

1.3 Real Crystal Structures

一.堆积

二.晶体结构的表达方法

三.典型晶体结构

四.多晶型现象和结构相变

五.晶体表面结构

What structure do the solids have? Can we predict it?

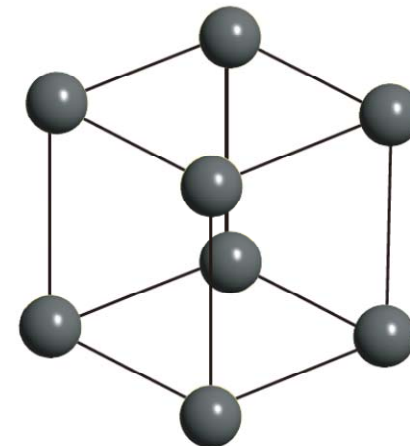
让我们来试着预测固体的结构

Consider inert elements (spheres). This could be anything with no directional bonding (noble gases, simple and noble metals)

考虑没有直接成键的元素，例如惰性气体、贵金属等

Just put the spheres together in order to fill all space. This should have the lowest energy. 将它们尽量密集地堆放在一起，这样它们将具有更低的能量（原因我们下一章阐述）

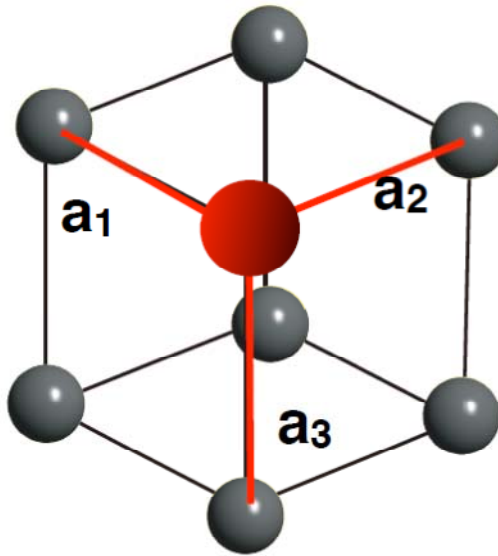
A simple cubic structure? 简立方？



Simple cubic 简立方

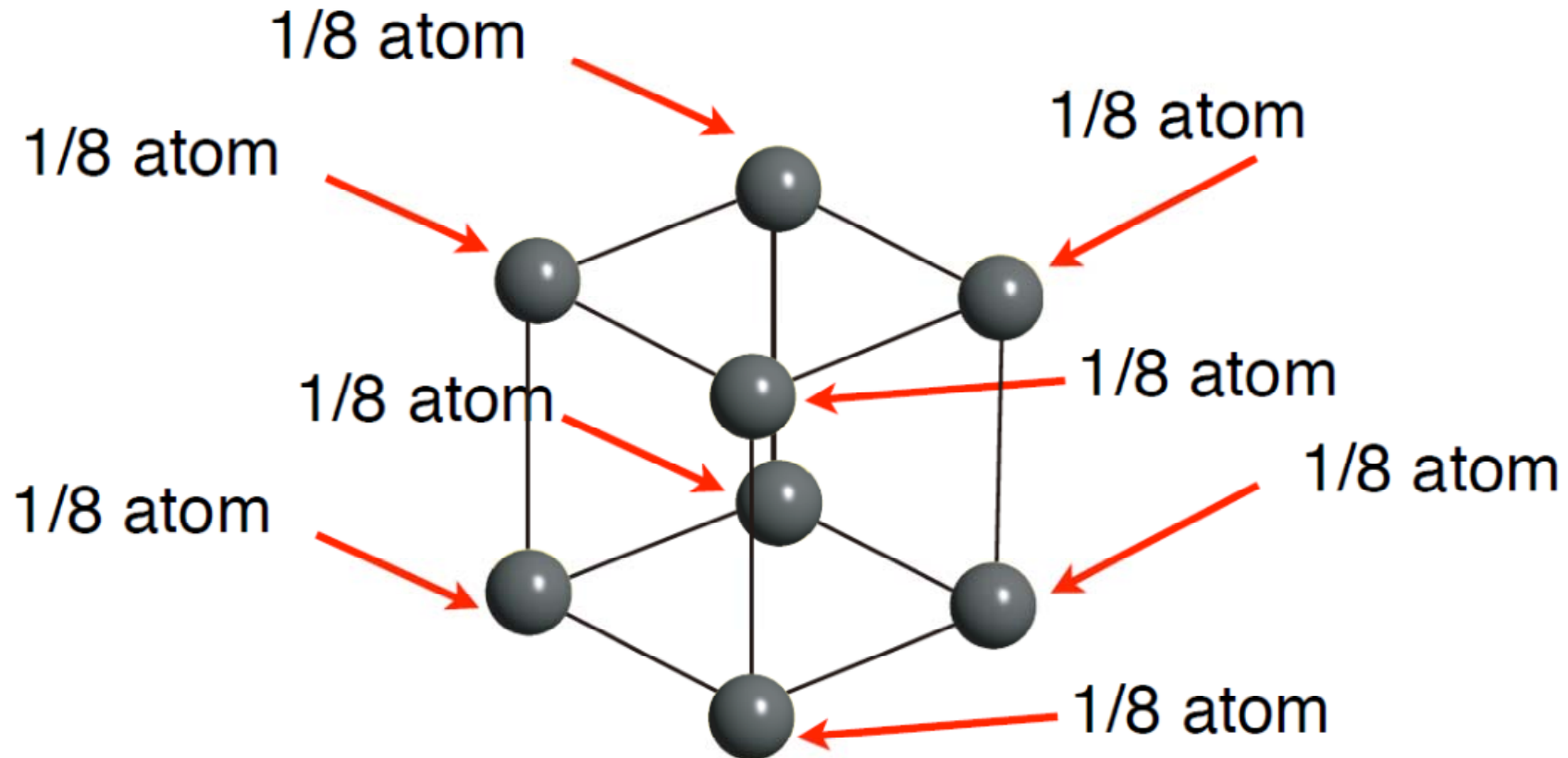
- The simple cubic structure is a Bravais lattice.
- The Wigner-Seitz cell is a cube
- The basis is one atom. So there is one atom per unit cell.

$$\mathbf{R}_{mno} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$$



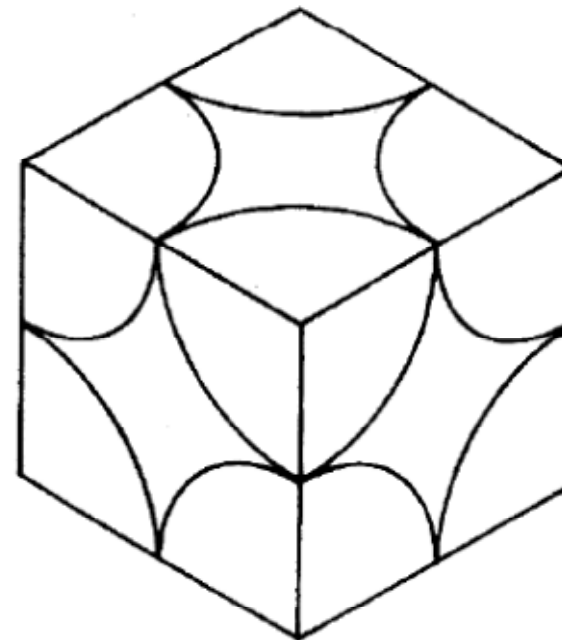
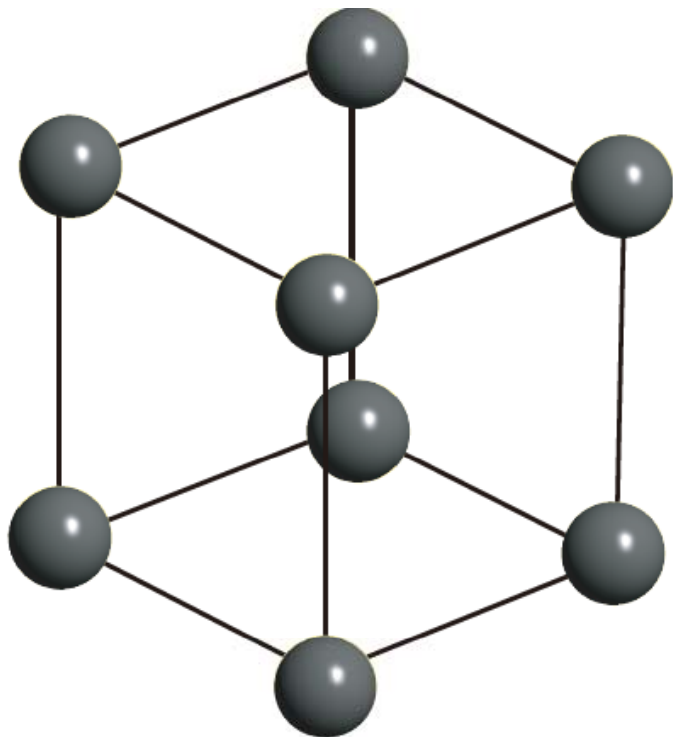
Simple cubic

- We can also simply count the atoms we see in one unit cell.
计算每个晶胞中的原子数目 $n=1$
- But we have to keep track of how many unit cells share these atoms.
要注意同一个原子有多少个晶胞分享



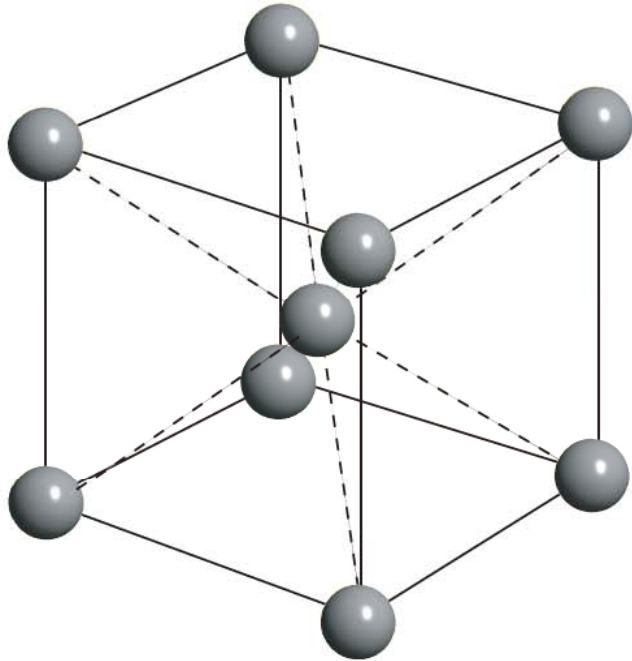
A simple cubic structure is not a good idea for packing spheres (they occupy only 52% of the total volume).

Only two elements crystallise in the simple cubic structure (F and O).

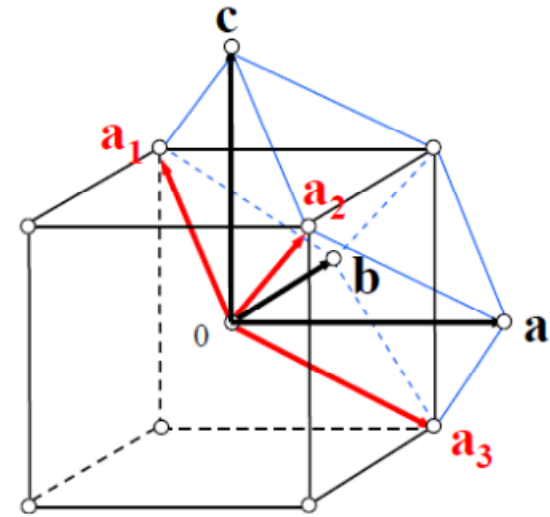


S.C., 52% full

Better packing



bcc:



- In the body-centred cubic (bcc) structure 68% of the total volume is occupied.

惯用晶胞中的原子数 $n = ?$

具有体心立方点阵排列的元素晶体有：

Li, Na, K, Rb, Cs, Ba, Cr, Nb, Ta, W 等，

它们原子的空间排列方式都相同，只是原子间

距有所不同。例如：

Li: $a=3.49,$

Ba $a=5.02,$

Fe $a=2.87,$

V $a=3.03,$

Cr $a=2.88,$

Ta $a=3.30,$

W $a=3.16,$

(单位 10^{-10} m)

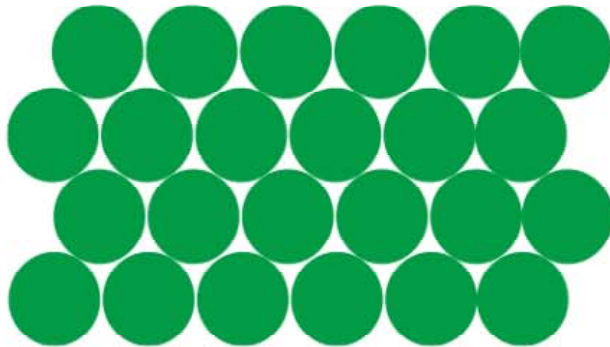
Close-packed structures 紧密堆结构



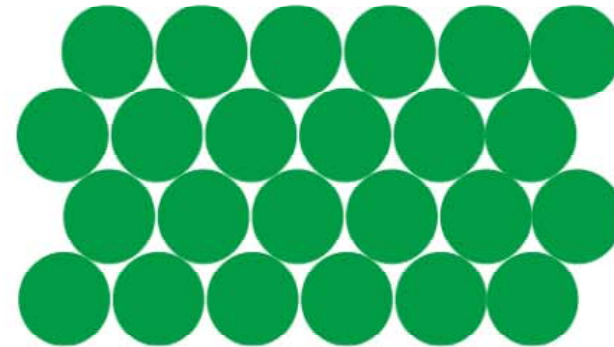
Close-packed structures 紧密堆结构

fcc and hcp 面心立方与密堆六方

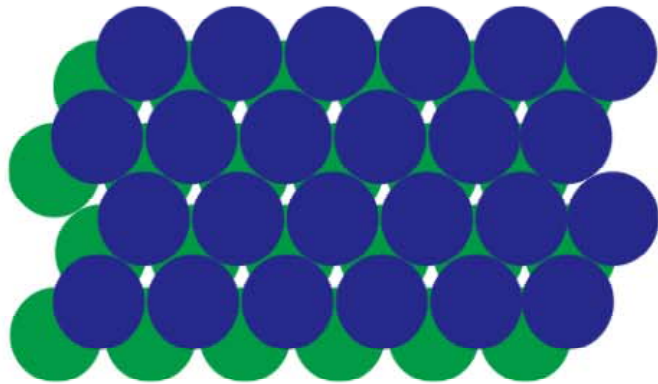
hcp
ABABAB...



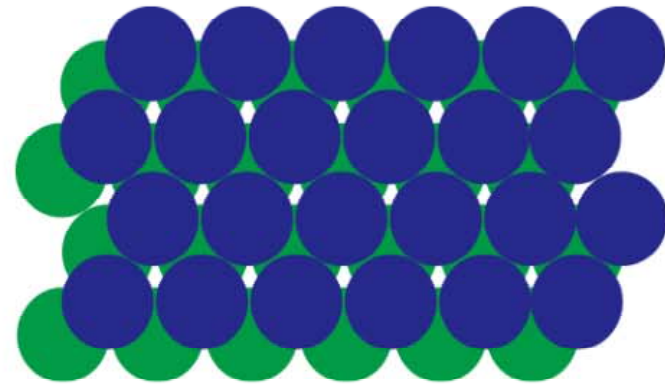
fcc
ABCABCABC...



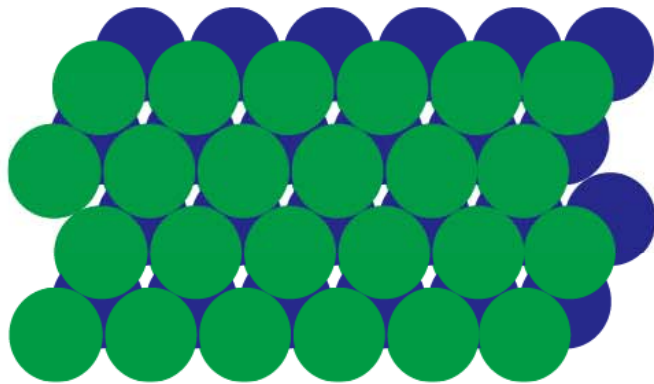
hcp
ABABAB...



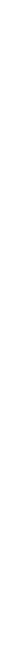
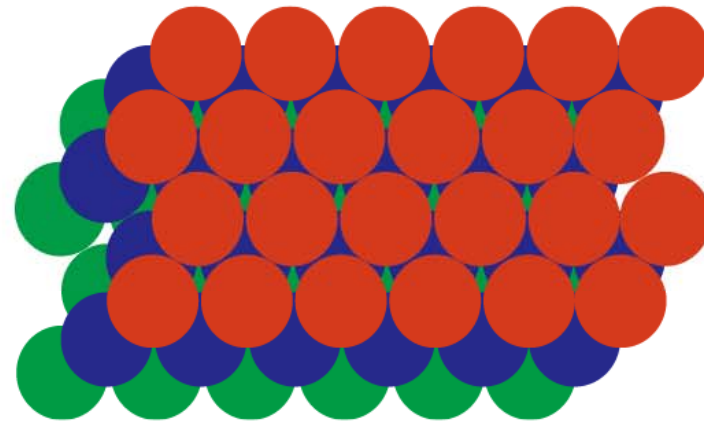
fcc
ABCABCABC...



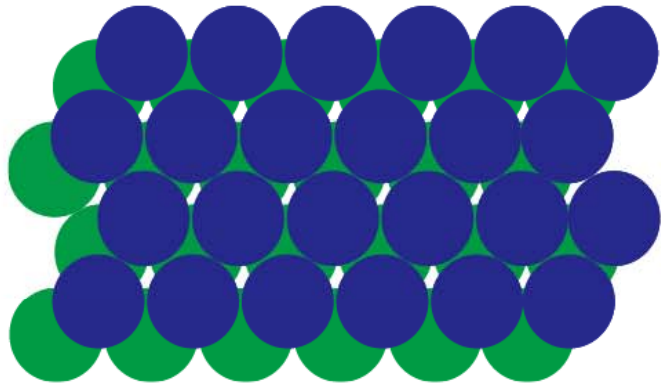
hcp
ABABAB...



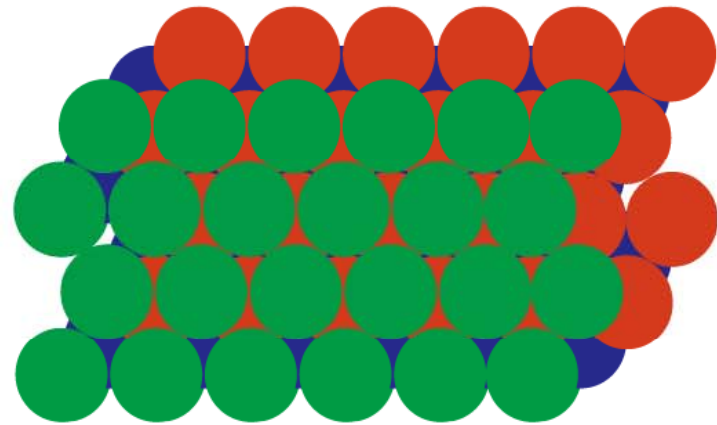
fcc
ABCABCABC...



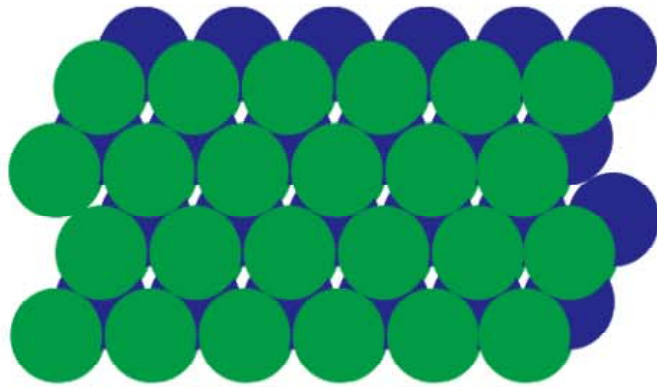
hcp
ABABAB...



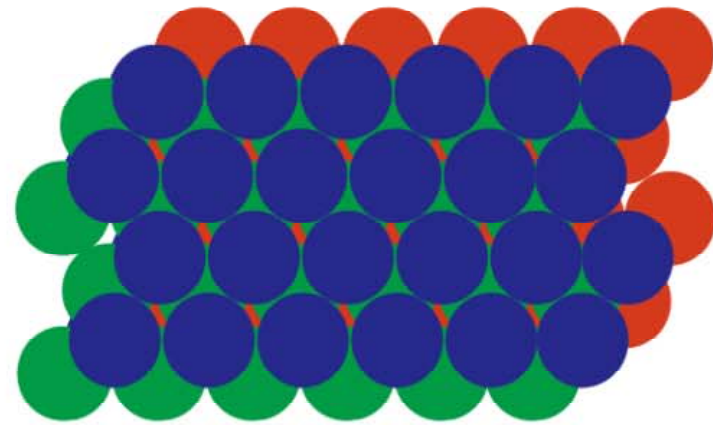
fcc
ABCABCABC...



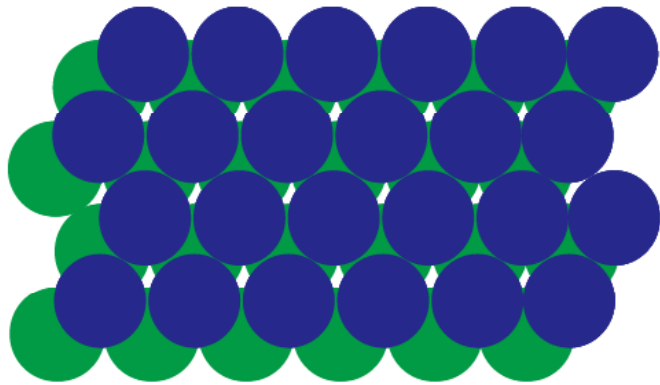
hcp
ABABAB...



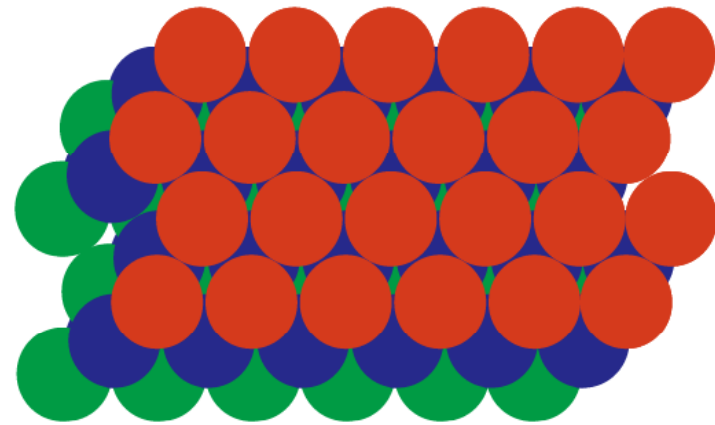
fcc
ABCABCABC...



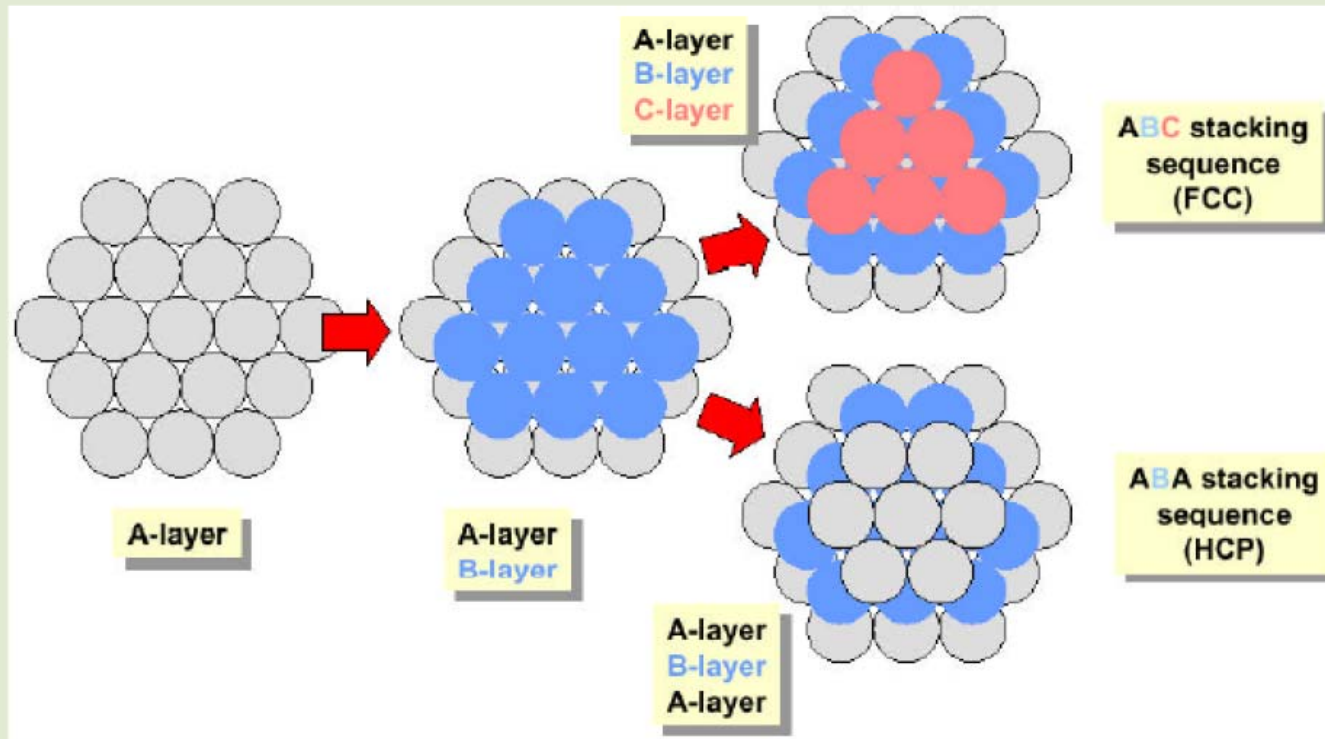
hcp
ABABAB...



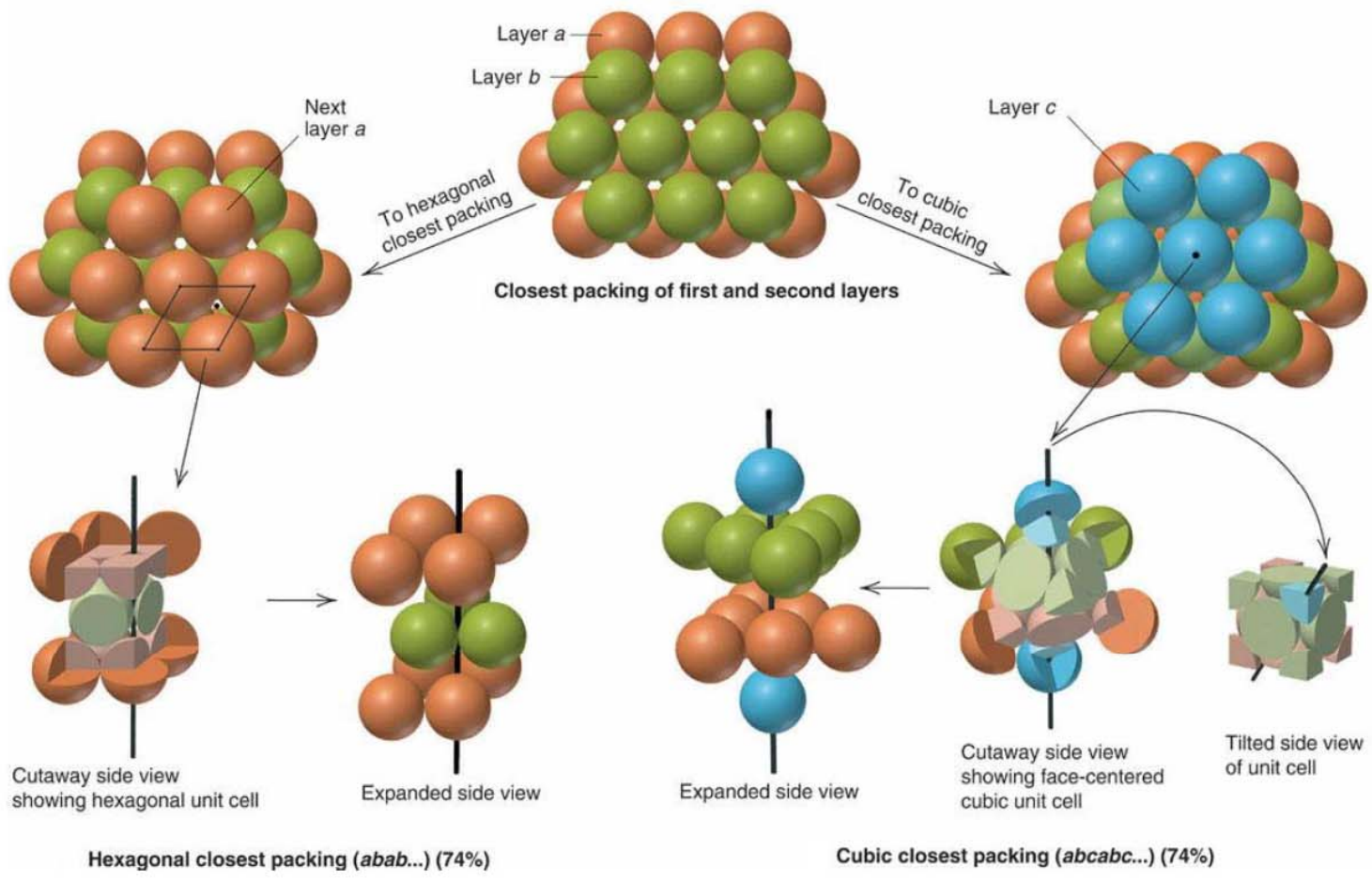
fcc
ABCABCABC...



The tightest way to pack spheres:



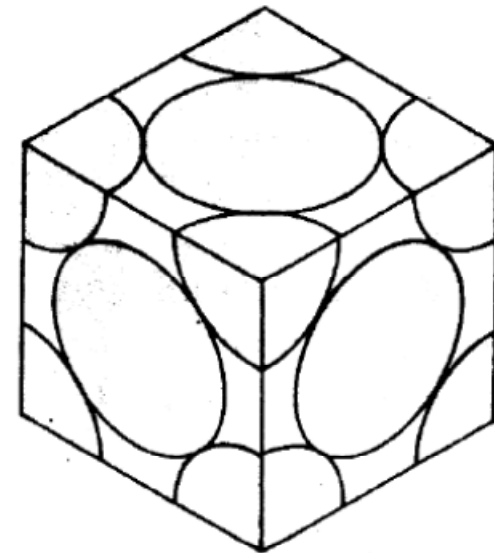
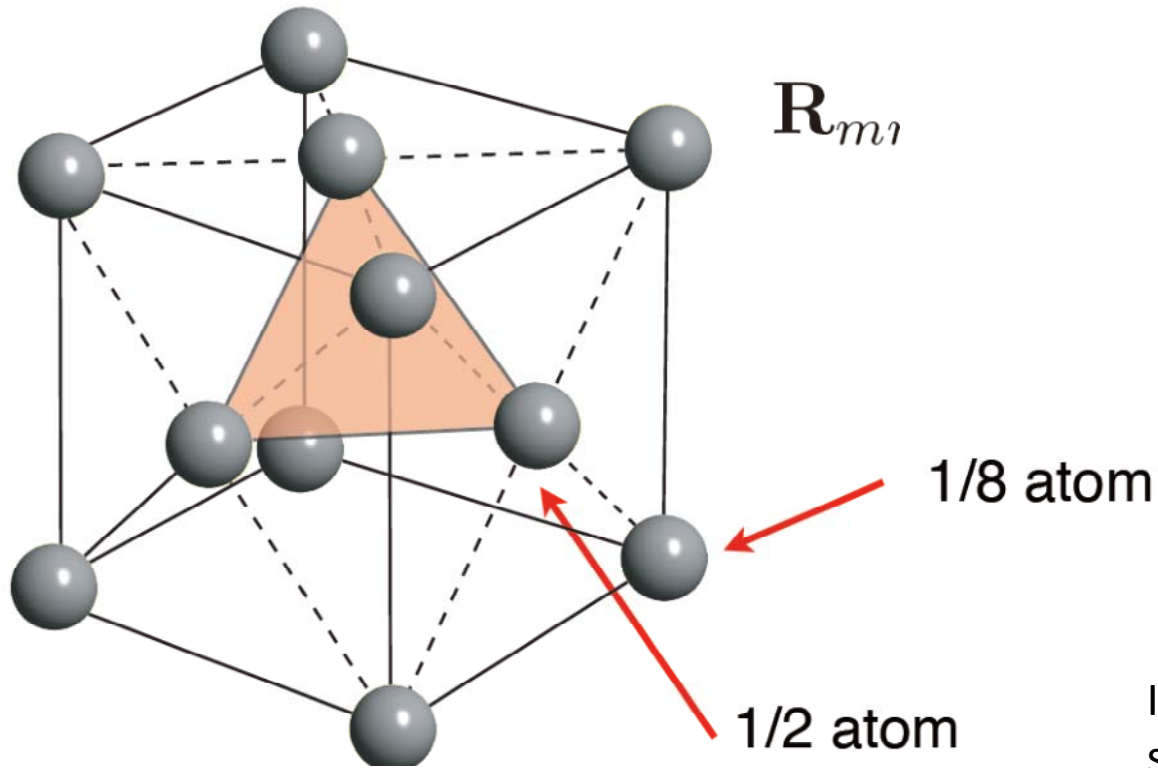
ABCABC... = fcc, ABAB... = hcp!



配位数都是12，堆积密度都为74%

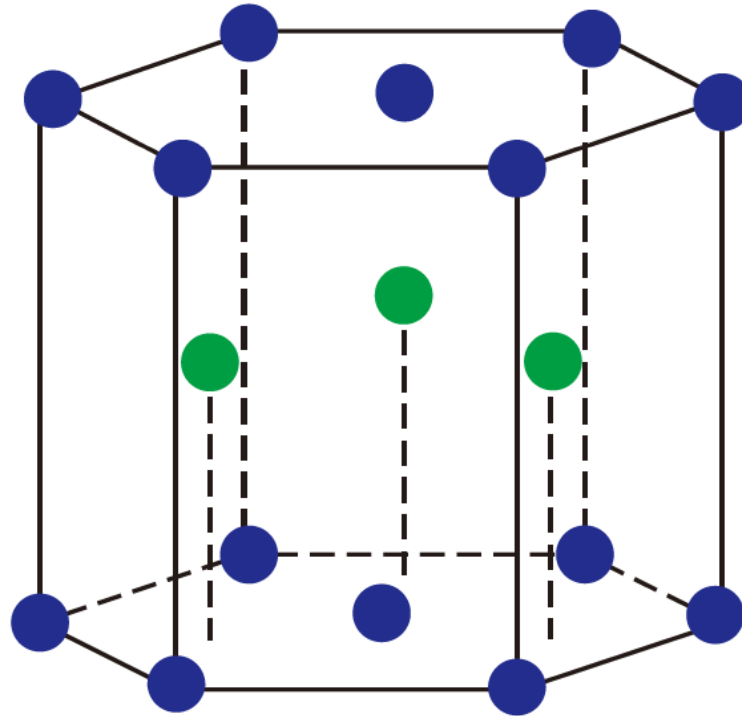
The unit cell of fcc structure

- The cubic unit cell contains more than one atom.



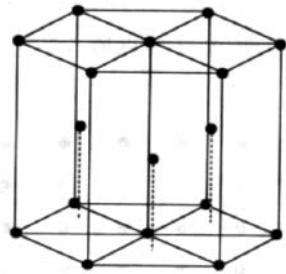
In the face-centred cubic (fcc) structure 74% of the total volume is occupied (slightly better than bcc with 68%)

The unit cell of hcp structure

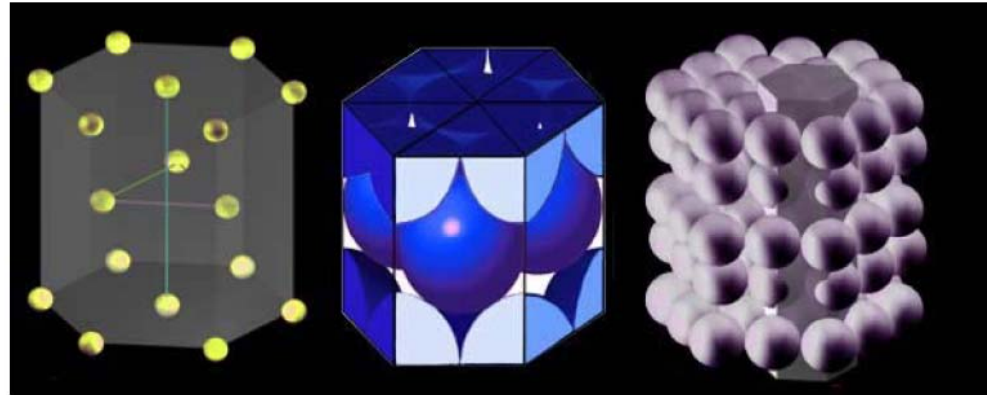


- The hcp lattice is NOT a Bravais lattice. It can be constructed from a Bravais lattice with a basis containing two atoms.
- the packing efficiency is of course exactly the same as for the fcc structure (74 % of space occupied).

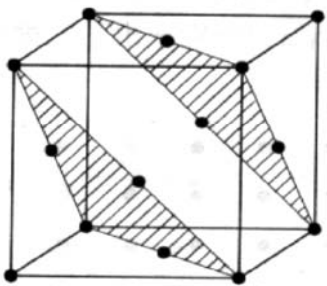
hcp不是布拉维格子！



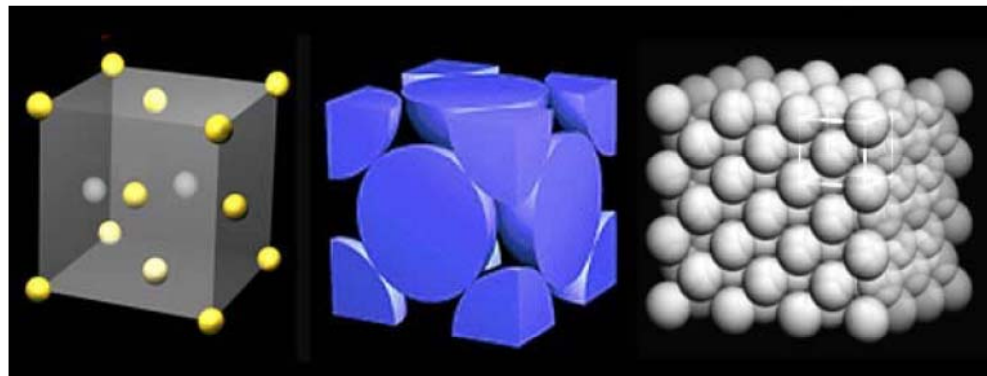
六角密排



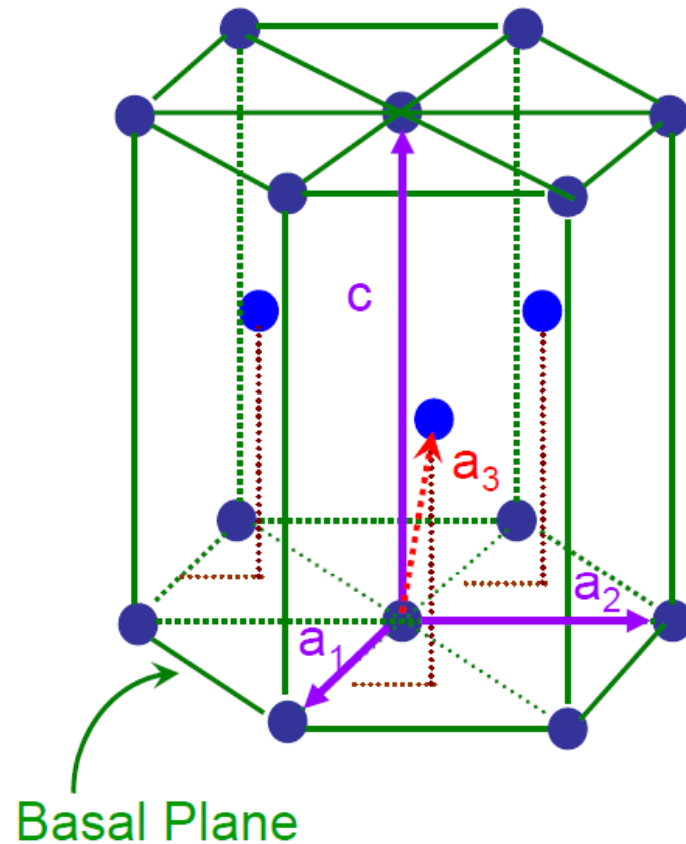
fcc是布拉维格子！



立方密排结构单元



Hexagonal Close-Packed lattice



$$|a_1| = |a_2|, \text{ with an included angle } 120^\circ$$

$$|c| = 1.633|a_1|$$

$$|a_1| = |a_2| = |a_3|$$

12 nearest neighbors

Transition metals : Sc, Y, Ti, Zr, Co...

IIA metals : Be, Mg

Hexagonal lattice + basis of 2 atoms at $(0,0,0)$ and $(2/3,1/3,1/2)$

Close packed structures -metal

fcc: Cu,Ag,Au,Al,Ca,Pb,Pt

hcp: Be,Mg,Zn,Cd,Gd,Tb,Dy,Ho,Er,Tm

晶体	c/a
Be	1.633
Mg	1.623
Zn	1.861
Cd	1.886
Co	1.622
Lu	1.586
Gd	1.592

hcp

Cu	a=3.16
Ag	a=4.09
Al	a=4.05
Au	a=4.08
Ca	a=5.58
Ni	a=3.52

fcc

除去ABAB...排列得到的hcp结构和ABCABC...排列得到的fcc结构，密堆积还可能有**无穷**多种排列方式，比如ABACABAC...等等。

多型性 (polytypism)：长重复周期的堆积方式。
例子：SiC, Pbl₂, Cdl₂

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)

Think peer review takes too long? One mathematician has waited four years to have his paper refereed, only to hear that the exhausted reviewers can't be certain whether his proof is correct. George Szpiro investigates.



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.

Nature, 3 July 2003

二. 晶体结构的表达方法

指出晶体所属的点阵、晶系、点群和空间群类型是在不同层次上对晶体结构做描述。

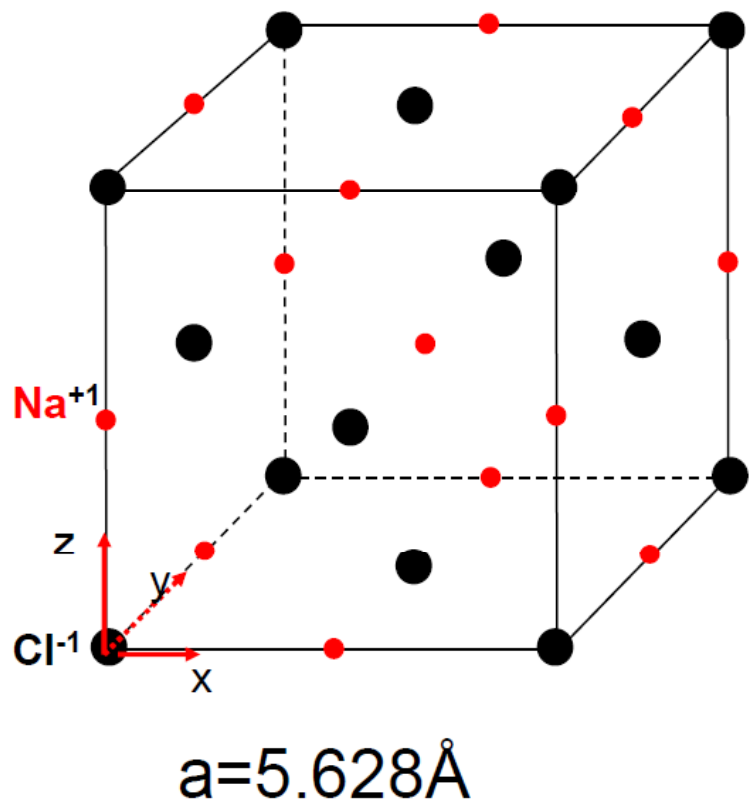
以NaCl为例说明。

面心立方点阵说明了它属于立方晶系，可以用 $a=b=c$, $\alpha = \beta = \gamma = 90^\circ$ 面心立方晶胞表示其原子周期排列特点。

点群为 O_h ，说明了它的外形具有的宏观对称性。

空间群为 O_h^5-Fm3m ，指出了它的原子排列规律。

至此我们才可以说对NaCl晶体的几何结构特点有了比较充分的认识。



对晶体结构几何特征的了解归结为绘出它的**结晶学晶胞**（包括基元中原子的种类、数量、相对取向及位置的点阵惯用原胞），**定出全部原子的位置，并确定出它的晶胞参量：**

a, b, c 和 α, β, γ

通过X光衍射等实验方法即可以做到这些。

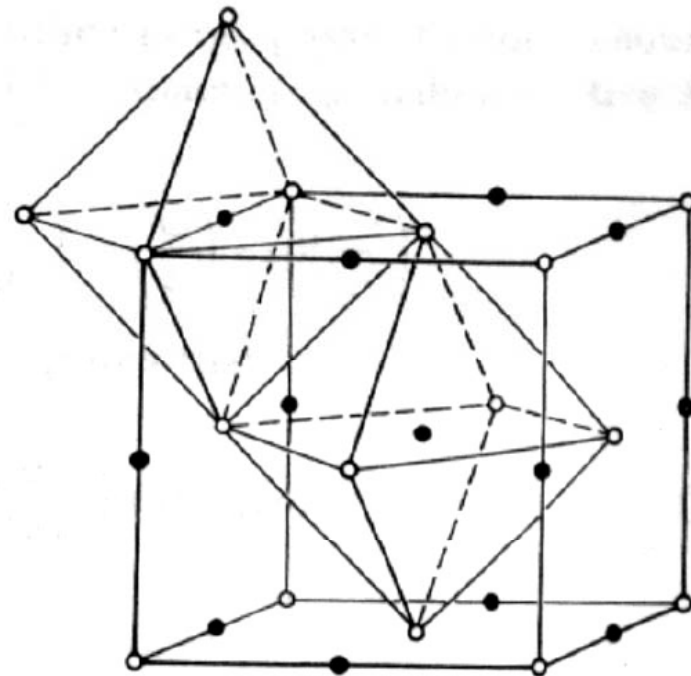
对 **NaCl** 晶体结构的测定，使我们得到了左面的反映其完整结构的晶胞图（测定原理见1.5节）

NaCl晶体为八面体群的说明： O_h ,

它的每个原子都处在不同原子组成的8面体体心位置。考虑它的晶场时就要注意到这个特点。

点群对称操作：

体对角线是3重轴；
3条棱边是4重轴；
棱对角线是2重轴，
体心是反演中心。



(b)

原子位置的表示：绘制晶胞时需要明确指出基元中各原子的位置。基元中第 j 个原子的中心位置相对于作为坐标原点的格点位置可以表示为： $r_j = x_j a + y_j b + z_j c$

如果以晶胞各边长度做单位， $0 \leq x_j, y_j, z_j, \leq 1$

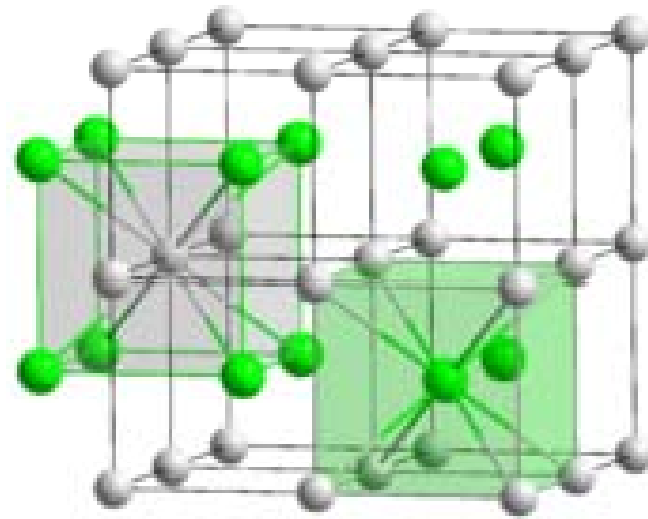
NaCl中，Cl原子位置为： $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2},$

Na原子位置为： $\frac{1}{2}\frac{1}{2}\frac{1}{2}, 00\frac{1}{2}, 0\frac{1}{2}0, \frac{1}{2}00,$

CsCl晶体为简立方晶胞，

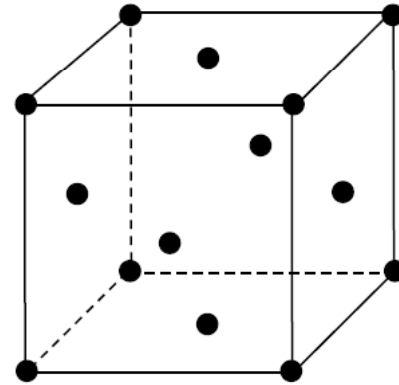
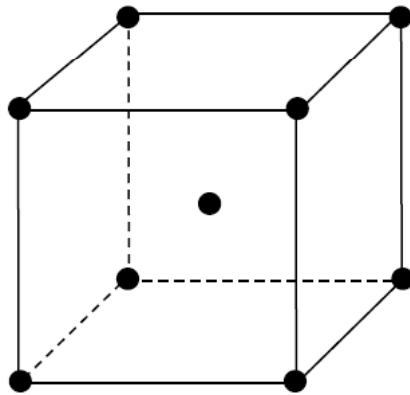
Cs原子在 $000,$

Cl原子在 $\frac{1}{2}\frac{1}{2}\frac{1}{2}。$



简单晶格和复式晶格：

许多元素晶体，其最小重复单元就是一个原子，知道了它的点阵类型，把阵点换成原子，就是它的晶胞，我们常称它具有简单晶格。例如：具有体心立方结构的碱金属Li、Na、K，和具有面心立方结构的Cu、Ag、Au晶体都是简单晶格。简单晶格晶体中所有原子是完全等价的，它们不仅化学性质相同而且在晶格中处于完全相同的位置，有完全相同的环境，比如近邻、次近邻原子数目、原子种类等。



但有些元素晶体和所有化合物晶体，其最小重复单位（**基元**）至少包含**2个或2个以上的原子**，它们的每一个原子虽然都构成同样的点阵类型（即同样的周期排列方式），但绘成晶胞时，要绘出基元原子之间位置上的相互关系，所以是同样的点阵类型的叠加，我们称这些**晶体具有复式晶格**。

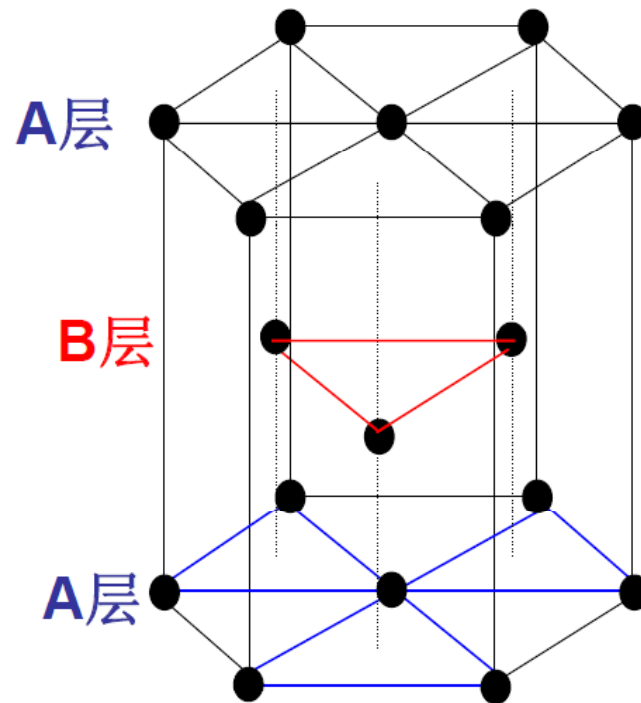
例如：**CsCl**晶体是两个原子各自构成简立方点阵后，沿晶胞对角线方向移动二分之一距离的叠加。

NaCl晶体是两个原子各自形成一个面心立方点阵后，沿立方边方向移动二分之一晶胞边长距离的叠加。

上述复式晶格中，每种原子自身是等价的，有完全相同的环境，但两类原子是不等价的，它们的几何环境是完全不同的。

CsCl晶体中，Cs离子的最近邻是8个Cl离子，而Cl离子的最近邻则是8个Cs离子，NaCl晶体中，Na离子的最近邻是6个Cl离子，Cl离子的最近邻则是6个Na离子。

元素晶体也不都是简单晶格，例如密堆六方（hcp）晶体Be, Mg, Zn, Gd等，它的基元包含2个原子，虽是同种原子，但它们的几何环境是不等价的，从一个A层原子看上下两层原子的三角形，和从一个B层原子看上下两层原子的三角形是不同的。它是复式晶格，它的基元有2个原子。



三. 典型晶体结构

在晶体结构报告中常按照化合物中各类原子的种类与数目参照晶体的化学性质进行分类，并用英文字母命名，科学文献中也常使用这种分类，介绍如下：

A 代表元素晶体。

A1 面心立方结构 (Cu), A2 为体心立方 (W)

A3 密堆六方结构 (Mg) A4 金刚石结构.....

B 代表AB型化合物，

。 B1 NaCl型结构； B2 CsCl型结构；

B3 闪锌矿型结构； B4 纤锌矿型结构；

C 代表AB₂型化合物

C1 萤石及反萤石结构 (CaF₂)

C2 黄铁矿 FeS₂

C3 赤铜矿 (Cu₂O)

其中每一小类都代表着许多结构基元排列相同、空间群相同的晶体。我们介绍其中经常提到的和最重要的几类：

A1

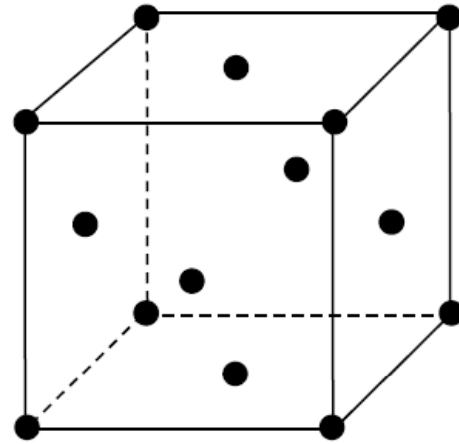
以元素晶体Cu为代表的晶体，具有面心立方点阵
(fcc)，

其晶胞内的原子坐标为： $000, 0\frac{1}{2}, 0\frac{1}{2}, 0\frac{1}{2}, 0\frac{1}{2}, 0\frac{1}{2}, 0\frac{1}{2}, 0\frac{1}{2}$

点群符号为： O_h

空间群符号： $O_h^5 (F_{m3m})$

原子最近邻 12 ， 次近邻 6 。



相同结构的元素晶体还有： $Ag, Au, Ni, Al, Pb, Pd, Pt,$
及固态稀有气体 $Ne, Ar, Kr, Xe.$

A2:

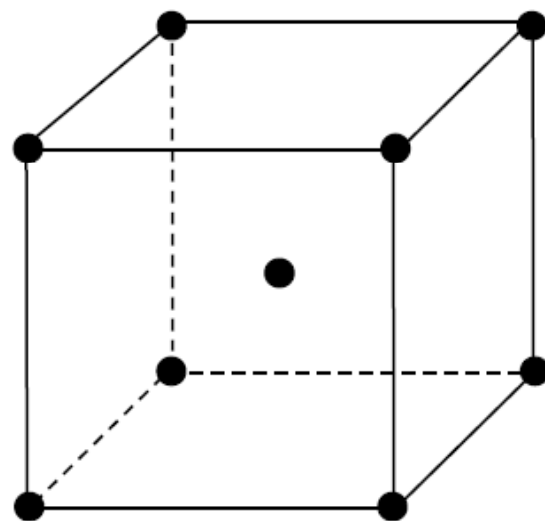
以金属钨为代表的元素晶体，体心立方点阵 **bcc**,

其原子坐标为： $000, \frac{1}{2} \frac{1}{2} \frac{1}{2}$,

点群符号为： O_h

空间群符号为： $O_h^9 (I_{m3m})$

最近邻为 8，次近邻为 6



相同结构的元素晶体有：碱金属Li,Na,K,Rb,Cs,

及金属Ba,V,Cr,Nb,Mo,Ta,W,Fe 等

A3: 以金属铋为代表的密堆六方结构hcp。

惯用晶胞

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

$$\gamma = 120^\circ$$

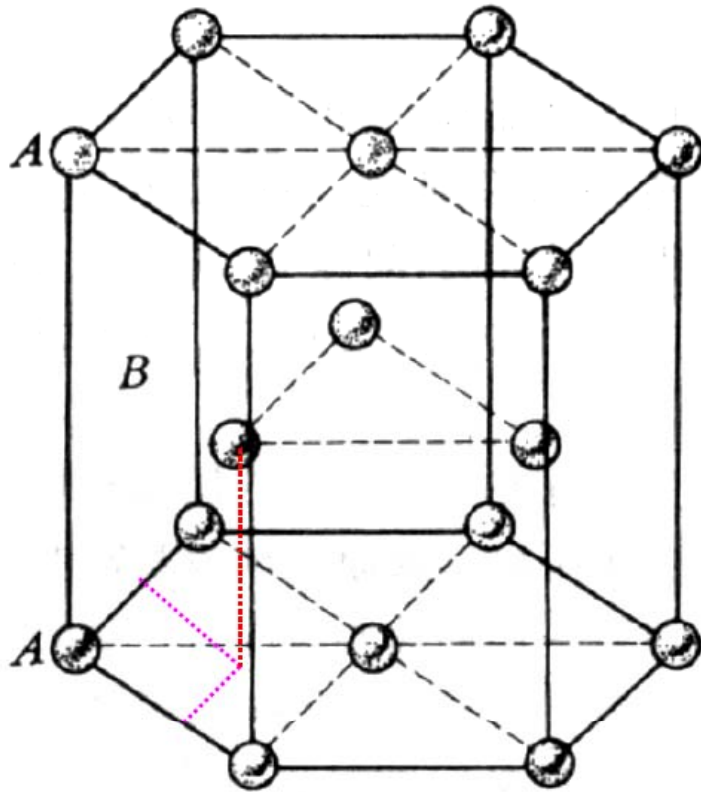
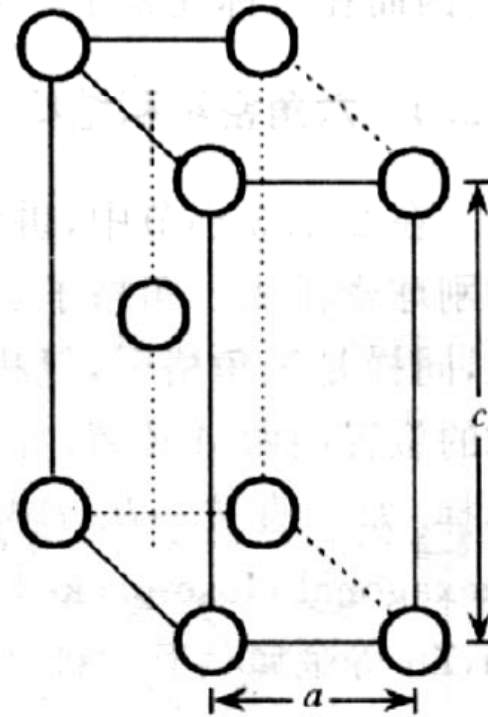


图 1-6 六角密排晶格的典型单元



(b)

hcp 结构原胞中原子坐标： $000, \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$,

点群符号： D_{6h}

空间群符号： $D_{6h}^4 P6_3/mmc$

hcp理想的密排比是： $\frac{c}{a} = 1.633$ （见习题1.2）

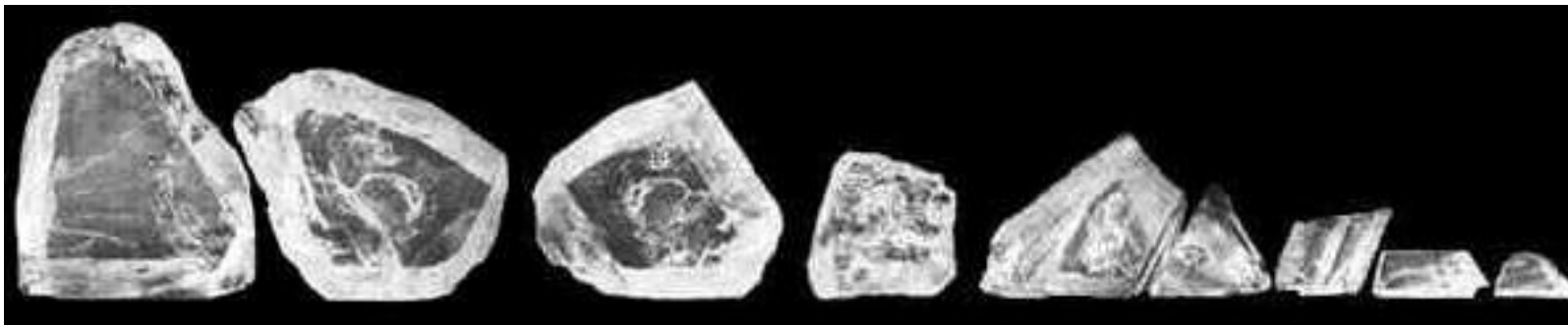
具有hcp结构的元素晶体有：Be, Mg, Sc, Y, Ti, Zr, Zn, Cd

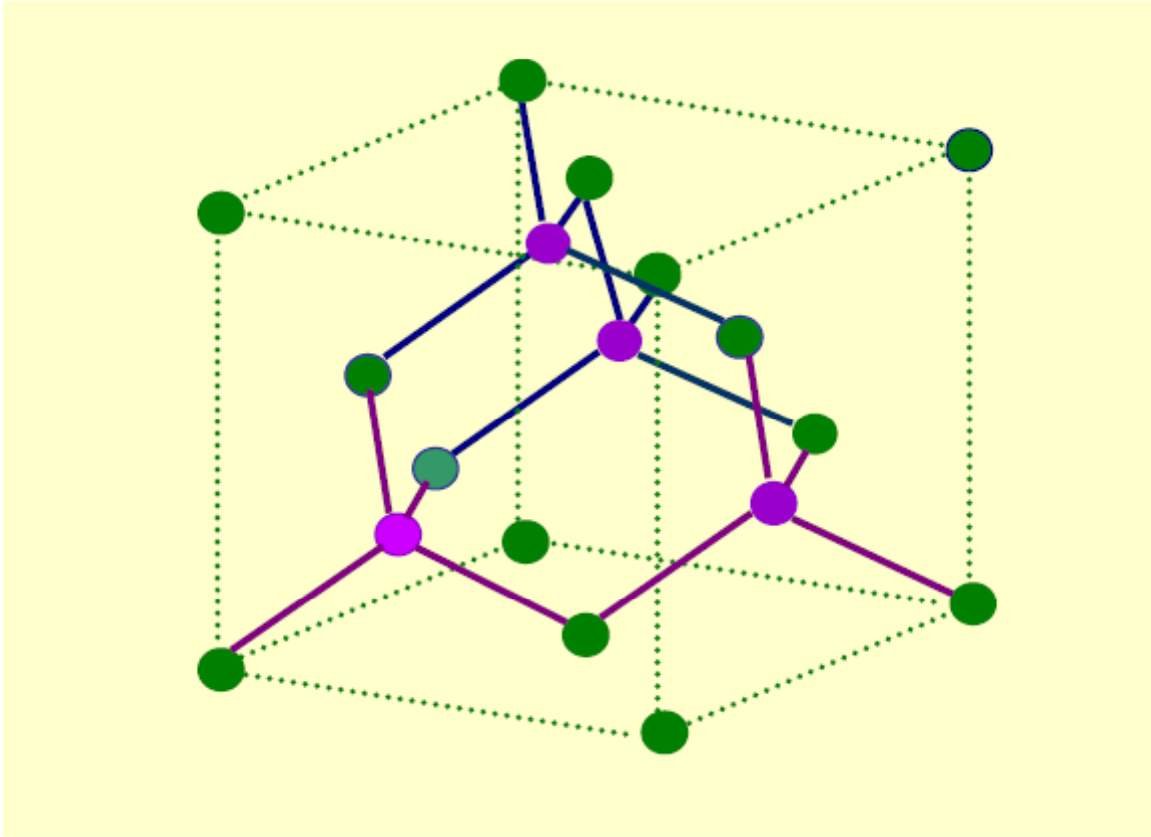
和大多数稀土金属Gd, Tb, Dy, Ho, Er, Tm, Lu

A4. 金刚石结构

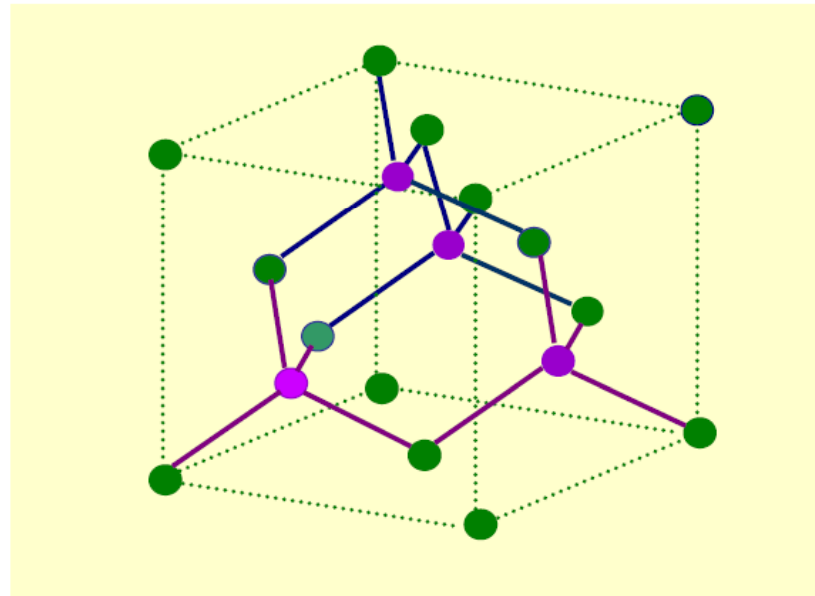
卡利南钻石（Cullinan Diamond, the）是迄今（2013年）发现的最大天然钻石原石，重3,106克拉，相当于612.2公克，于1905年1月26日发现于南非的卡利南矿场。英国国王爱德华七世拥有时，将它切割为9大块及许多小块，其中9大块分别命名为卡利南一～九世（Cullinan I～IX），皆为英国王室所收藏。

卡利南一世：别名“大非洲之星”（Great Star of Africa, the），曾为世界最大的切割钻石，现仅次于登基五十周年（Golden Jubilee Diamond, the）。装饰在皇家权杖上，于伦敦塔展示。

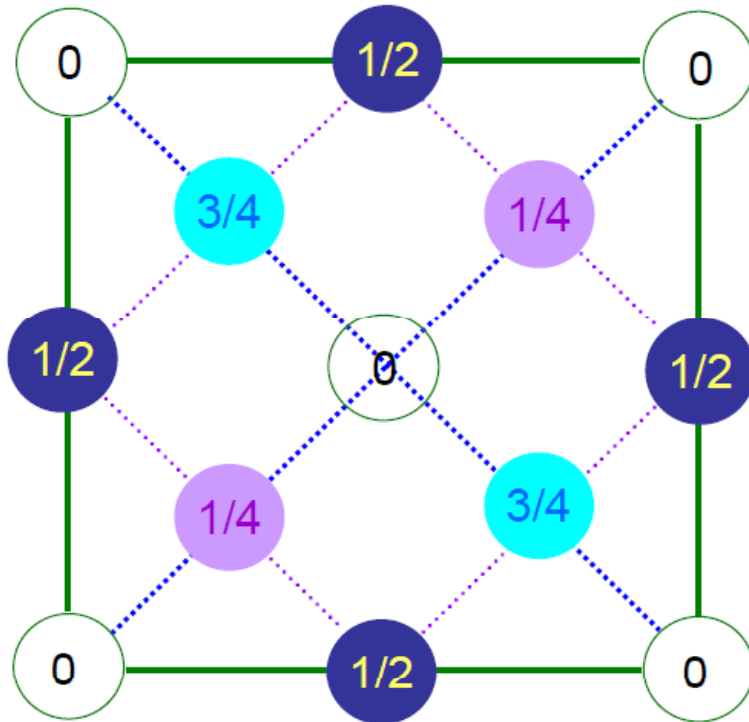




它是由两个fcc点阵, 每个点阵放上同种原子, 沿体对角线平移 $1/4$ 体对角线长穿套起来的, 这个结构的Bravais点阵是fcc点阵, 它的初基基元包含两个原子, 基元中两个原子的坐标用惯用晶胞的晶轴写出就是 (000) 和 $(1/4, 1/4, 1/4)$, 将这两个原子组成的基元按fcc点阵的排列便可得金刚石结构, 惯用晶胞中有4个基元, 共有8个原子。



金刚石晶胞中的原子位置, 有两种不同晶格位置。



$$000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0,$$

$$\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4},$$

即基元包含**2**个原子, 各自形成面心立方点阵, 沿体对角线移动四分之一叠加而成。但**每个原子都处在同种原子的四面体中, 所以具有这种结构的晶体, 其原子是共价键结合。** Kittel p13

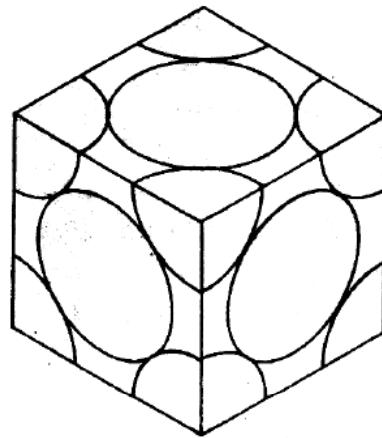
金刚石结构点群符号： O_h

空间群符号： $O_h^7(F_{d3m})$

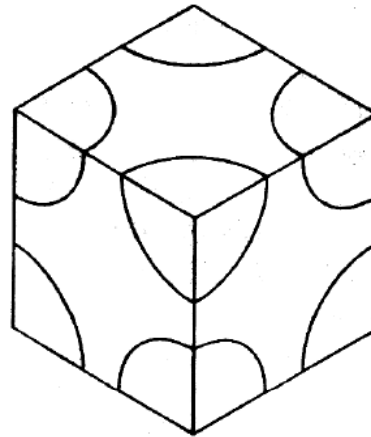
具有相同结构的元素晶体有：C:a=3.567 Si:a=5.430;

Ge:a=5.658; α -Sn(灰锡):a=6.49。

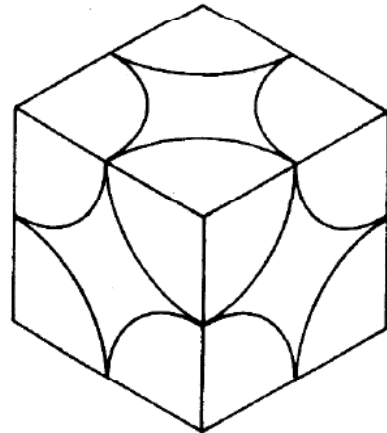
金刚石拥有四面体型成键特征，每个原子有4个最近邻和12个次近邻。金刚石结构是比较空的，在总体积中，已被硬球填充的最大比率只有0.34，远低于密堆积结构的填充率0.74。它是周期表中第IV族元素具有方向性共价键结合的典型例证。



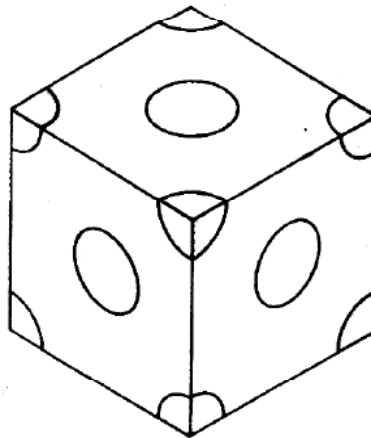
F.C.C., 74% full



B.C.C., 68% full



S.C., 52% full



Diamond, 34% full

不同立方结构中，按刚性球形原子模型计算出所占总体积的比例：

Figure 1-30 Filling factors for identical spheres in contact, in four common cubic structures. After C. Wert and R. Thomson, *Physics of Solids* (McGraw-Hill, 2nd edition, 1970).

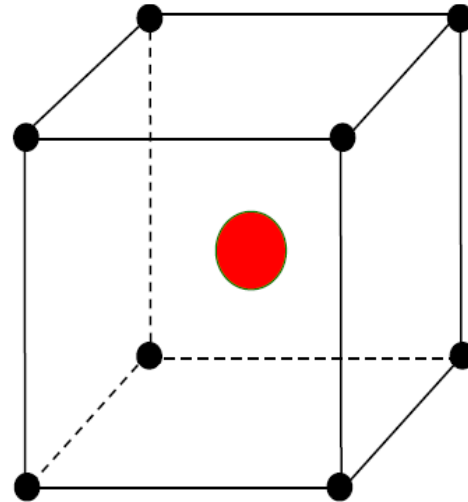
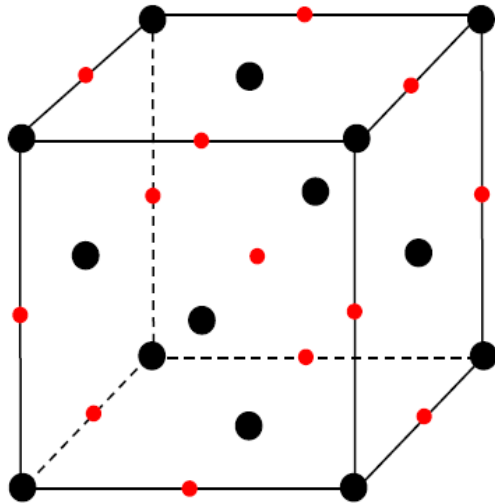
B1: NaCl型结构, 前面已讲, 从略。

B2: CsCl型结构, 结构图见前, 点群符号: O_h

空间群: $O_h^1(P_{m3m})$ 晶胞中原子位置: $000, \frac{1}{2} \frac{1}{2} \frac{1}{2}$

最近邻 8个异号离子, 次近邻 6个同号离子。

这是两类可以形成离子性结合的典型结构。



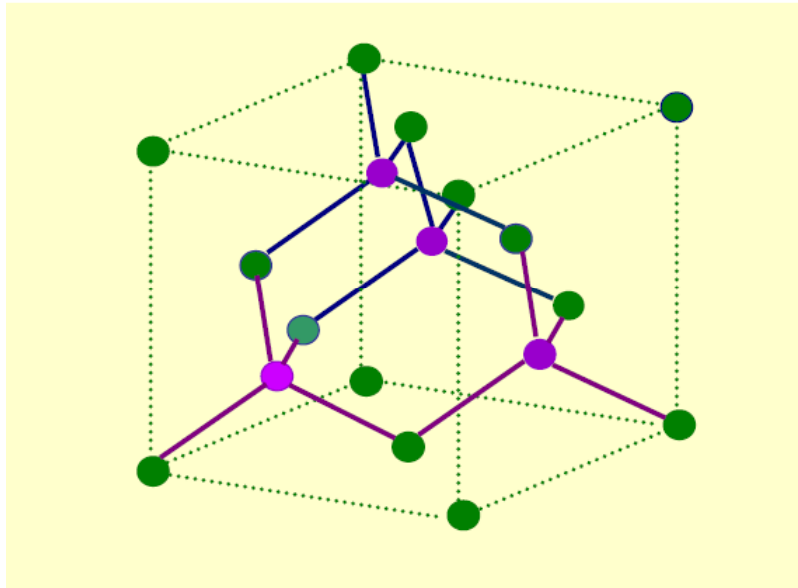
B3: 闪锌矿结构（立方ZnS），

fcc，结构类似金刚石，原子位置相同，只是基元换成ZnS分子，因此对称性降低，点群为： T_d

空间群为： $T_d^2(F_{43m})$

硫原子坐标： $000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0,$

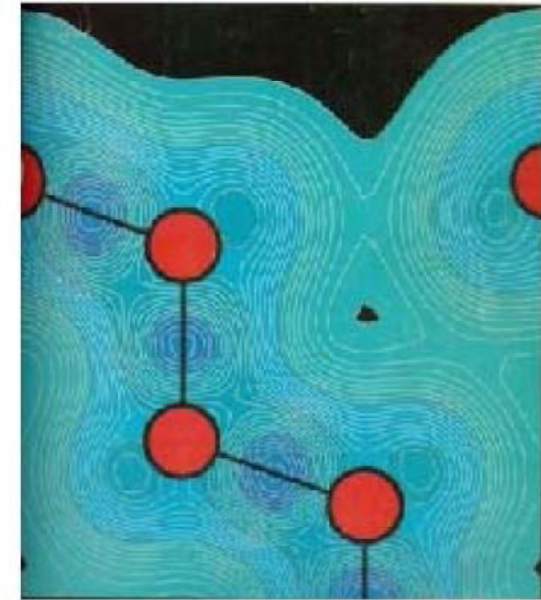
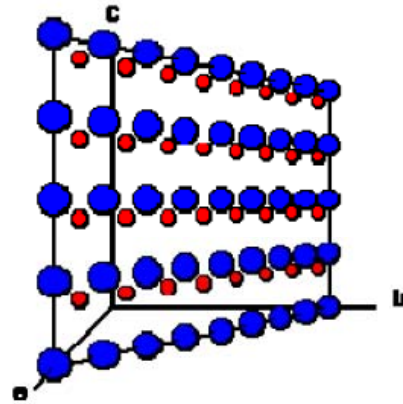
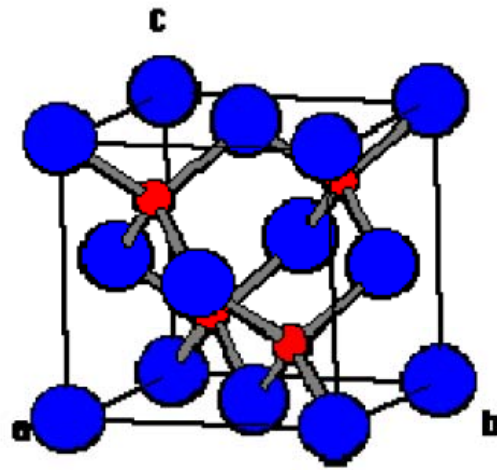
锌原子坐标： $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4},$



很多 II-VI 族, III-V 族

化合物具有此结构，是重要的
半导体和发光材料。例如：
GaAs, InSb, SiC

见 Kittel 14 页 图 24



ZnS的(110)面。可以看到在该面上原子的zig-zag排列方式。锯齿形的Zn-S原子链

金刚石结构的Si(110)面上的原子zig-zag排列方式和价电子密度分布的计算结果。（现在运用STM可以直接观察到，不过结果与此不同，因为表面重构）。

B4: 纤锌矿（六角ZnS）

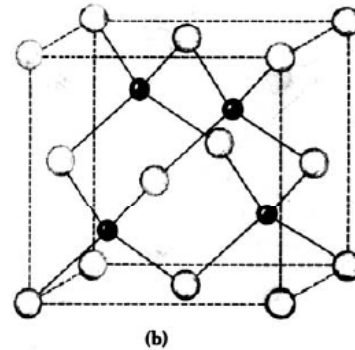
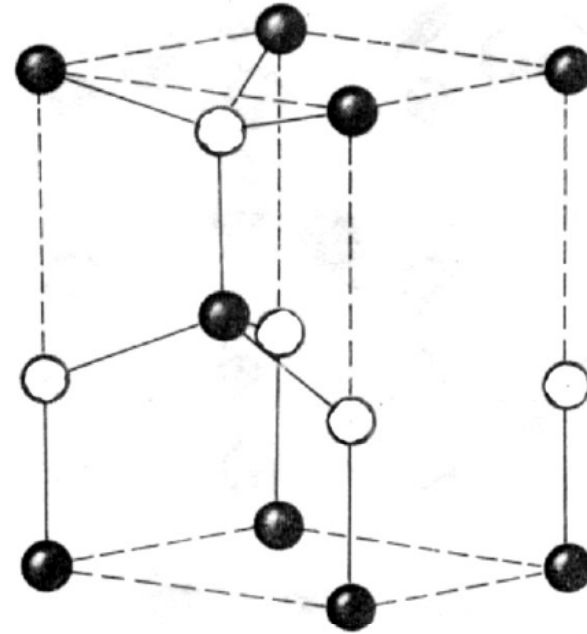
晶胞如右图（下方是立方结构）它的两种原子位置分别是：

$$000, \frac{1}{3}, \frac{2}{3},$$

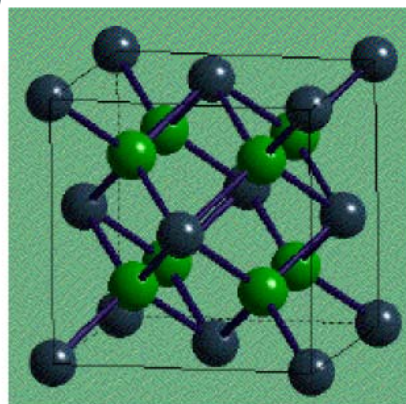
$$00\frac{3}{8}, \frac{1}{3}, \frac{2}{3}, \frac{7}{8}$$

点群： C_{6v}

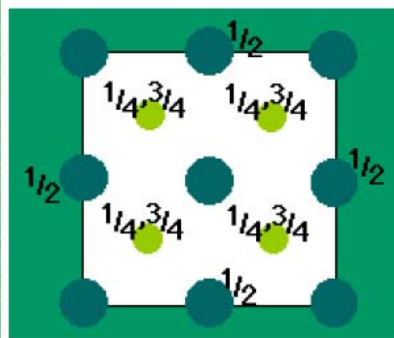
空间群： $C_{6v}^4(P6_3mc)$



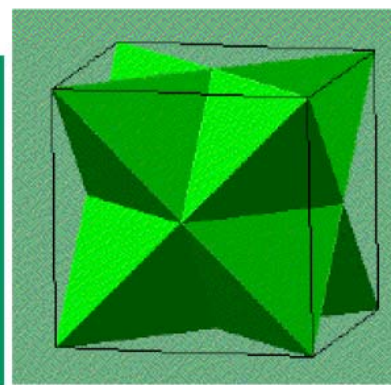
C1: 萤石结构



Fluorite A-cell



Plan view



FCa_4 Tetrahedra

空间群: O_h^5 (Fm3m)

Ca^{2+} 坐标: (0,0,0)

F-坐标: $(1/4, 1/4, 1/4; 1/4, 1/4, 3/4)$.

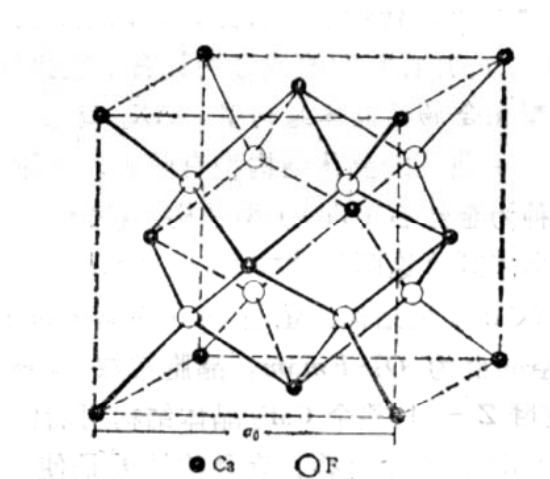
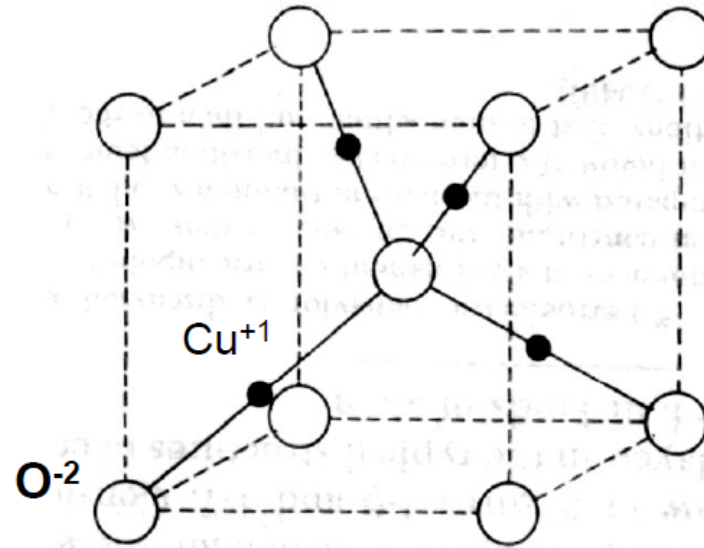
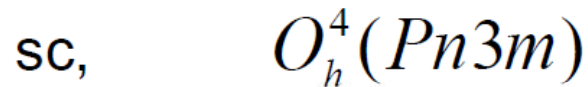
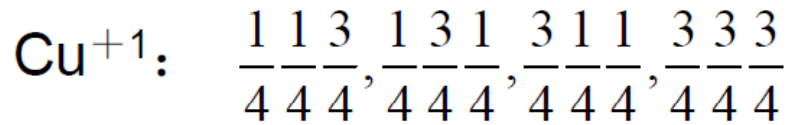
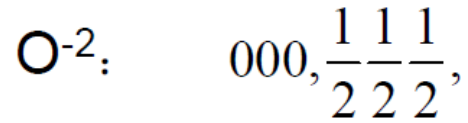


图 5.14 萤石 (CaF_2) 晶体结构模型。

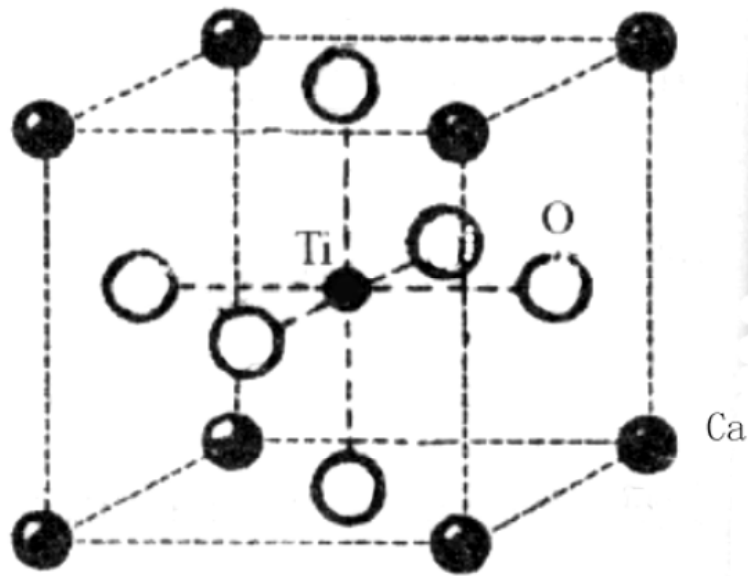
C3: 赤铜矿 (Cu_2O)



结构特点：它的每个氧离子都处在Cu 离子的四面体中，所以体对角线方向有一个三重对称轴，符合立方晶系的最低要求。

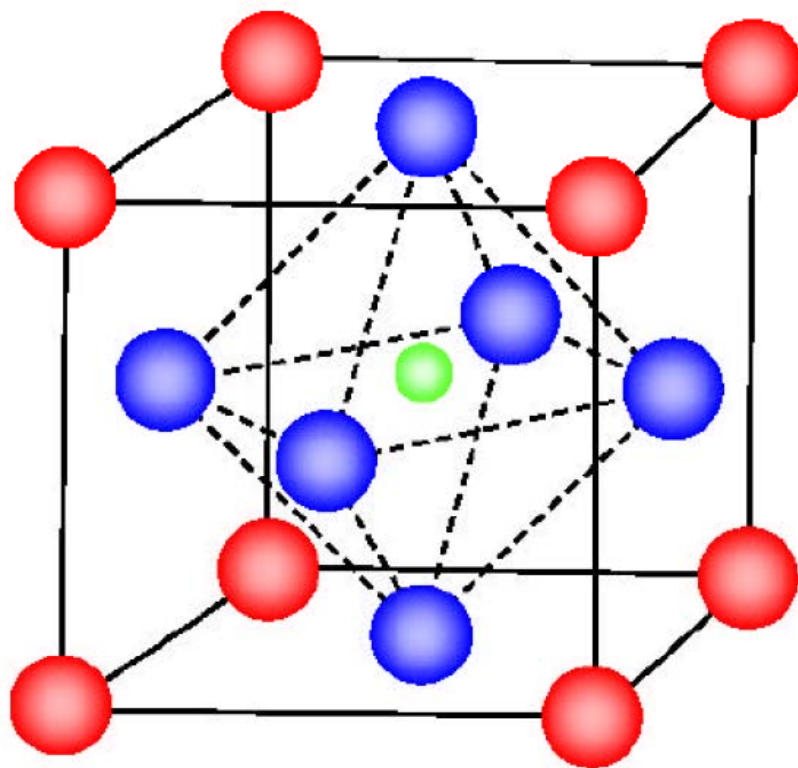
E 钙钛矿 CaTiO_3 : sc, 点群: O_h 空间群: $O_h^1(P_{m3m})$

这是一个很特殊的结构，每个基元有 5 个原子，各自组成简立方点阵，相互套购叠加而成。



BaTiO_3 结构

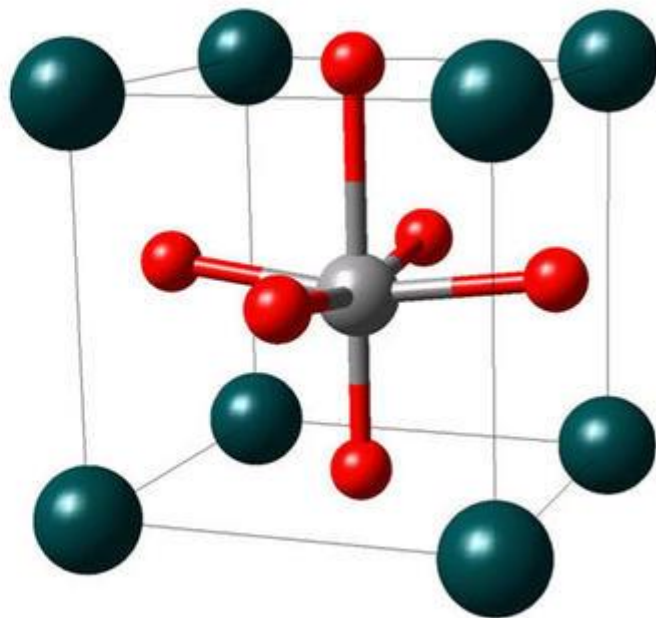
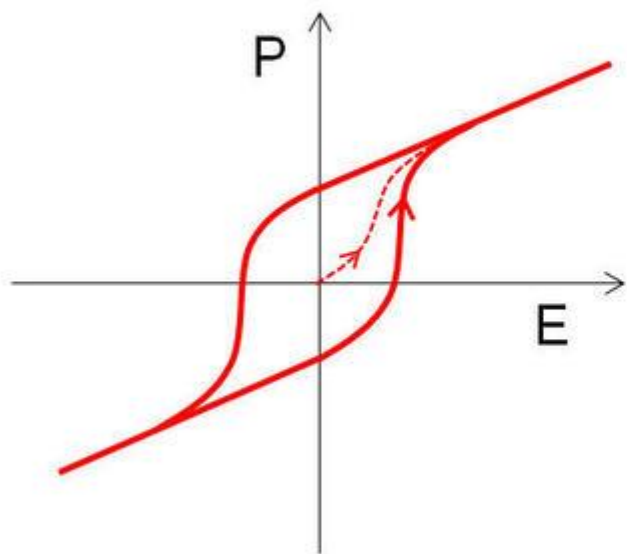
Perovskite Type Structure ABO_3 鈦酸鈣結構

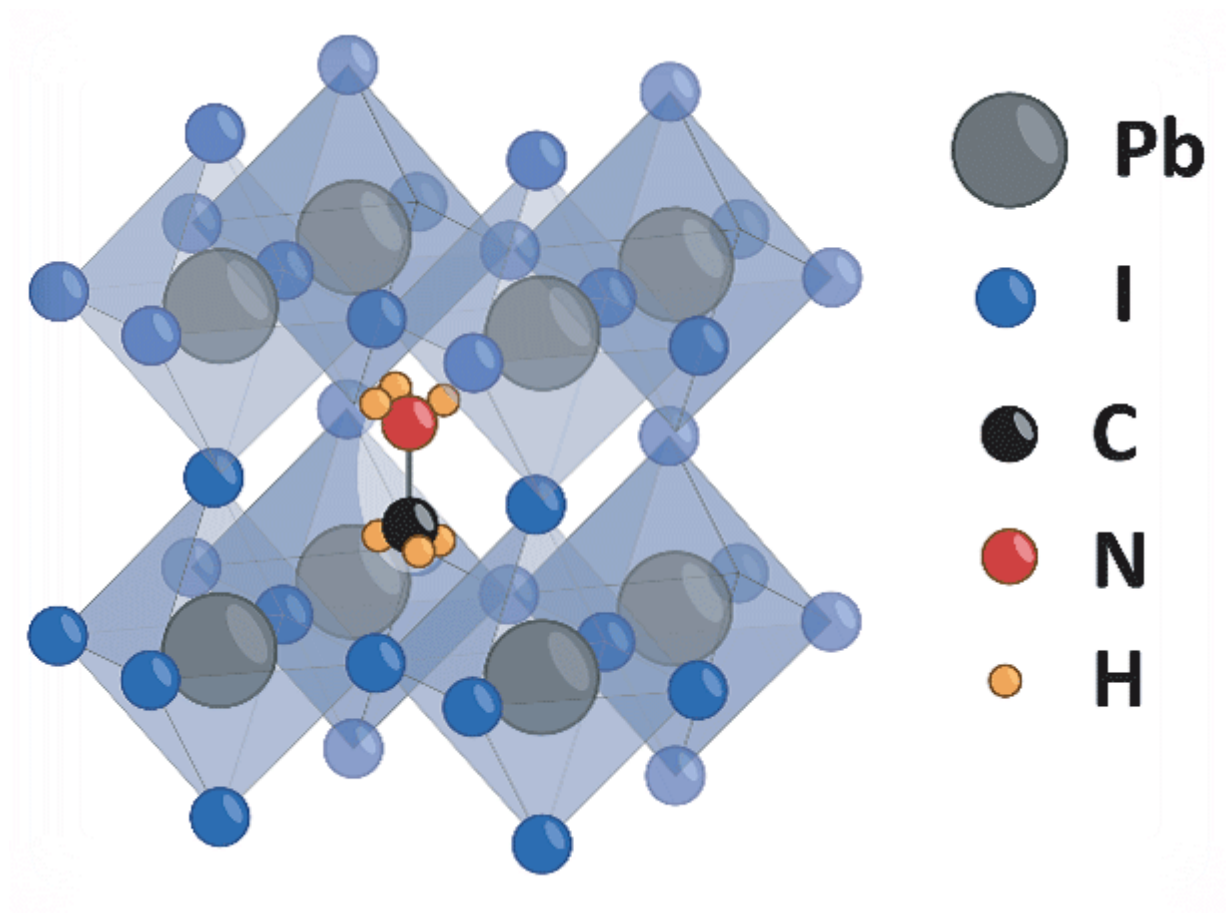


- **A - cation:**
cubic lattice
- **B - cation:**
body centered
- **O - anion:**
face centered

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





Pb

I

C

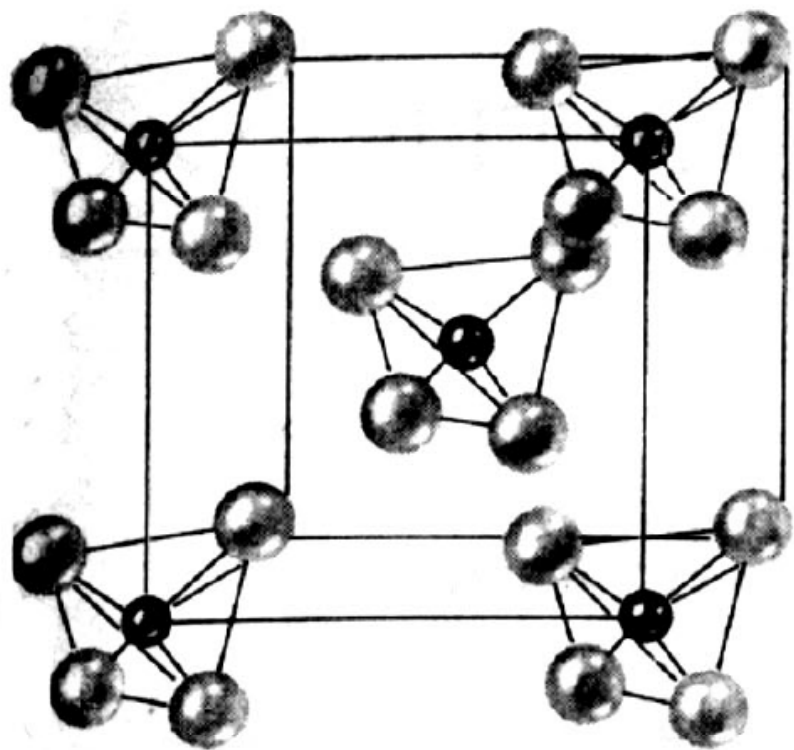
N

H

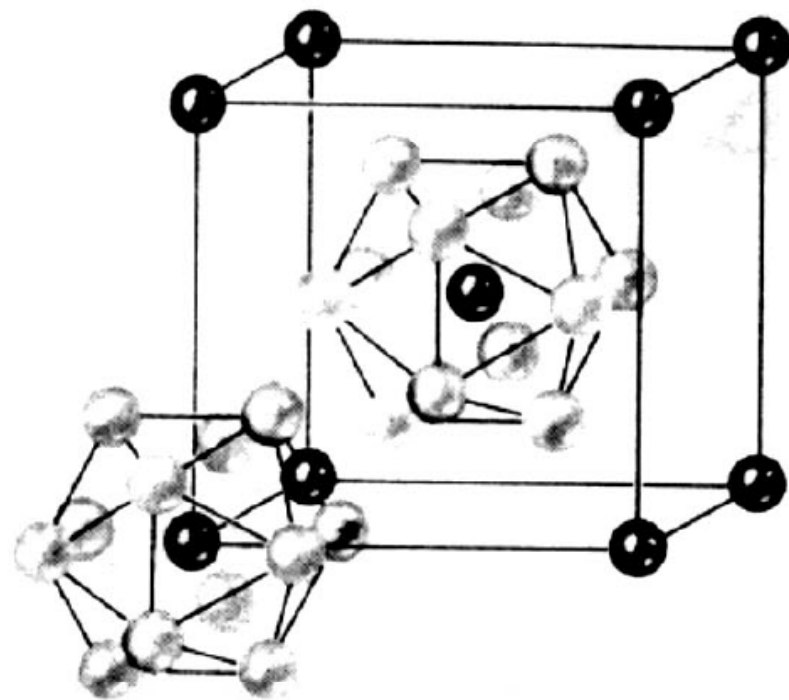
MAPbI₃

Perovskite solar cell

复杂合金结构



SiF₄合金: ^(a)Si在F的四面体中, 有**3**重轴,



MoAl₁₂; WAl₁₂合金

比较重要的还有：尖晶石 MgAl_2O_4 $O_h^7(F_{3dm})$

石榴石 $(\text{Fe,Mn})_3\text{Al}_2(\text{SiO}_4)_3$ $O_h^{10}(I_{a3d})$

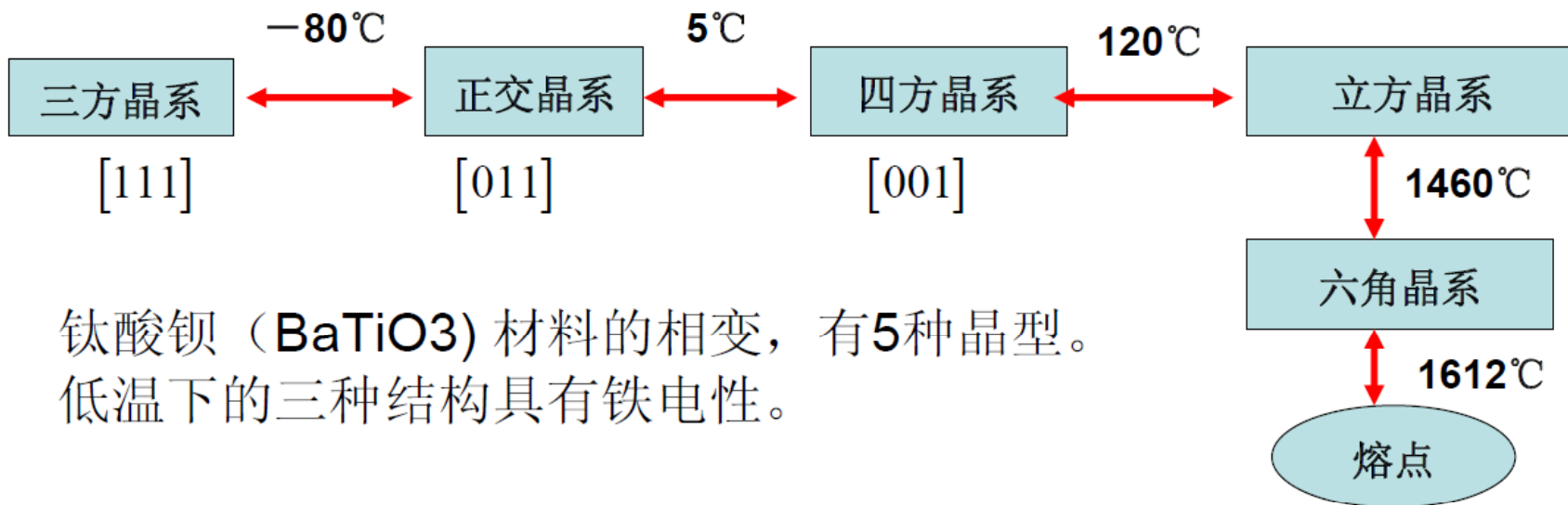
以上我们介绍的例子多数是立方晶系，1975年从
Crystal data No1 中所列出的 5572 种无机化合物中统计，

立方晶系	30%
六方晶系	11%
四方晶系	14%
三方晶系	12%
正交晶系	18%
单斜晶系	14%
三斜晶系	2%

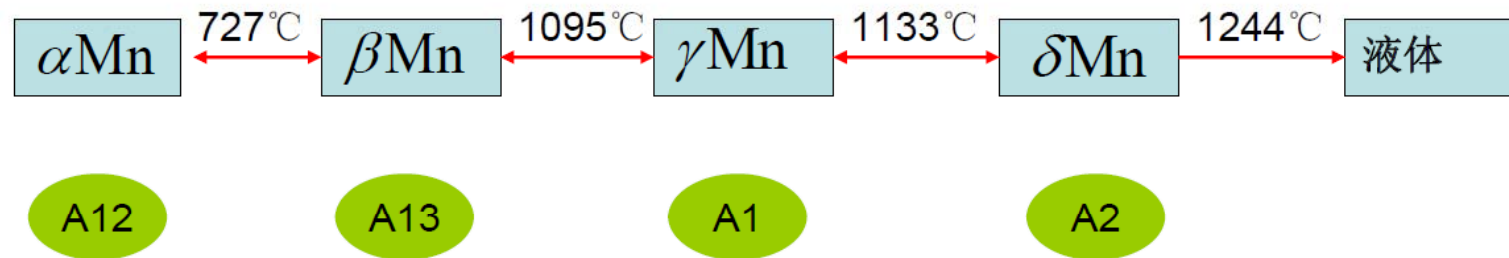
有机化合物和蛋白质晶体则不同，接近80%的晶体都属于正交和单斜晶系。

四. 多晶型现象和结构相变

同一种材料在不同的环境下，可以有不同的结晶状态，所以它的晶体结构可能不是唯一的，会随着环境温度、压力的变化而变化。

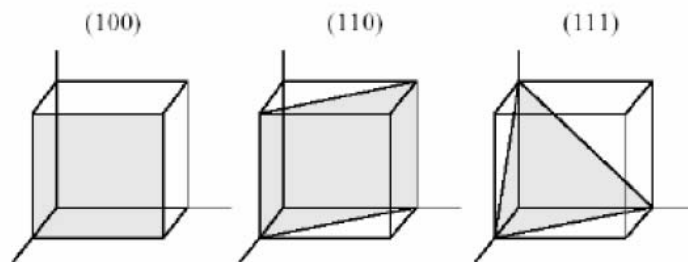


钛酸钡 (BaTiO_3) 材料的相变，有5种晶型。
低温下的三种结构具有铁电性。



锰金属晶体结构随温度发生变化，低温下为A12型，基元含有58个原子，A13型基元有20个原子，A1是fcc，A2是bcc.

五. 晶体表面结构



Science 282, 946 (1998)

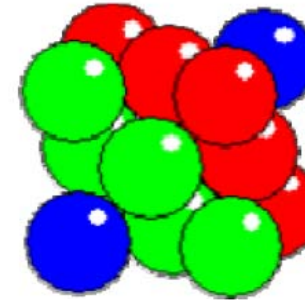
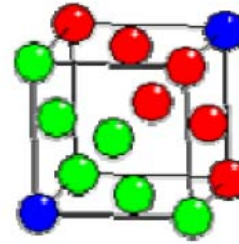
GaN(0001) spiral growth mode

(Feenstra, *J. Vac. Sci. Technol. A* 16,

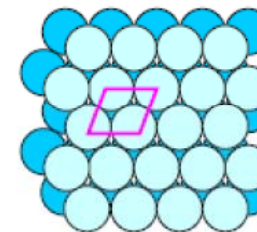
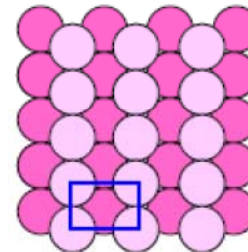
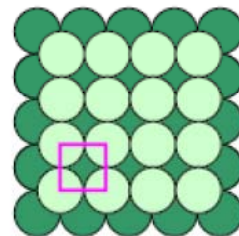
1641 (1998).)

Fcc 表面

fcc metals



	<i>fcc(100)</i>	<i>fcc(110)</i>	<i>fcc(111)</i>
- <i>symmetry</i>	4-fold	2-fold	3-fold
- <i>coordination number</i>	8	7	9
- <i>roughness</i>	smooth	rough	atomically smooth

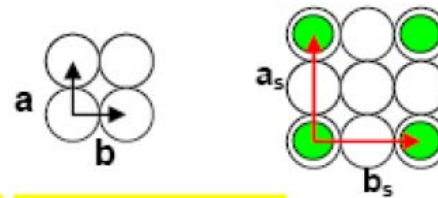


表面重构

Wood notation

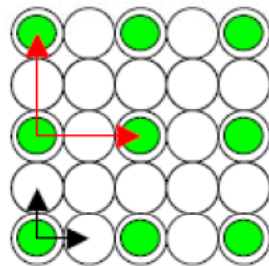
Substrate unit cell : a, b

Surface unit cell : a_s, b_s



$M(hkl) - (|a_s|/|a|) \times (|b_s|/|b|) R \theta^\circ$ (rotation angle) - Adsorbate

eg1) Ni(100)-2x2-O



$$|a_s|/|a| = 2a/a = 2$$

$$|b_s|/|b| = 2b/b = 2$$

$$\text{angle} = 0$$

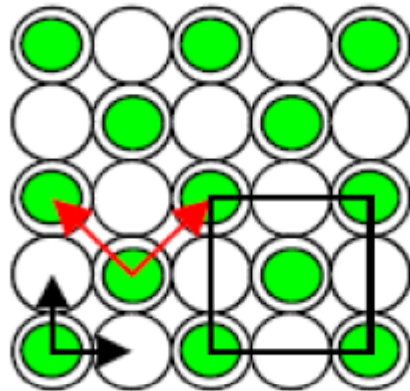
$$\therefore 2 \times 2 \text{ or } p(2 \times 2)$$

$$a_s = 2a + 0b$$

$$b_s = 0a + 2b$$

$$\text{Matix notation: } \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$$

eg2) Ni(100)-c(2x2)-CO or Ni(100)- $\sqrt{2} \times \sqrt{2}$ R45°-CO



$$a_s = a + b$$

$$b_s = a - b$$

$$|a_s|/|a| = \sqrt{2} a/a = \sqrt{2}$$

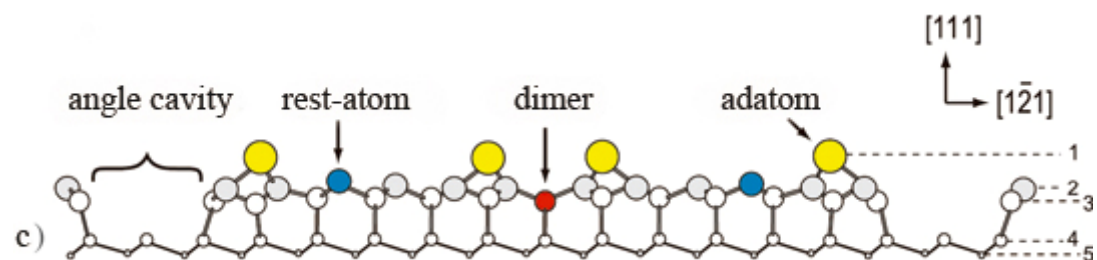
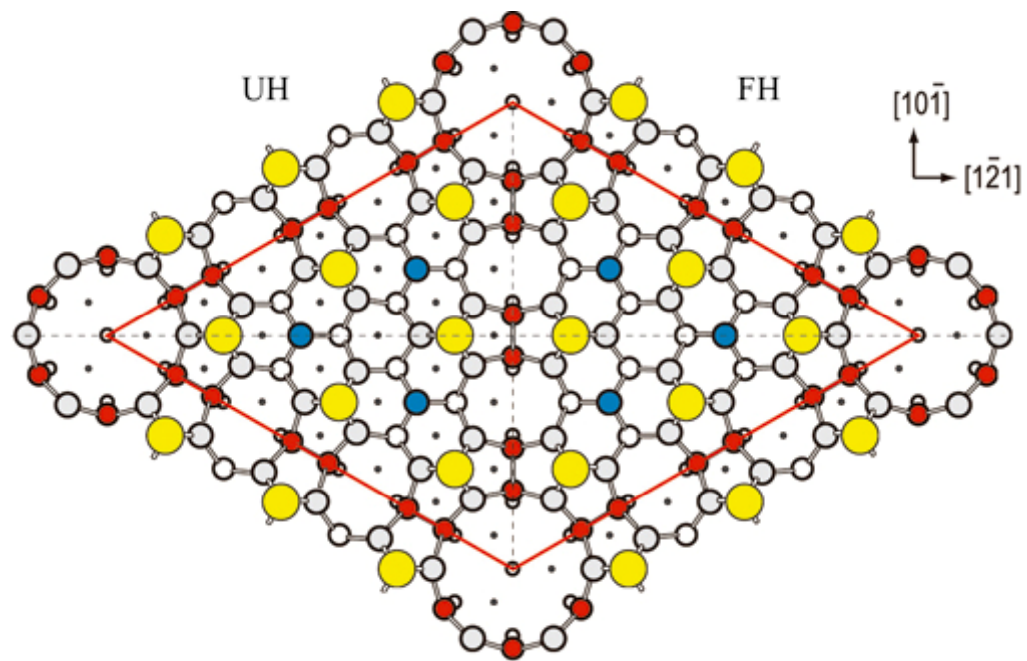
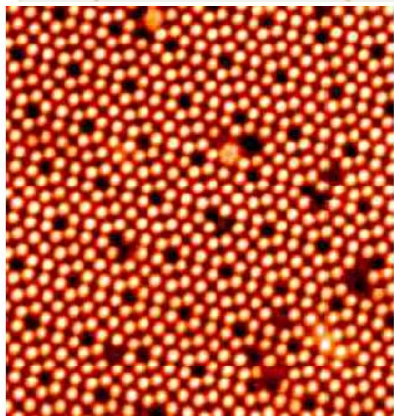
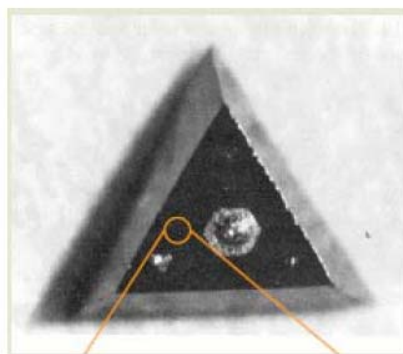
$$|b_s|/|b| = \sqrt{2} b/b = \sqrt{2}$$

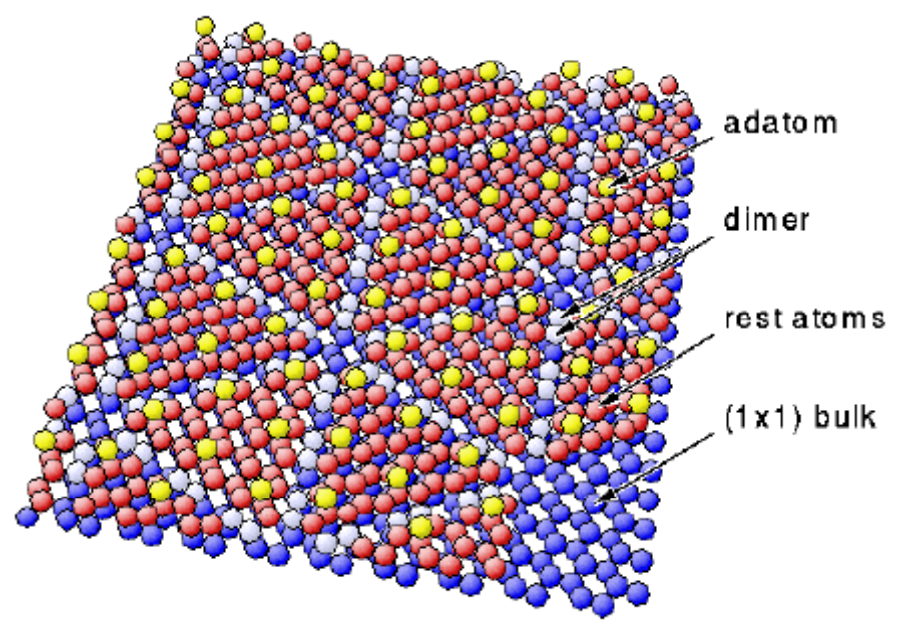
angle = R45

$\therefore \sqrt{2} \times \sqrt{2}$ R45°
or c(2x2)

真实例子：

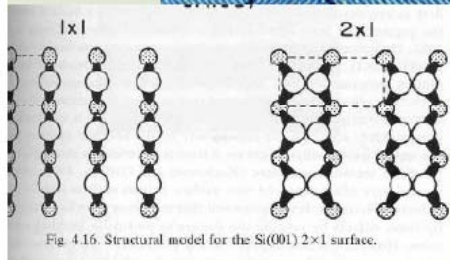
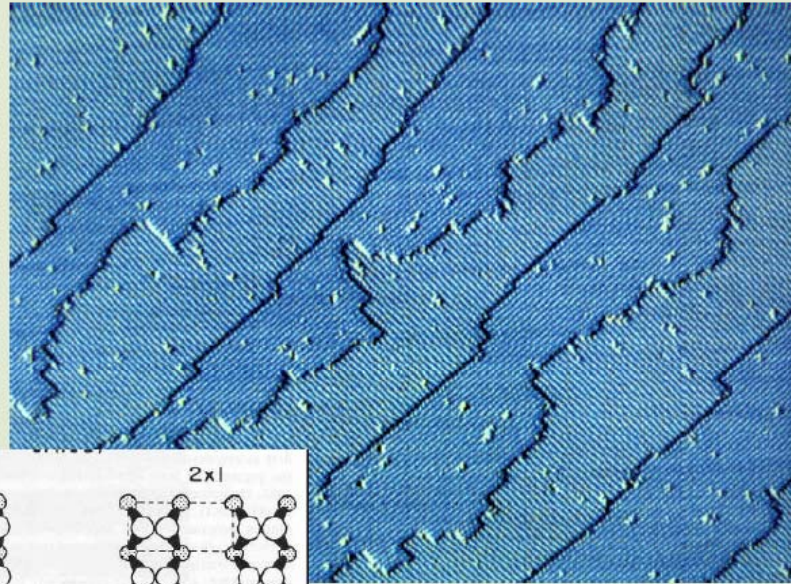
(1) Si(111)-7x7



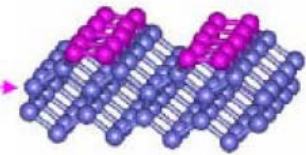
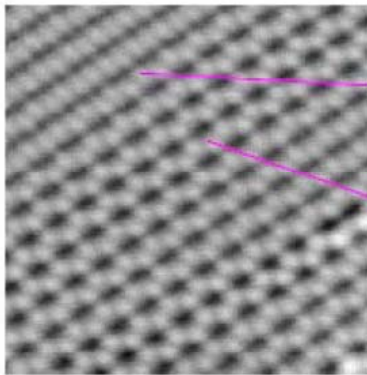


(2) Si(100)

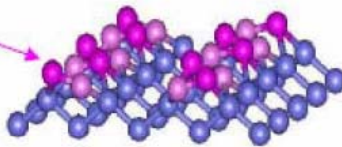
Actual Si(001) surface under STM (Kariotis and Lagally, 1991)



Surface reconstruction (表面重構)

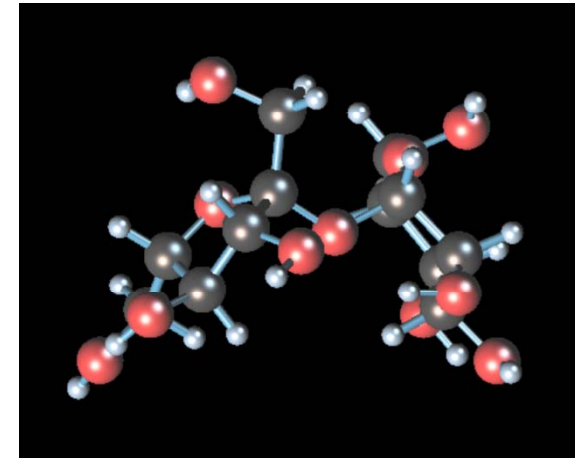
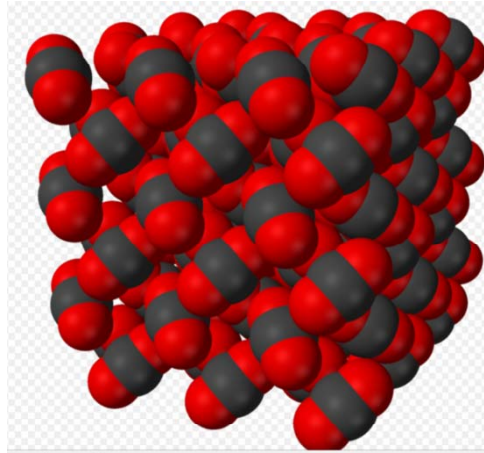
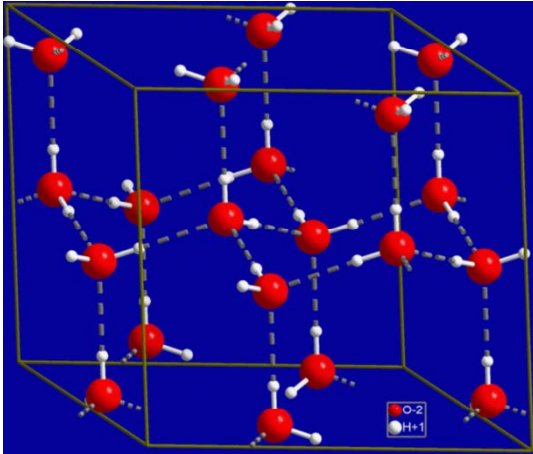


Si(100)-2x1



Si(100)-4x2

molecular crystals (molecules are not round, complicated structures)



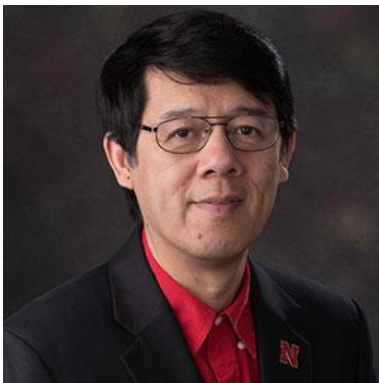
ice



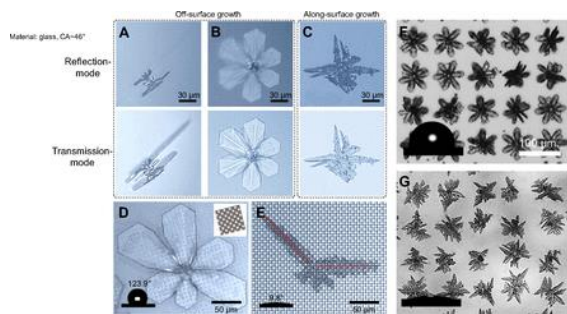
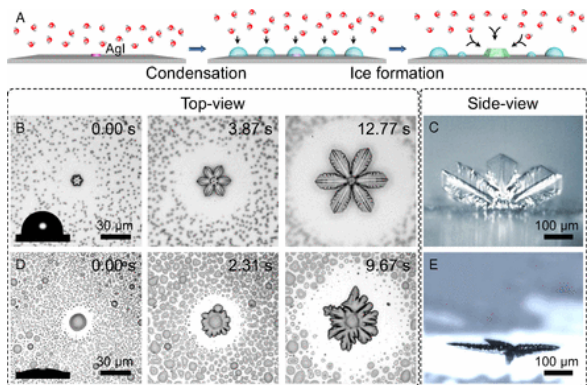
Dry ice



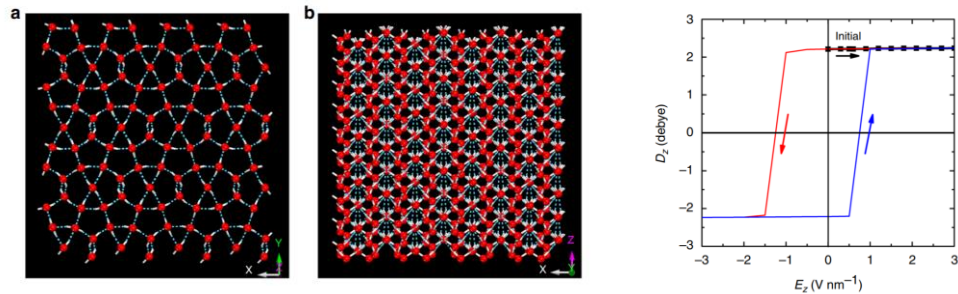
Sucrose crystal



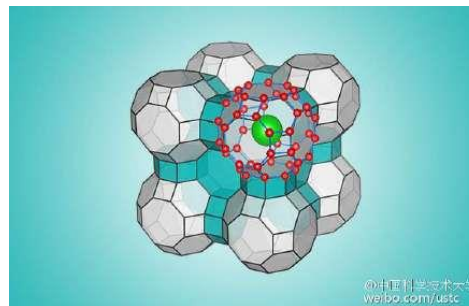
Xiaocheng Zeng



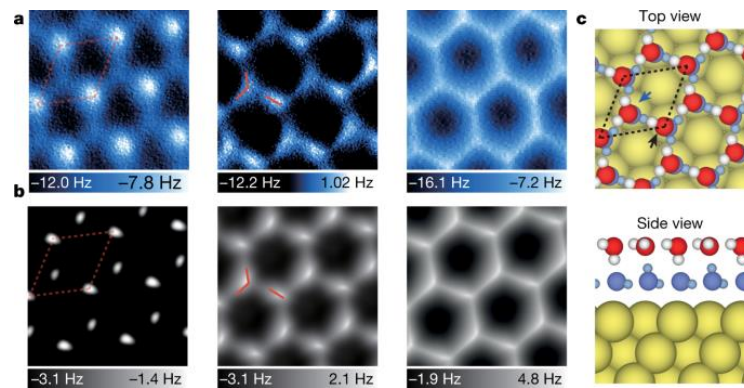
X. Zeng ice formation PNAS (2017)



X. Zeng ice χ Nat. Commun. (2019)



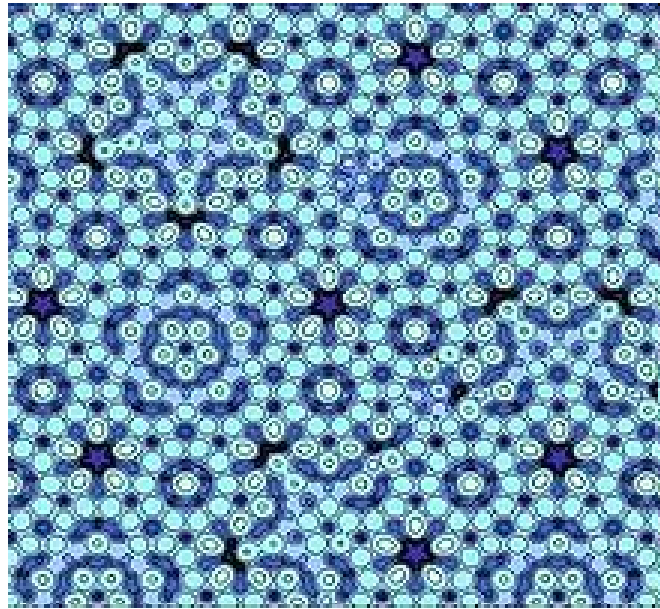
X. Zeng ice cage Sci. Adv. (2016)



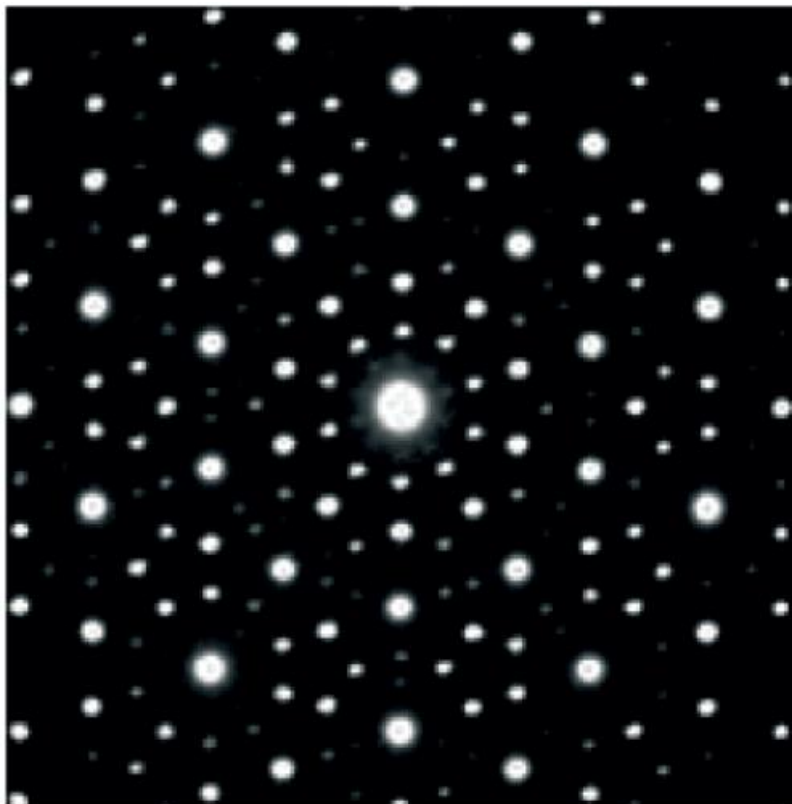
X. Zeng and Y. Jiang 2D ice Nature (2020)

Quasicrystal (准晶)

亦称为“准晶”或“拟晶”，是一种介于晶体和非晶体之间的固体。准晶体具有与晶体相似的长程有序的原子排列；但是准晶体不具备晶体的平移对称性。根据晶体局限定理（crystallographic restriction theorem），普通晶体只能具有二次、三次、四次或六次旋转对称性，但是准晶的布拉格衍射图具有其他的对称性，例如五次对称性或者更高的如六次以上的对称性。

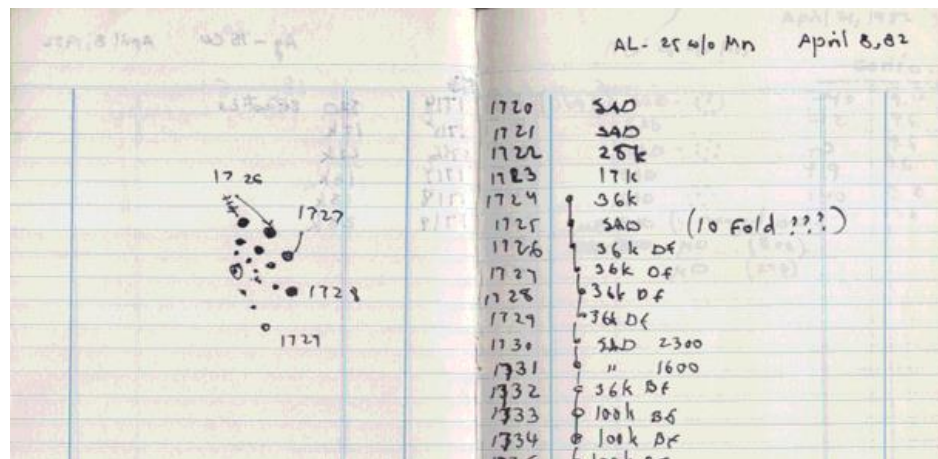


银铝合金准晶的原子模型



图一 丹尼尔·舍特曼得到的衍射图案具有十重对称性：即将图案旋转十分之一圆周角（ 36° ）所得到的图案与原来的图案相同。

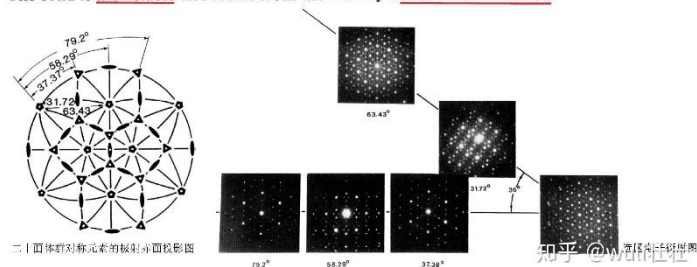
准晶的电子衍射图像



Metallic Phase with Long-Range Orientational Order and No Translational Symmetry

D. Shechtman and I. Blech

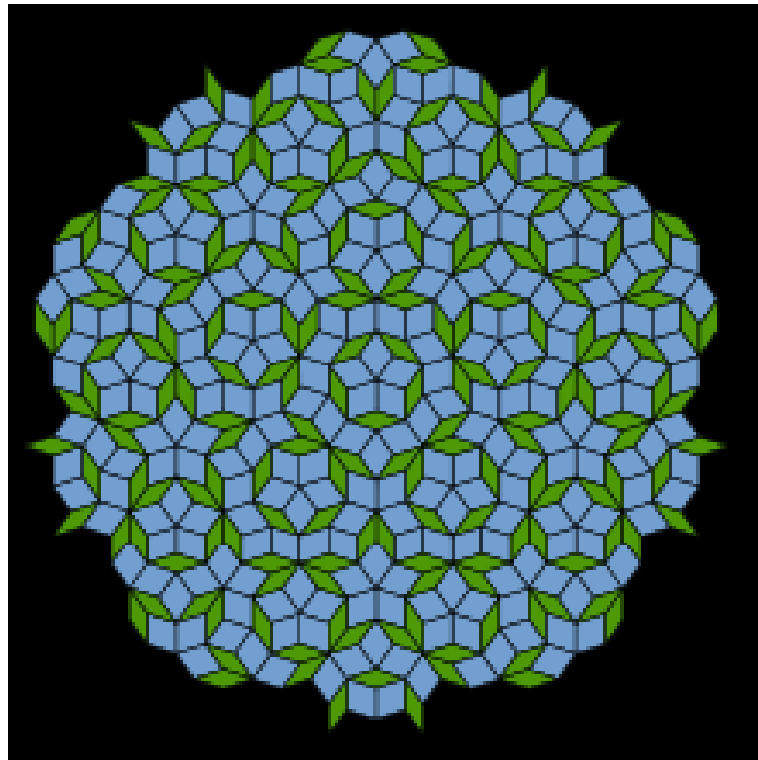
We have observed a metallic solid (Al-14-at.-%-Mn) with long-range orientational order, but with icosahedral point group symmetry, which is inconsistent with lattice translations. Its diffraction spots are as sharp as those of crystals but cannot be indexed to any Bravais lattice. The solid is metastable and forms from the melt by a first-order transition.



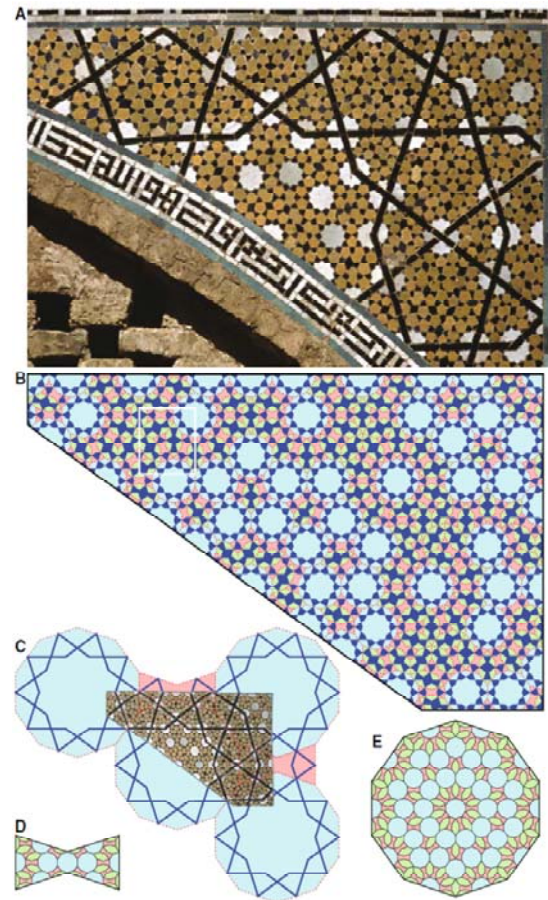
知乎 @ 物理社区

准晶体的结构在20世纪之前就已经被建筑师熟知，例如在伊朗伊斯法罕的清真寺，上面瓷砖的图案就是按照准晶样式排列。

1961年，数学家瓦罗提出了用不同形状的拼图铺满平面的拼图问题。数学家们已经知道，可以用单一形状的拼图拼满一个平面，例如任意形状的四边形或者正六边形，但是当增加拼图单元的种类时，就能够构造出更多的拼满一个平面的方法。两年后，瓦罗的学生Robert Berger构造了一系列不具有周期性的拼图方法。之后铺满平面所需要的拼图种类越来越少，1976年Roger Penrose构造了一系列只需要两种拼图的方法，这种方法拼出来的图案具有五次对称性。



二维Penrose拼图：两种菱形



清真寺瓷砖图案

自然界的准晶体：2009年，Science 报道在一种khatyrkite(铝锌铜矿)岩石中找到准晶体。



Natural Quasicrystals

Luca Bindi, *et al.*

Science **324**, 1306 (2009);

DOI: 10.1126/science.1170827

Natural Quasicrystals

Luca Bindi,¹ Paul J. Steinhardt,^{2*} Nan Yao,³ Peter J. Lu⁴



Quasicrystals are solids whose atomic arrangements have symmetries that are forbidden for periodic crystals, including configurations with fivefold symmetry. All examples identified to date have been synthesized in the laboratory under controlled conditions. Here we present evidence of a naturally occurring icosahedral quasicrystal that includes six distinct fivefold symmetry axes. The mineral, an alloy of aluminum, copper, and iron, occurs as micrometer-sized grains associated with crystalline khatyrkite and cupalite in samples reported to have come from the Koryak Mountains in Russia. The results suggest that quasicrystals can form and remain stable under geologic conditions, although there remain open questions as to how this mineral formed naturally.

知乎 @wuli壮壮

QUASICRYSTALS

Dirac electrons in a dodecagonal graphene quasicrystal

Sung Joon Ahn^{1*}, Pilkyung Moon^{2,3*}, Tae-Hoon Kim^{4*}, Hyun-Woo Kim¹, Ha-Chul Shin¹, Eun Hye Kim¹, Hyun Woo Cha⁴, Se-Jong Kahng⁵, Philip Kim⁶, Mikito Koshino⁷, Young-Woo Son^{8,†}, Cheol-Woong Yang^{4,†}, Joung Reel Ahn^{1,9,†}

Quantum states of quasiparticles in solids are dictated by symmetry. We have experimentally demonstrated quantum states of Dirac electrons in a two-dimensional quasicrystal without translational symmetry. A dodecagonal quasicrystalline order was realized by epitaxial growth of twisted bilayer graphene rotated exactly 30°. We grew the graphene quasicrystal up to a millimeter scale on a silicon carbide surface while maintaining the single rotation angle over an entire sample and successfully isolated the quasicrystal from a substrate, demonstrating its structural and chemical stability under ambient conditions. Multiple Dirac cones replicated with the 12-fold rotational symmetry were observed in angle-resolved photoemission spectra, which revealed anomalous strong interlayer coupling with quasi-periodicity. Our study provides a way to explore physical properties of relativistic fermions with controllable quasicrystalline orders.

Ahn *et al.*, *Science* **361**, 782–786 (2018) 24 August 2018

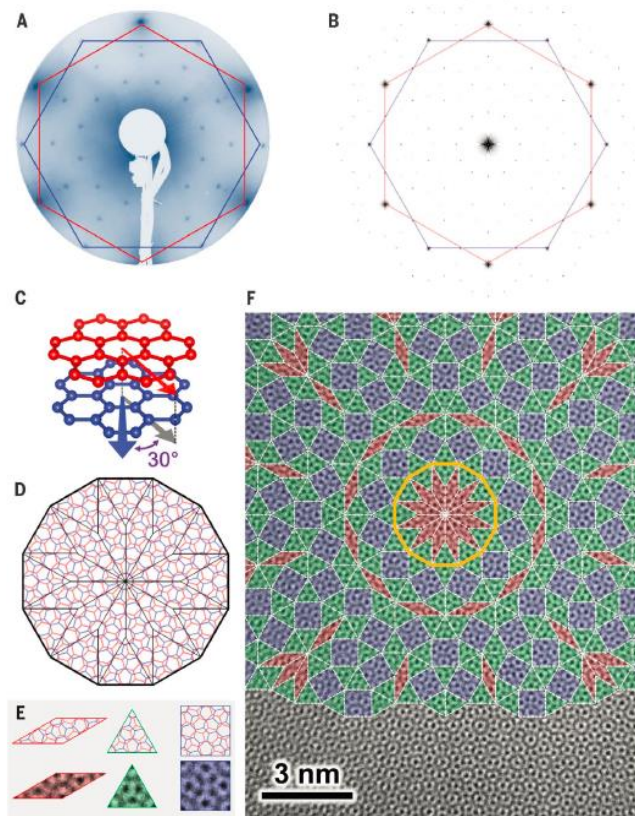


Fig. 1. A LEED pattern and a TEM image of graphene quasicrystal. (A) A LEED pattern of graphene quasicrystal. (B) A Fourier-transformed pattern of graphene quasicrystal (see also fig. S6 in SM). (C and D) An atomic structure model of TBG with R30°. (E) Atomic structures and TEM images of Stampfli tiles [rhombuses (red), equilateral triangles (green), and squares (blue)]. (F) A false-colored TEM image of graphene quasicrystal mapped with 12-fold Stampfli-inflation tiling.



© The Nobel Foundation. Photo: U. Montan

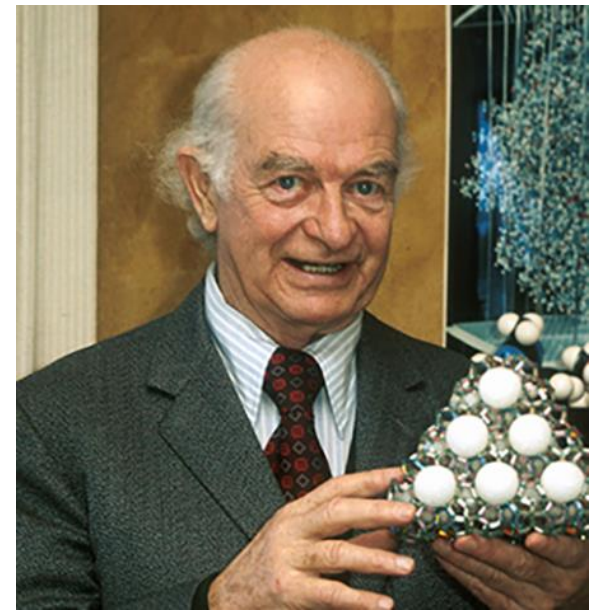
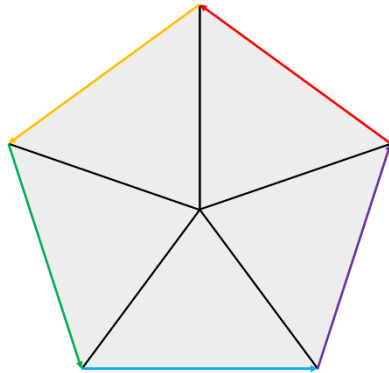
Dan Shechtman
The Nobel Prize in Chemistry 2011

Born: 24 January 1941, Tel Aviv, British Mandate of Palestine (now Israel)

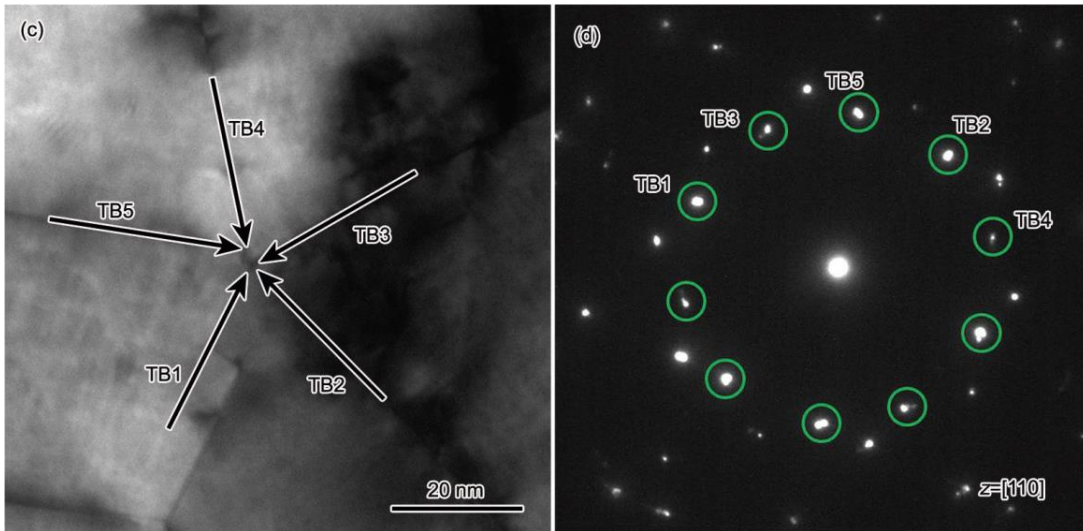
Affiliation at the time of the award: Technion - Israel Institute of Technology,
Haifa, Israel

Prize motivation: "for the discovery of quasicrystals."

Prize share: 1/1



Linus Pauling



准晶

✿ “Metallic Phase with Long-Range Orientational Order and No Translational Symmetry”, *Phys. Rev. Lett.*, **53**, 1951 (1984)

✿ 鲍林直到死都认为不存在准晶。

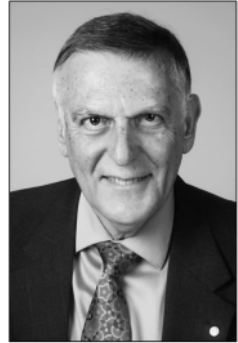
*“Danny Shechtman is talking nonsense, **there are no quasi-crystals, just quasi-scientists.**”*

— *Linus Pauling*

A few years before he died, Pauling wrote to Shechtman to suggest a truce of sorts:

*“And the letter says, ‘Professor Shechtman, may I propose to you to write the joint Shechtman-Pauling paper on quasi-periodic materials? And you will be first,’ he says. And I answered him with a letter: ‘Professor Pauling, I’ll be delighted to write this paper with you, but before we even start we **have to agree that quasi-periodic materials do exist.**’ He wrote me back and said, ‘**Well, that may be too early for that.**’ And that was the end of our communication.”*

— *Dan Shechtman*



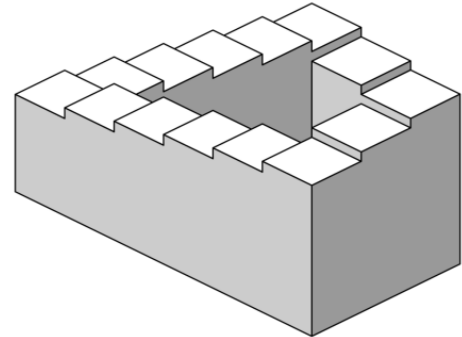
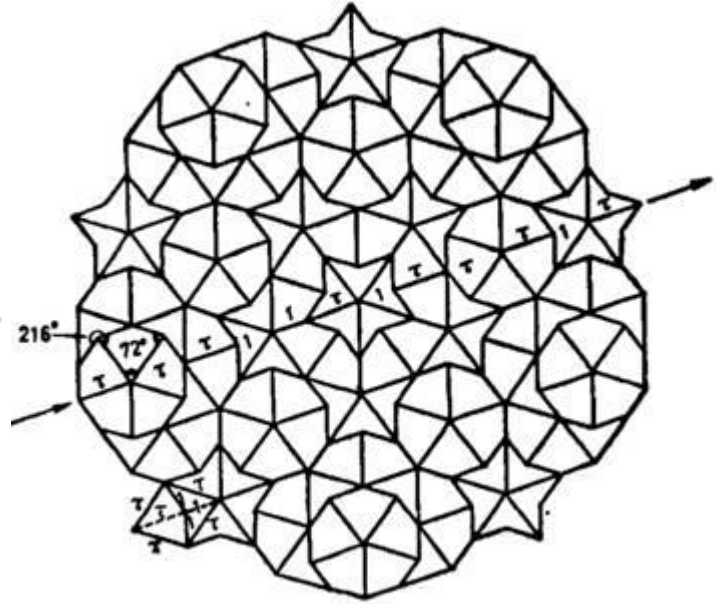
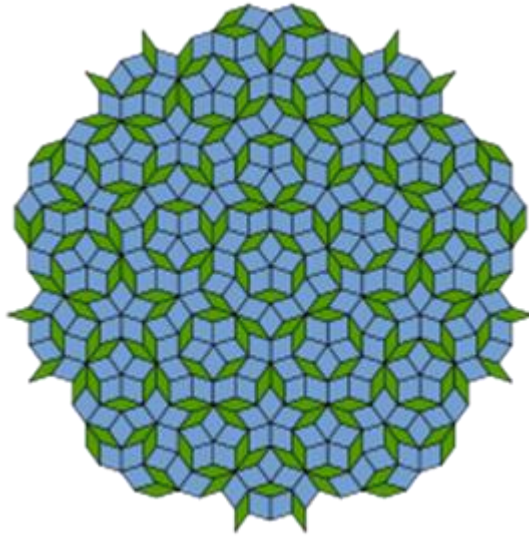
Dan Shechtman
2011 Nobel Prize
in Chemistry



Linus Pauling
(1901–1994)
Nobel Prize in
Chemistry (1954)
Nobel Peace
Prize (1962)



Roger Penrose
Nobel Prize winner, 2020

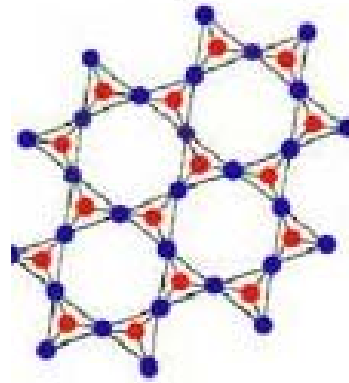


Amorphous or non-crystal solid (非晶)

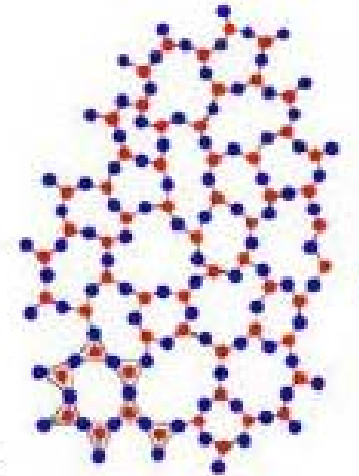
An **amorphous solid** is a solid in which there is no long-range order or repeating pattern in the positions of its atoms or molecules.



Crystalline SiO_2
(Quartz)



Amorphous SiO_2
(Glass)



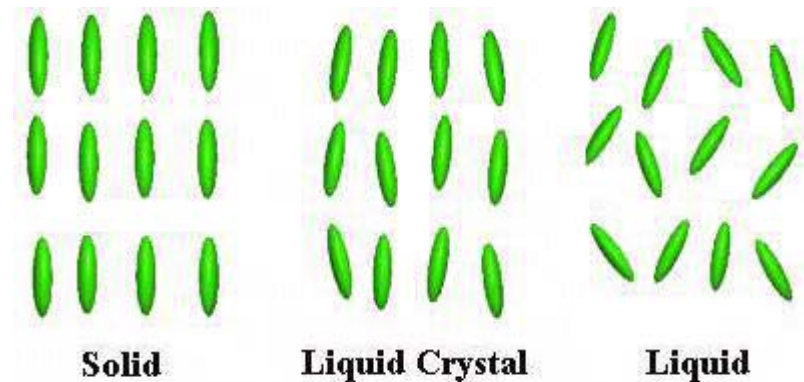
• Si • O



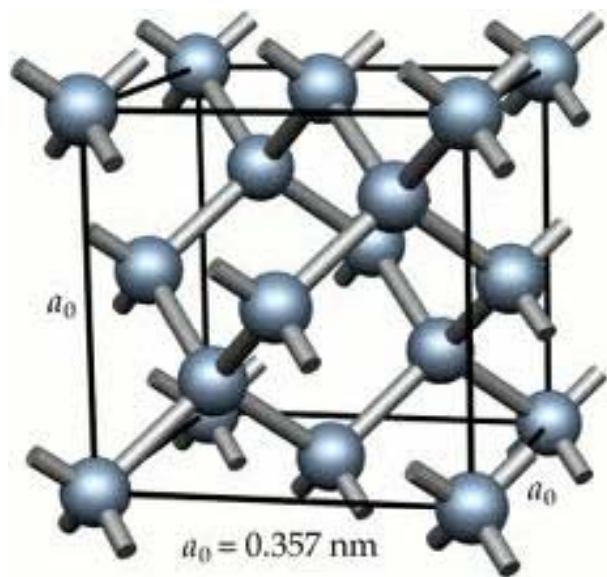
Liquid crystal (液晶)

1888年在匈牙利工作的奥地利植物学家和化学家莱尼切尔(Friedrich Reinitzer)发现他所研究的一种胆固醇物质好像有2个熔点：在145.5 C时融化成为一种混浊的液体，直到178.5C时液体中的混浊物不见了，出现一个完全透明的液相。他写信给德国物理学家勒曼(Otto Lehmann)，勒曼是一位晶体光学专家，1889年，勒曼确定那种混浊的物质是一种新的物相，并且将其命名为液晶。液晶的光学性质强烈依赖于方向。80年后，法国理论物理学家德让(Pieere-Gilles de Gennes)发现了液晶与超导体、磁性材料之间极好的类似，他解释了为什么液晶中的分子是有序排列的，他因此获得了1991年诺贝尔物理奖。

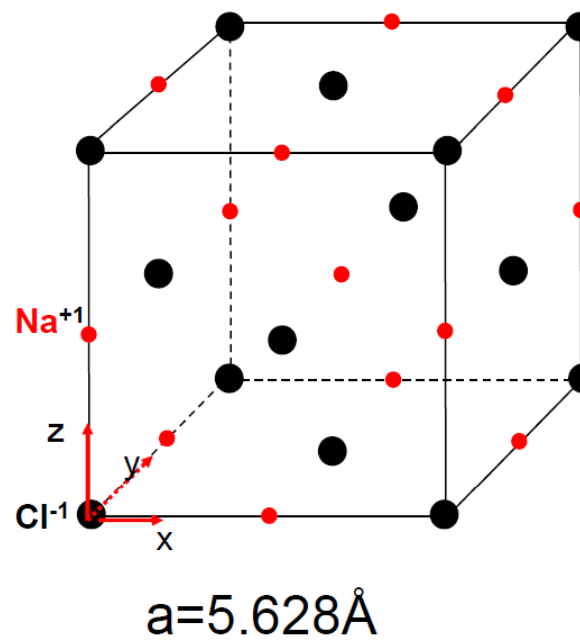
液晶与颜料相混合，只要几伏的电压就可以改变一个颜色，因此可以用来做显示器。



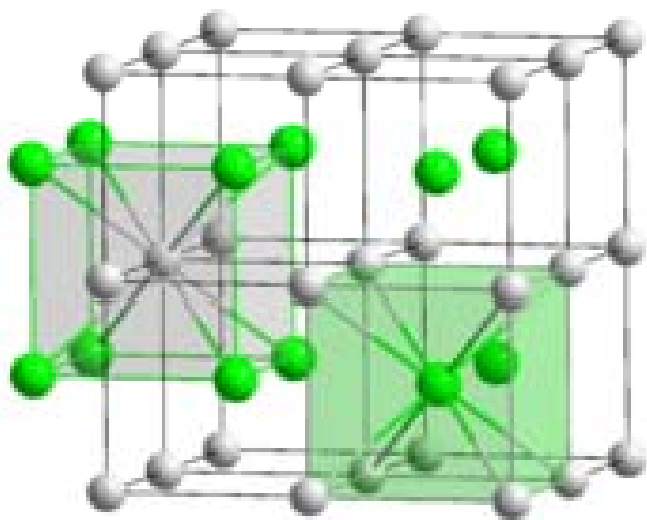
金刚石



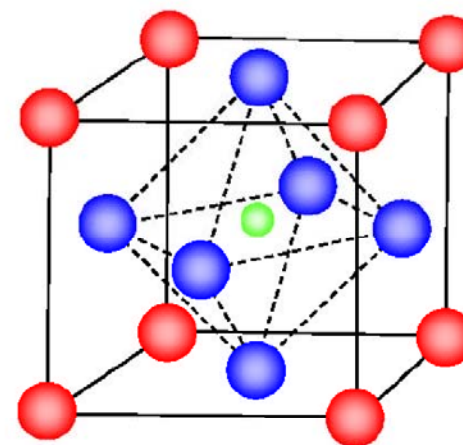
NaCl



CsCl



钙钛矿



习题

1.8 (黄昆书1.1) 如果将等体积球分别排成下列结构, 求证钢球所占体积与总体积之比为:

简单立方: 0.52; 体心立方: 0.68; 面心立方: 0.74; 六角密堆: 0.74; 金刚石: 0.34

1.9 试证六方密堆结构中 $c/a=1.633$ 。又: 金属Na在273K因马氏体相变从体心立方转变为六角密堆结构, 假定相变时金属密度维持不变, 已知立方相的晶格常数 $a=0.423\text{nm}$, 设六角密堆结构相的 c/a 维持理想值, 试求其晶格常数。

1.10 (阎守胜书 2.6) 可在面心立方晶体中掺入外来原子, 掺杂原子填入四面体或八面体位置, 即掺杂原子周围的晶格原子分别处在正四面体或正八面体的顶点位置上。试给出这些间隙位置的所在。