RbBr	3.43	3.43	0.76				
RbI	3.66	3.64	0.69				
CsF	3.00	3.05	1.24				
CsCl	3.51	3.50	0.93				
AgF	2.46	2.62	0.93				
AgCl	2.77	3.07	0.70				
AgBr	2.89	3.21	0.65				

Does the model  
work well?



# Radius Test: Zincblende Structure

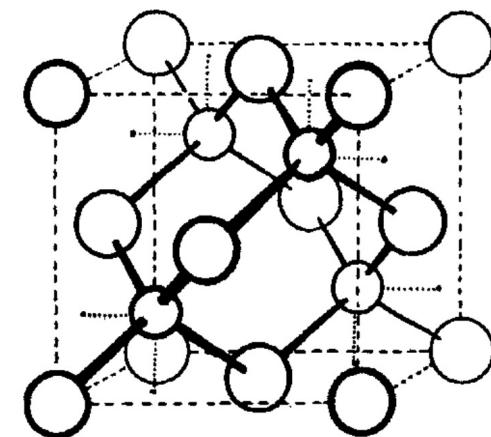
SOME CRYSTALS WITH TETRAHEDRALLY COORDINATED STRUCTURES (150)<sup>a</sup>

Compound	Sphalerite M-X (Å)	Wurtzite M-X (Å)	Ionic radius sum <sup>b</sup> (Å)	$r_M/r_X$
BeO	—	1.64, 1.65	1.62	0.22
BeS	2.10	—	2.04	0.17
ZnO	—	1.95, 1.98	2.03	0.53
ZnS	2.36	2.33, 2.33	2.45	0.40
CdS	2.52	2.51, 2.53	2.67	0.53
HgS	2.53	—	2.79	0.60
MnS	2.43	2.41, 2.44	2.50	0.43
CuF	1.85	—	2.20	0.71
CuCl	2.35	—	2.63	0.53
CuBr	2.46	—	2.76	0.49
CuI	2.62	—	2.96	0.44
AgI	2.80	—	3.24	0.58

<sup>a</sup> The interatomic distances in these compounds can be closely reproduced by a special set of covalent radii (114, p. 179).

<sup>b</sup> The ionic radius sum has been multiplied by 0.95 to allow for the change from 6- to 4-coordination (see Appendix).

Does the model work well?

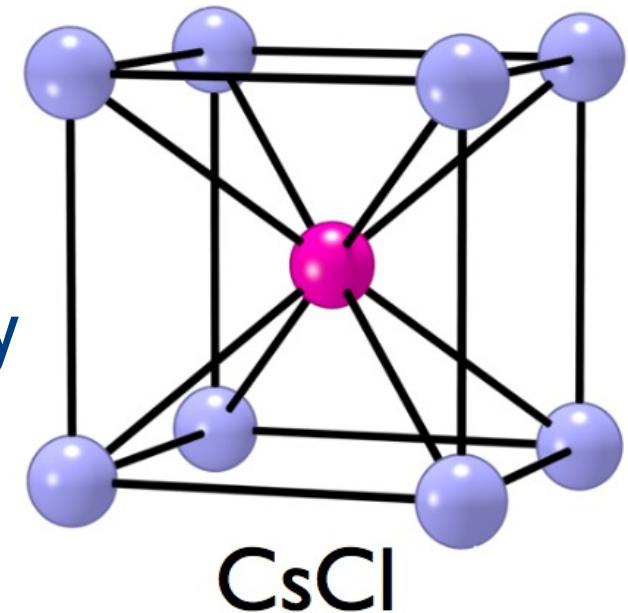


\* CuF was mis-assigned: “The existence and chemical stability of cuprous fluoride”, A. Walsh et al, Chemical Science 3, 2565 (2012)

# Derive Radius Ratio: CsCl

**Task:** Calculate the critical radius ratio ( $r_{\text{Cs}}/r_{\text{Cl}}$ ) for which the CsCl structure is stable

**Approach:** Inspect the geometry of the structure to find a relationship between  $r_{\text{Cs}}$  and  $r_{\text{Cl}}$



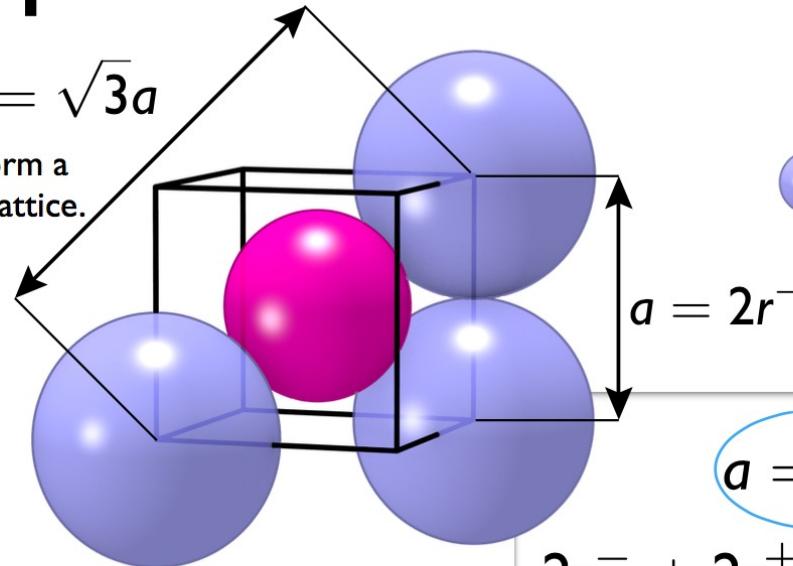
**Hint:** The critical point is where the Cl ions touch, which will happen when  $a = 2r_{\text{Cl}}$

# Radius Ratio Example: CsCl

## Example: CsCl

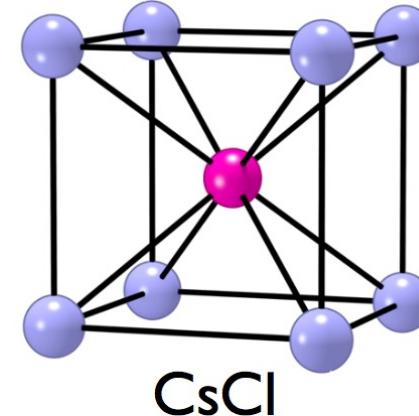
$$2r^- + 2r^+ = \sqrt{3}a$$

In CsCl anions form a simple cubic sub-lattice.  
Therefore  $2r^- = a$



$$\frac{r^+}{r^-} = (\sqrt{3} - 1) = 0.732$$

That is, if the cation radius  $r^+ > 0.732 r^-$   
the predicted structure is that of CsCl.



$$a = 2r^-$$

$$2r^- + 2r^+ = \sqrt{3}a$$

$$\cancel{2r^- + 2r^+} = \cancel{2r^-} = 2\sqrt{3}r^-$$

$$r^- + r^+ = \sqrt{3}r^-$$

$$r^+ = (\sqrt{3} - 1)r^-$$

# Summary: Crystals 1

## Class outcomes:

- Define the terms allotrope (1 element) and polymorph (>2 elements), with examples
- Describe common AB structure types: rocksalt, caesium chloride, zincblende, wurtzite
- Understand and apply radius ratio rules to predict stable structures for ionic solids

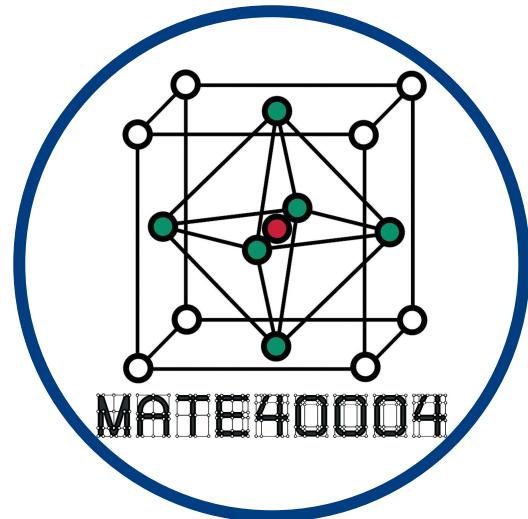
MATE40004 – Structure 1

## Crystallography

# F. Crystals 2

Professor Aron Walsh

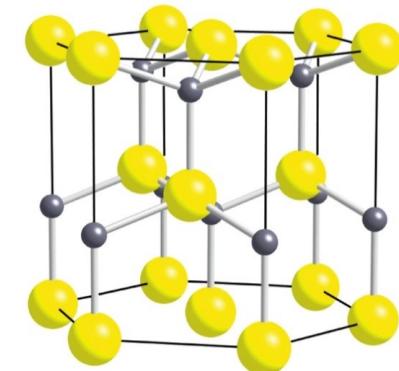
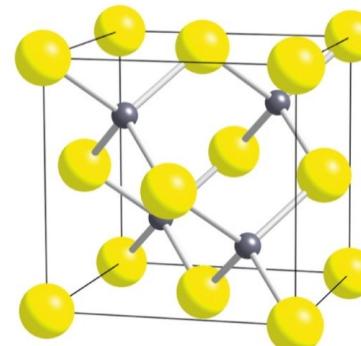
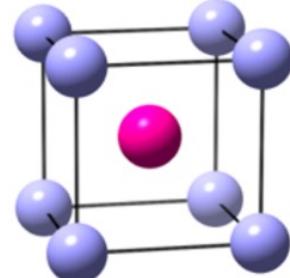
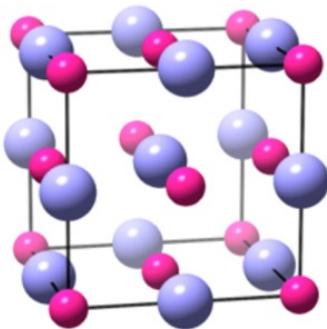
Department of Materials  
Imperial College London



<http://www.imperial.ac.uk/people/a.walsh>

# Recap: Binary Crystal Structures

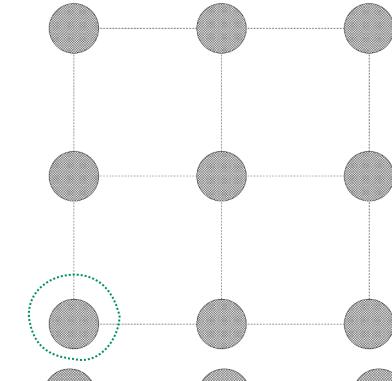
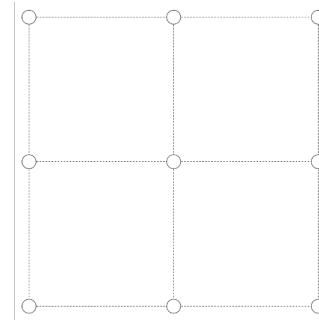
Type	Prototype	Mineral Name	Based on	Coordination
B1	NaCl	Rocksalt	FCC	6+6
B2	CsCl	None	SC	8+8
B3	ZnS	Zincblende	FCC	4+4
B4	ZnS	Wurtzite	HCP	4+4



# Recap: Lattice vs Crystal

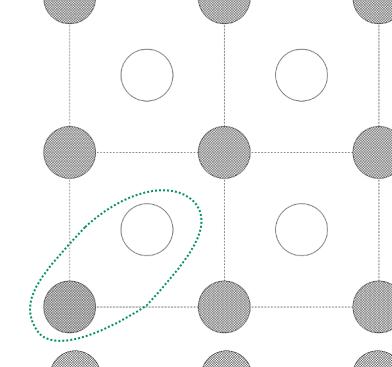
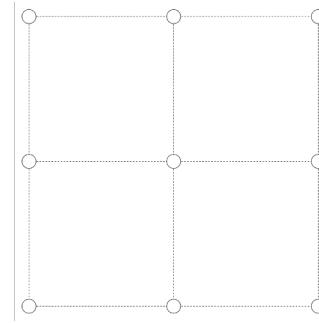
## Primitive cubic

1 lattice point x  
1 atom motif



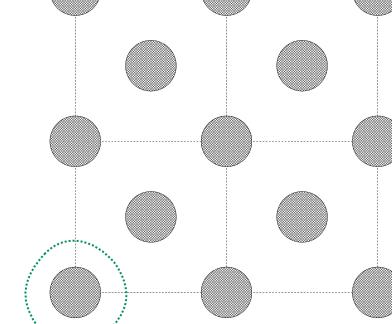
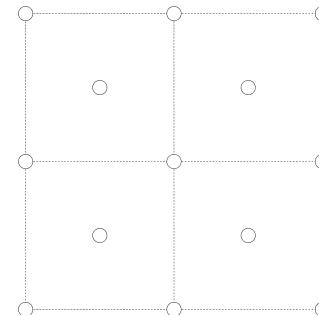
## CsCl

1 lattice point x  
2 atom motif



## Body-centred cubic

2 lattice points x  
1 atom motif



# Outline of Crystallography

---

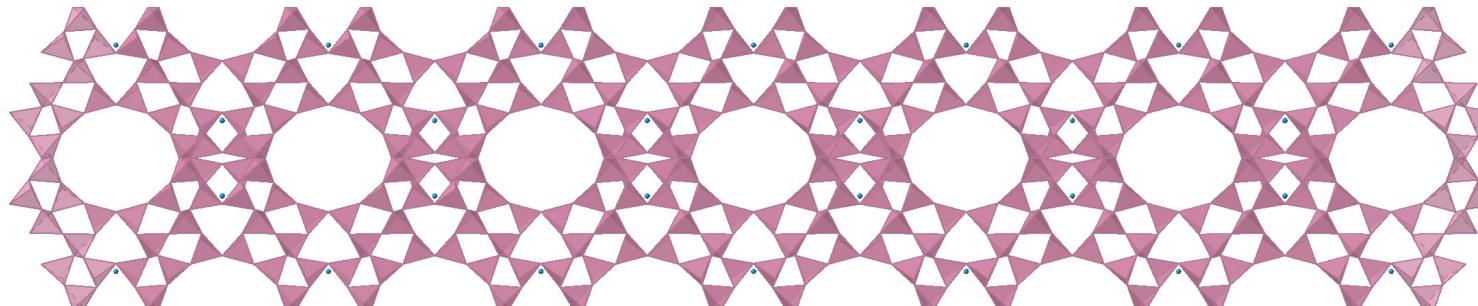
- A. Lattices
- B. Symmetry
- C. Geometry
- D. Packing
- E. Crystals 1
- F. Crystals 2
- G. Diffraction

# More Complex Crystal Structures

We covered the B class of Strukturbericht,  
but there are many more....

Label	Type	Examples
A	Elemental	A1 (FCC); A2 (BCC); A3 (HCP)
B	1:1	B1 (NaCl); B2 (CsCl); B3 (ZnS)
C	1:2	C1 ( $\text{CaF}_2$ ); C2 ( $\text{FeS}_2$ ); C3 ( $\text{Cu}_2\text{O}$ )

E, F, G, H, I, J, K, L ... O = Organics; S = Silicates



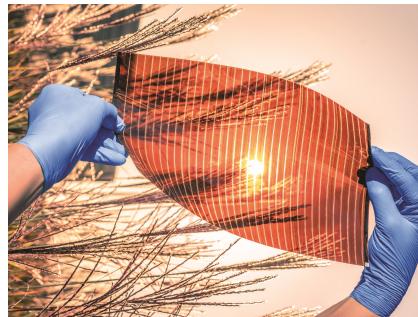
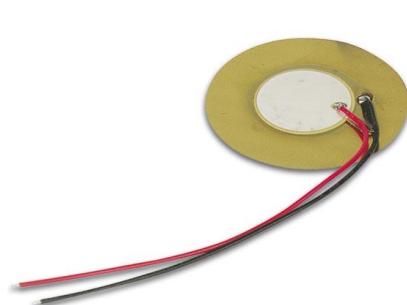
Zeolite X  
Aluminosilicate

# Structural Case Study of Perovskites

**Perovskite:** mineral form of  $\text{CaTiO}_3$  and the name given to  $\text{ABX}_3$  materials with the same structure

Perovskites exhibit structural and chemical flexibility, with a wide range of materials properties:

- **Conductivity:** insulators, metals, superconductors
- **Ferroelectricity:** switchable electric polarisation
- **Magnetism:** long-range alignment of electron spins



# Structural Case Study of Perovskites

NEWS FEATURE • 25 JUNE 2019

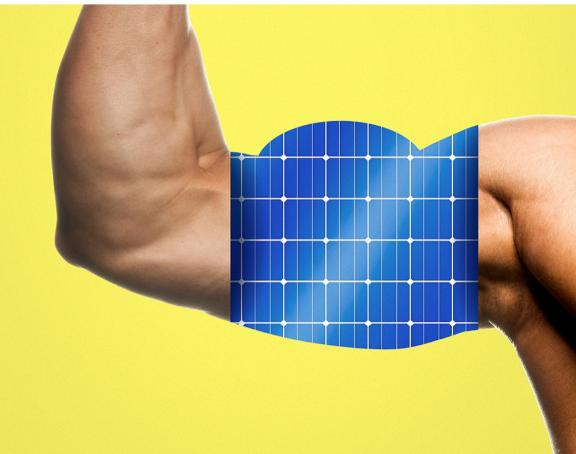
## The reality behind solar power's next star material

Companies say they are close to commercializing cheap perovskite films that could disrupt solar power — but are they too optimistic?

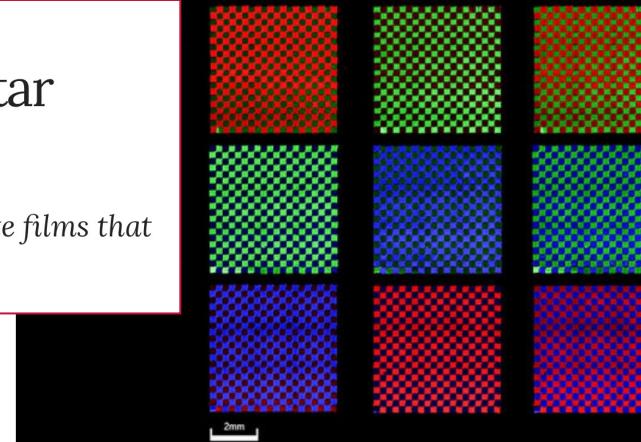
### Power From Commercial Perovskite Solar Cells Is Coming Soon

Oxford PV's tandem silicon-perovskite solar modules aim to beat the best panels on the market

By Jean Kumagai



TOP  
TECH  
2019  
SPECIAL REPORT



When combined with polarizing filters, 3D-printed perovskite nanowires produce adjustable multicolor displays. N. ZHOU ET AL., SCI. ADV. 5, EAAV8141 (2019)

### LEDs created from wonder material could revolutionize lighting and displays

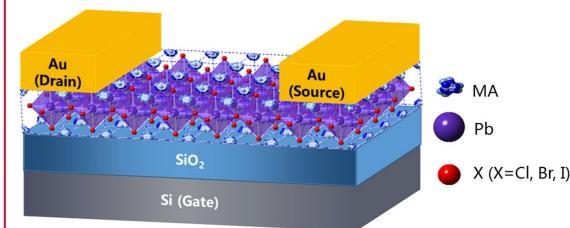
By Robert F. Service | Jun. 4, 2019, 4:45 PM



### Hail the Perovskite Transistors

Researchers have created a field-effect transistor using a single-crystal, "paint-on" perovskite

By David Schneider



# Count Lev von Perovski (1792–1856)

Mineralogist and Minister of Internal Affairs of Russia



Lev von Perovski

Perovski established the  
Russian Geological Society



Gustav Rose

Gustav Rose (Prussia)  
discovered a new mineral  
in the Ural Mountains in  
1839 and named it  
*Perovskite*

# Structural Case Study of Perovskites

1. Geometry of perovskite structure
2. Radius ratio rules for  $\text{ABX}_3$
3. Polymorphism and phase transitions

# Cubic Perovskite Aristotype

Aristotype: the simplest and most symmetric member of a structural family (the parent structure)

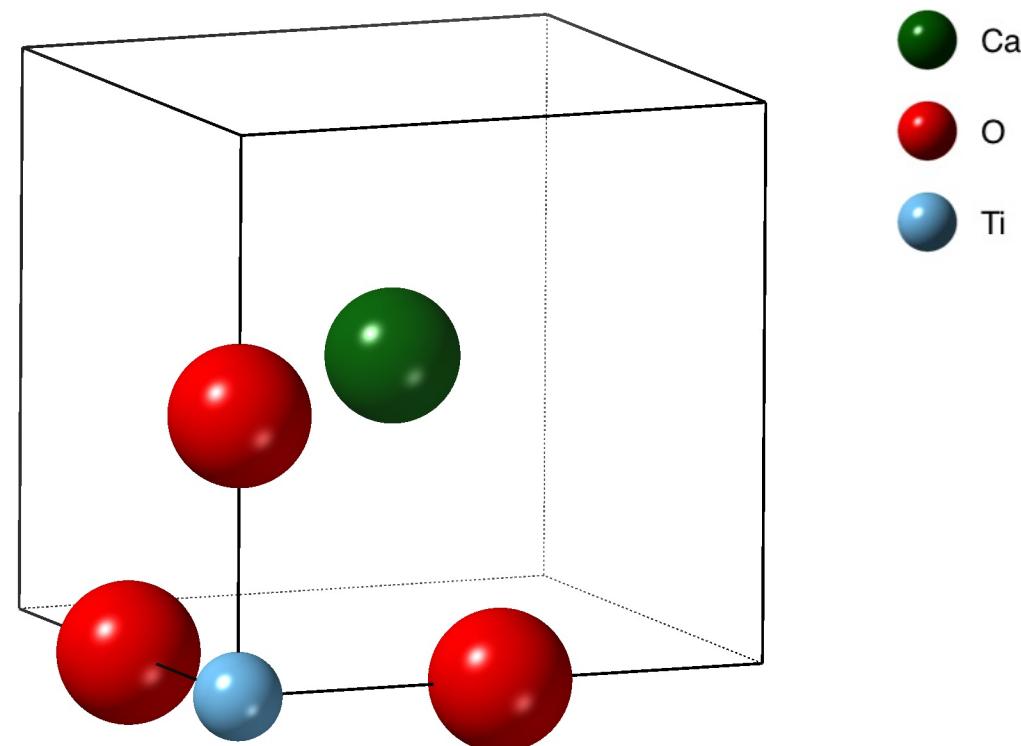
Ca \_\_\_\_\_

Ti \_\_\_\_\_

O1 \_\_\_\_\_

O2 \_\_\_\_\_

O3 \_\_\_\_\_

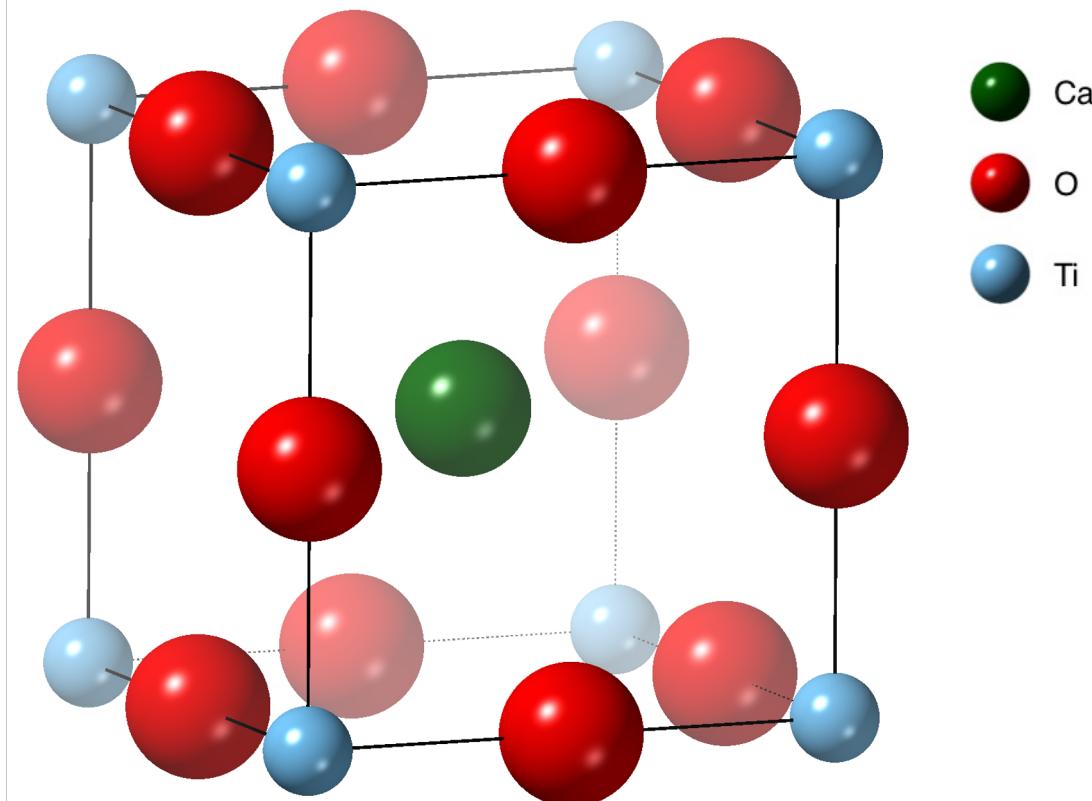


Primitive lattice with a motif of 5 atoms

# Cubic Perovskite Aristotype

Aristotype: the simplest and most symmetric member of a structural family (the parent structure)

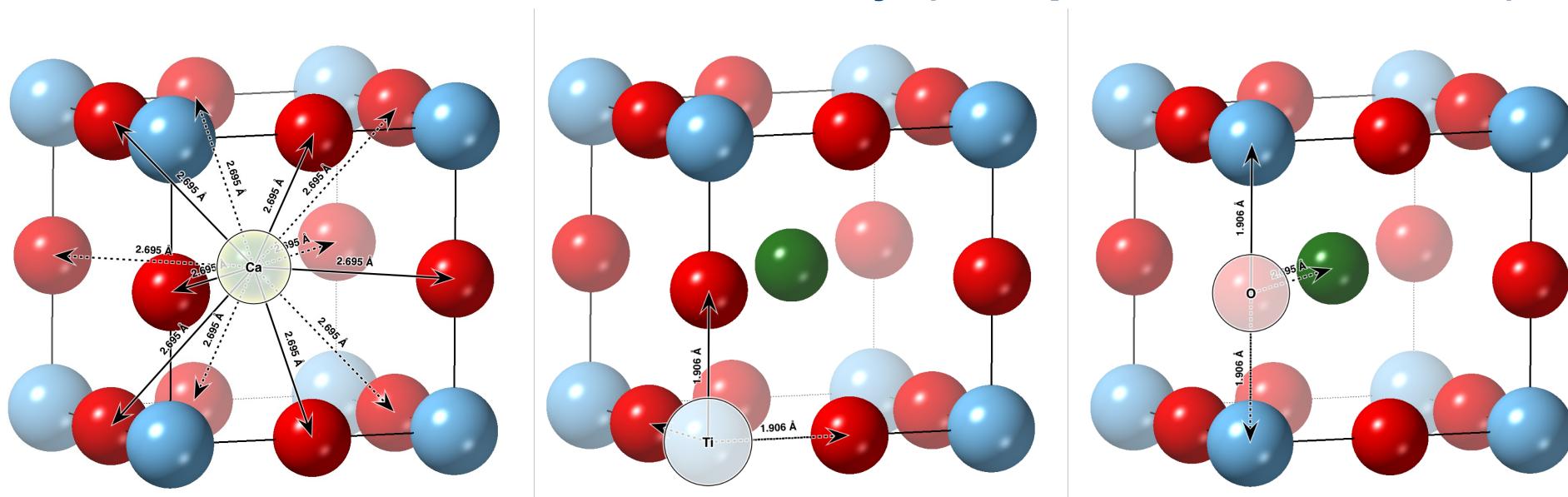
The same cubic crystal structure is adopted by 100s of  $ABX_3$  compounds



Full unit cell representation

# Cubic Perovskite Aristotype

Aristotype: the simplest and most symmetric member of a structural family (the parent structure)



A site

12 coordinate  
(cuboctahedral)

B site

6 coordinate  
(octahedral)

X site

2 coordinate  
(linear)

# Warning: Unit Cell Definitions

Two  $\text{ABX}_3$  perovskites unit cells common in the literature, which are easy to distinguish

## Origin at A-site

A: 0,0,0  
B:  $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$   
X:  $\frac{1}{2}$ ,  $\frac{1}{2}$ , 0  
 $\frac{1}{2}$ , 0,  $\frac{1}{2}$   
0,  $\frac{1}{2}$ ,  $\frac{1}{2}$

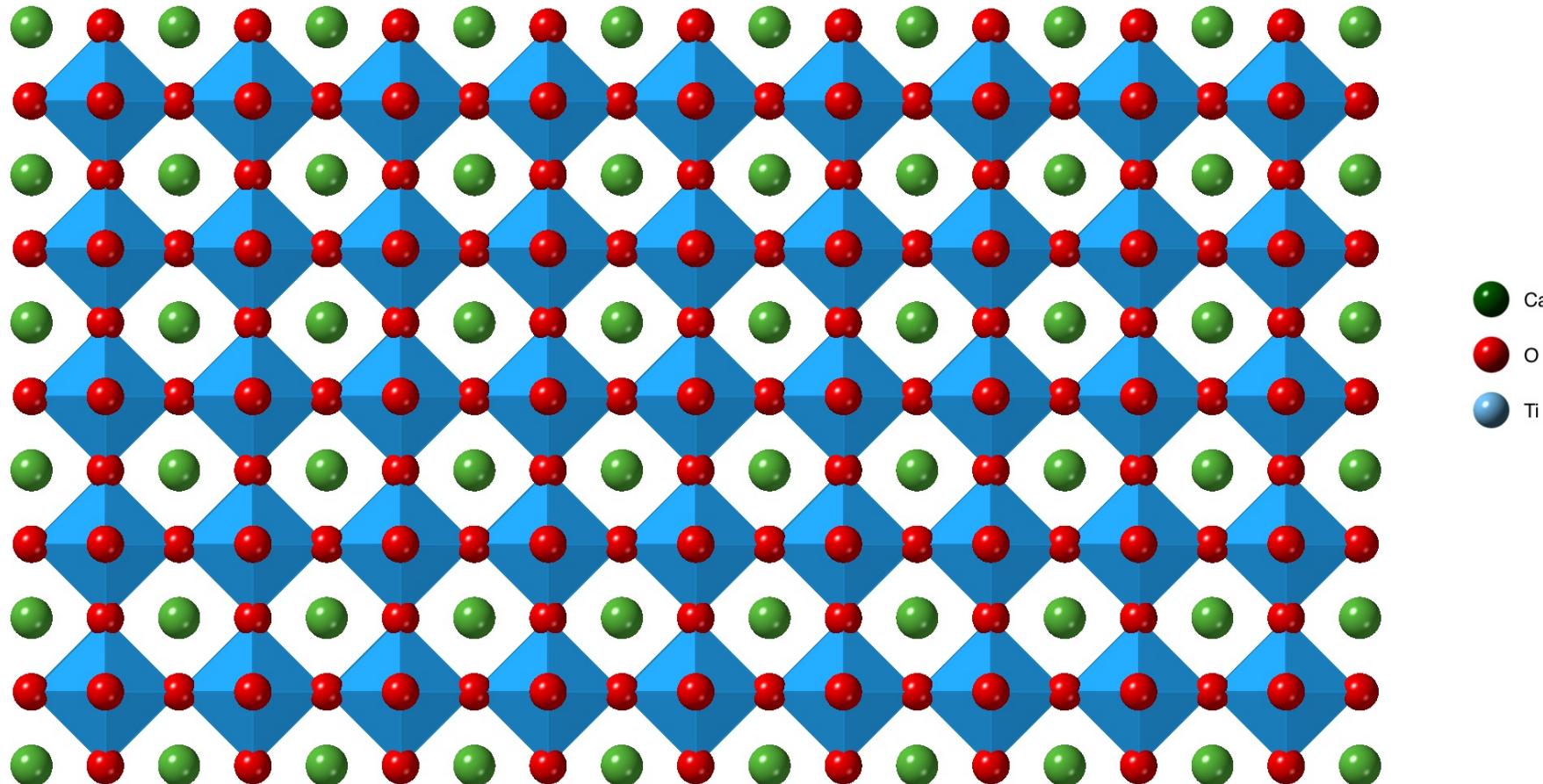
## Origin at B-site

A:  $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$   
B: 0, 0, 0  
X: 0, 0,  $\frac{1}{2}$   
0,  $\frac{1}{2}$ , 0  
 $\frac{1}{2}$ , 0, 0

Each coordinate  
is shifted by  $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$

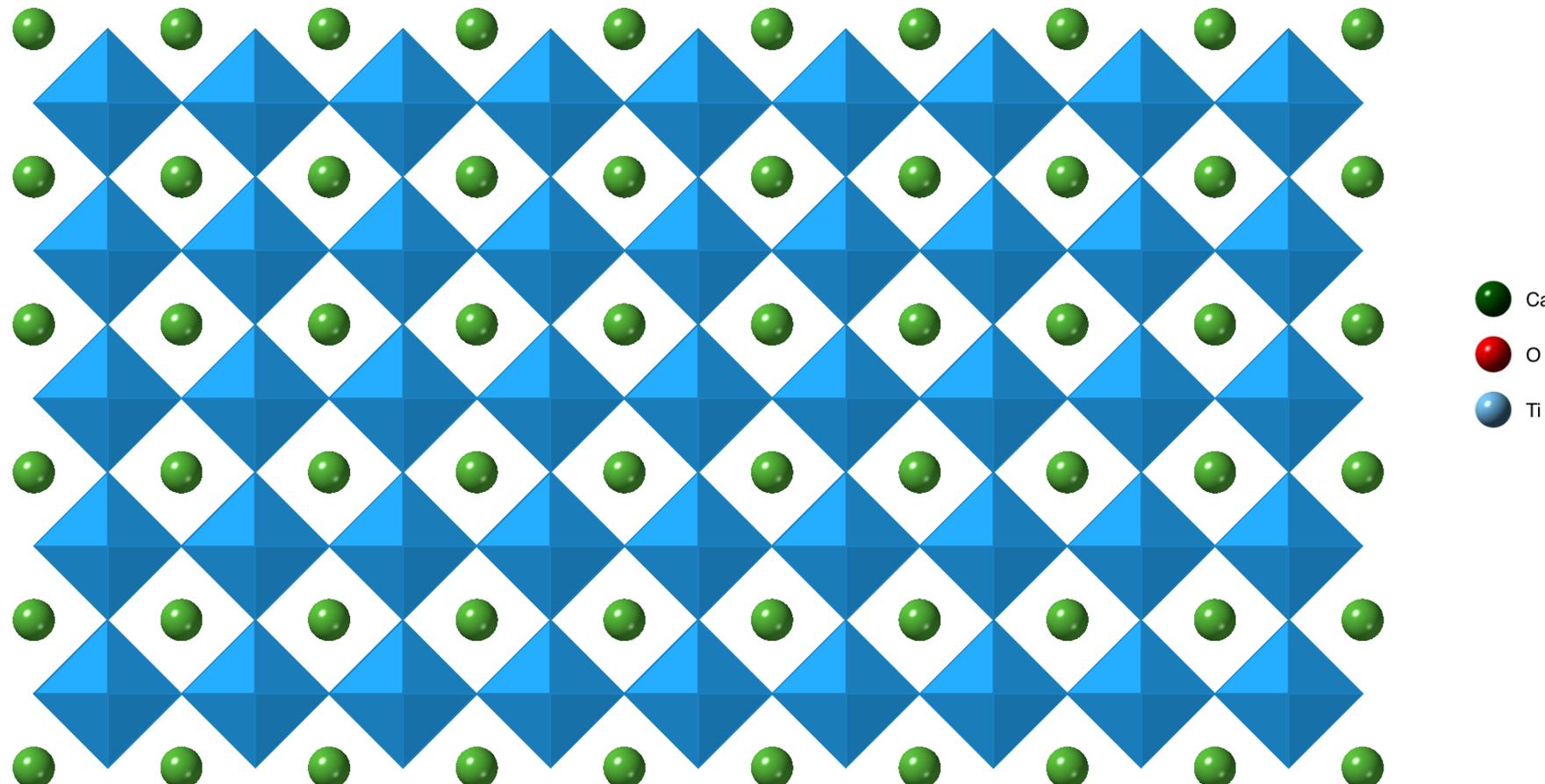
# Cubic Perovskite Aristotype

Common representation showing 3D corner-sharing octahedral network of  $\text{BX}_6$  units



# Cubic Perovskite Aristotype

Common representation showing 3D corner-sharing octahedral network of  $\text{BX}_6$  units



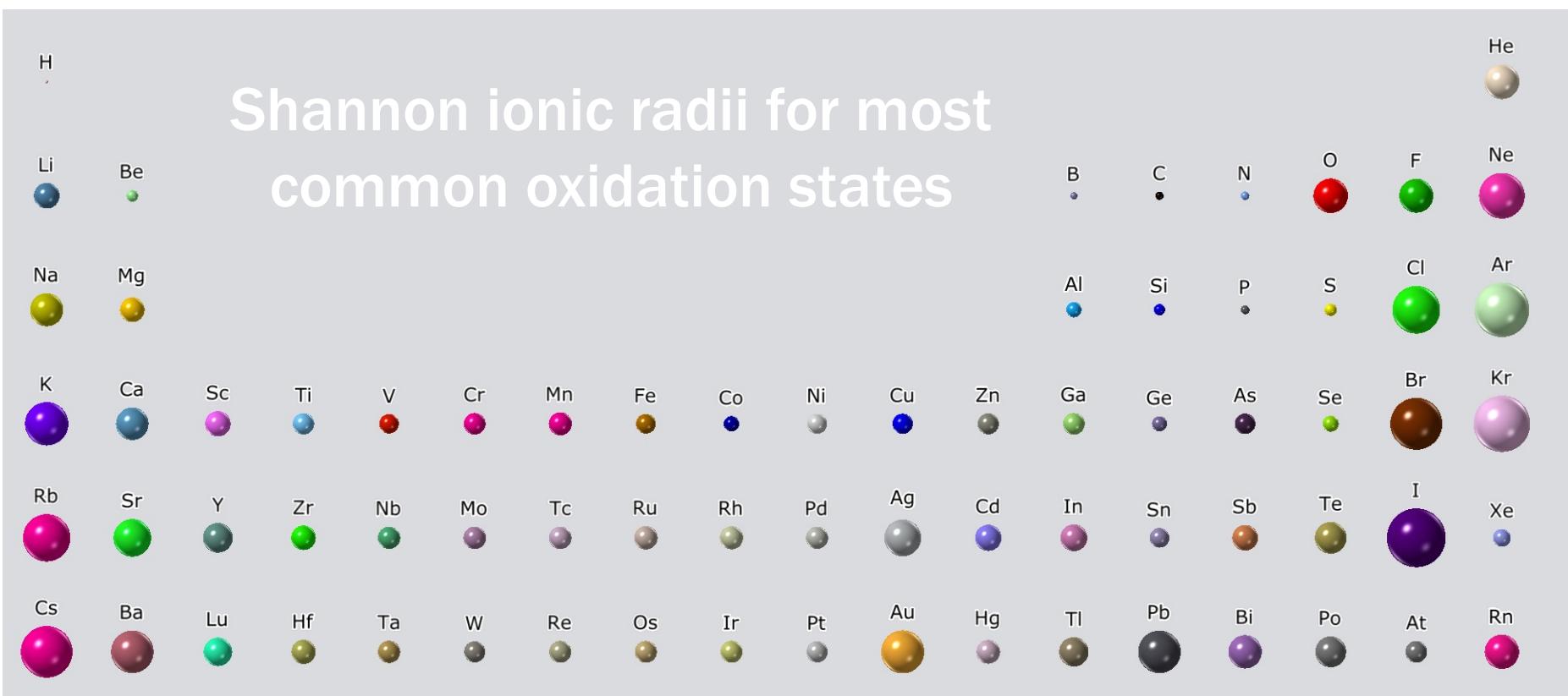
# Structural Case Study of Perovskites

1. Geometry of perovskite structure
2. Radius ratio rules for  $\text{ABX}_3$
3. Polymorphism and phase transitions

# Forming a Stable Perovskite

Allowed combinations of elements are determined by their size (radius) and charge (oxidation state)

Shannon ionic radii for most common oxidation states



# Allowed Combinations of Charge

For charge neutrality, the formal oxidation states must obey:  $A + B = 3X$

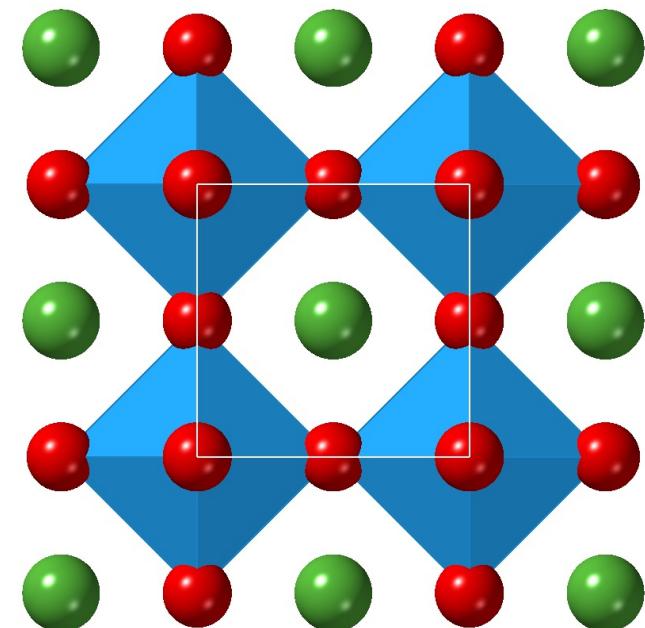
Valence rules for 1:1:3 perovskites

$X = 2^-$  (Oxides;  $A + B = 6^+$ )

- $A = 1^+$ ,  $B = 5^+$  (e.g.  $\text{KTaO}_3$ )
- $A = 2^+$ ,  $B = 4^+$  (e.g.  $\text{SrTiO}_3$ )
- $A = 3^+$ ,  $B = 3^+$  (e.g.  $\text{GdFeO}_3$ )

$X = 1^-$  (Halides;  $A + B = 3^+$ )

- $A = 1^+$ ,  $B = 2^+$  (e.g.  $\text{CsSnI}_3$ )

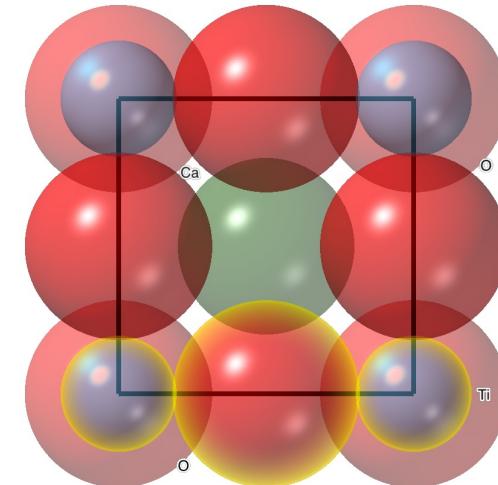
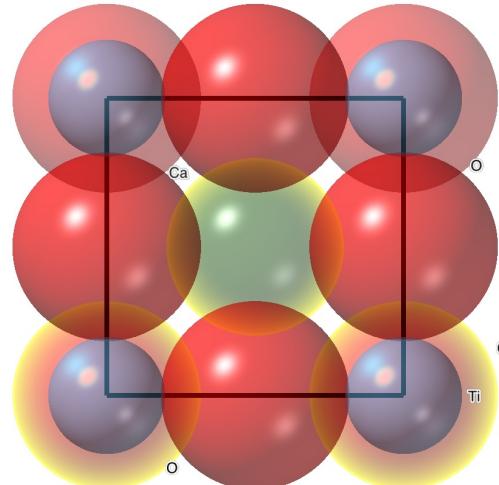


# Allowed Combinations of Size

Extension of radius ratio rules that we already covered for AB binary compounds

Ideal lattice spacing ( $a$ ) of the cubic perovskite:

$$a = \sqrt{2}(r_A + r_X) = 2(r_B + r_X)$$



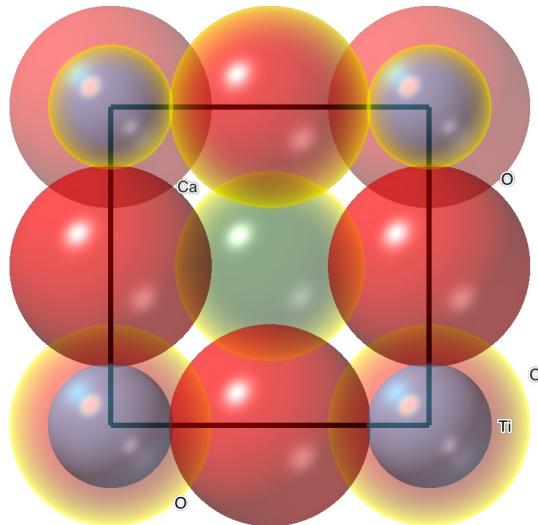
Reminder: find directions where atoms “touch” (close packed) and relate to length of unit cell (black square)

# Goldschmidt Tolerance Factor

Simple geometric descriptor ( $\alpha$ ) of structural stability and distortions of perovskites

$$\alpha = \frac{\sqrt{2}(r_A + r_X)}{2(r_B + r_X)} = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

0.7 - 1.1  
is typically accessible

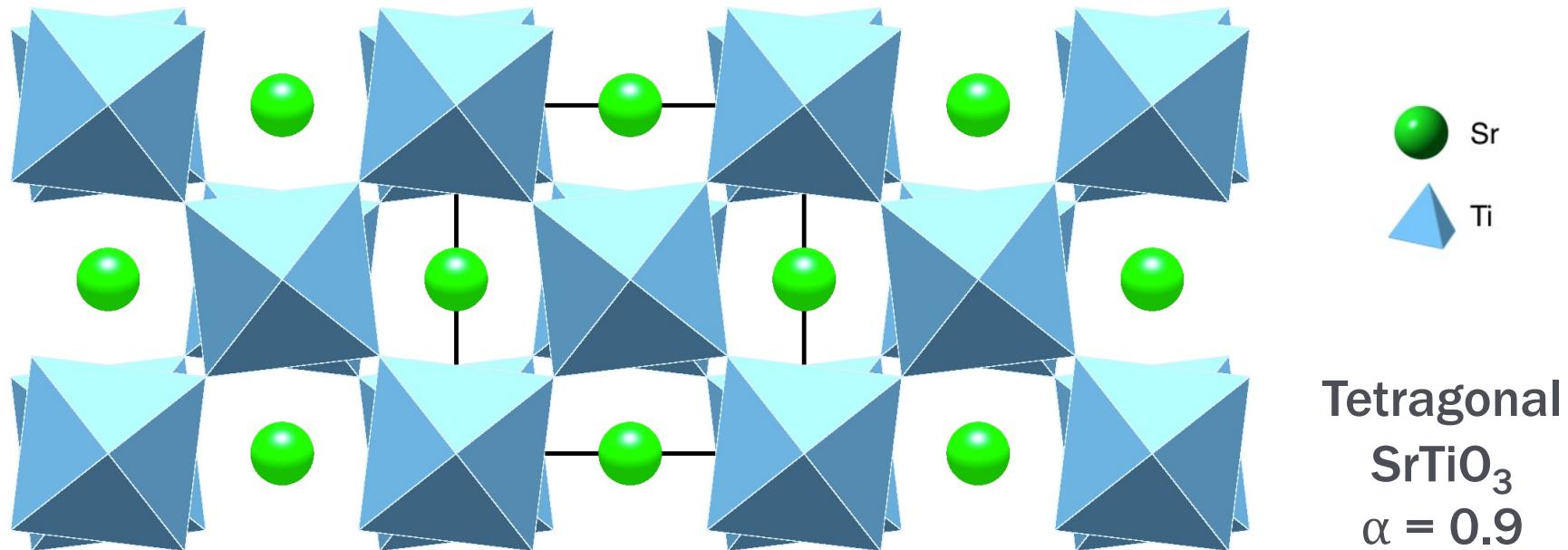


The three different sized elements results in structural “frustration”

If  $\alpha \sim 1$  the three building blocks have compatible sizes and the cubic perovskite structure should be stable

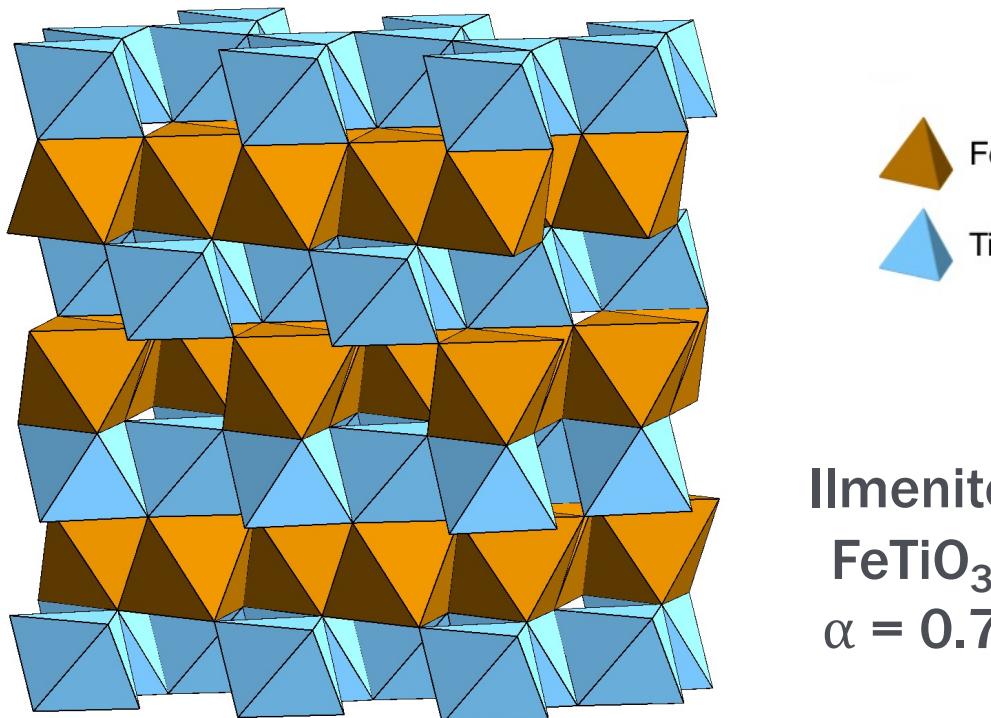
## $\alpha < 1$ – Octahedral Tilting

A-site is too small to fit in the cuboctahedral cavity.  
The octahedral cages tilt to form lower symmetry  
phases (e.g. tetragonal or orthorhombic)



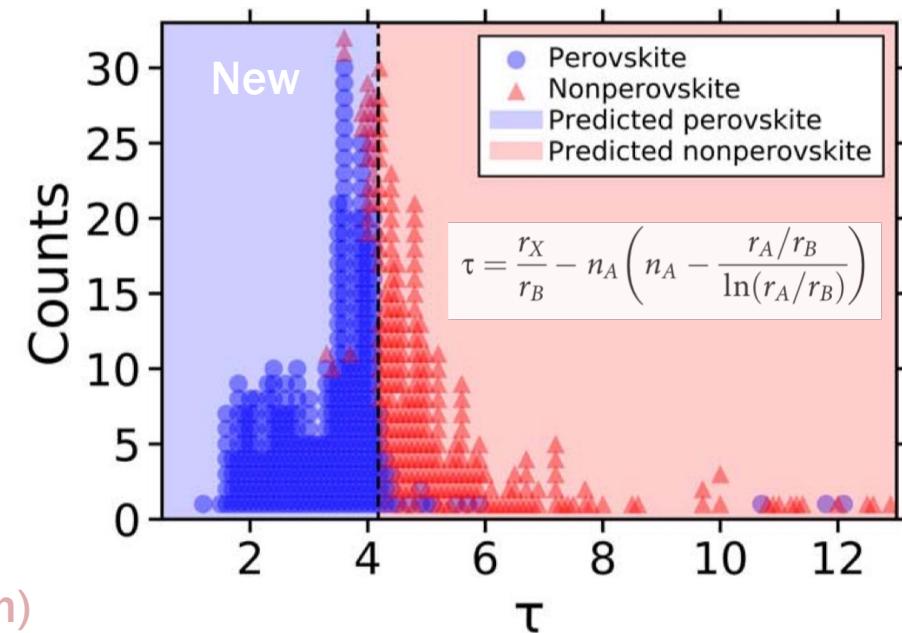
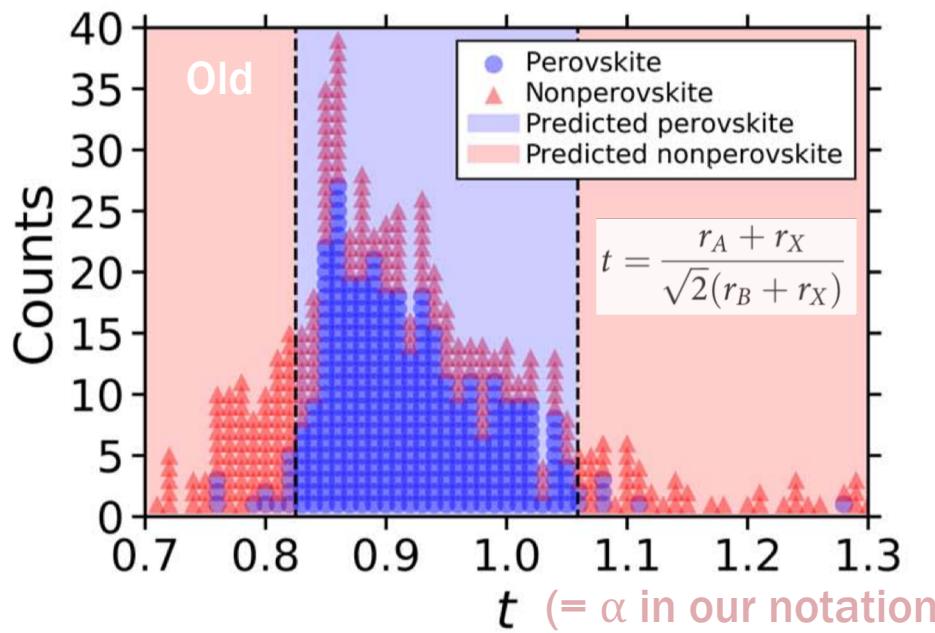
## $\alpha \ll 1$ – Non-Perovskite Phases

Size mismatch is too large to maintain a perovskite-like structure. Edge or face-sharing octahedral networks become favoured



# Tolerance Factor Developments

Recent research has tried to make more robust models incorporating variable ionic radii<sup>1</sup>, molecular components<sup>2</sup>, and statistical analysis<sup>3</sup>

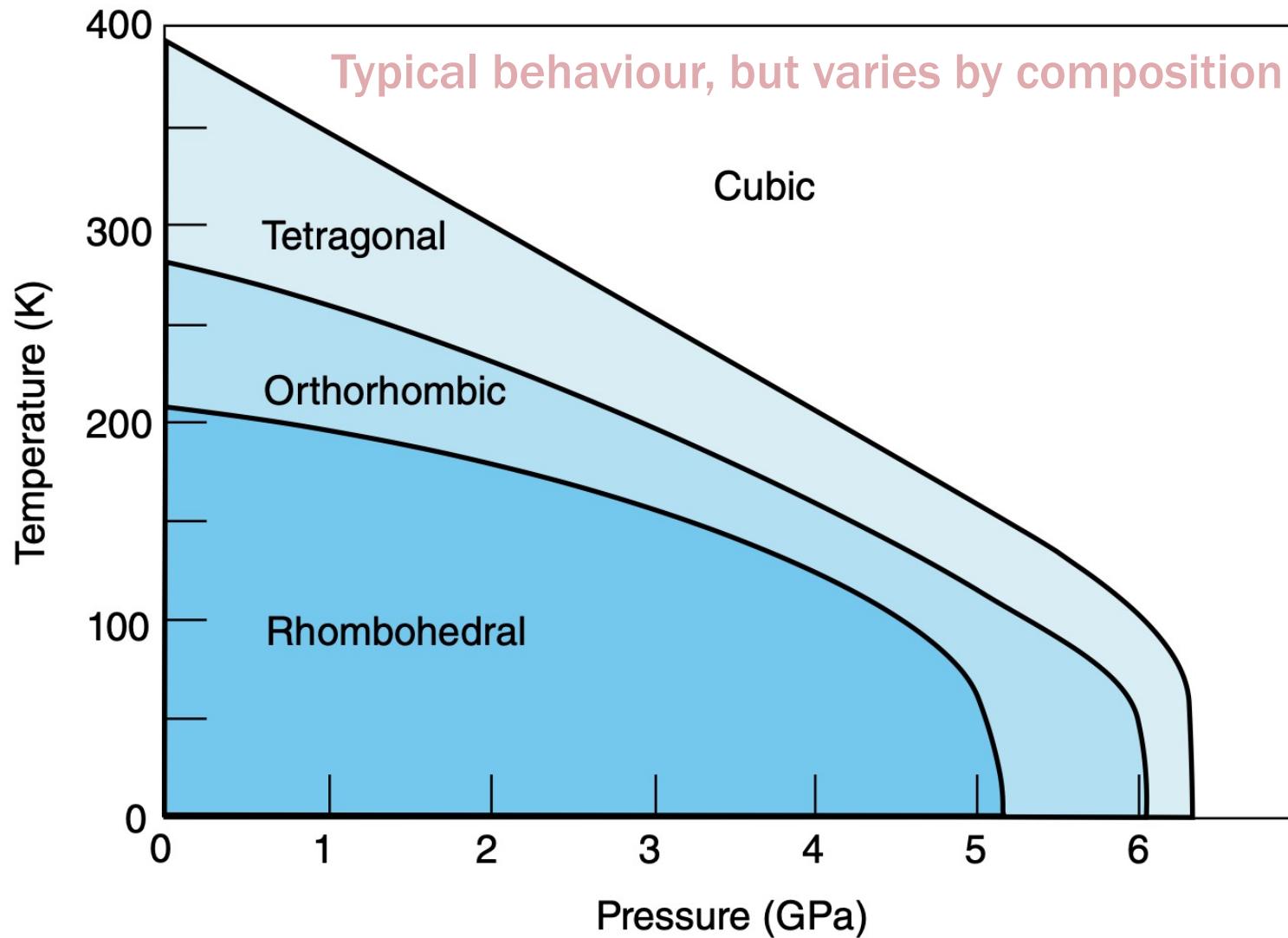


<sup>1</sup>W. Travis et al, Chem. Sci. 7, 4548 (2016); <sup>2</sup>G. Kieslich et al, Chem. Sci. 6, 3430 (2015); <sup>3</sup>C. J. Bartel et al, Science Advances 5, eaav0693 (2020)

# Structural Case Study of Perovskites

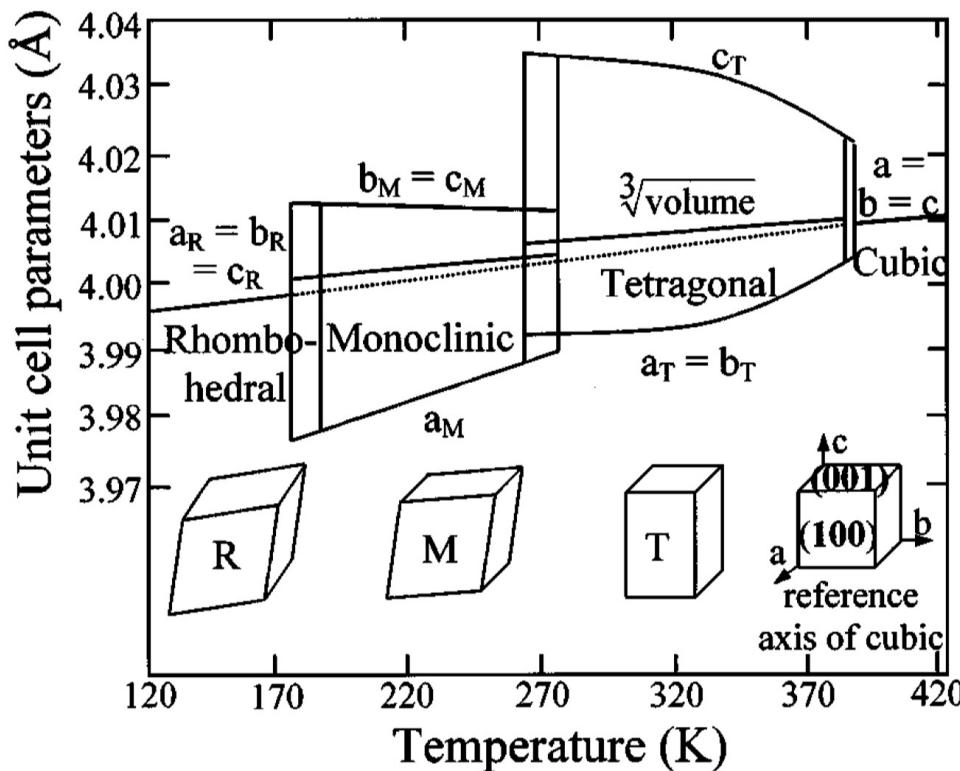
1. Geometry of perovskite structure
2. Radius ratio rules for  $\text{ABX}_3$
3. Polymorphism and phase transitions

# Perovskite Phase Transitions



# Perovskite Phase Transitions

The cubic perovskite phase is usually formed at high temperature. Cooling results in a series of phase transitions with increasing distortions

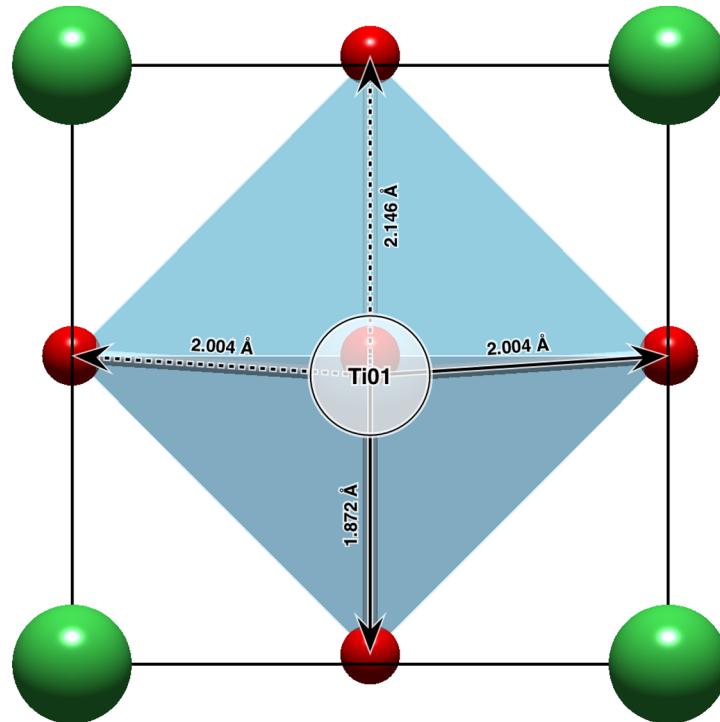


Change in the structural parameters of  $\text{BaTiO}_3$  from X-ray diffraction measurements

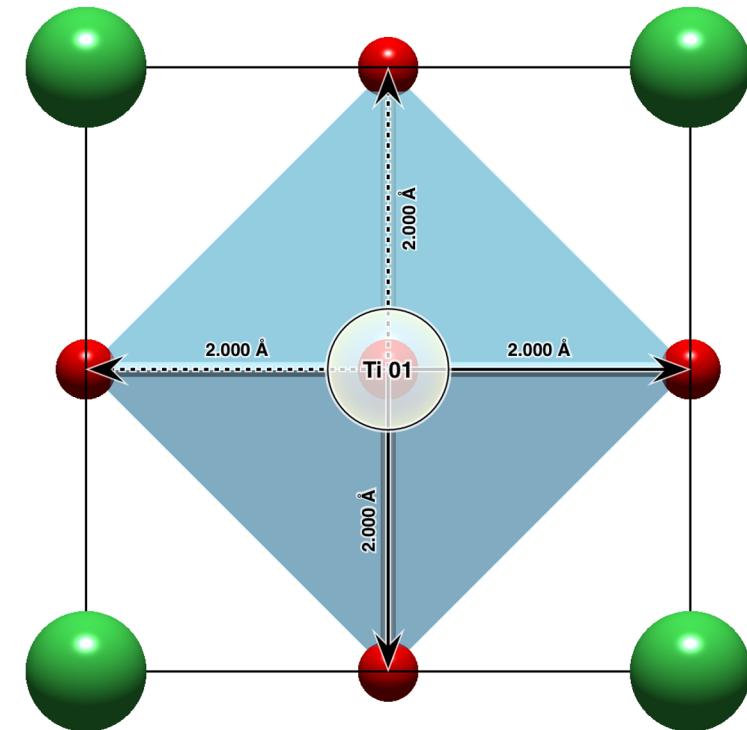
M. K. Lee et al, Appl. Phys. Lett.  
77, 3547 (2000)

# Perovskite Phase Transitions

$278 \text{ K} < T < 393 \text{ K}$  tetragonal (left) and  
 $T > 393 \text{ K}$  cubic (right) structures of  $\text{BaTiO}_3$



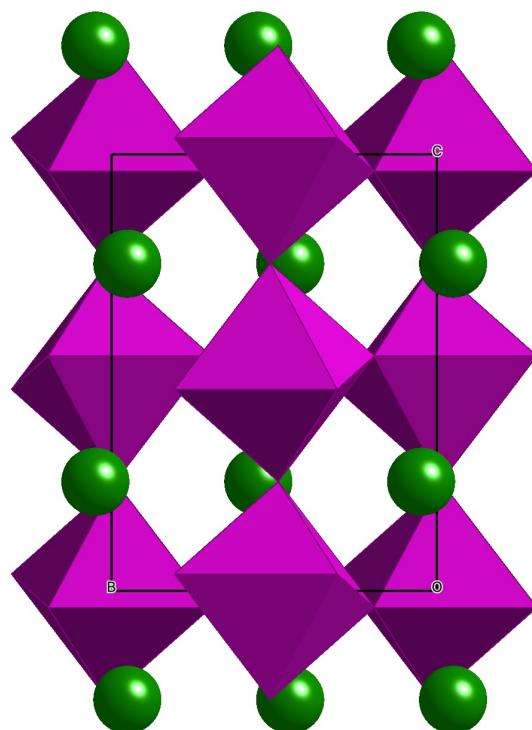
$$\begin{aligned}a &= b = 3.999 \text{ \AA} \\c &= 4.018 \text{ \AA}\end{aligned}$$



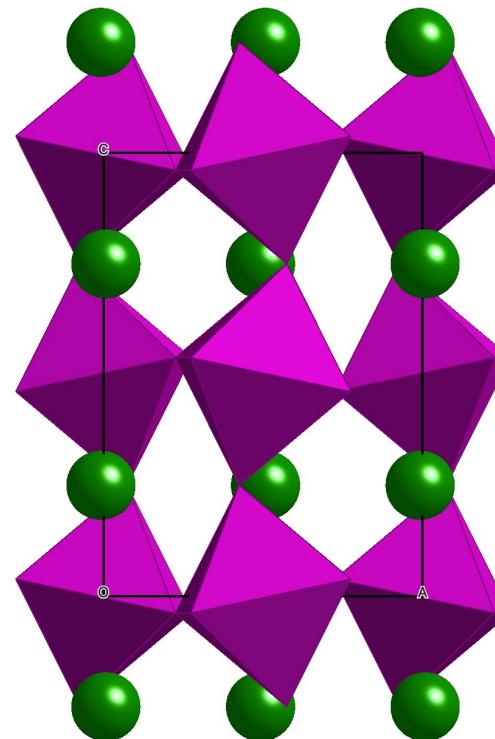
$$a = b = c = 3.996 \text{ \AA}$$

# Perovskite Phase Transitions

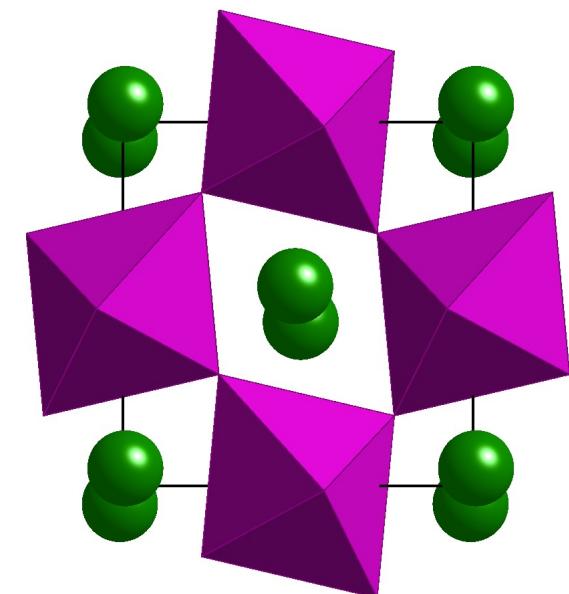
Room temperature orthorhombic structure of  
 $\text{LaMnO}_3$  with a complex octahedral tilting pattern



<100> view

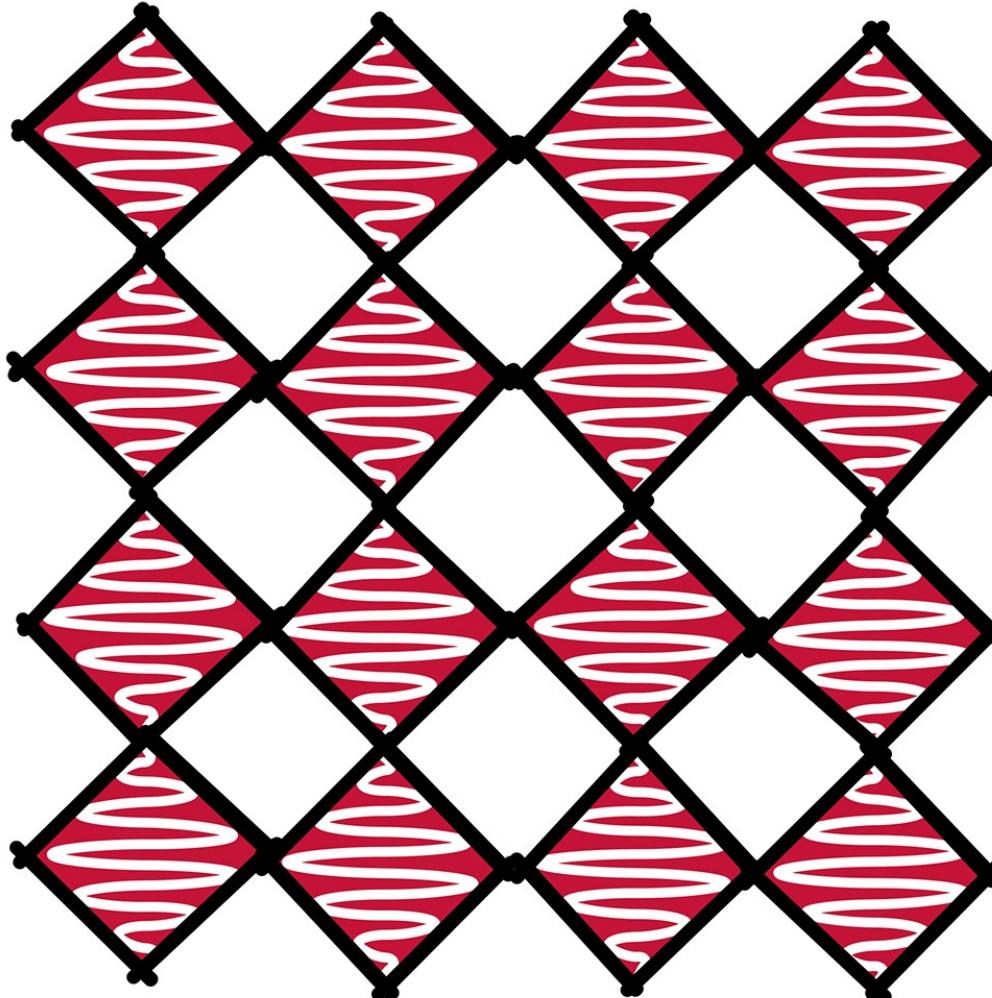


<010> view



<001> view

# Perovskite Phase Transitions

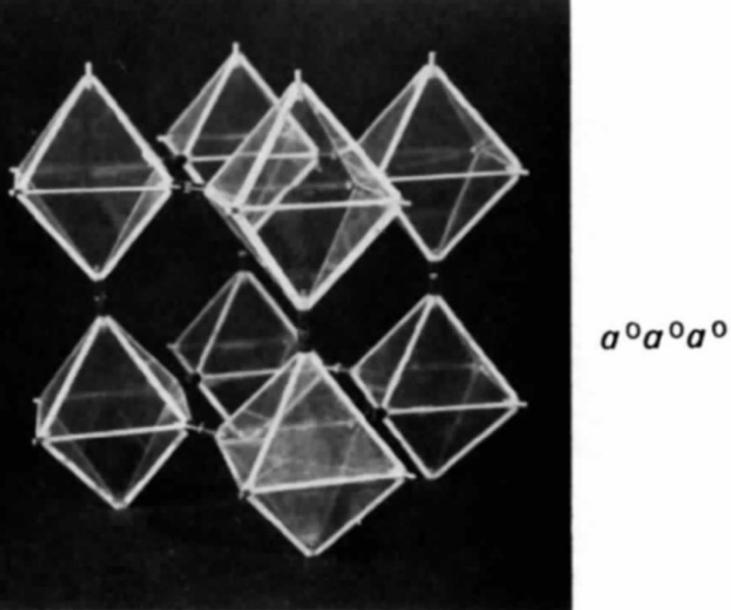


High flexibility of  
a corner-sharing  
network

Cooperative  
structural  
distortion

# Description of Perovskite Polymorphs

Distortions in perovskites are often geometrically simple, but difficult to describe using standard crystallographic language

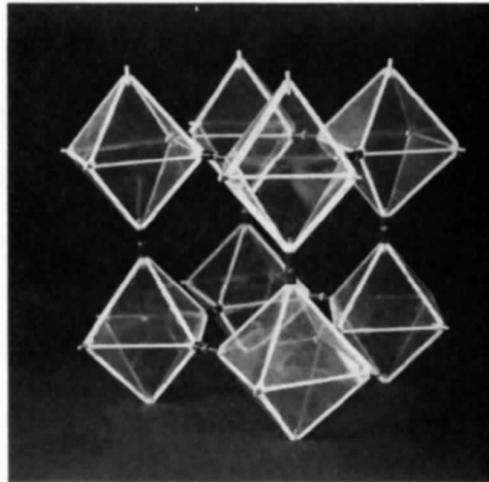
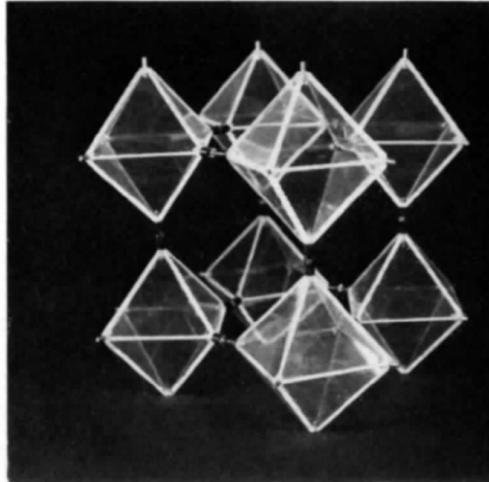


## Glazer Perovskite Tilting Notation

- Sequence of three axes
- Superscript: 0 (no tilt);  
+ (in phase tilt); - (out of phase)
- Limitation: tilting amplitude and octahedral distortions are not described

$a^0a^0a^0$  = perfect cubic phase

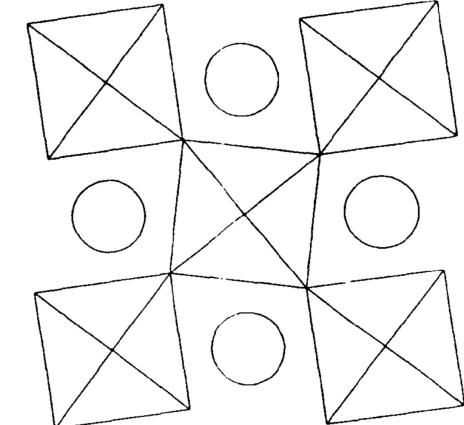
# Examples of Glazer Notation



1 tilt (tetragonal)

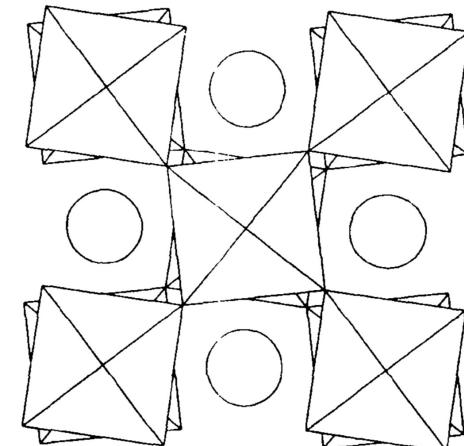
In phase  
along the c axis

$\langle 001 \rangle$



1 tilt (tetragonal)

Out-of-phase  
along the c axis

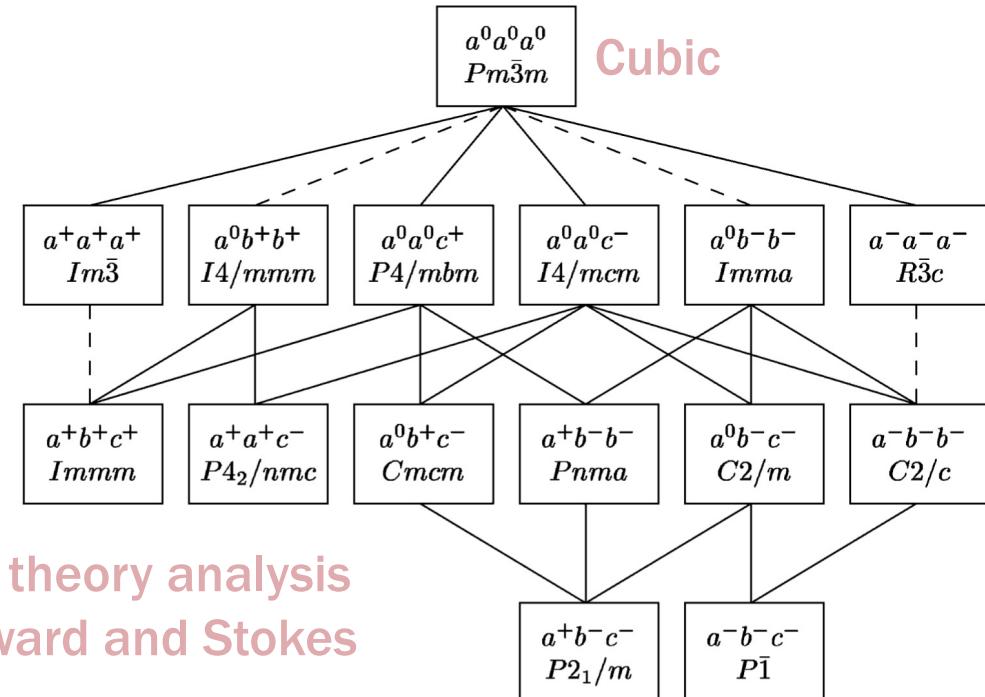


# Advanced: Glazer Notation Applications

Search of all tilting patterns and application of group theory to phase transition sequences

Tilt system number	Tilt system symbol
Three-tilt systems	
1	$a^+b^+c^+$
2	$a^+b^+b^+$
3	$a^+a^+a^+$
4	$a^+b^+c^-$
5	$a^+a^+c^-$
6	$a^+b^+b^-$
7	$a^+a^+a^-$
8	$a^+b^-c^-$
9	$a^+a^-c^-$
10	$a^+b^-b^-$
11	$a^+a^-a^-$
12	$a^-b^-c^-$
13	$a^-b^-b^-$
14	$a^-a^-a^-$
Two-tilt systems	
15	$a^0b^+c^+$
16	$a^0b^+b^+$
17	$a^0b^+c^-$
18	$a^0b^+b^-$
19	$a^0b^-c^-$
20	$a^0b^-b^-$
One-tilt systems	
21	$a^0a^0c^+$
22	$a^0a^0c^-$
Zero-tilt systems	
23	$a^0a^0a^0$

Possible phase transitions



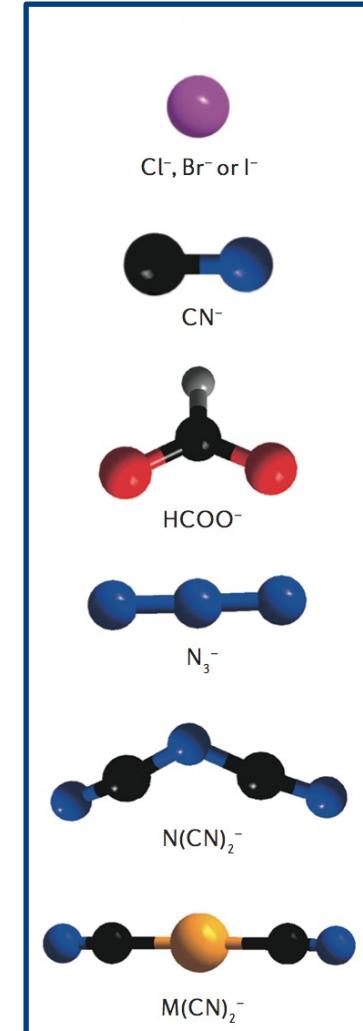
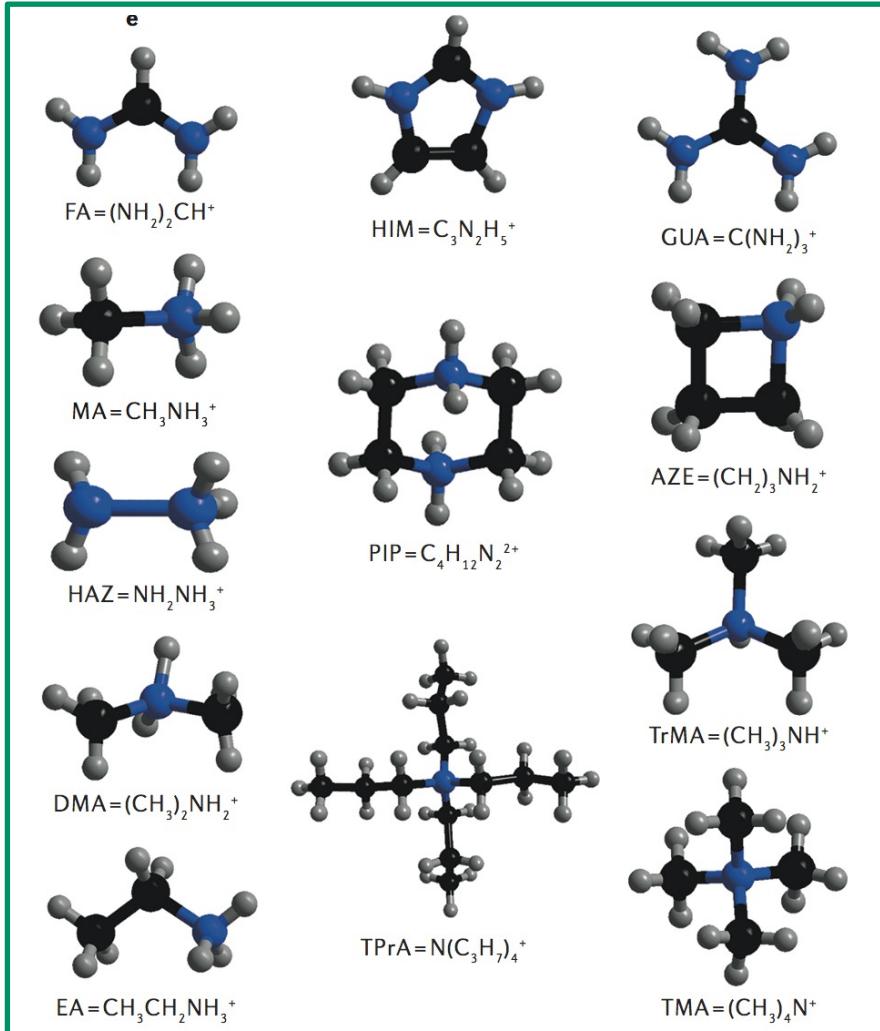
Group theory analysis  
by Howard and Stokes

P. M. Woodward, Acta. Cryst. B 53, 32 (1997)

C. J. Howard and H. T. Stokes, Acta Cryst. B 54, 782 (1998)

# Growing Family of Hybrid Perovskites

Molecular  
**A<sup>+</sup> site**  
Longer chains  
lead to 0-2D  
structures



# Is “X” a Perovskite?

**COMMENT**

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## What Defines a Perovskite?

*Joachim Breternitz\* and Susan Schorr\**

From our point of view, three major points must be obeyed for a material to be called a perovskite:

- 1) A stoichiometry of  $ABX_3$ , or at least a ratio A:B:X of 1:1:3
- 2) The B-cation coordination needs to be octahedral (or distorted octahedra)
- 3) The  $[BX_6]$  octahedra need to be organized in an all-corner sharing 3D network

# Is “X” a Perovskite?

## What Defines a Halide Perovskite?



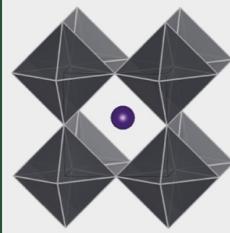
Cite This: ACS Energy Lett. 2020, 5, 604–610



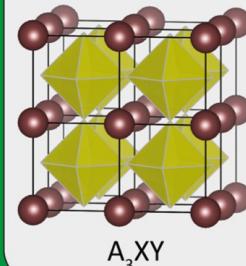
Read Online

Metal halide perovskites

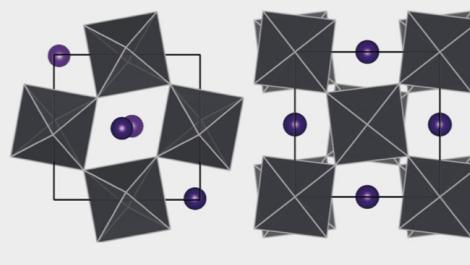
a) Cubic perovskites



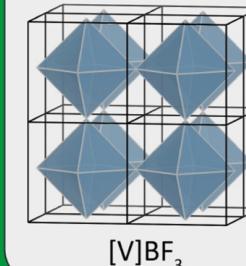
b) Anti perovskites



c) Distorted perovskites

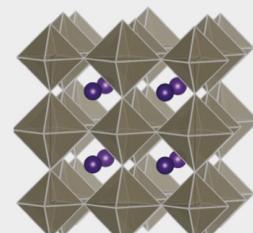
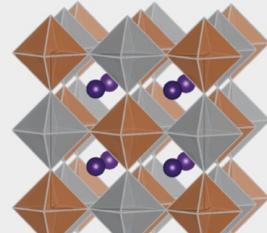


d) Vacant perovskites

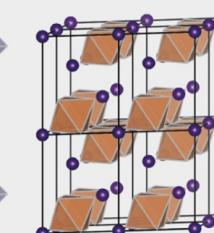
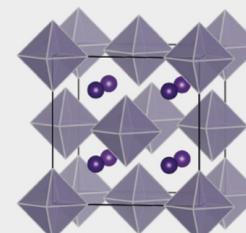


e)

Ordered perovskites



f) Vacancy ordered perovskites



# Is “X” a Perovskite?

## What Defines a Halide Perovskite?



Cite This: ACS Energy Lett. 2020, 5, 604–610

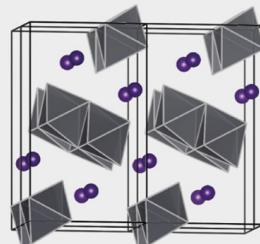


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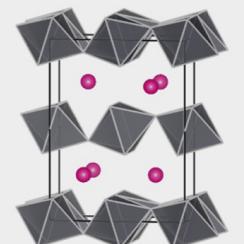
Not metal halide perovskites

a)

$ABX_3$  post-perovskites



1D



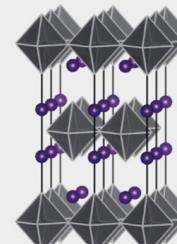
2D



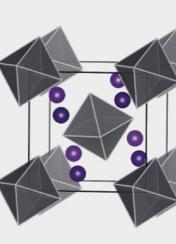
1D

b)

A-B(II)-X alternative stoichiometries



$Cs_2PbX_4$



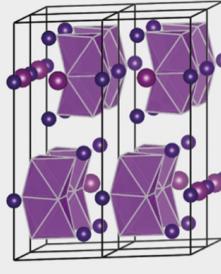
$Cs_4PbX_6$



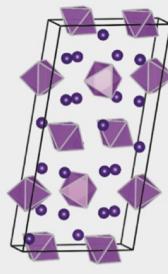
$CsPb_2X_5$

c)

Ternary bismuth halides



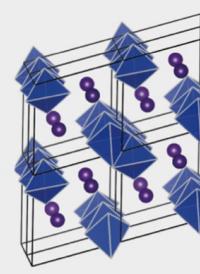
$Cs_3Bi_2I_9$



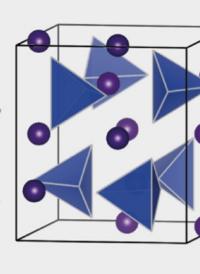
$Cs_3BiX_6$

d)

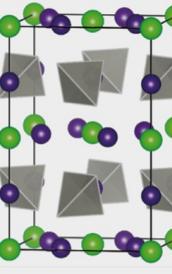
Tetrahedral ternary (transition) metal halides



$A_3B_2X_5$



M(I)



$A_2BX_3$



M(II)

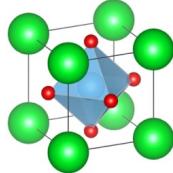
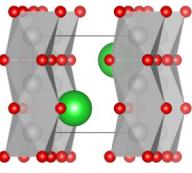
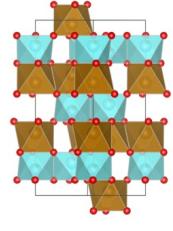
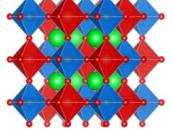
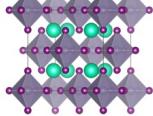
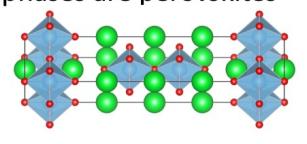
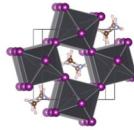
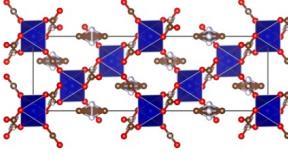


$A_2BX_4$

# Is “X” a Perovskite?



Robert Palgrave  
@Robert\_Palgrave

	Structural Purity			
Compositional Purity		STRUCTURE PURIST <i>Only corner sharing BX<sub>6</sub> octahedra</i>	STRUCTURE NEUTRAL <i>Let's try and keep the coordination numbers about right</i>	STRUCTURE REBEL <i>Anything goes!</i>
	COMPOSITION PURIST <i>ABX<sub>3</sub> only A and B are metallic elements</i>	<i>Hardline perovskite conservative</i> “SrTiO <sub>3</sub> is a perovskite” 	“Hexagonal perovskites are perovskites” 	“Ilmenite is a perovskite” 
	COMPOSITION NEUTRAL <i>ABX<sub>3</sub> is more of a guideline</i>	“Double perovskites are perovskites” 	“Cs <sub>2</sub> SnI <sub>6</sub> is a perovskite” 	“Ruddlesden Popper phases are perovskites” 
	COMPOSITION REBEL <i>Anything goes!</i>	<i>All PV researchers</i> “CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> is a perovskite” 	“A MOF is a perovskite” 	<i>Radical perovskite anarchy</i> 

# Summary: Crystals 2

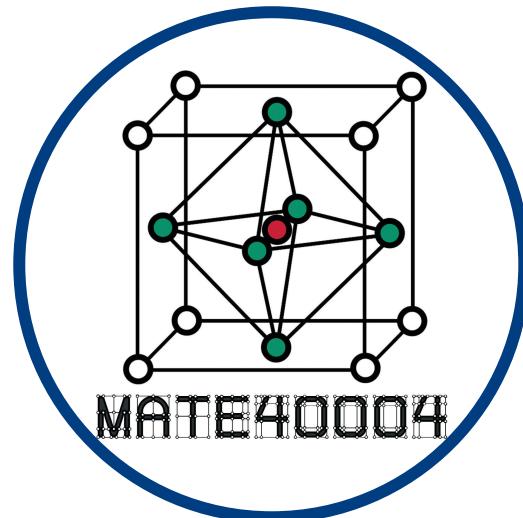
## Class outcomes:

- Describe the perovskite crystal structure
- Understand the extension of radius ratio principles to more complex crystals
- Assess the feasibility of a hypothetical perovskite material composition based on size and charge requirements

MATE40004 – Structure 1

**Crystallography**  
**G. Diffraction**

**Professor Aron Walsh**  
Department of Materials  
Imperial College London



<http://www.imperial.ac.uk/people/a.walsh>

# Day 1: Building Blocks of Crystals

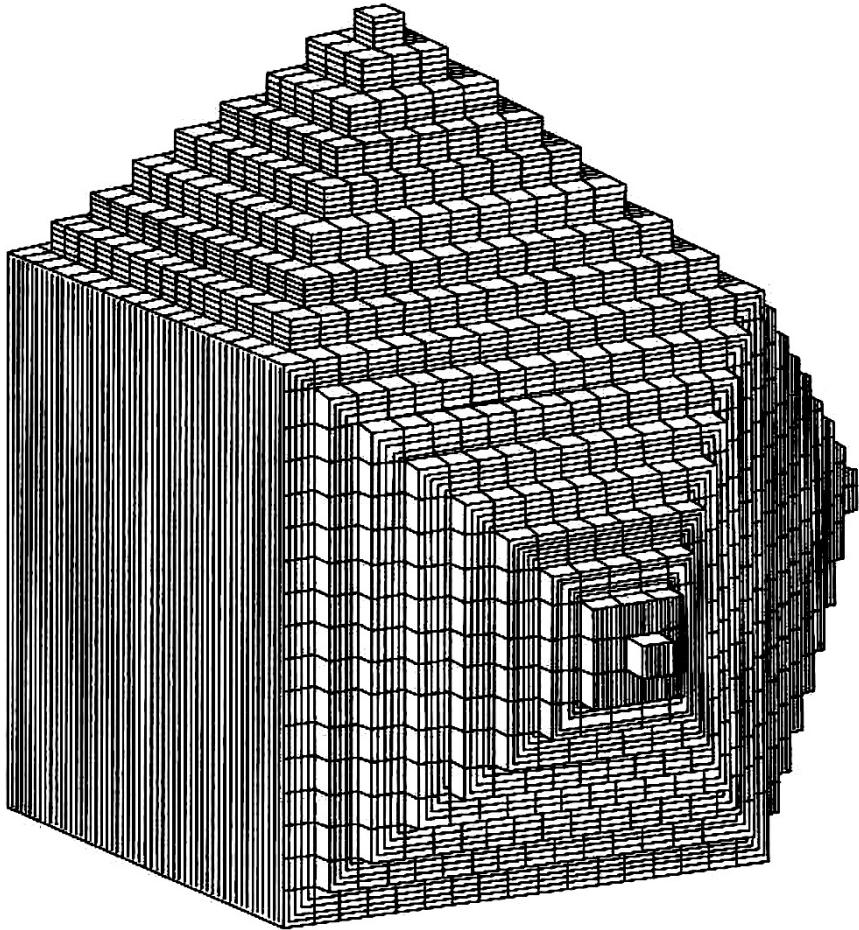


Image: Kittel, Solid-State Physics (1953)

The structure of a crystalline material can be described by a unit cell repeated by translational symmetry

A macroscopic crystal will contain more than  $10^{20}$  unit cells

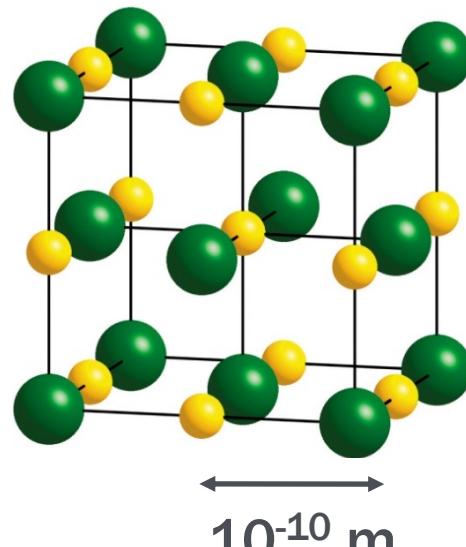
# Why X-ray Crystallography?

Macroscopic  
Crystal



$10^{-1}$  m

Microscopic  
Unit Cell



$10^{-10}$  m

Electromagnetic  
Spectrum

Radio

$\lambda = 10^3$  m

Microwave

$\lambda = 10^{-2}$  m

Visible

$\lambda = 10^{-6}$  m

X-ray

$\lambda = 10^{-10}$  m

Gamma-ray

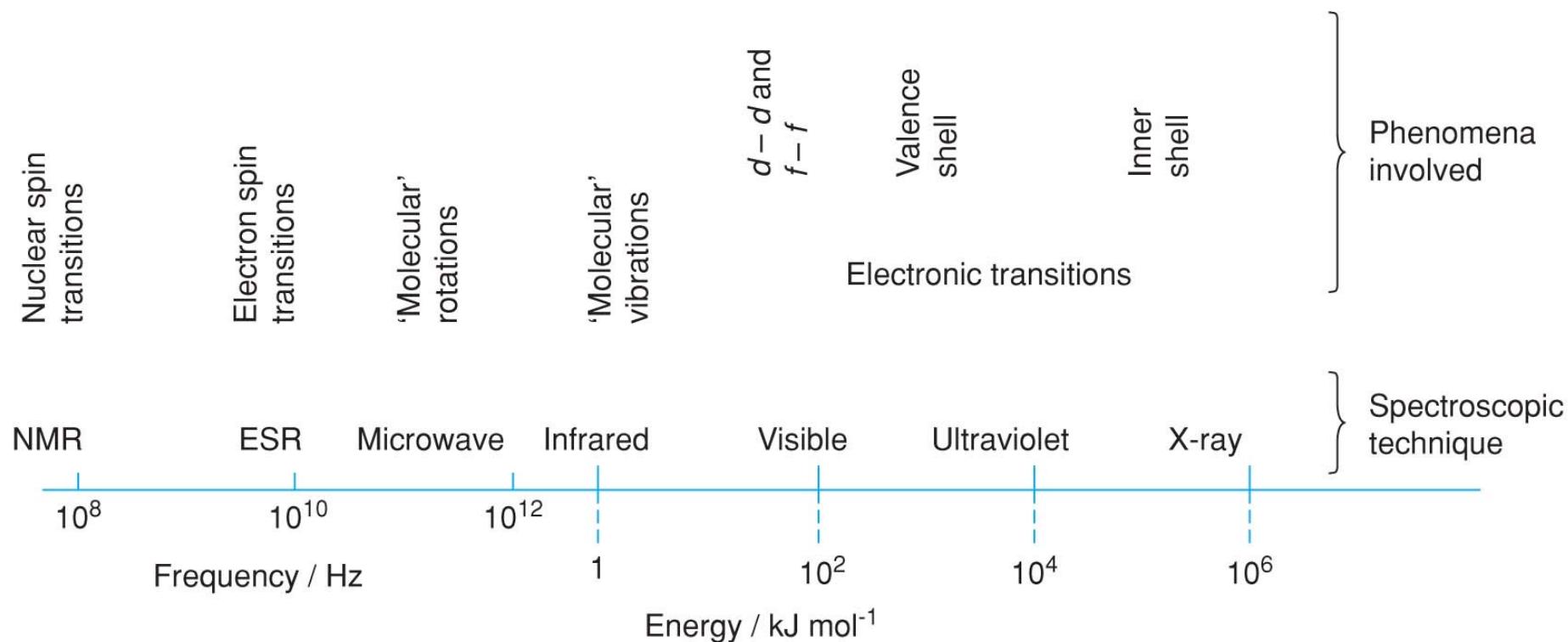
$\lambda = 10^{-12}$  m

The wavelength of X-rays is comparable to the interatomic spacing in crystals



# Probing the Structure of Materials

Many techniques probe solids using absorption or emission of radiation: spectroscopy



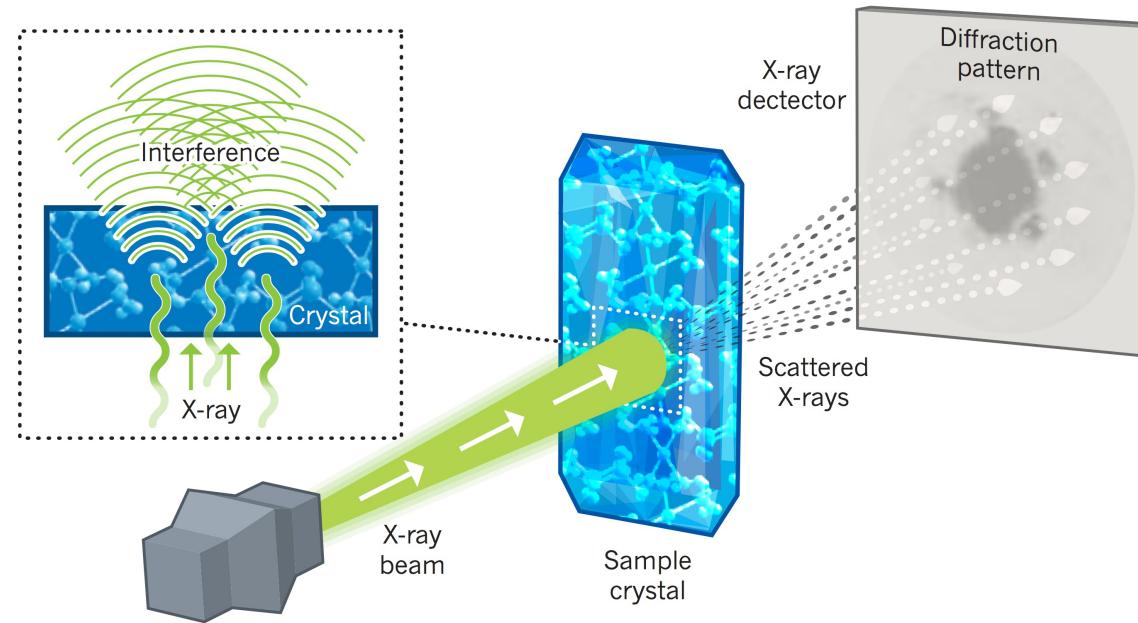
# Diffraction Techniques

Wavelength of incoming radiation is fixed (monochromatic) and intensity is measured  
diffraction is distinct from spectroscopy

## Why use X-rays?

- Spacing between atoms in crystals ( $1\text{--}3 \text{ \AA}$ ) is similar to the wavelength of an X-ray
- Electron clouds of atoms scatter X-rays with intensity proportional to the atomic number ( $Z$ )

# Early History of X-ray Diffraction

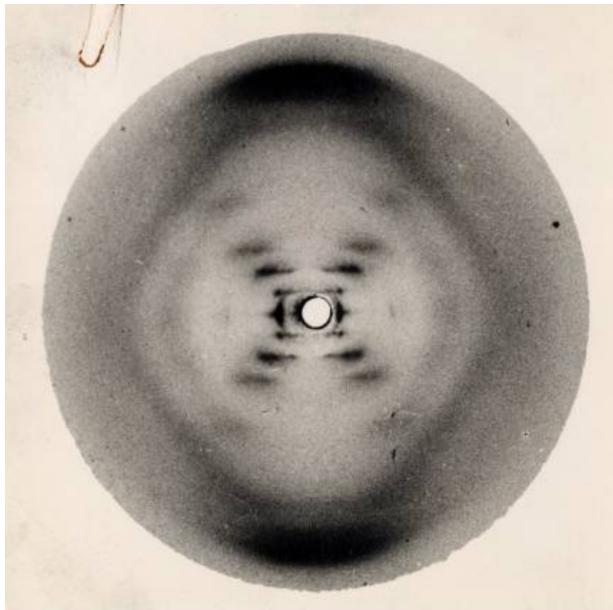


- (1895) Röntgen – Discovery of X-rays
- (1912) von Laue – X-ray diffraction of  $\text{CuSO}_4$
- (1912) Braggs – Law of diffraction
- (1913) Braggs – Complete structure of  $\text{NaCl}$

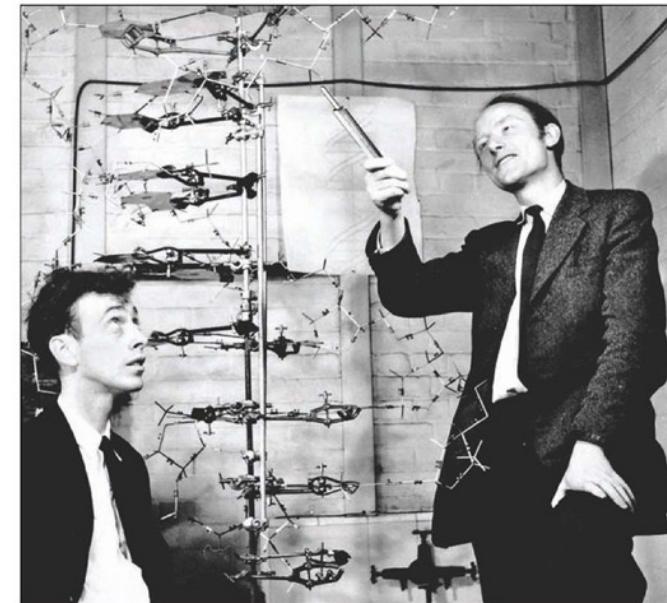


# Double Helix of DNA

The structure of DNA was an early success of X-ray crystallography (and physical science) – Nature (1953)



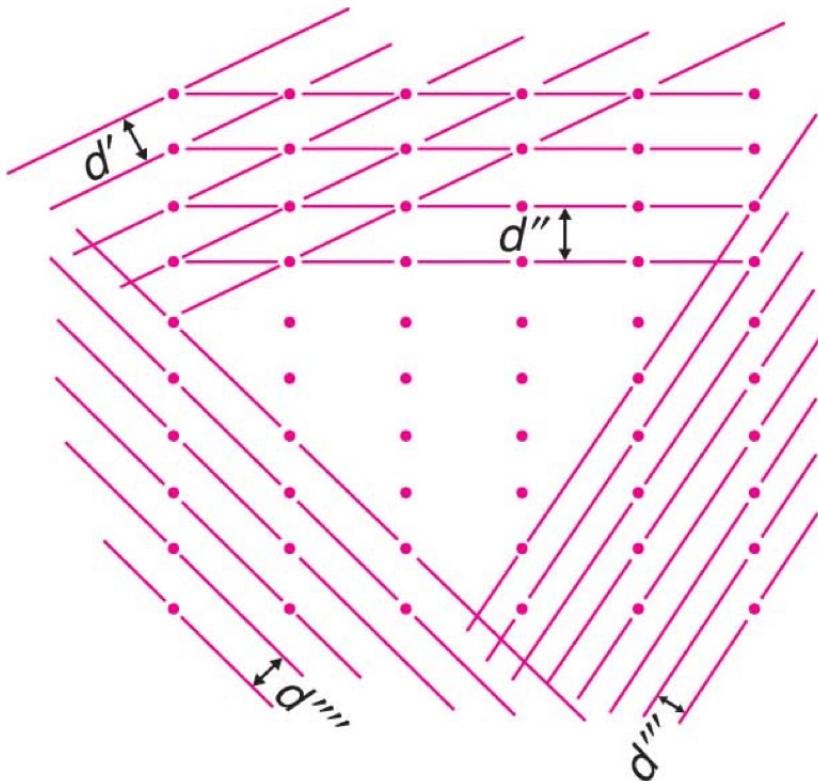
Rosalind Franklin's X-ray image of DNA  
("photo 51") – Kings College (1952)



Watson and Crick at  
University of Cambridge

# Distance Between Lattice Planes ( $hkl$ )

Recall, a crystal has an infinite series of parallel lattice planes. Each plane is separated by  $d_{hkl}$



For a cubic, tetragonal, or orthorhombic cell:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Lattice vectors

More complex expressions exist for other crystal systems

# $d_{hkl}$ Spacing (for Reference Only)

Crystal System	$d_{hkl}$
Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$
Triclinic	$\frac{1}{d^2} = h^2 \frac{b^2 c^2 \sin^2 \alpha}{V^2} + k^2 \frac{a^2 c^2 \sin^2 \beta}{V^2} + l^2 \frac{a^2 b^2 \sin^2 \gamma}{V^2}$ $+ 2hk \frac{abc^2 (\cos \alpha \cos \beta - \cos \gamma)}{V^2} + 2kl \frac{a^2 bc (\cos \beta \cos \gamma - \cos \alpha)}{V^2}$ $+ 2lh \frac{ab^2 c (\cos \gamma \cos \alpha - \cos \beta)}{V^2}$

# $d_{hkl}$ Spacing Values

$a = 4 \text{ (\AA)}$	$d_{hkl}$
(100)	4.0 Å
(110)	2.8 Å
(111)	2.3 Å

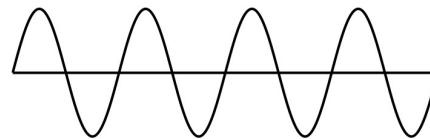
$a = 6, b = 3, c = 2 \text{ (\AA)}$	$d_{hkl}$
(100)	6.0 Å
(110)	2.6 Å
(111)	1.6 Å

Higher Miller index [ $h+k+l$ ] = shorter  $d$  spacing

# Refresh: Wave Interference

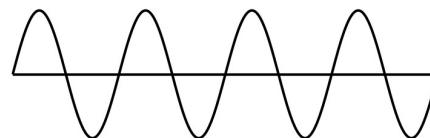
Constructive  
Interference

Wave 1



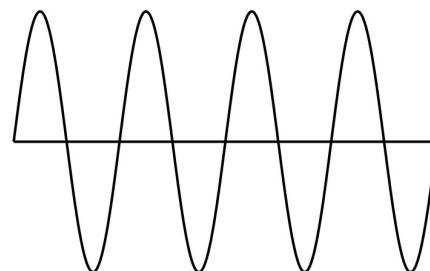
+

Wave 2

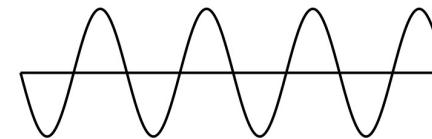


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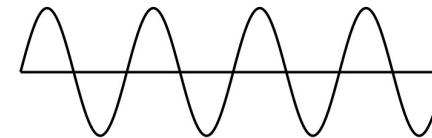
Combined  
Wave



Destructive  
Interference



+

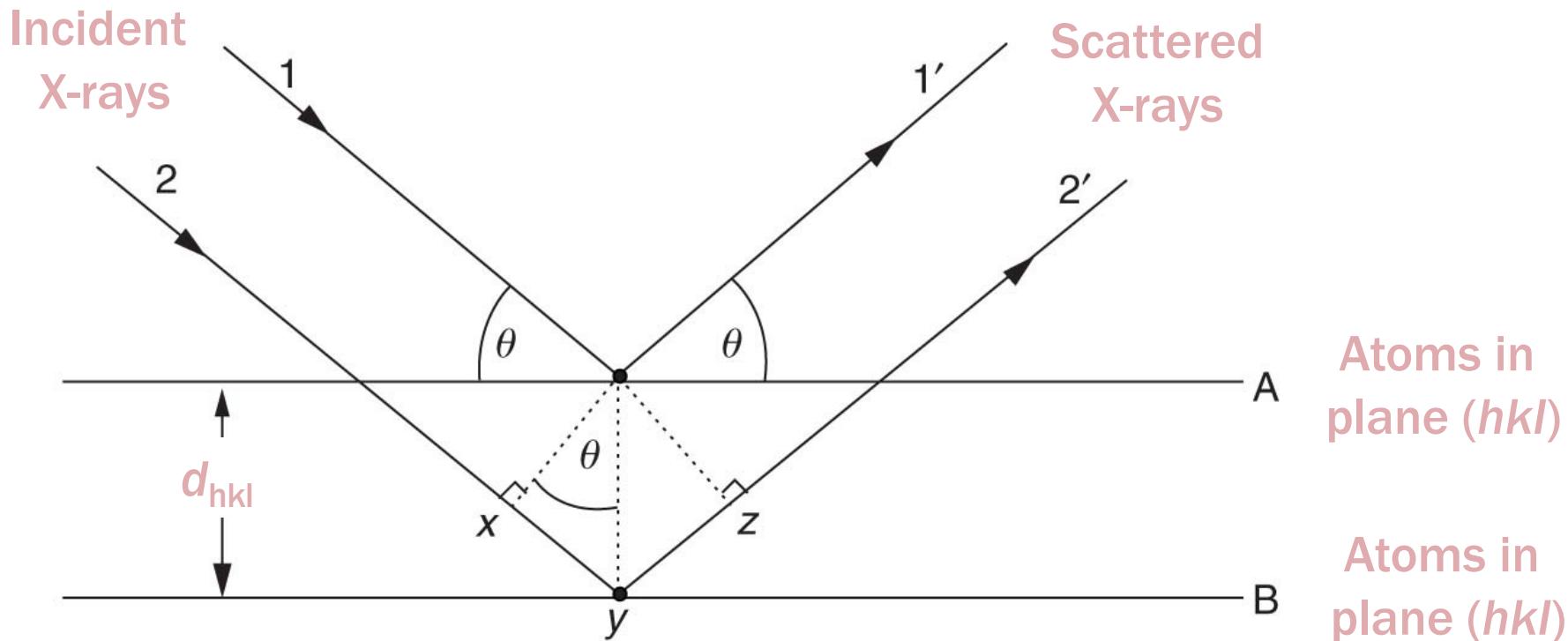


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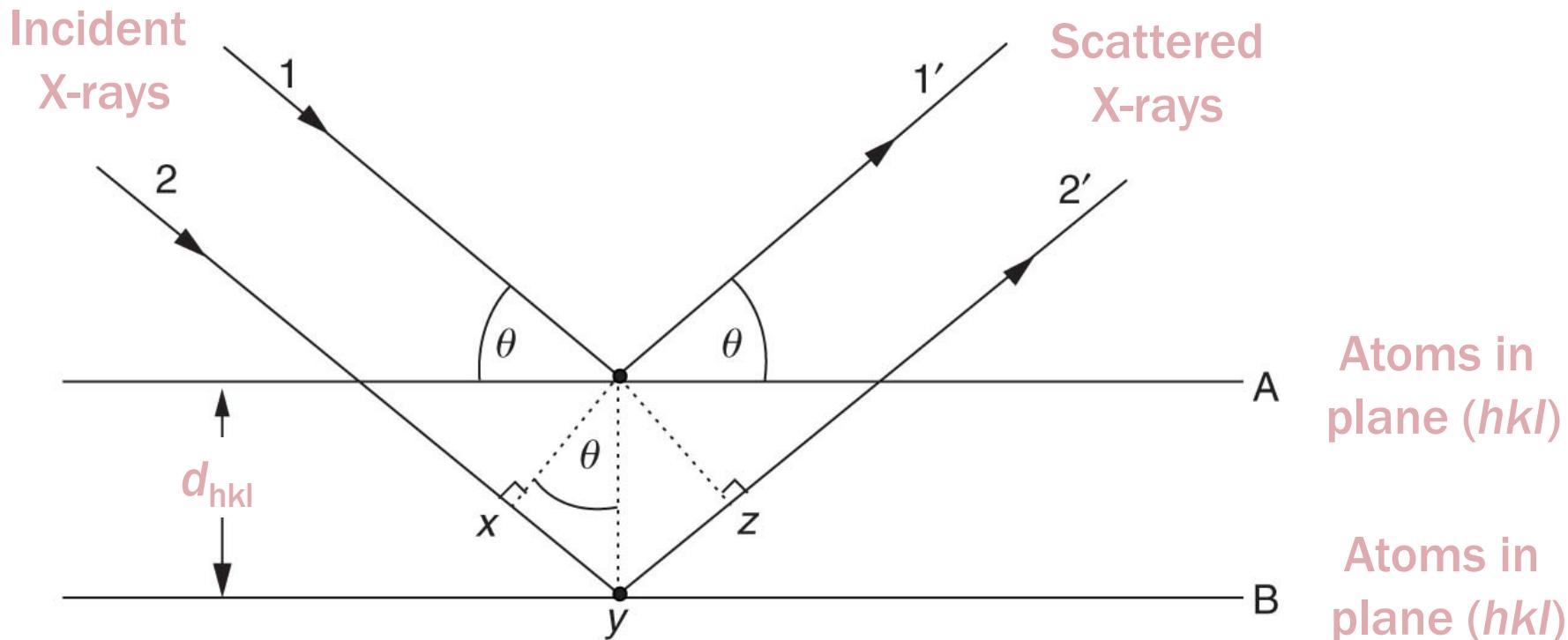
# Bragg's Law (or Condition)

Scattering of X-rays (1 and 2) will be in phase if the extra distance travelled by 2 is an integer of X-ray wavelengths ( $\lambda$ )



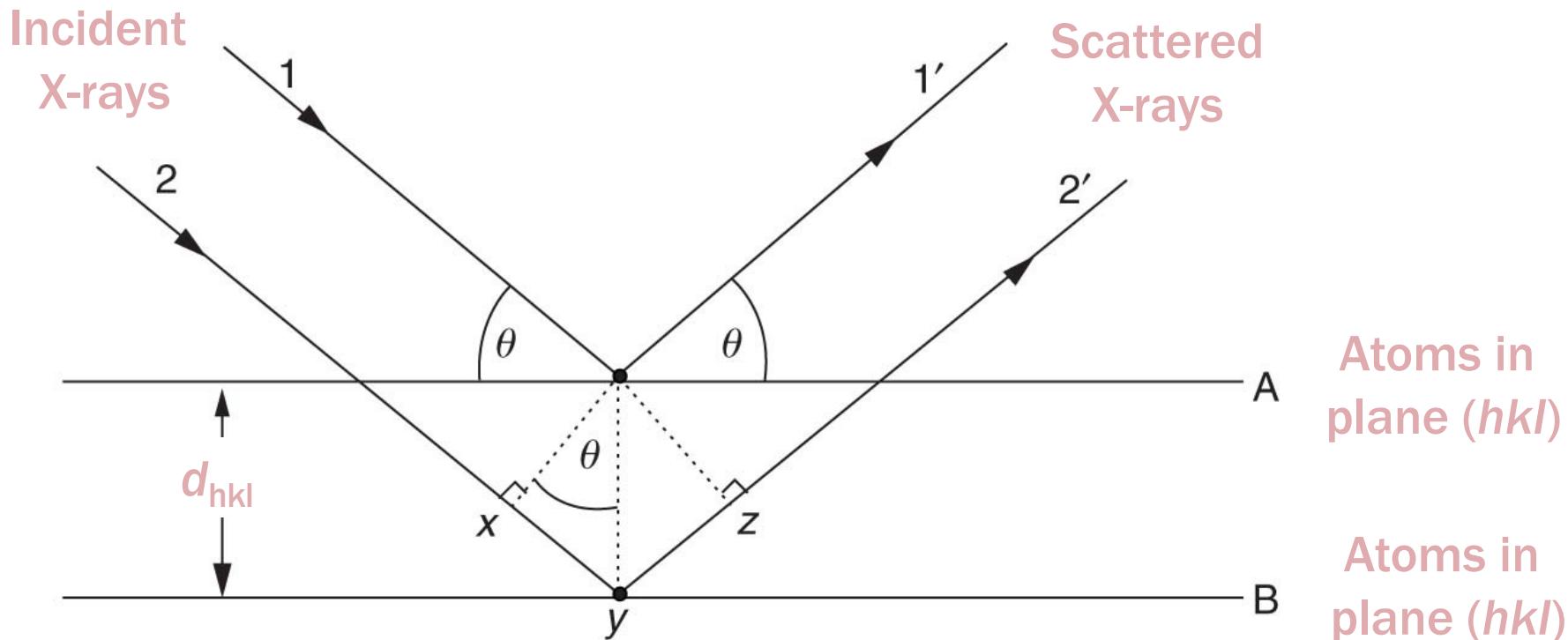
# Bragg's Law

$$\text{Path difference} = xy + yz = 2d_{hkl} \sin\theta = n\lambda$$



# Bragg's Law

Bragg's Law relates  $d$ -spacing, angles of diffraction maxima, and X-ray wavelength:  $2d_{hkl} \sin\theta = n\lambda$



# Using Bragg's Law, $2\Theta = 2\sin^{-1}(\lambda/2d)$

**Example:** Calculate diffraction angle ( $2\Theta$ ) for an X-ray wavelength of 1.5406 Å and lattice with  $a = 6$  Å

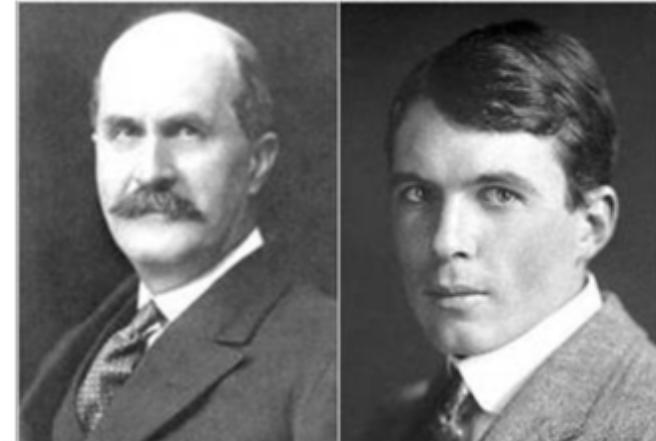
$(hkl)$	$d_{hkl}$	$2\Theta$
(100)	6.0 Å	14.75°
(110)	4.2 Å	20.92°
(111)	3.5 Å	25.70°
(544)	0.8 Å	151.52°

Note: Bragg angle is  $\Theta$ ; diffraction angle is  $2\Theta$   
(measured angle by which X-ray beam is turned)

# The Bragg Family

**William Henry Bragg (1862–1942)**

**William Laurence Bragg (1890–1971)**

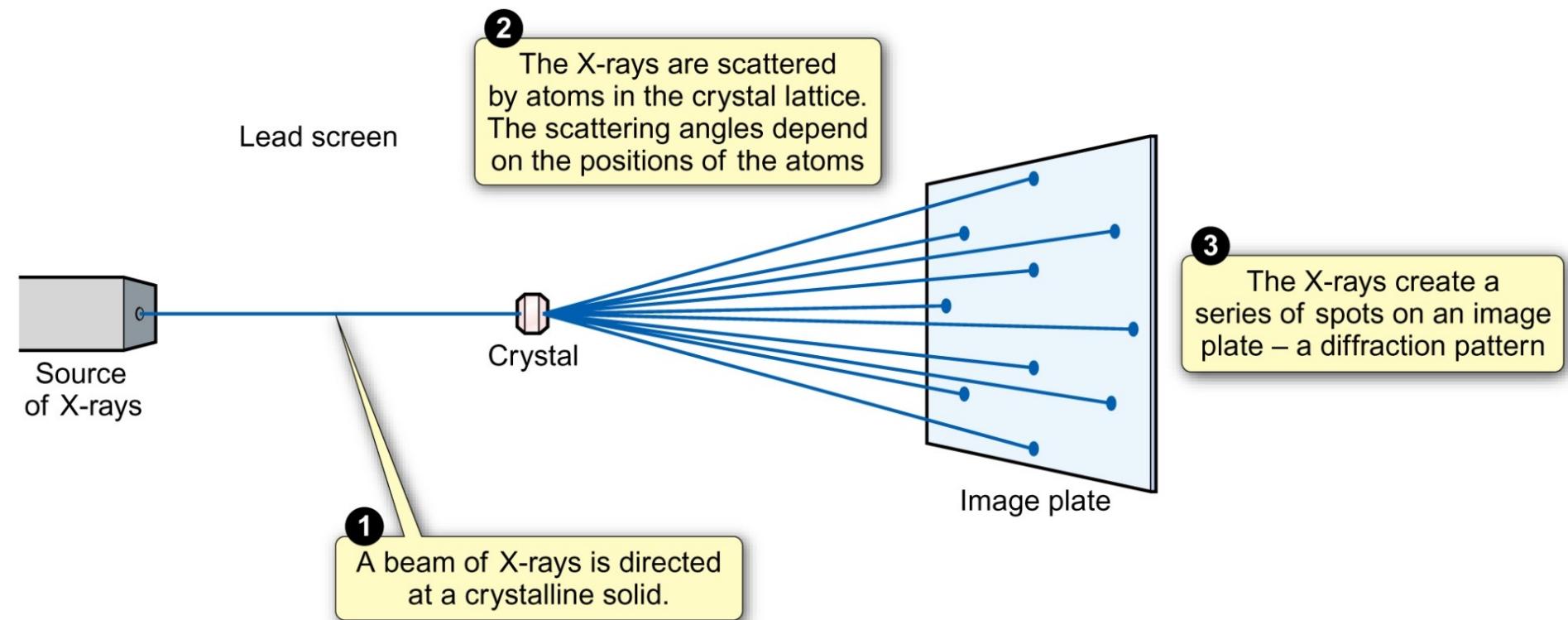


**Physics Nobel in 1915: "For their services in the analysis of crystal structure by means of X-ray" – WL Bragg was 25!**

Supporters of women in science: student Kathleen Lonsdale became 1<sup>st</sup> female professor at UCL and 1<sup>st</sup> female Fellow of the Royal Society



# X-ray Diffraction Experiment

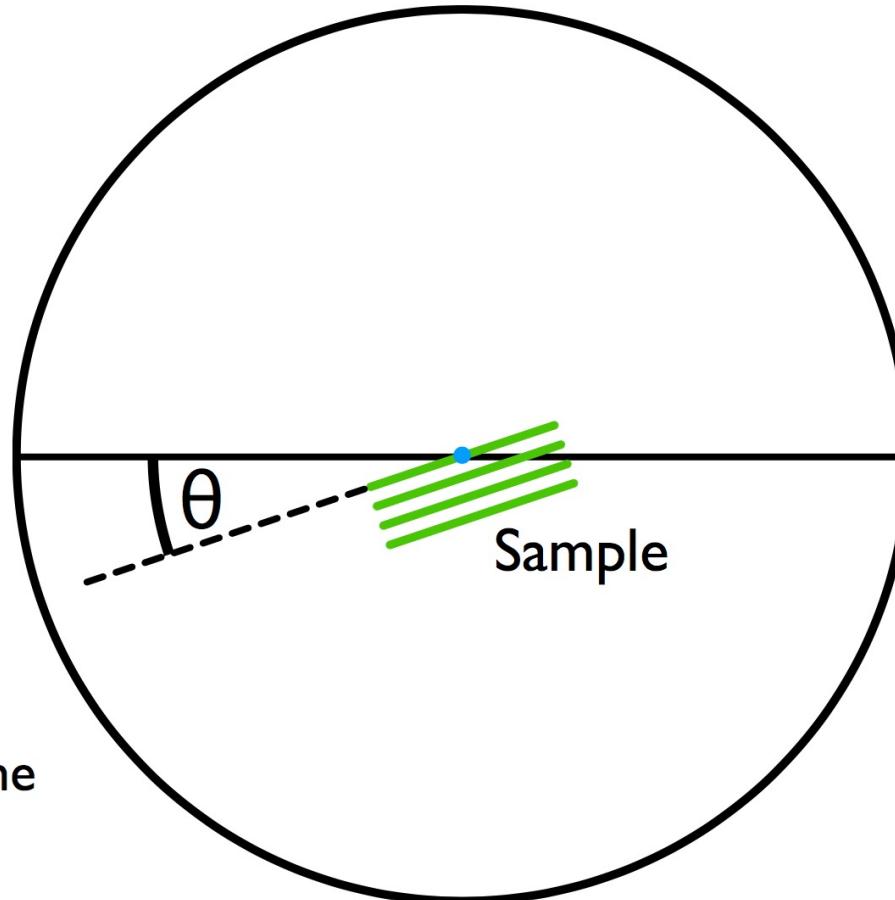


# Modern X-ray Diffractometer



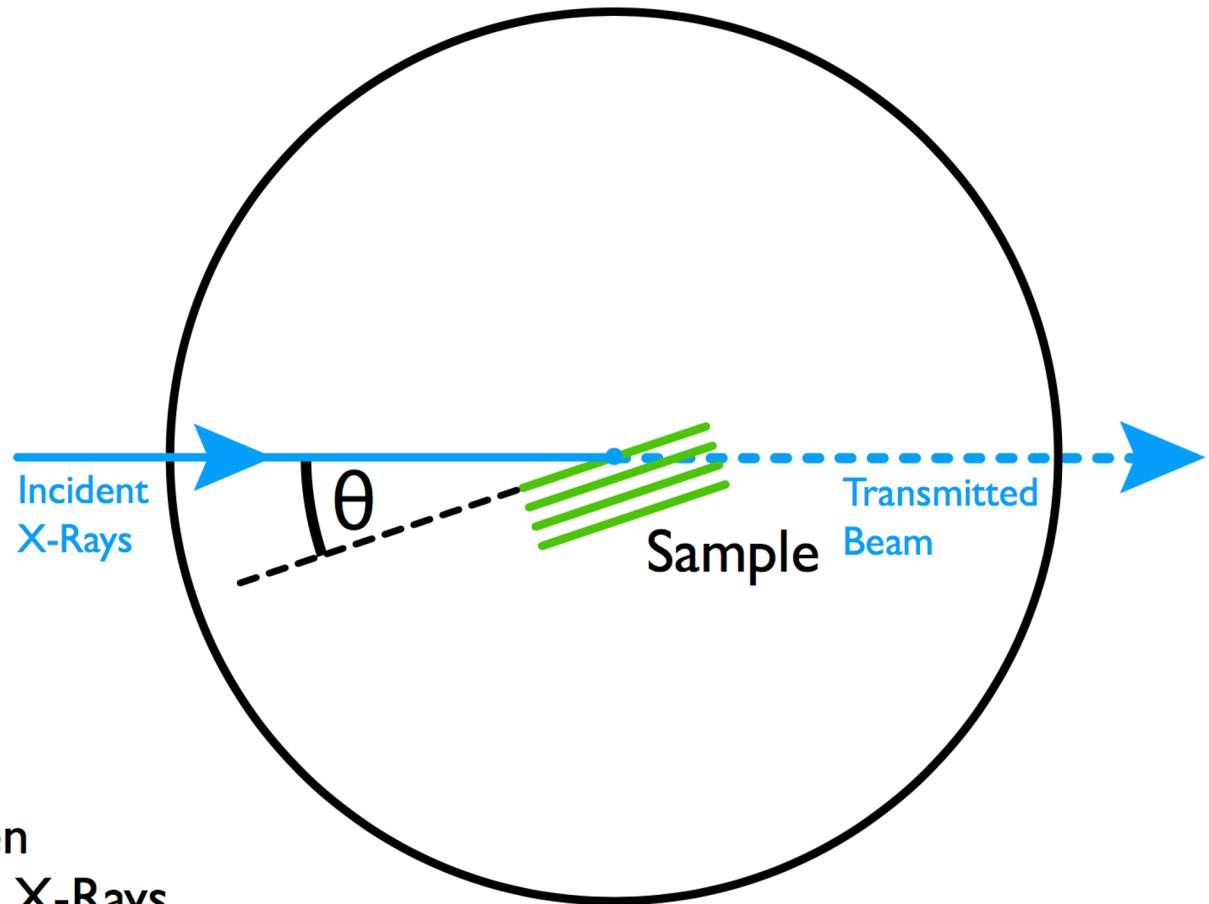
One vendor: <https://www.rigaku.com/products/xrd/smartlab>

# X-ray Diffractometer



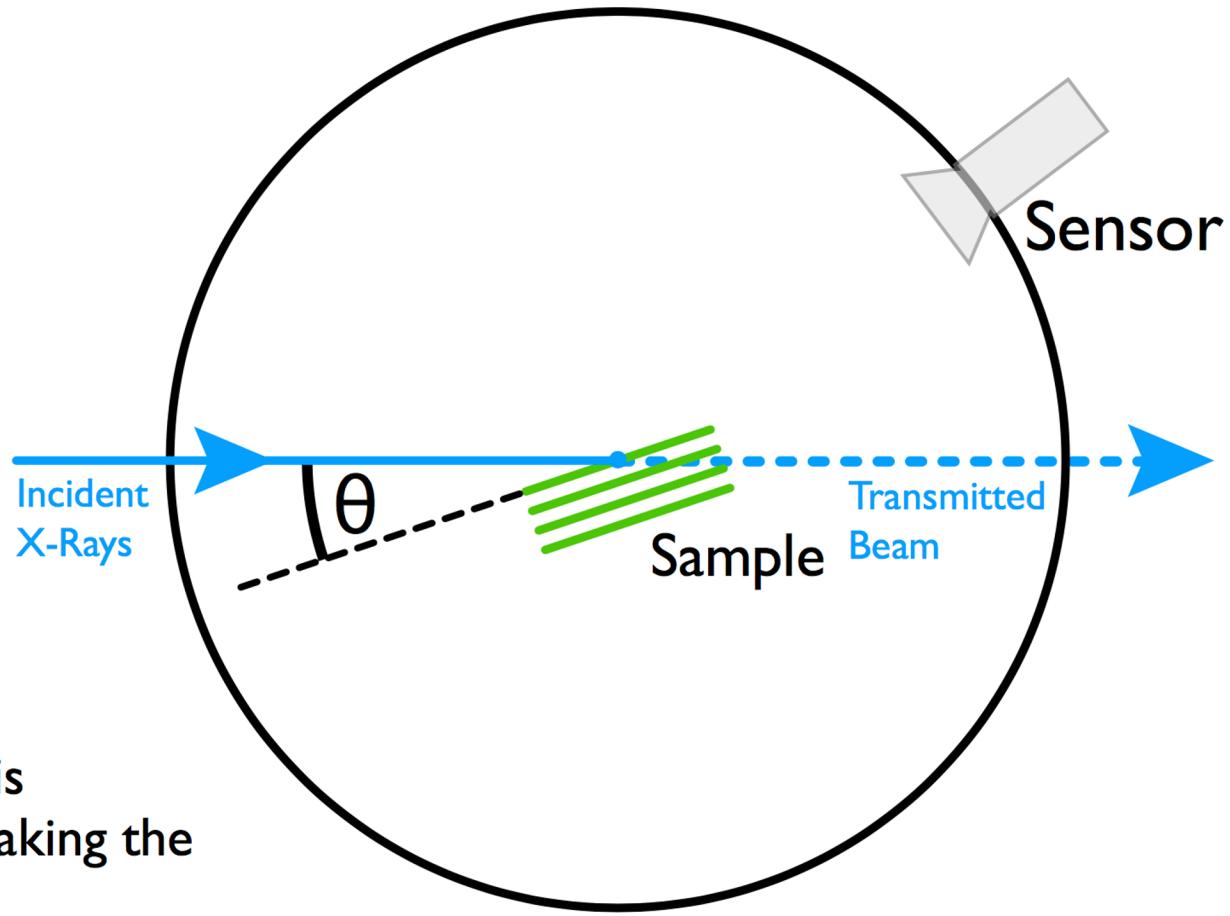
- A sample is mounted within the chamber of the X-Ray diffractometer at an angle  $\theta$ .

# X-ray Diffractometer

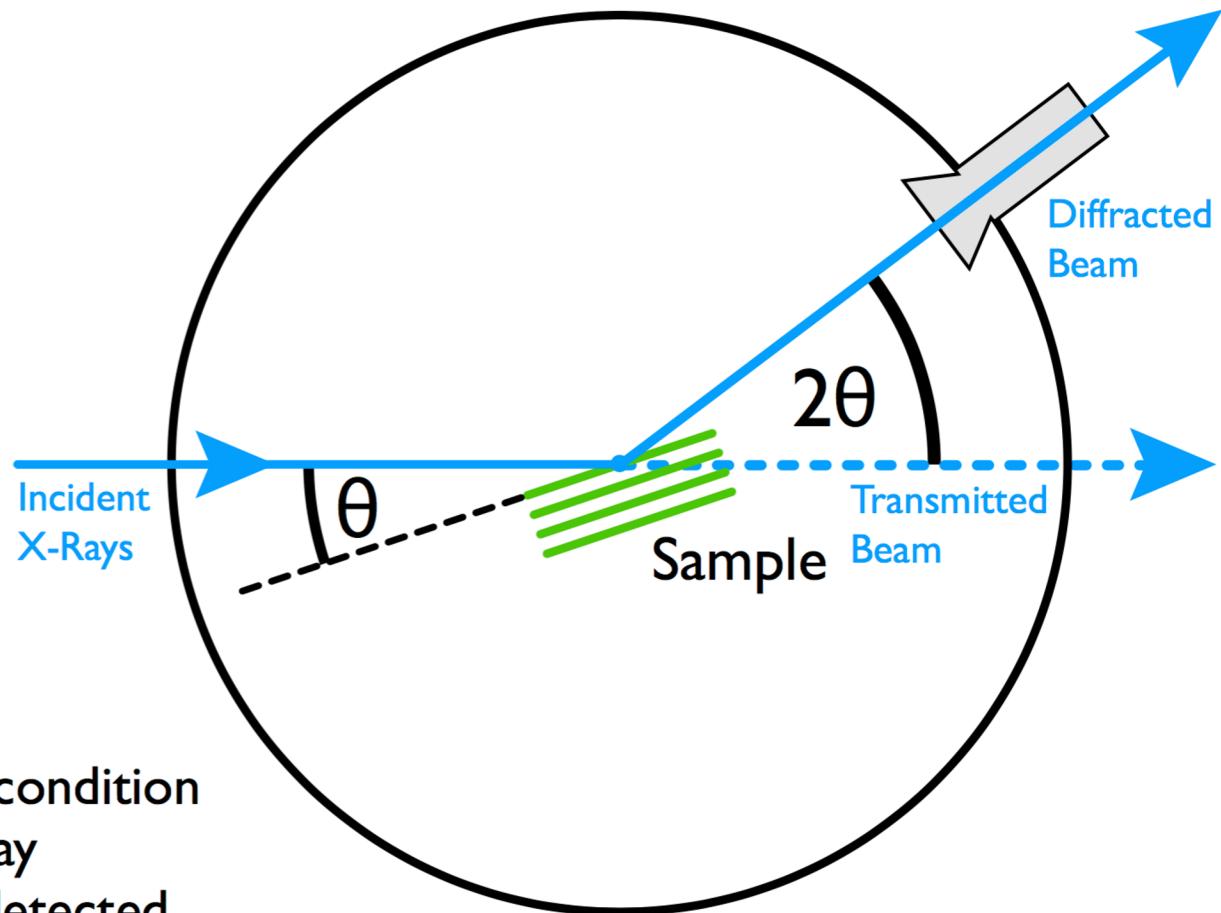


- The sample is then interrogated with X-Rays.

# X-ray Diffractometer

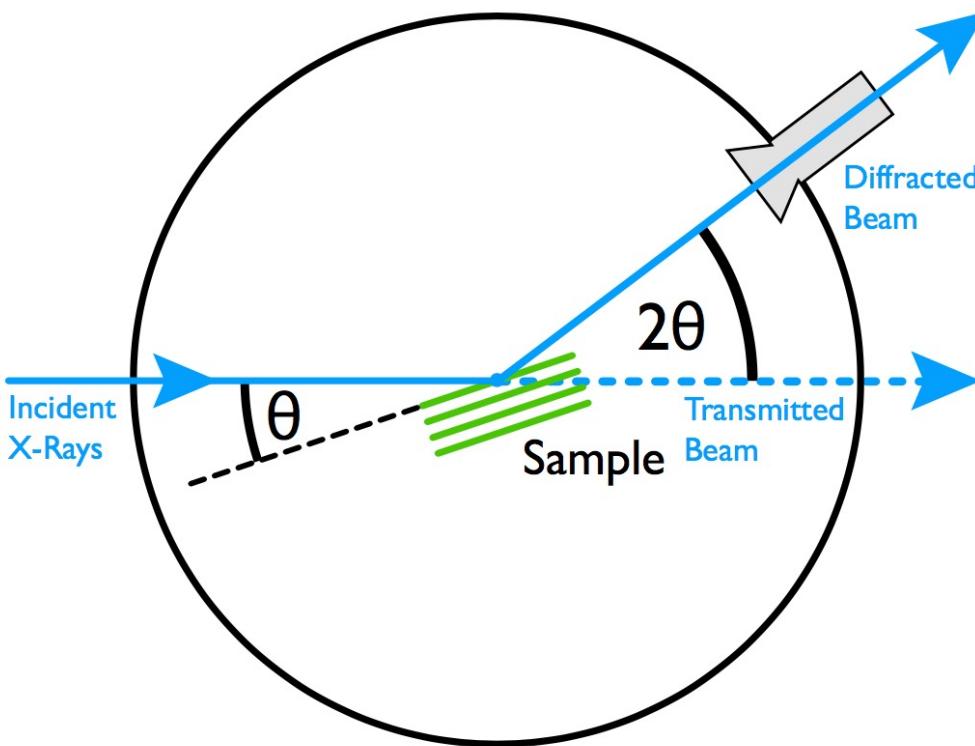


# X-ray Diffractometer



- When the Bragg condition is met, a high X-ray intensity will be detected.

# X-ray Diffractometer



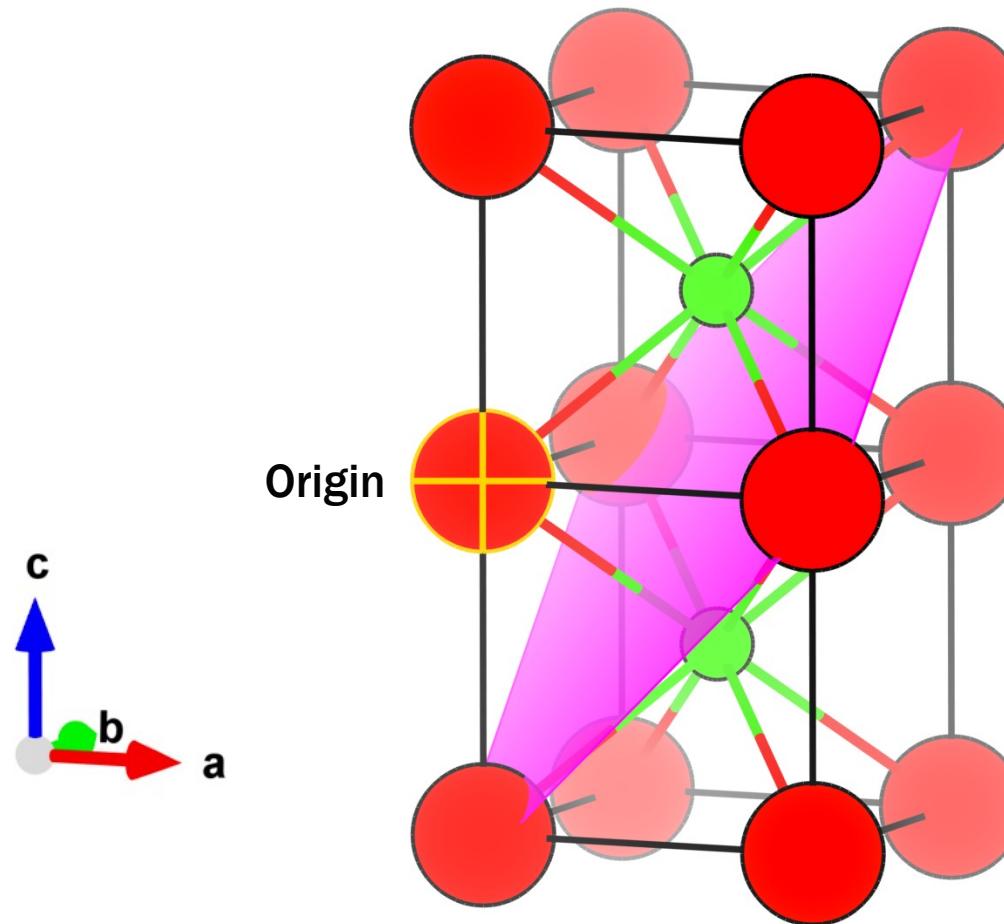
- Diffraction occurs when the Bragg condition is met: when the crystallite is in an orientation with respect to the incident X-ray beam such that:

$$\theta = \sin^{-1} \left\{ \frac{\lambda}{2d_{hkl}} \right\}$$

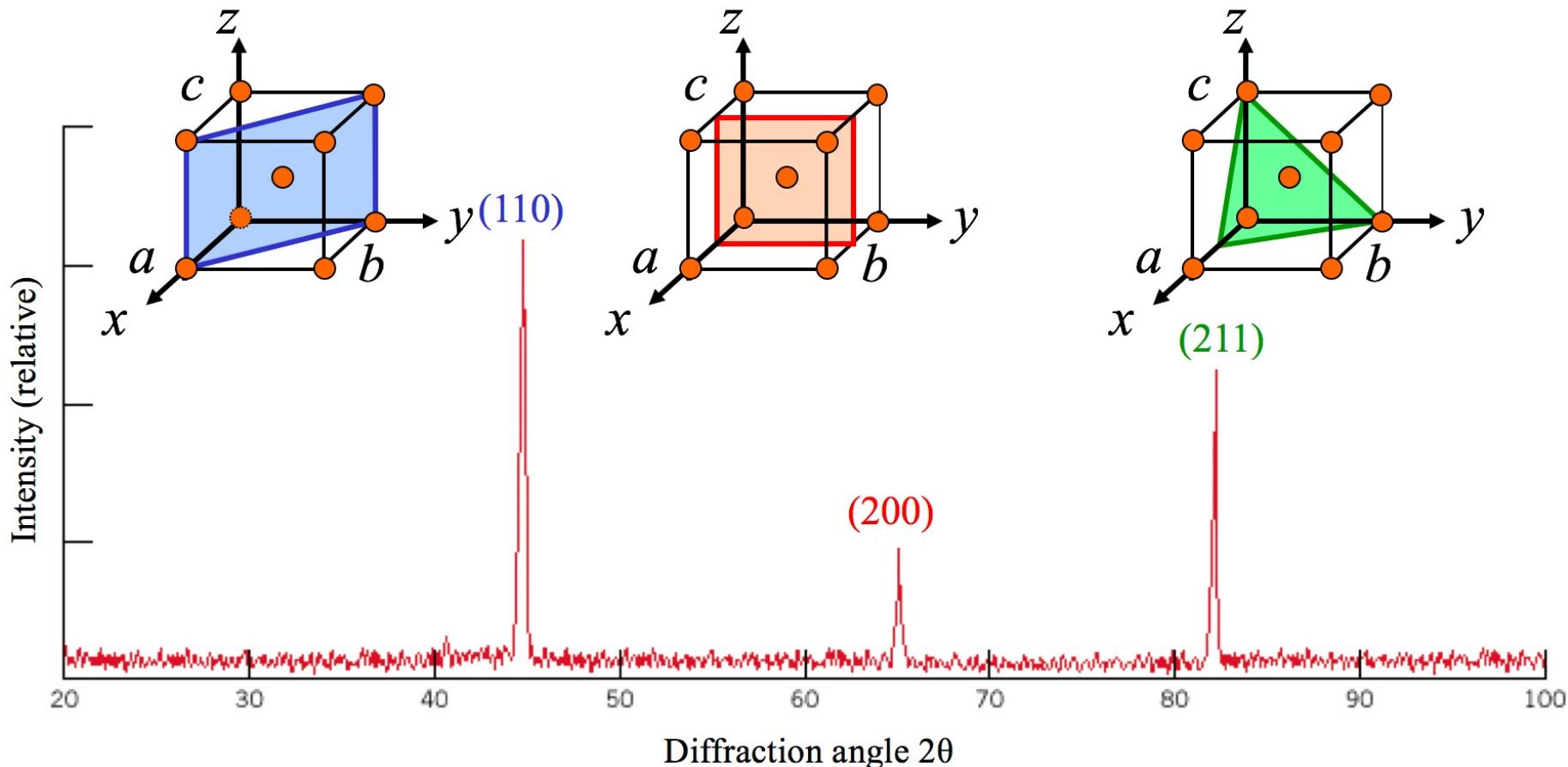
Diffraction peaks are often referred to as “reflections” (technically incorrect). Scattering due to  $(hkl)$  is labelled a  $(hkl)$  reflection

# Quiz

What is the Miller Index of the pink plane?



# Diffraction Pattern (bcc Fe)

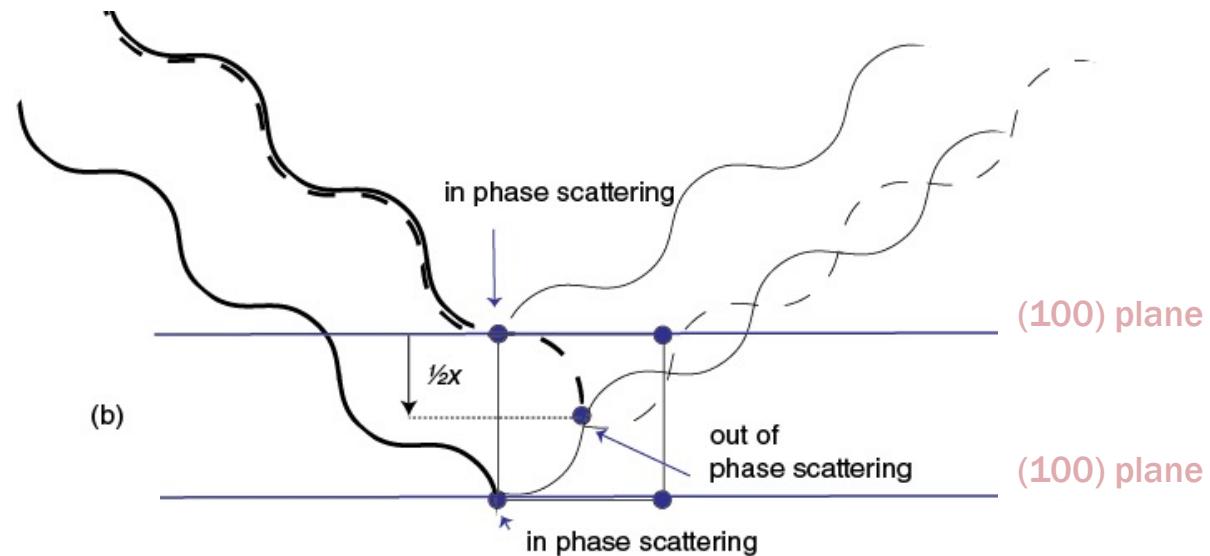
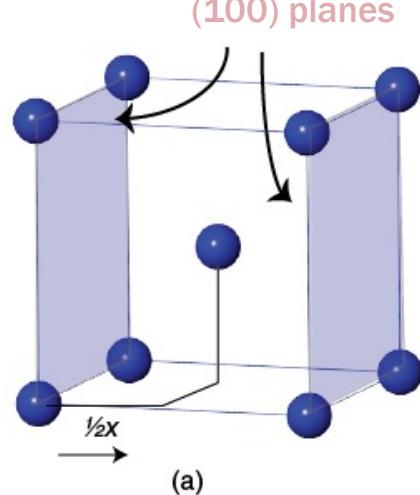


Where is the (100) peak?

# Systematic Absences

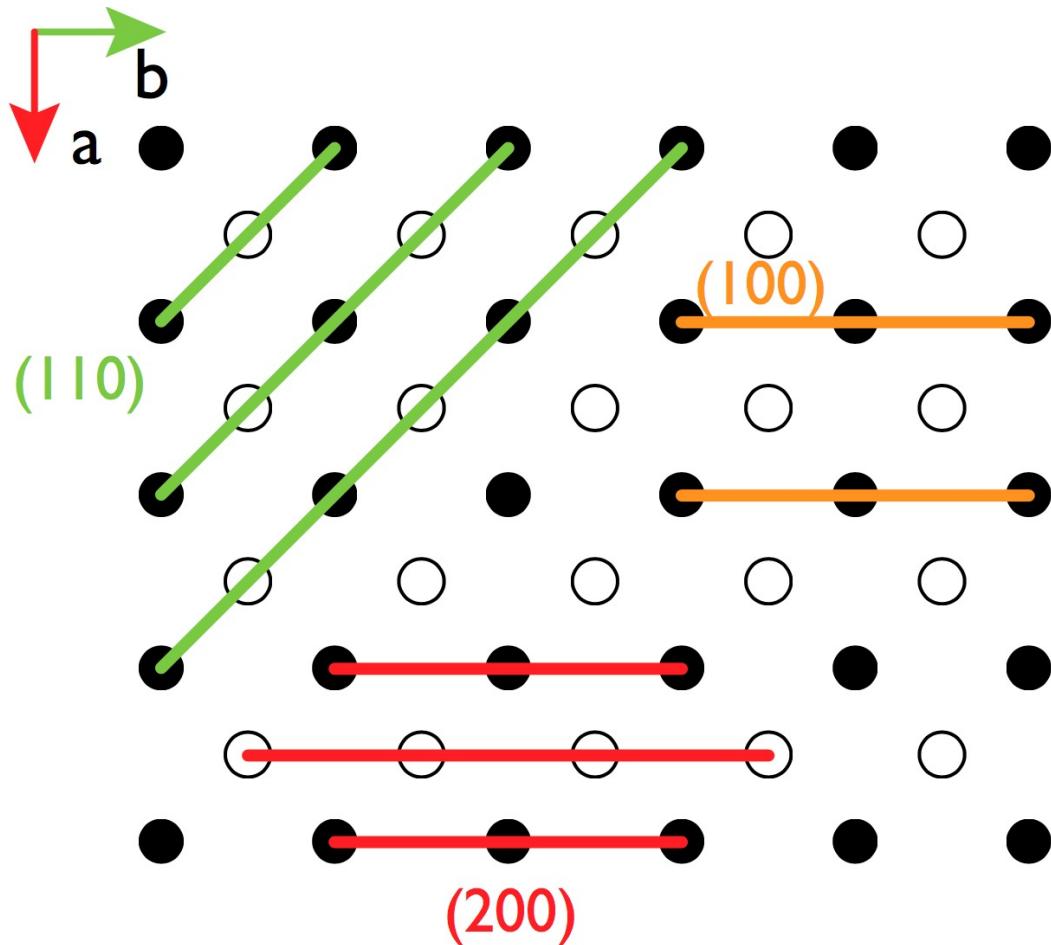
Bragg's Law is only guaranteed for primitive lattices

**Systematic Absences:** For structures with atoms in the unit cell centre (bcc) or faces (fcc), additional X-ray scattering can lead to out-of-phase contributions that cancel diffracted intensity



# Systematic Absences: bcc

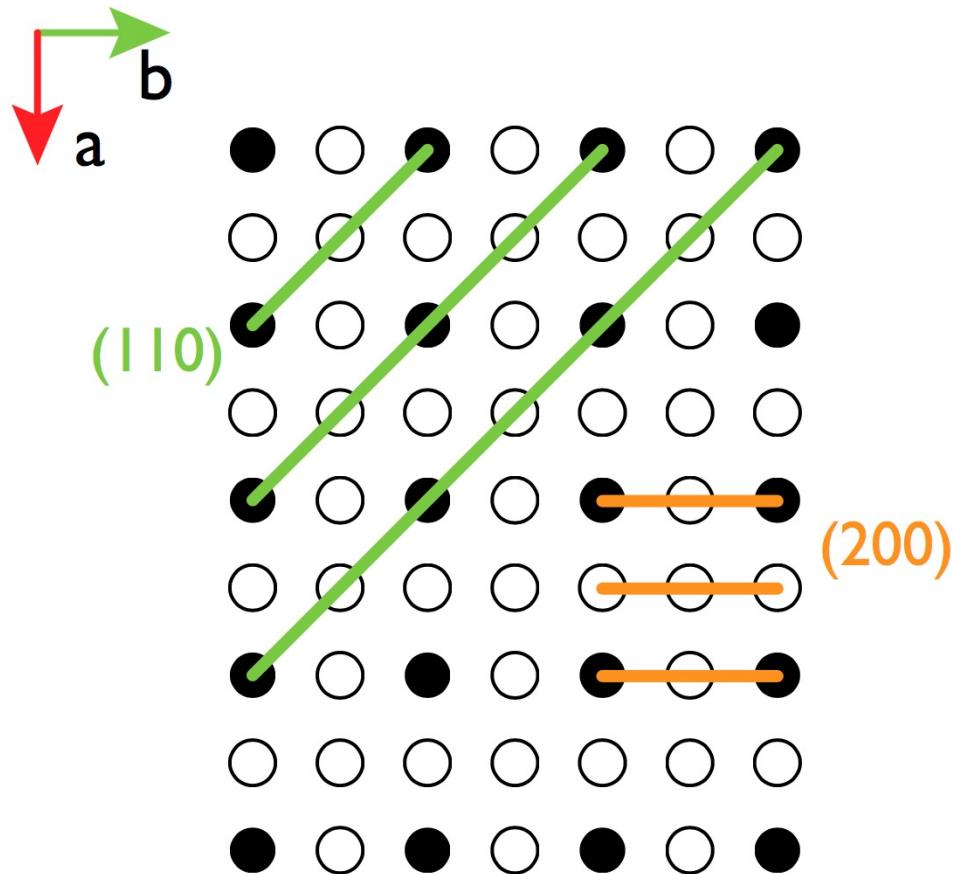
Active  $(hkl)$  planes should pass through all lattice points



- Plan view of BCC lattice.
- Open points = body centres.
- $(110)$  and  $(200)$  pass through all lattice points.
- $(100)$  does not.

# Systematic Absences: fcc

Active  $(hkl)$  planes should pass through all lattice points



- Plan view of FCC lattice (LiF with NaCl structure).
- Open points = face centres points.
- $(200)$  passes through all lattice points.
- $(110)$  does not.

# Rules for Systematic Absences

Simple Cubic  
(primitive)

All reflections allowed

BCC

$h+k+l = \text{EVEN}$

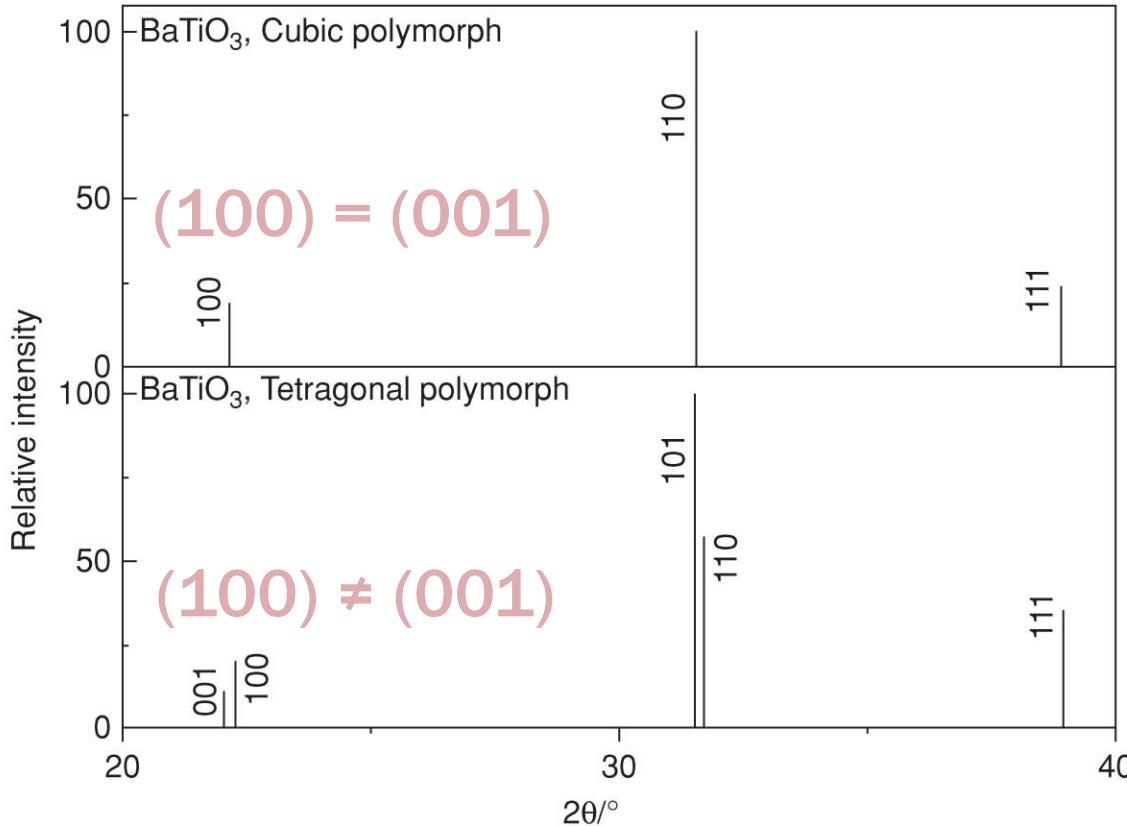
FCC

$h, k$  and  $l$  must either be  
**all odd or all even**

The rules will be explored in more detail in 2<sup>nd</sup> year (Structure 2)

# X-ray Diffraction Patterns

As covered in last lecture, many perovskites display a tetragonal-to-cubic phase transition at high temperature

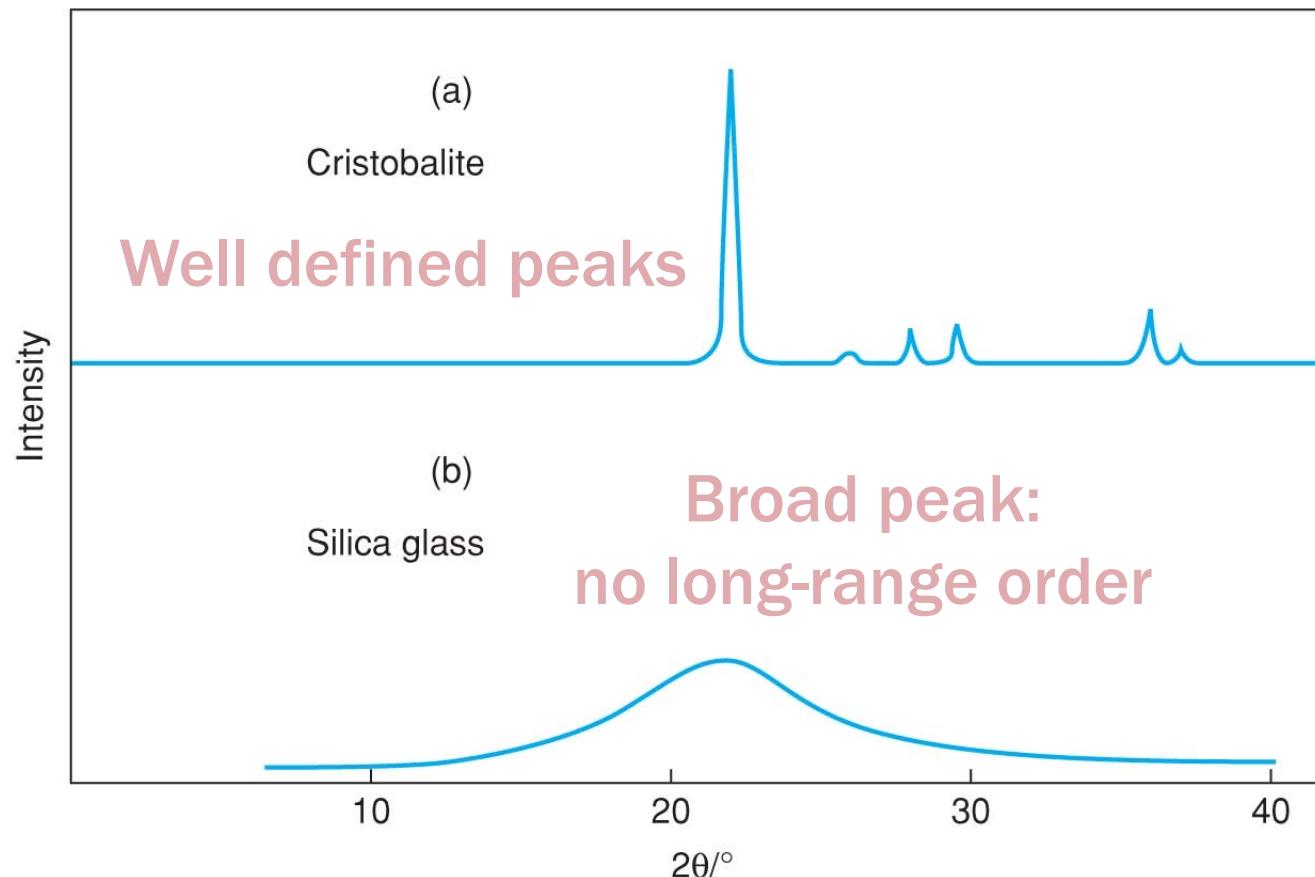


Higher symmetry  
results in fewer peaks

Peak splitting after  
phase transition

# X-ray Diffraction Patterns

Measured diffraction patterns for two forms of  $\text{SiO}_2$ :  
(a) is crystalline and (b) is amorphous (glass state)

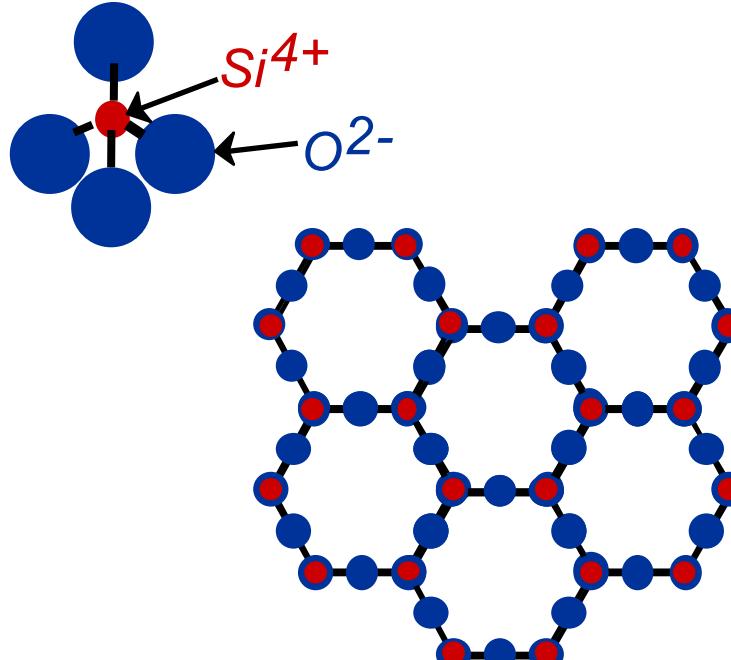


# Non-Crystalline Compounds

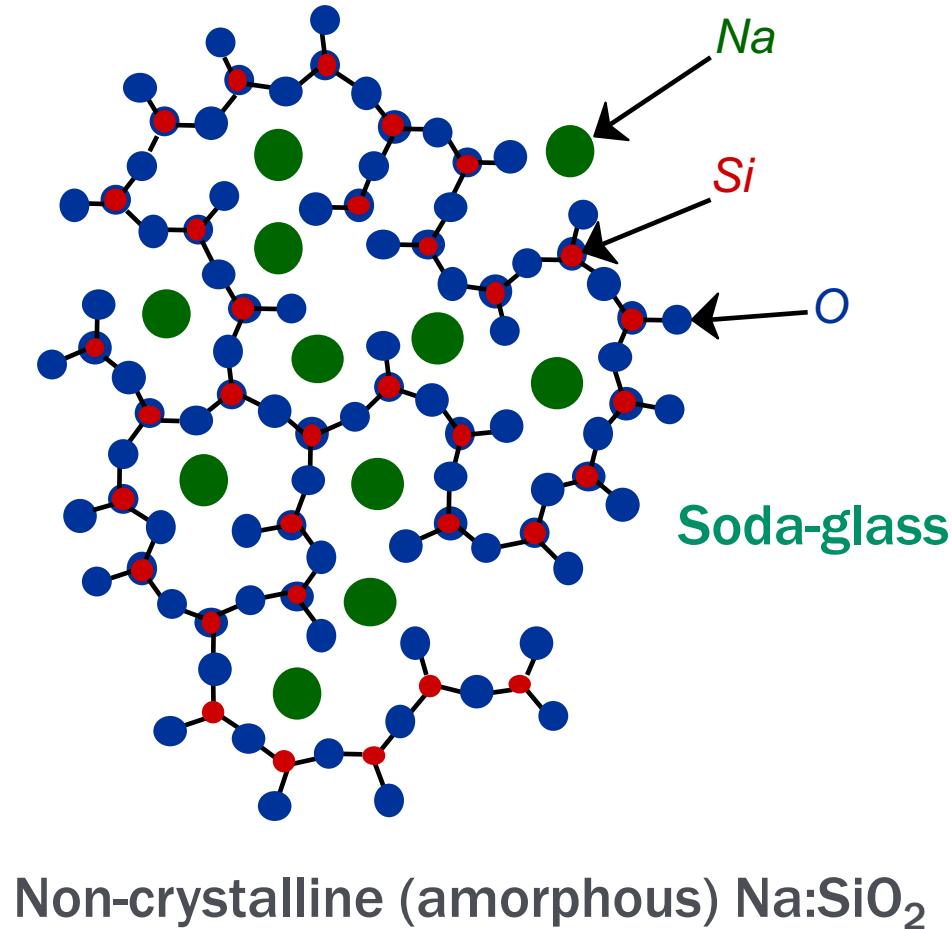
We focused on crystalline materials, but there are classes of compounds with no long-range ordered structure

Building block:

$\text{SiO}_4$  tetrahedron



Crystalline  $\text{SiO}_2$



Non-crystalline (amorphous)  $\text{Na:SiO}_2$

# Summary: Diffraction

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## Class outcomes:

- Calculate spacing between lattice planes
- Derive Bragg's Law
- Apply Bragg's Law to predict diffraction angles
- Describe systematic absences for simple lattices