Chap 2 Three-dimensional lattices

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Monoatomic lattices

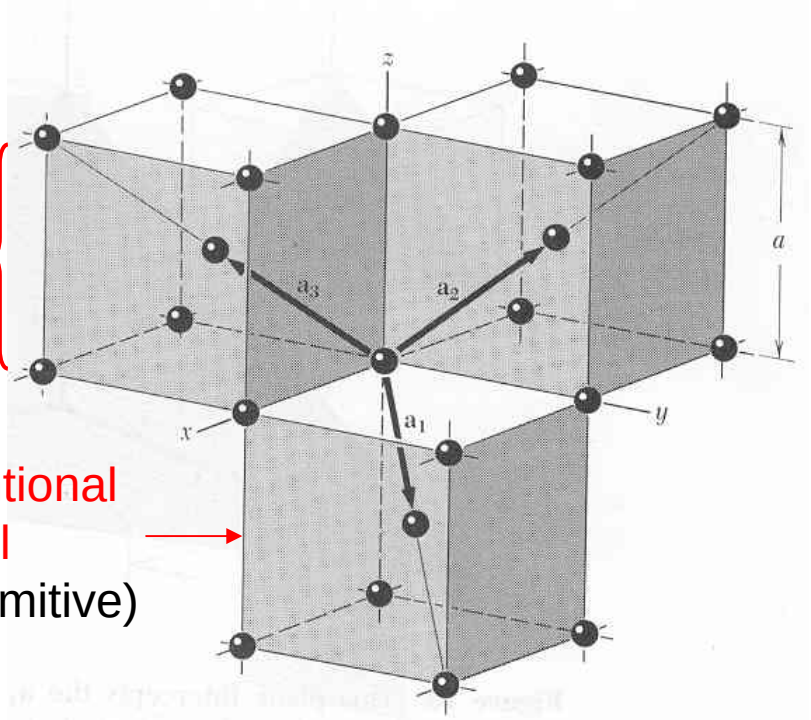
Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

H^1 4K hcp 3.75 6.12																	He^4 2K hcp 3.57 5.83
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N_2)	O complex (O_2)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21	← Crystal structure → ← a lattice parameter, in Å → ← c lattice parameter, in Å →										Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl_2)	Ar 4K fcc 5.31
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br_2)	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I_2)	Xe 4K fcc 6.13
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 *ABAC*	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —
Fr —	Ra —	Ac fcc 5.31															

Ce fcc 5.16	Pr hex. 3.67 *ABAC*	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55
Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 *ABAC*	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —

1) bcc lattice (Li, Na, K, Rb, Cs… etc)



One possible choice of primitive vectors

$$\vec{a}_1 = \frac{a}{2}(\ \hat{x}+\hat{y}-\hat{z}),$$

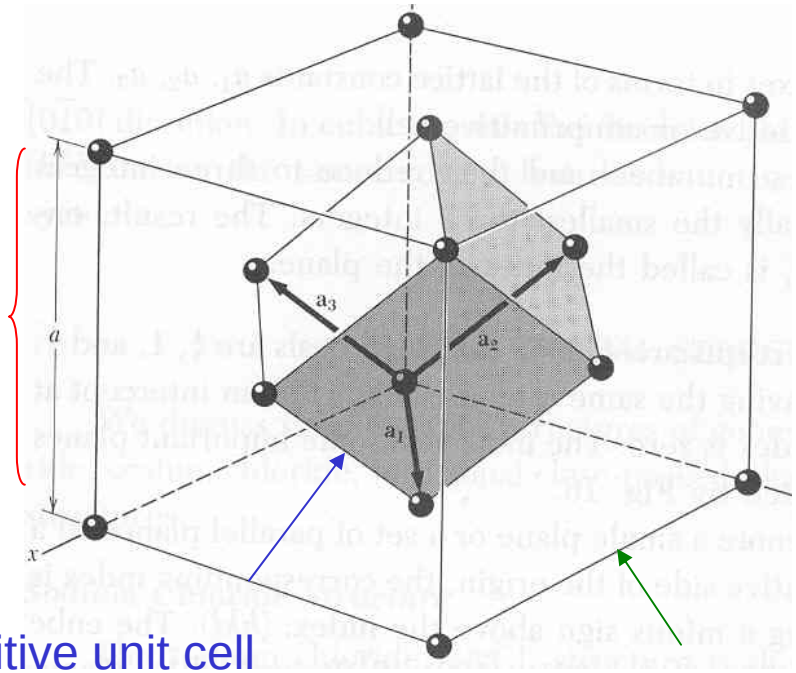
$$\vec{a}_2 = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z}),$$

$$\vec{a}_3 = \frac{a}{2}(\ \hat{x}-\hat{y}+\hat{z}).$$

• A bcc lattice is a Bravais lattice.
But we can also treat it as a cubic lattice with a 2-point basis
(to take advantage of the cubic symmetry)

2) fcc lattice (Ne, Ar, Kr, Xe, Al, Cu, Ag, Au… etc)

lattice constant



primitive unit cell

conventional unit cell

One possible choice of primitive vectors

$$\vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y}),$$

$$\vec{a}_2 = \frac{a}{2}(\hat{y} + \hat{z}),$$

$$\vec{a}_3 = \frac{a}{2}(\hat{z} + \hat{x}).$$

• A fcc lattice is also a Bravais lattice, but we can treat it as a cubic lattice with a 4 point basis.

3) hcp lattice (Be, Mg… etc)

= a hexagonal lattice + a 2-point basis

= 2 overlapping “hexagonal lattices”

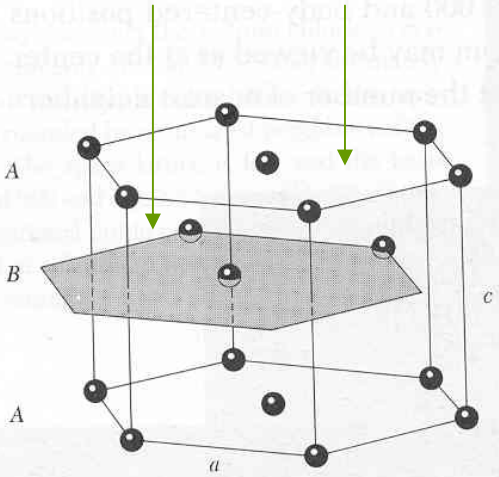
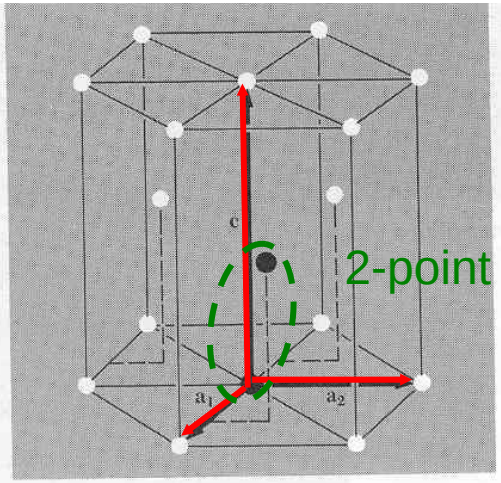


Figure 22 The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters a and c are indicated, where a is in the basal plane and c is the magnitude of the axis $\mathbf{a}_3$ of Fig. 14.

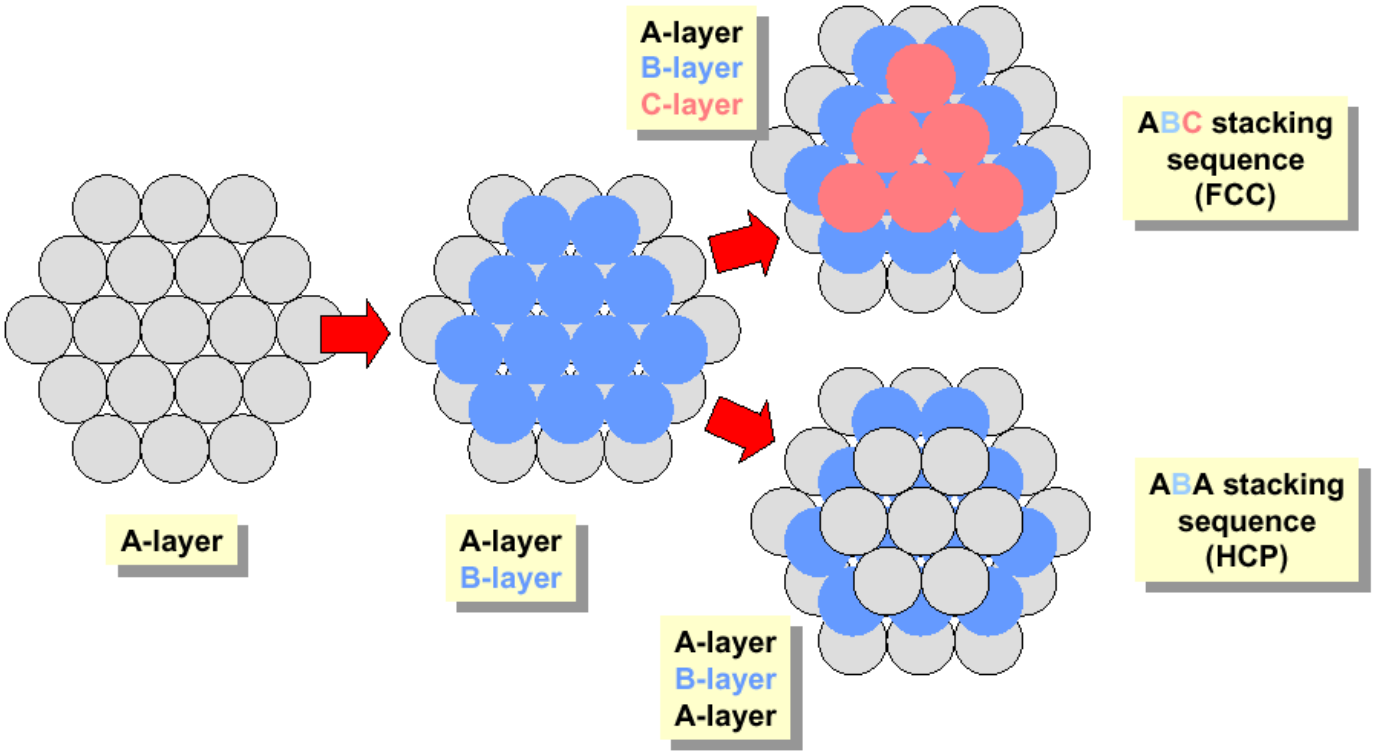


2-point basis

Figure 23 The primitive cell has $a_1 = a_2$, with an included angle of 120°. The c axis (or $\mathbf{a}_3$) is normal to the plane of $\mathbf{a}_1$ and $\mathbf{a}_2$. The ideal hcp structure has $c = 1.633\,a$. The two atoms of one basis are shown as solid circles. One atom of the basis is at the origin; the other atom is at $\frac{2}{3}\frac{1}{3}\frac{1}{2}$, which means at the position $\mathbf{r} = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$.

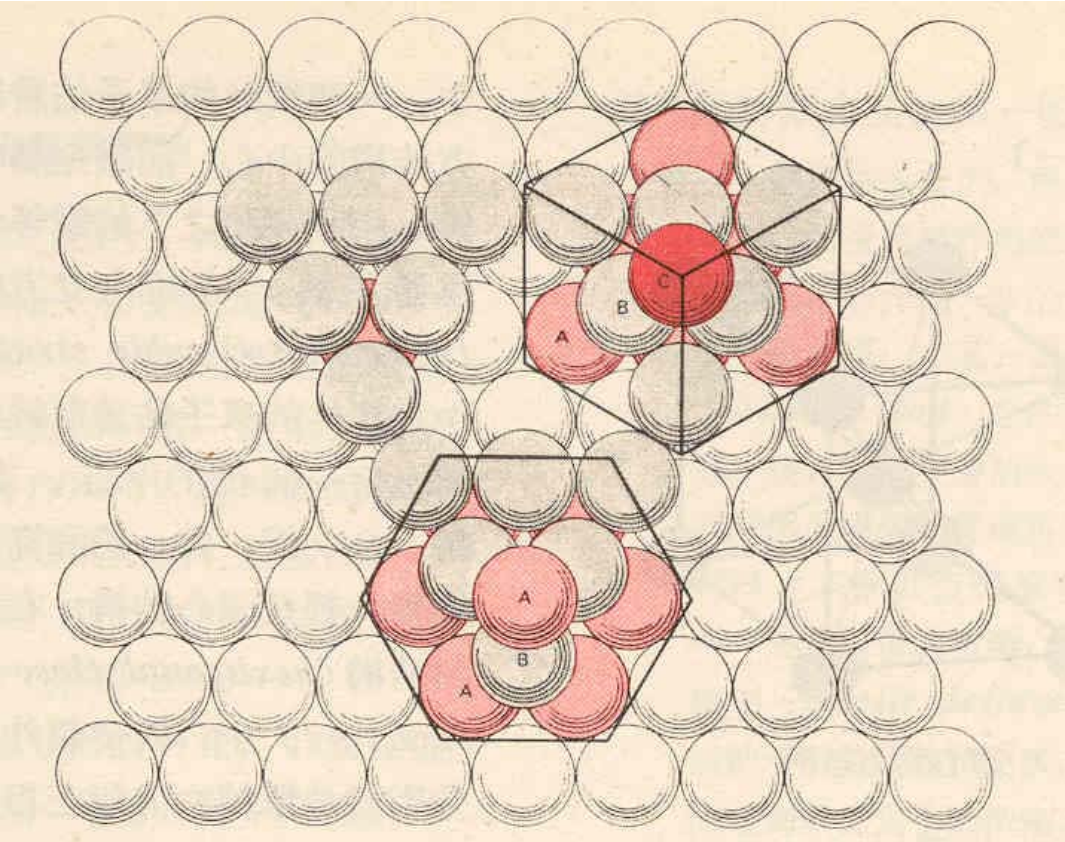
- Primitive vectors: $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{c}$ [$c=2a\sqrt{(2/3)}$ for hcp]
- The 2 atoms of the basis are located at $\mathbf{d}_1=0$ and at $\mathbf{d}_2 = (2/3)\,\mathbf{a}_1 + (1/3)\,\mathbf{a}_2 + (1/2)\mathbf{c}$

The tightest way to pack spheres:



- ABCABC…= fcc, ABAB…= hcp
- Other close packed structures: ABABCAB… etc.

Viewing from different angles



- coordination number (配位數) = 12, packing fraction ≈ 74%

  (Cf: bcc, coordination number = 8, packing fraction ≈ 68%)

Kepler's conjecture (1611): The packing fraction of spheres in 3-dim $\leq \pi/\sqrt{18}$

Does the proof stack up?

(the value of fcc and hcp)

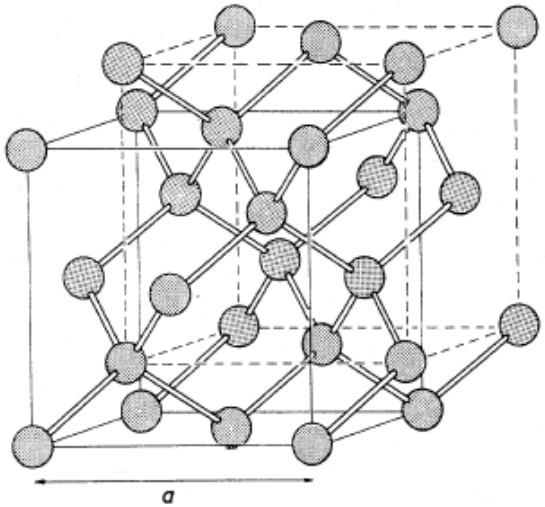
… the editors of the *Annals of Mathematics* agreed to publish it, provided it was accepted by a panel of 12 referees. In 2003, after 4 years of work, the head of the referee's panel reported that the panel were "99% certain" of the correctness of the proof… (from wiki)

Grocers the world over know the most efficient way to stack spheres — but a mathematical proof for the method has brought reviewers to their knees.

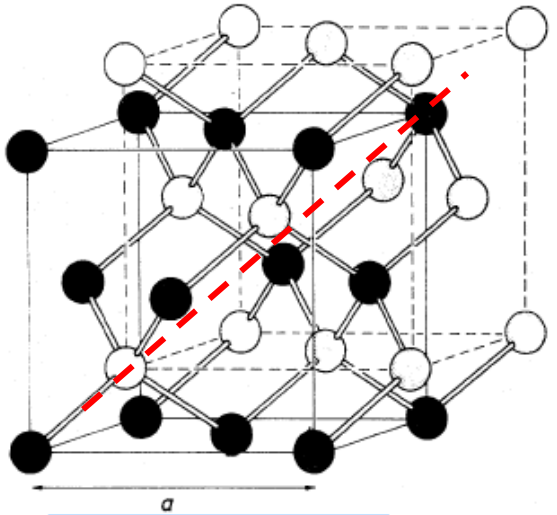
4) Diamond structure (C, Si, Ge… etc)

= 2 overlapping fcc lattices (one is displaced along the main diagonal by 1/4)

= fcc lattice + a 2-point basis, $\mathbf{d}_1=\mathbf{0}$, $\mathbf{d}_2=(a/4)(\mathbf{x}+\mathbf{y}+\mathbf{z})$



diamond-type (Si, Ge)



ZnS-type (GaAs)

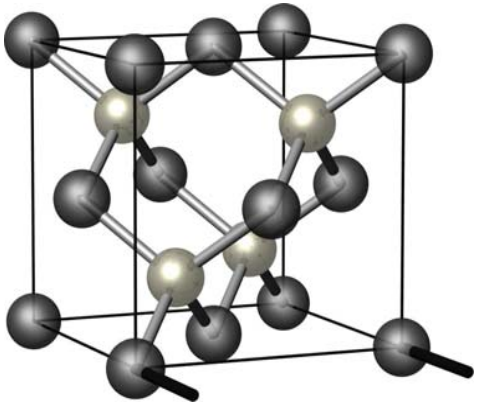
- Very low packing fraction (～ 36%)
- If the two atoms on the basis are different, then it is called a Zincblend (閃鋅) structure (GaAs, ZnS… etc).

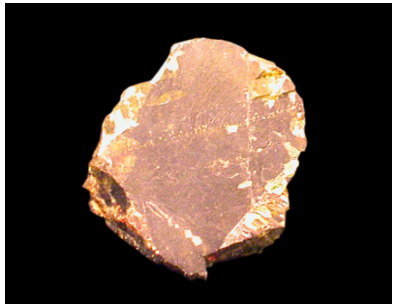
It is a familiar structure with an unfamiliar name.

Crystal structure of compound

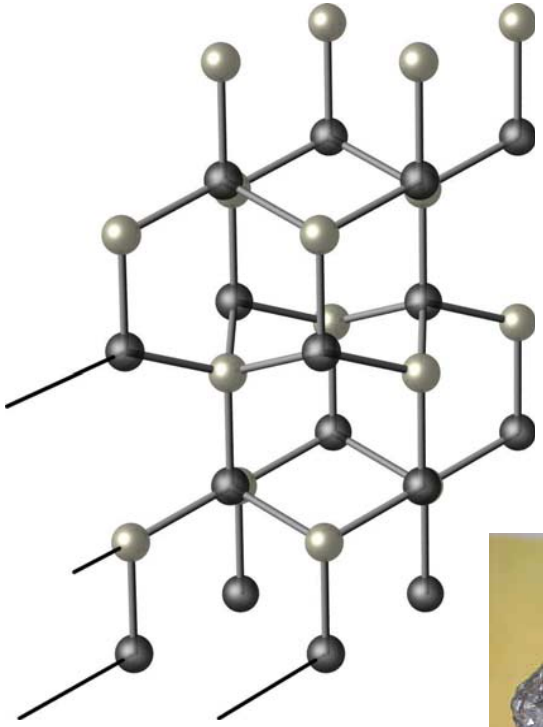
Here we mention 3 examples

1. Zincblend (or Zinc Sulfide) structure (see previous page)

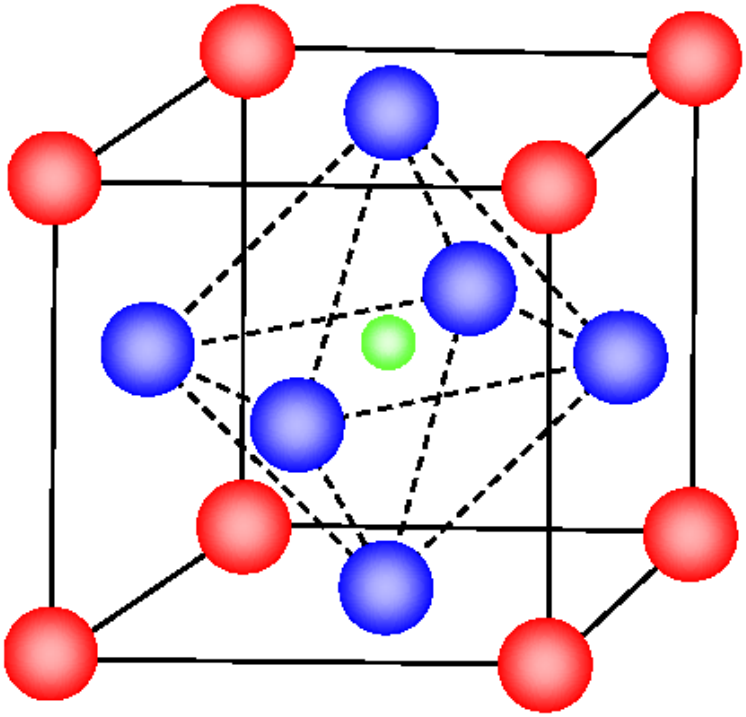




2. Wurtzite (or Zinc oxide, 纖鋅) structure
= 2 overlapping hcp lattices



3. Perovskite (鈣鈦礦 or 鈦酸鈣) structure, ABO_3 (1839)



A - cation: cubic lattice

B - cation: body centered

O - anion: face centered

oxidation state		examples
II / IV	A^{2+} / B^{4+}	$BaTiO_3$ $Pb(Zr,Ti)O_3$
I / V	A^{+} / B^{5+}	$KTaO_3$
III / III	A^{3+} / B^{3+}	$LaMnO_3$

application: nonlinear resistors (PTC), SMD-capacitors, piezoelectric sensors and actuators, pyro-detectors, ferroelectric memory

Positive Temperature Coefficient

Surface Mount Device

Symmetries of 3D crystals

POINT AND SPACE GROUPS OF BRAVAIS LATTICES AND CRYSTAL STRUCTURES

	BRAVAIS LATTICE (BASIS OF SPHERICAL SYMMETRY)	CRYSTAL STRUCTURE (BASIS OF ARBITRARY SYMMETRY)
Number of point groups:	7 ("the 7 crystal systems")	32 ("the 32 crystallographic point groups")
Number of space groups:	14 ("the 14 Bravais lattices")	230 ("the 230 space groups")

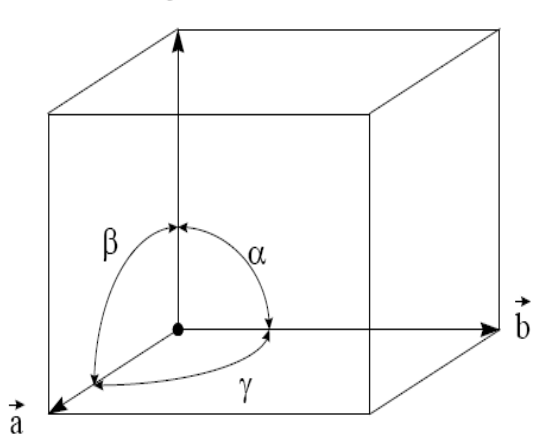
Ashcroft and Mermin, p.120

Note:

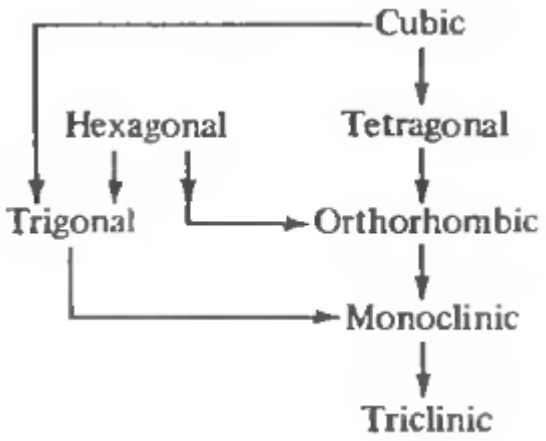
1. The Bravais lattices were studied by M.L. Frankenheim in 1842, who found that there were 15 Bravais lattices. This was corrected to 14 by A. Bravais in 1848.
2. The 230 space groups were enumerated by Fydorov, Schonflies, and Barlow in the 1890's.

7 point groups (aka 7 "crystal systems")

- primitive cell



- Heirarchy of symmetries

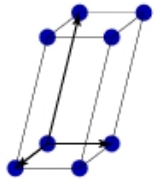
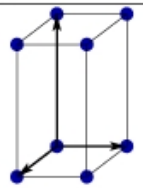
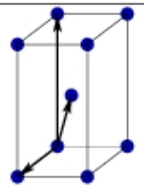
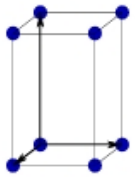
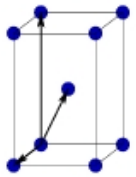
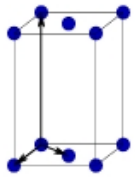
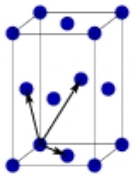
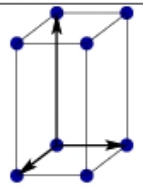
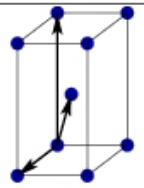
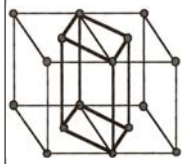
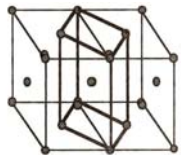
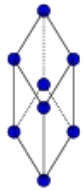
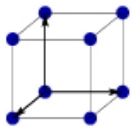
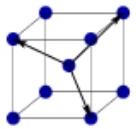
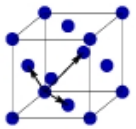
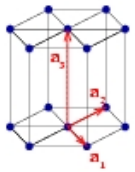


Crystal System	Lattice Parameters	Lattice Angles
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$
Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90°$
Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$
Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	a = b ≠ c	$\alpha = \beta = 90°, \gamma = 120°$
Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90°, \beta \neq 90°$
Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90°$

trigonal

http://matsci.uah.edu/courseware/mts721/

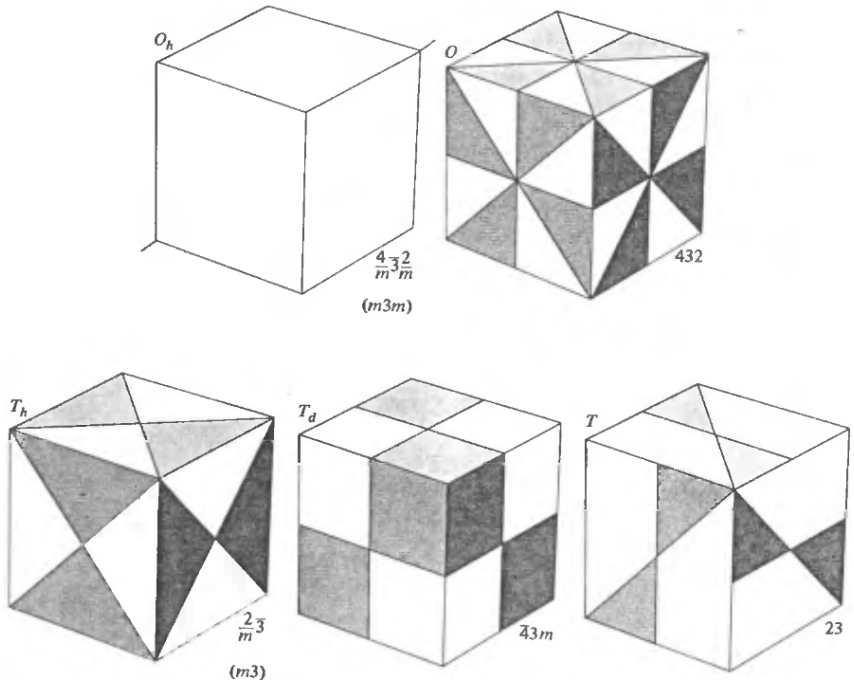
14 space groups (14 Bravais lattices)

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$			Same as S and tetragonal	VC
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

http://www.theory.nipne.ro/~dragos/Solid/FYS230-Exercises.html

32 point groups for crystal structure

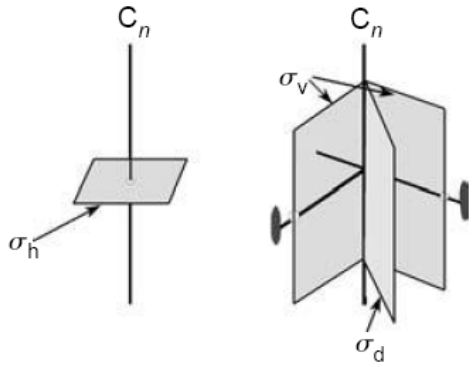
- 5 cubic point groups



- 27 non-cubic point groups

Ashcroft and Mermin, p.121,122

27 non-cubic point groups:



SCHOEN-FLIES	HEXAGONAL	TETRAGONAL	TRIGONAL	ORTHO-RHOMBIC	MONOCLINIC	TRICLINIC	INTER-NATIONAL
C_n	C_6 6	C_4 4	C_3 3		C_2 2	C_1 1	n
C_{nv}	C_{6v} $6mm$	C_{4v} $4mm$	C_{3v} $3m$	C_{2v} $2mm$			nmm (n even) nm (n odd)
C_{nh}	C_{6h} $6/m$	C_{4h} $4/m$			C_{2h} $2/m$		n/m
	C_{3h} $\bar{6}$				C_{1h} ($\bar{2}$) m		$\bar{n}$
S_n		S_4 $\bar{4}$	S_6 (C_{3i}) $\bar{3}$			S_2 (C_i) $\bar{1}$	
D_n	D_6 622	D_4 422	D_3 32	D_2 (V) 222			$n22$ (n even) $n2$ (n odd)
D_{nh}	D_{6h} $6/mmm$	D_{4h} $4/mmm$		D_{2h} (mmm) (V_h) $2/mmm$			$\frac{n}{m}\frac{2}{m}\frac{2}{m}$ (n/mmm)
	D_{3h} $\bar{6}2m$						$\bar{n}2m$ (n even) $\bar{n}\frac{2}{m}$ (n odd)
D_{nd}		D_{2d} (V_d) $\bar{4}2m$	D_{3d} ($\bar{3}m$) $\bar{3}\frac{2}{m}$				

S_n: These groups contain only an n-fold rotation-reflection axis.

D_n: In addition to an n-fold rotation axis, these groups contain a 2-fold axis perpendicular to the n-fold axis, plus as many additional 2-fold axes as are required by the existence of the n-fold axis.

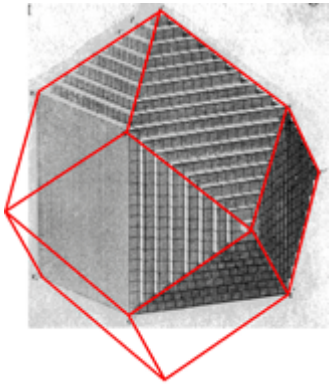
D_{nh}: These (the most symmetric of the groups) contain all the elements of D_n plus a mirror plane perpendicular to the n-fold axis.

D_{nd}: These contain the elements of D_n plus mirror planes containing the n-fold axis, which bisect the angles between the 2-fold axes.

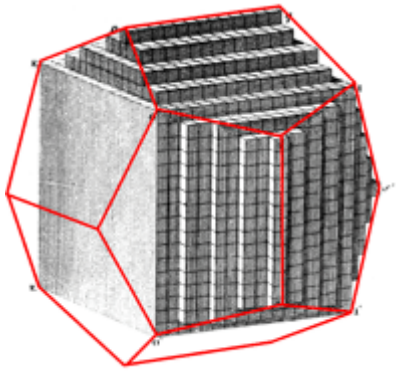
Microscopic symmetry ↔ macroscopic properties

- appearance

Prob.2.9: Haüy's law regarding the angles between crystal faces

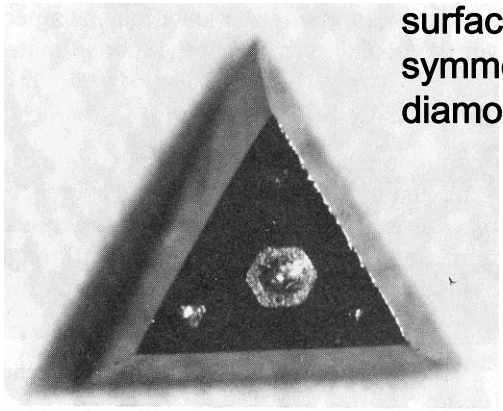


Rhomb-dodecahedron

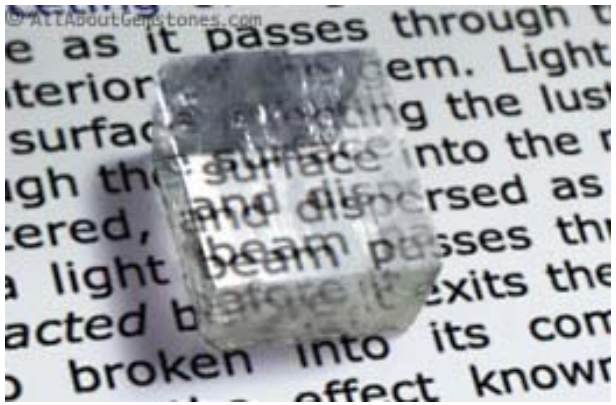


Pentagon-dodecahedron

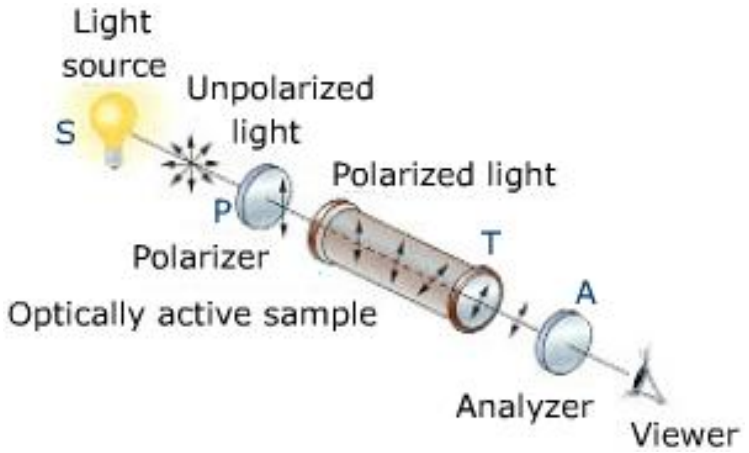
Al melt on Si {111} surface reveals the symmetry of the diamond lattice



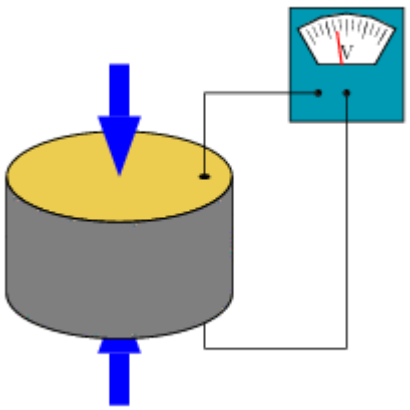
- birefringence (eg. Calcite) 方解石



- optical activity 旋光性



• piezoelectricity 壓電 (eg. Quartz)



• piezoelectricity are only possible in crystals that have no center of inversion symmetry

• Of the 32 crystallographic point groups, 21 have no inversion symmetry (thus can support piezoelectricity). However, Cubic-432 (i.e. O) is impossible, so only 20.
for details, see

capsicum.me.utexas.edu/ChE386K/docs/20a_Physical_Properties.ppt

• pyroelectricity 熱電 (eg. LiTaO3, Lithium Tantalate 鉭酸鋰)

• The 20 piezoelectric crystal classes can be divided into 2 classes: polar and nonploar.

• Polar point groups have a “unique” axis that is not repeated in any direction (They are: 1, 2, m, 2mm, 3, 3m, 4, 4mm, 6, 6mm).
They can support spontaneous polarization without any mechanical stress, such as pyroelectricity.

A pyroelectric can be repeatedly heated and cooled to generate electrical power. (~ a heat engine)