第七章 晶体学基础

Fundamentals of Crystallography

物质三种聚集态
- 气态
- 液态
- 固态
  - 晶体
  - 非晶体
  - 准晶体

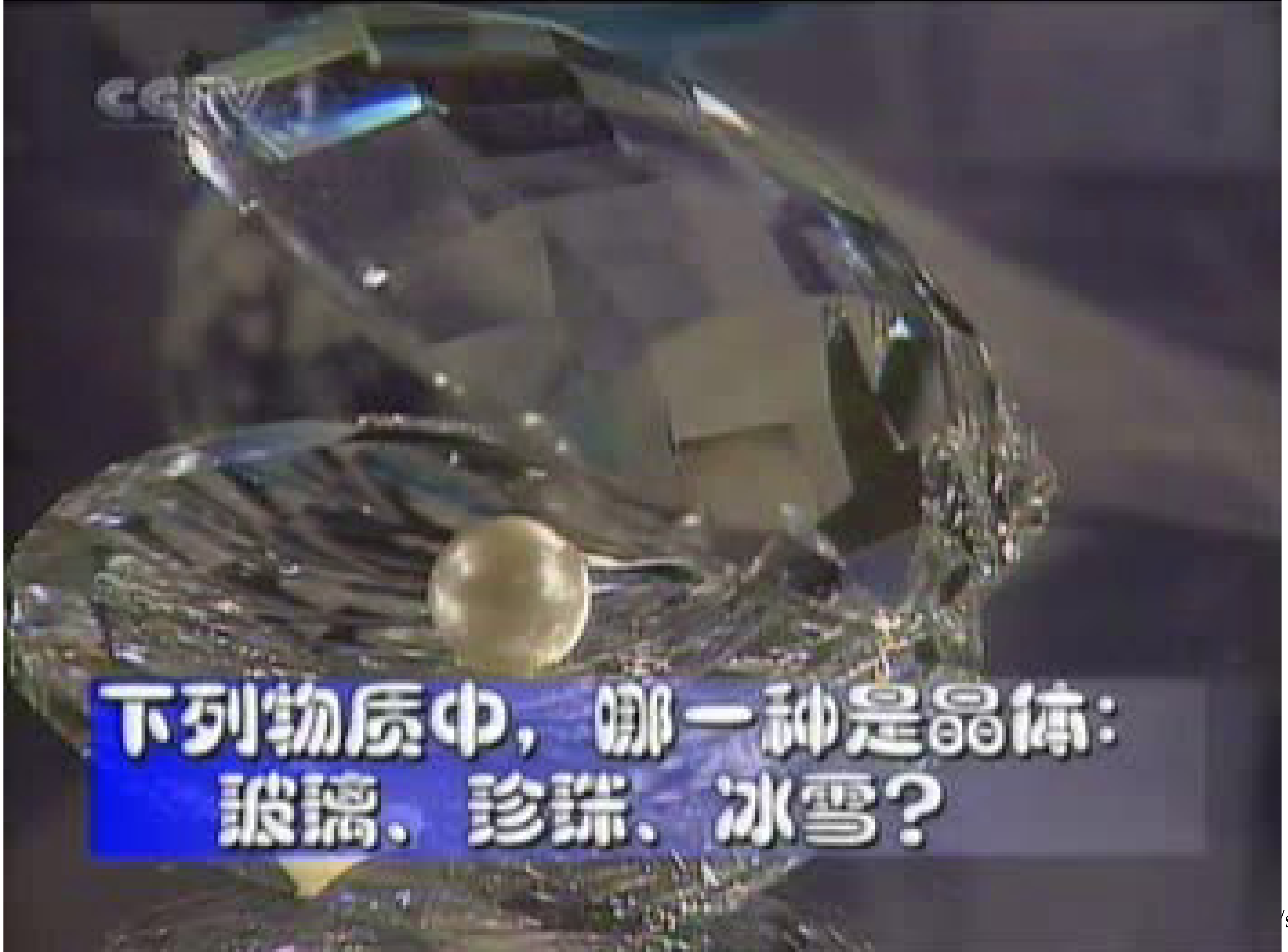
§ 7.1 晶体学基础

7.1.1 晶体的特征



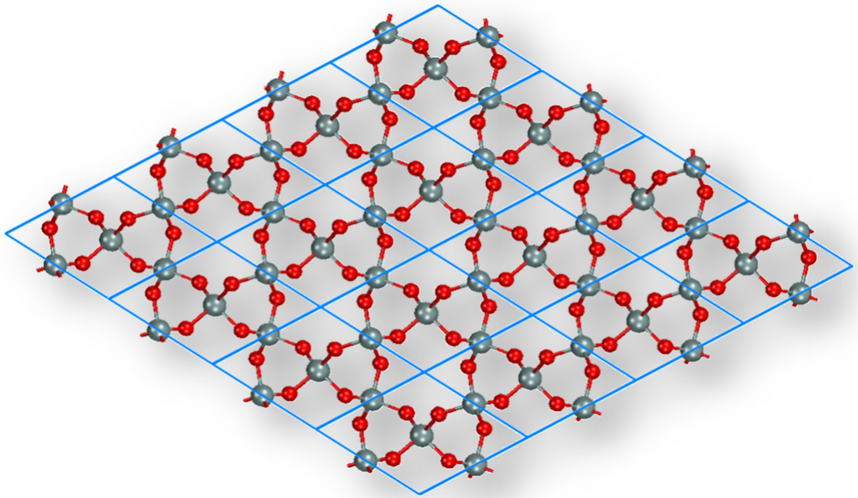




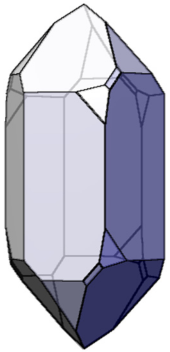


下列物质中，哪一种是晶体：
玻璃、珍珠、冰雪？

1. 晶体的均匀性和各向异性

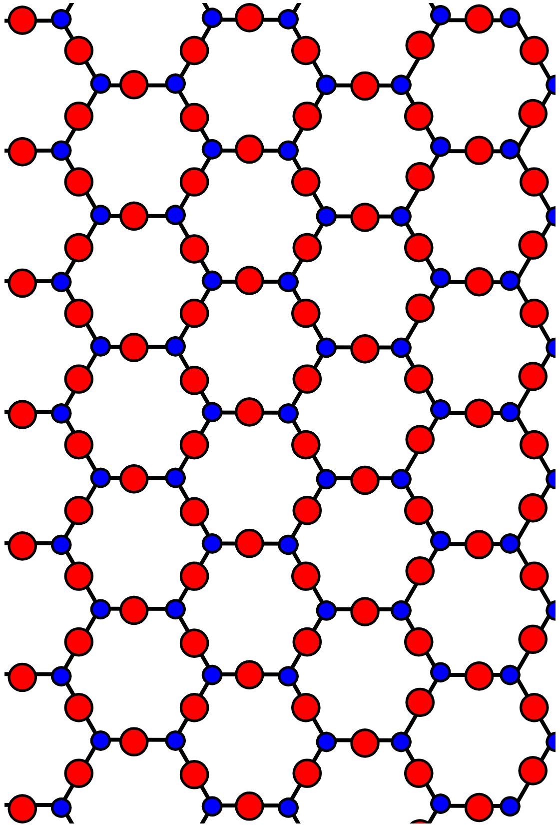
i. 晶体的均匀性



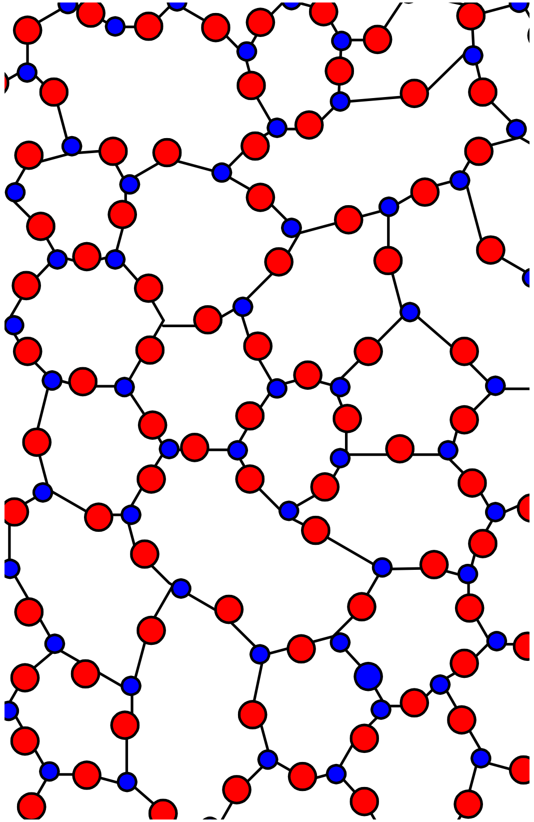
Long-range-order



α-石英

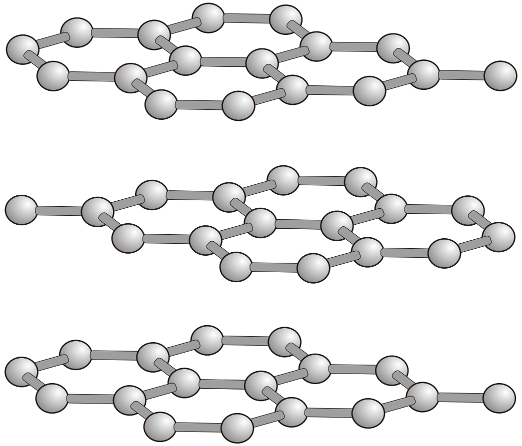


Crystalline Solid

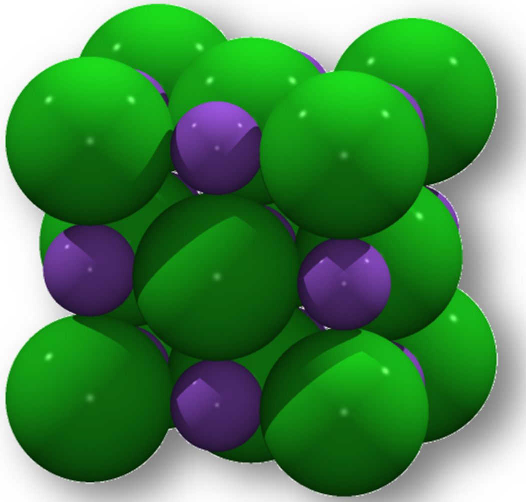


Glass
(Amorphous Solid)

ii. 晶体的各向异性

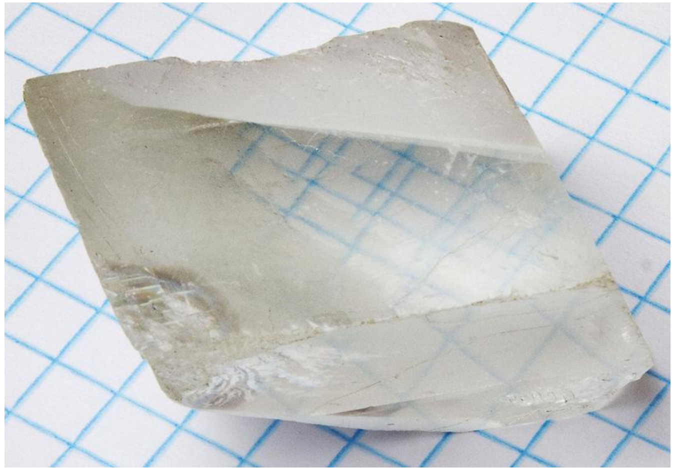


石墨

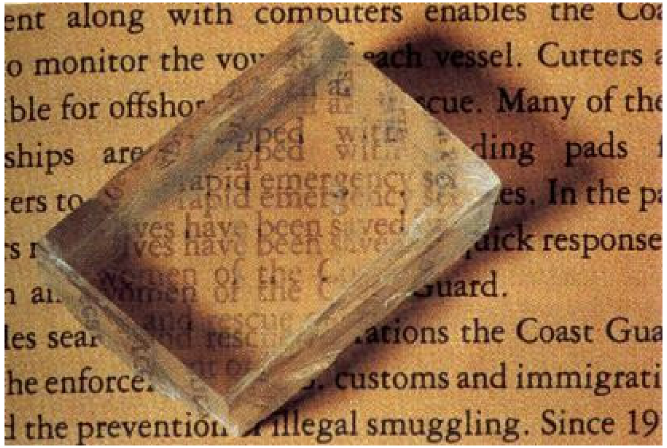


NaCl

c、$b+c$、$a+b+c$方向上的拉力比为1:2:4



方解石晶体的双折射现象



iii. 晶体的自限性

$F+V=E+2$

(F:晶面 V:顶点 E:晶棱)

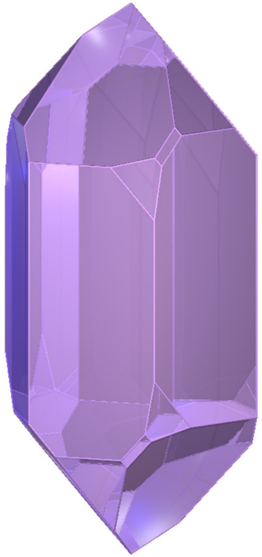
NaCl晶体常为立方体，立方体有6个面，12条棱，8个顶点

iv. 晶面角守恒定理

v. 晶体具有确定的熔点

vi. 晶体对X射线产生衍射

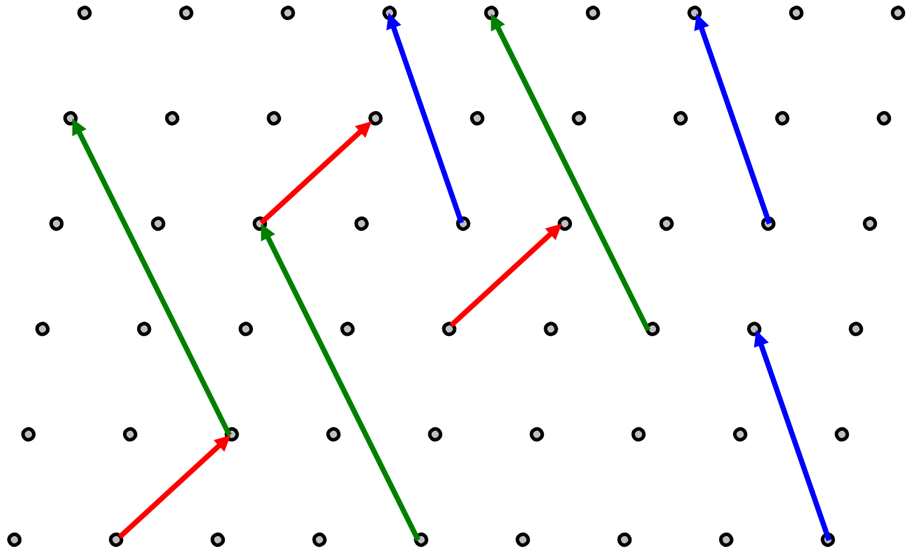
vii. 晶体具有对称性



结构决定性质，性质反映结构

7.1.2 点阵(lattice)

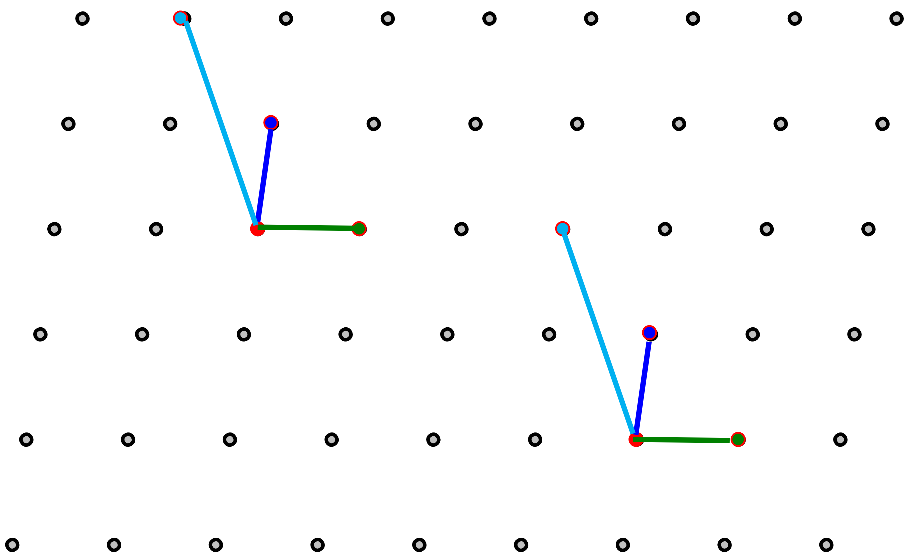
晶体的周期性→抽象成点阵

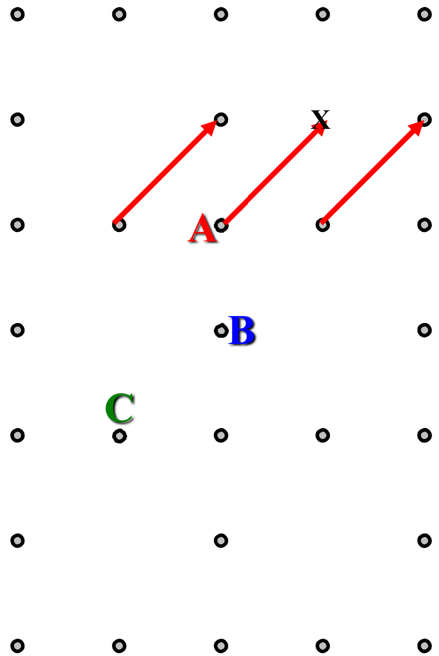


点阵是一组无限的点，连结其中任意两点可得一向量，将各个点按此向量平移能使它复原

本质：平移对称性

平移操作，平移群



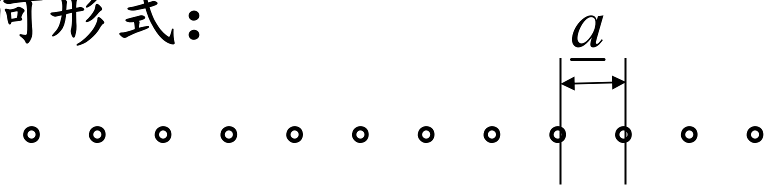


点阵中每个点都具有完全相同的周围环境

1. 直线点阵(one-dimensional lattice)

定义：在一维方向上等间隔排列的无穷点列

几何形式：



。**点阵点**，相邻两点间的距离$\underline{a}$叫**基本周期**。

平移群：点阵的代数形式，能使点阵复原的全部平移向量集称为平移群。

$$\boxed{\underline{T}_m = m\underline{a}}$$

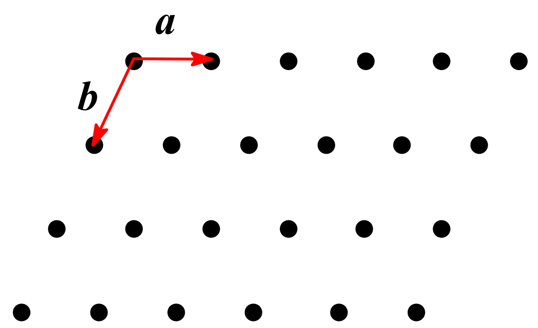
基本周期$\underline{a}$，平移素向量； $m = 0, \pm1, \pm2, \ldots$

2. 平面点阵：

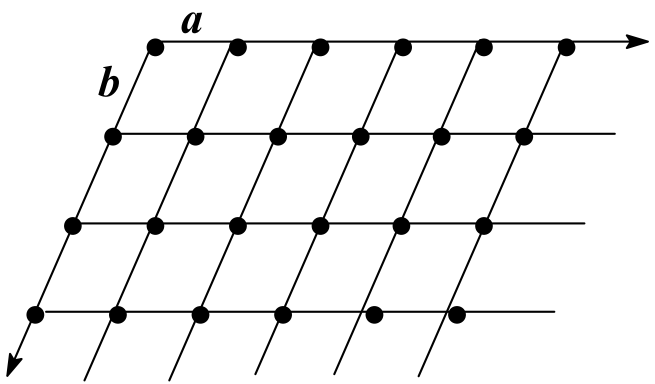
定义：在二维方向上等周期排布点阵叫平面点阵。平面点阵中，可以找到两个独立的不平行的基本向量。

平移群表示：

$$\boxed{\underline{T}_{m,n} = m\underline{a} + n\underline{b}}$$

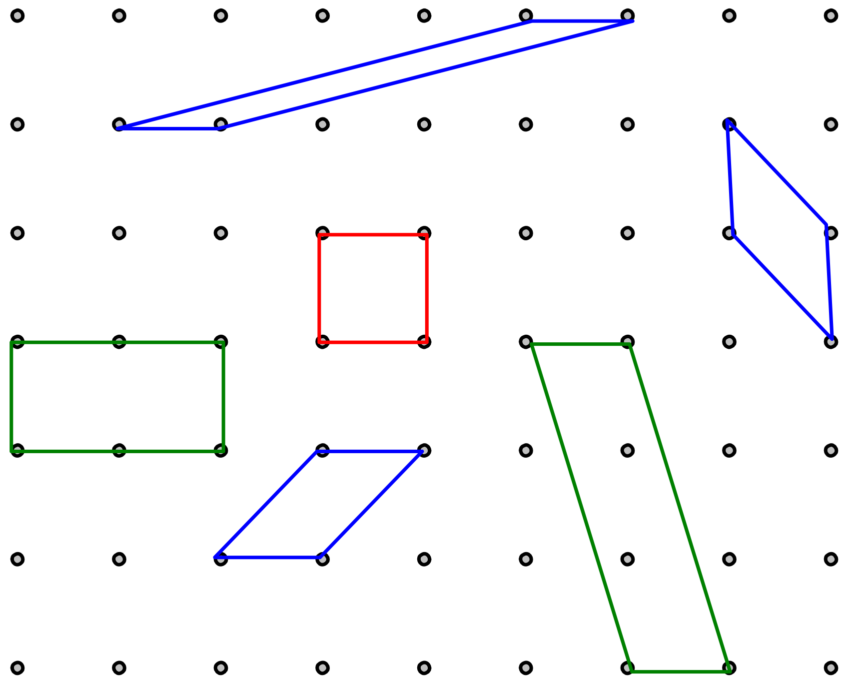


几何形式



平面格子：沿二个方向将全部点阵点连结起来，即得到平面格子。整个平面点阵可视为无数个这样的平行四边形格子并置而成。

格子



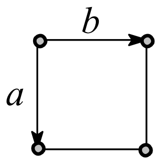
素单位：摊到**一个**点阵点的单位 (**素格子**)

复单位：摊到**一个以上**点阵点的单位 (**复格子**)

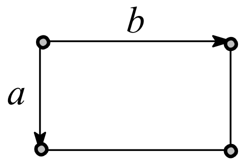
正当单位：尽量选取具有较**规则形状**的、**面积较小**的平行四边形单位(**正当格子**)

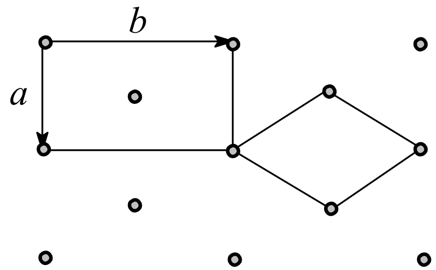
平面点阵的正当单位可有四种形状，五种型式

正方



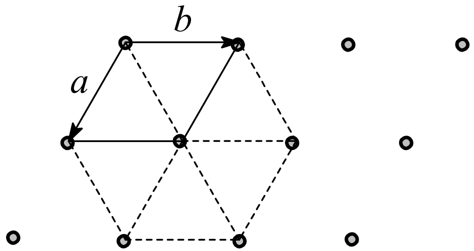
$a=b \quad a\wedge b=90^\circ$





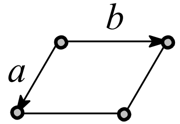
矩形　　　　矩形(带心)

$a\neq b \quad a\wedge b=90^\circ$



六方

$a=b \quad a\wedge b=120^\circ$

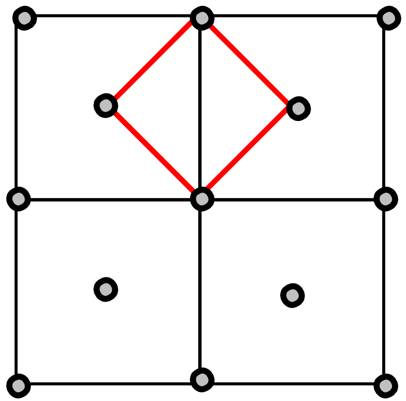


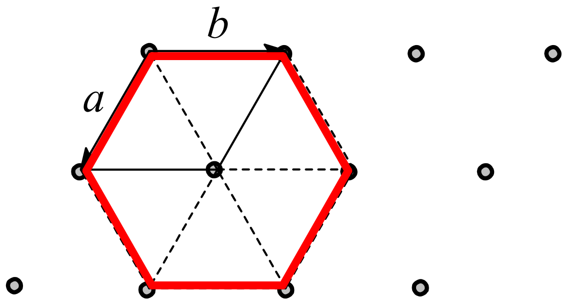
$a\neq b \quad a\wedge b\neq 90^\circ$

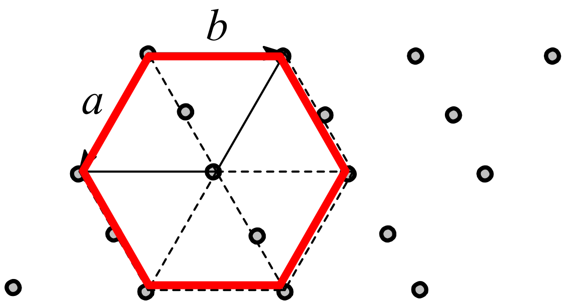
一般平行四边形

为什么只有这几种呢？

1. 保证对称性不降低
2. 不能划出更小的简单格子







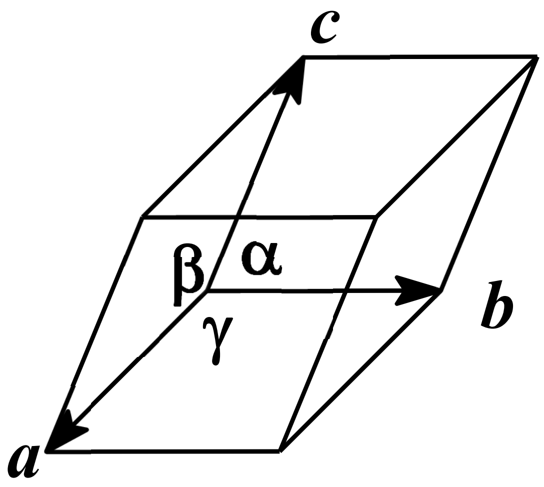
4. 空间点阵：阵点分布在三维空间的点阵

平移群表示：

$$\boxed{\underline{T}_{m,n,p} = m\underline{a} + n\underline{b} + p\underline{c}} \qquad (m, n, p = 0, \pm 1, \pm 2, \ldots)$$

空间点阵可划分为许多平行六面体格子

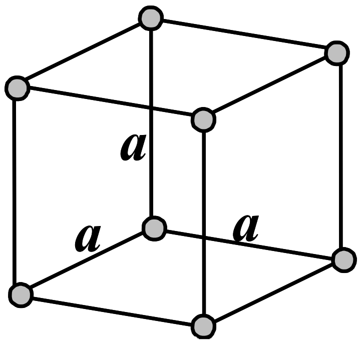
正当单位：按较规则形状、体积较小的原则，空间点阵的正当单位可有6种形状，14种**空间点阵形式**或叫14种**布拉维(Bravias)格子**



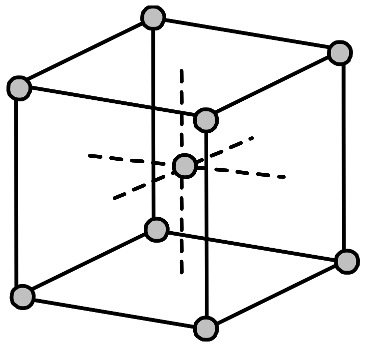
对正当单位，选一点为原点，选以原点出发的三个不相平行的向量$\underline{a}$, $\underline{b}$, $\underline{c}$为向量，**右手定则**，食中姆指为三个方向*a*, *b*, *c*

$\alpha = \underline{b} \wedge \underline{c} \quad \beta = \underline{c} \wedge \underline{a} \quad \gamma = \underline{a} \wedge \underline{b}$

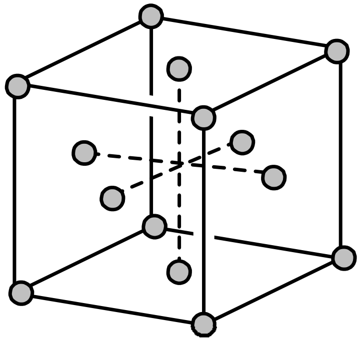
$a, b, c, \alpha, \beta, \gamma$为描述点阵正当单位的一套参量



cP



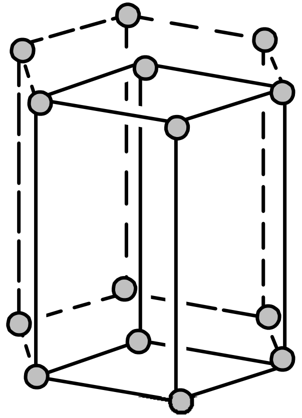
cI



cF

立方 **c**ubic $a = b = c$, $\alpha = \beta = \gamma = 90^{o}$

P-简单(Primitive) **I**-体心(Body centred) **F**-面心(All-face centred)



hP

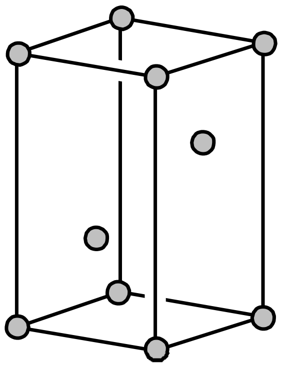
六方P

***h*exagonal (P)**

$a = b \neq c$,

$\alpha = \beta = 90^{o}$,

$\gamma = 120^{o}$



hR

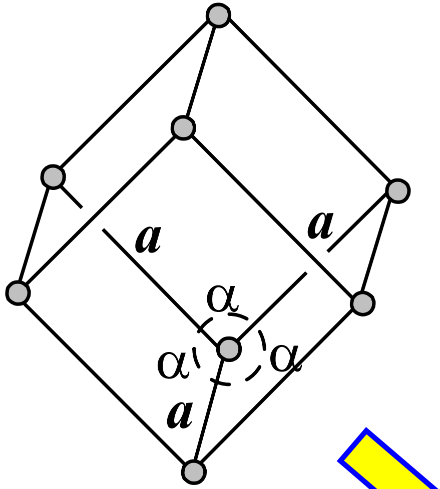
*R*心六方

***h*exagonal (*R*)**

$a = b \neq c$,

$\alpha = \beta = 90^{o}$,

$\gamma = 120^{o}$

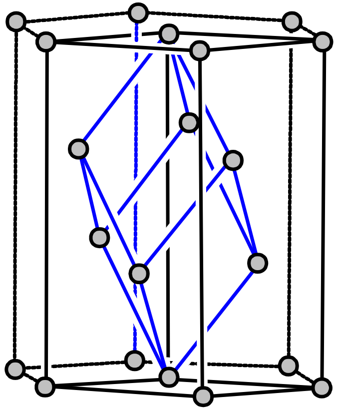


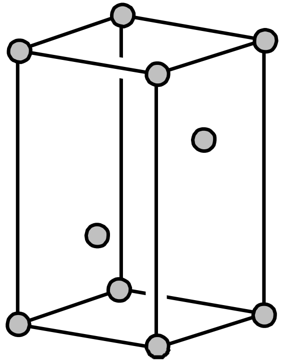
菱面体

Rhombohedral (R)

$a = b = c,$

$\alpha = \beta = \gamma \neq 90^{o}$





hR

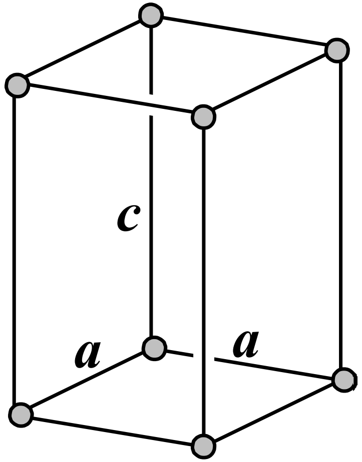
*R*心六方

***h*exagonal (*R*)**

$a = b \neq c,$

$\alpha = \beta = 90^{o},$

$\gamma = 120^{o}$



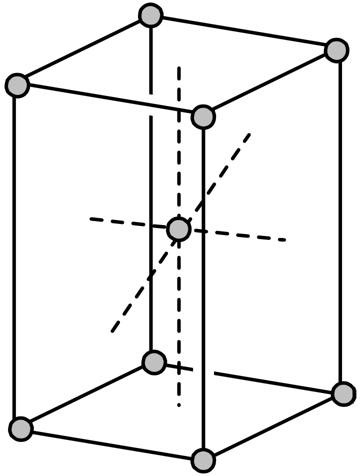
tP

四方

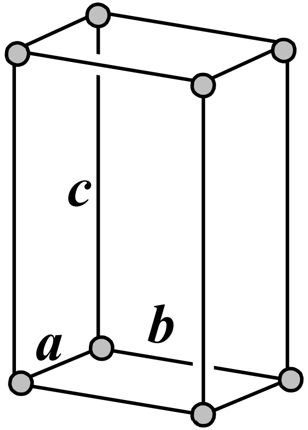
tetragonal (P I)

$a = b \neq c,$

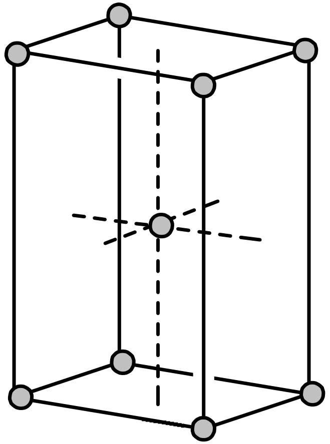
$\alpha = \beta = \gamma = 90^o$



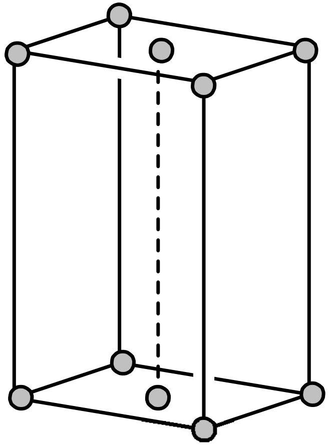
tI



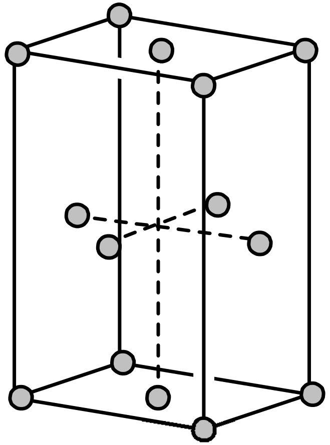
oP



oI



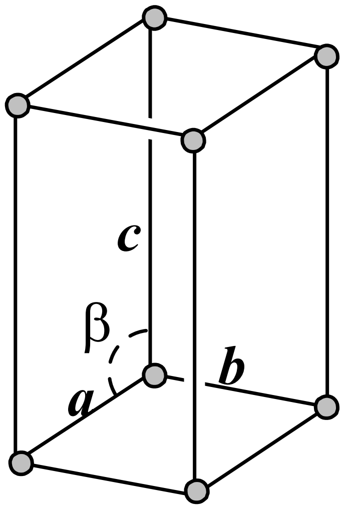
oC



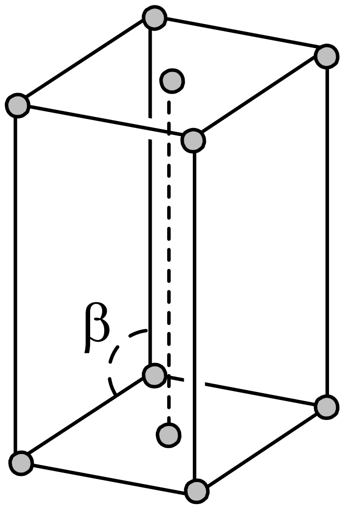
oF

正交 **orthorhombic** $a \neq b \neq c, \alpha = \beta = \gamma = 90^o$

C-底心(C-face centred)



mP



mC

单斜

***m*onoclinic (P C)**

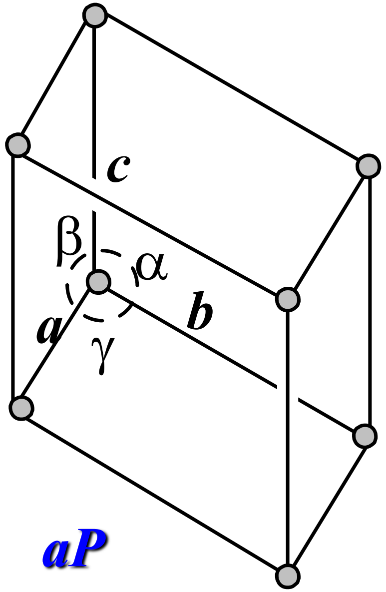
$a \neq b \neq c,\ \alpha = \gamma = 90^{o},\ \beta \neq 90^{o}$

三斜

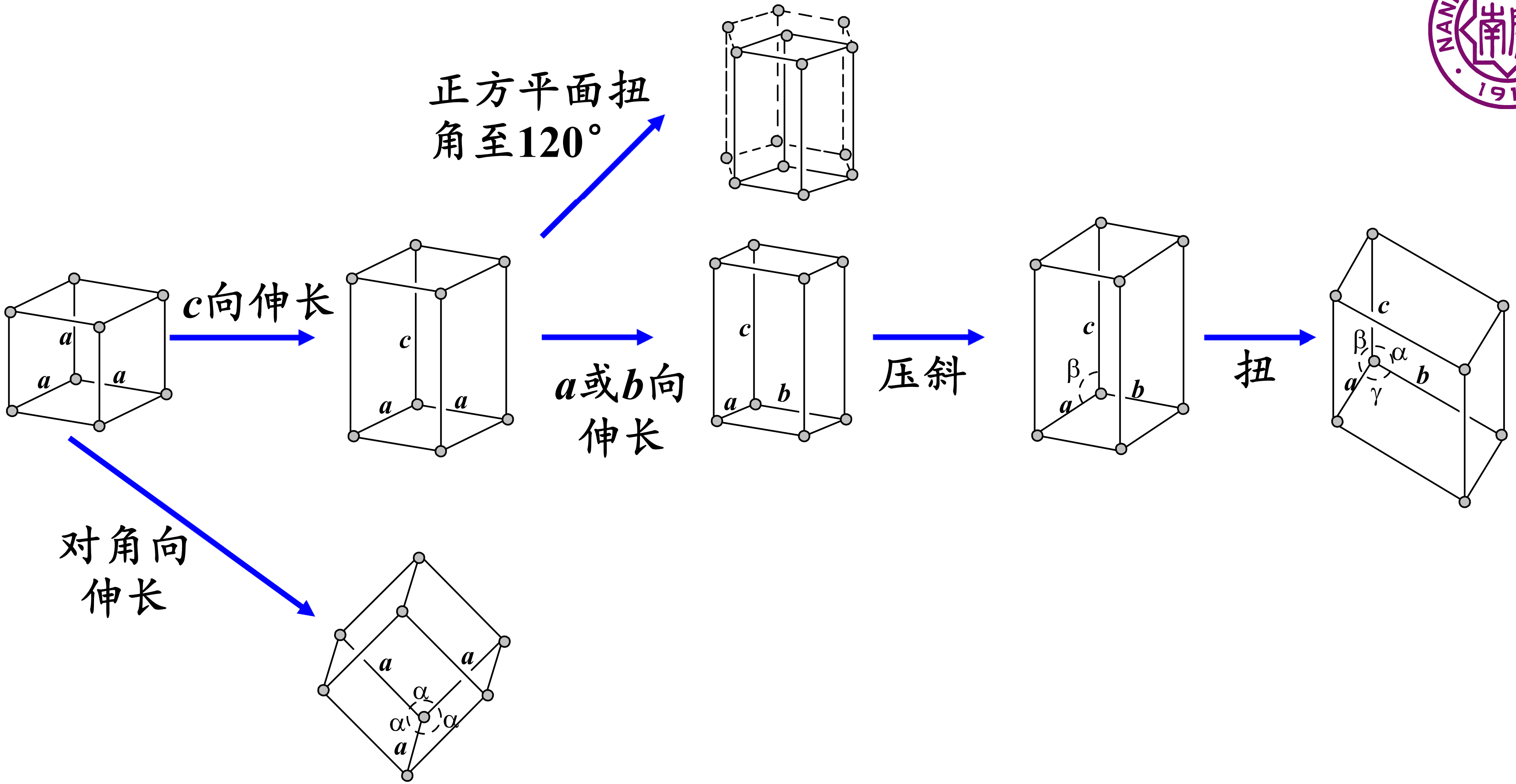
***a*northic (P)**

(triclinic)

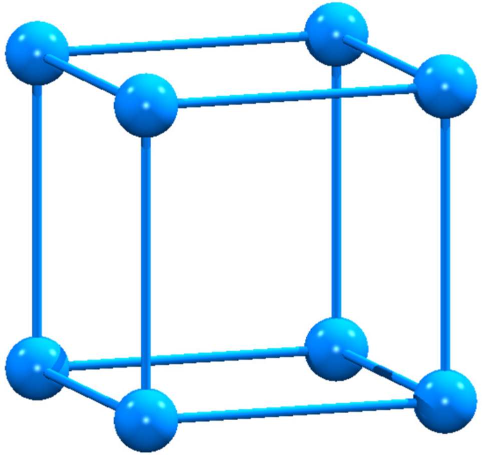
$a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90^{o}$



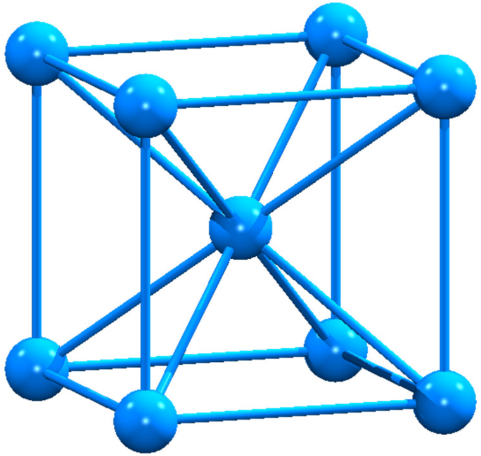
aP


c向伸长
正方平面扭角至120°
a或b向伸长
压斜
扭
对角向伸长
a
b
c
α
β
γ

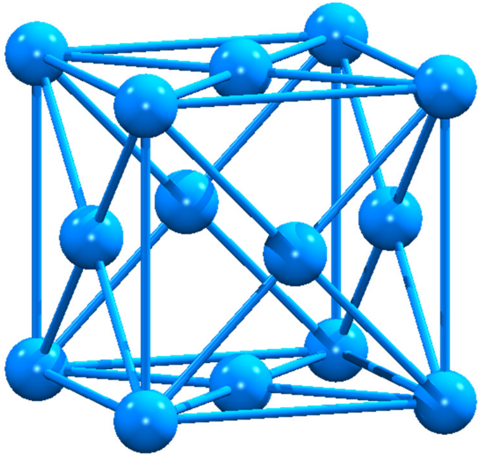
格子模型



cP

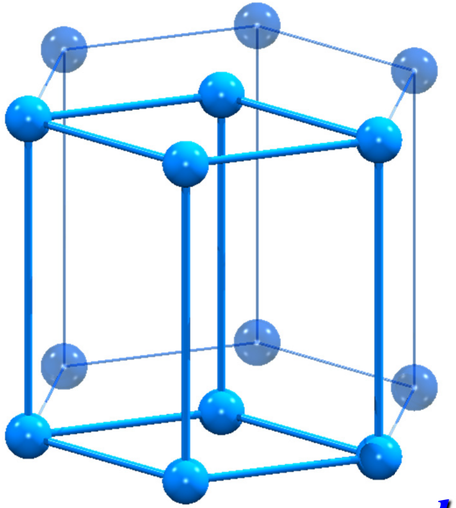


cI

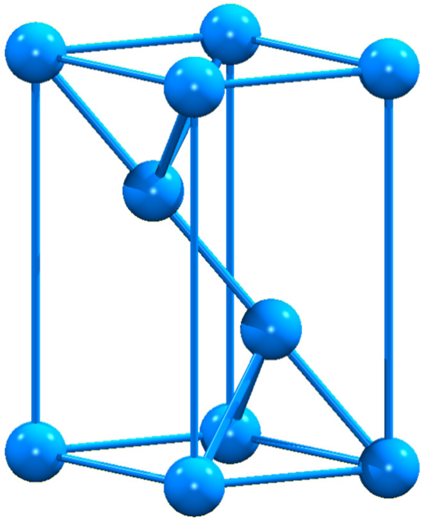


cF

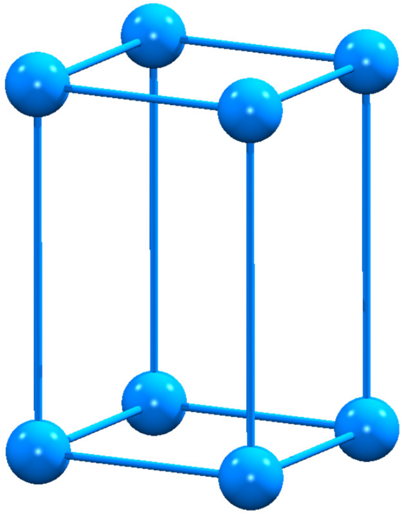
格子模型



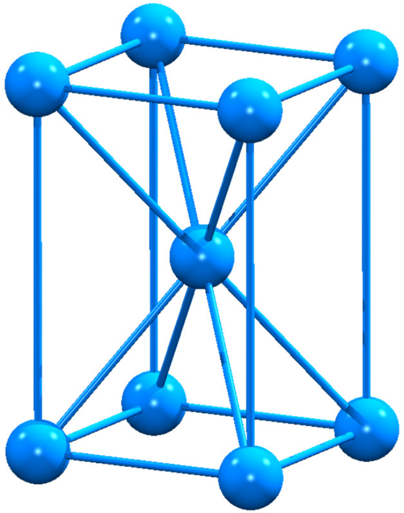
hP



hR

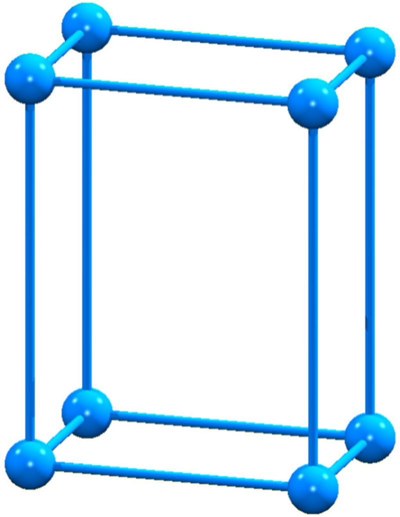


tP

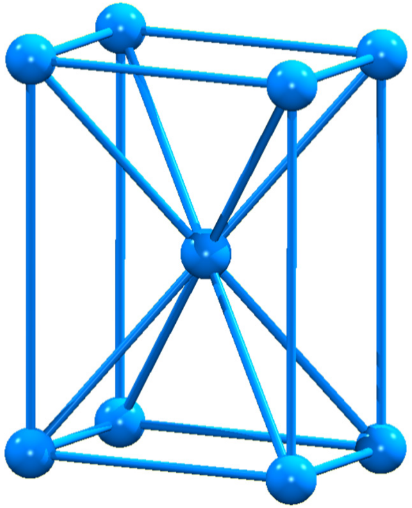


tI

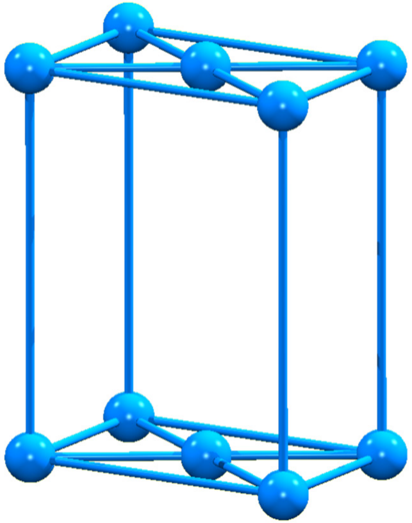
格子模型



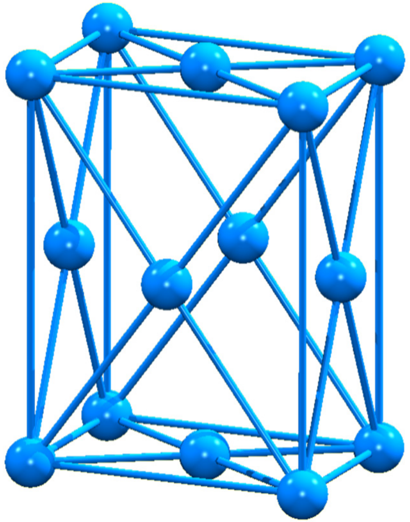
oP



oI

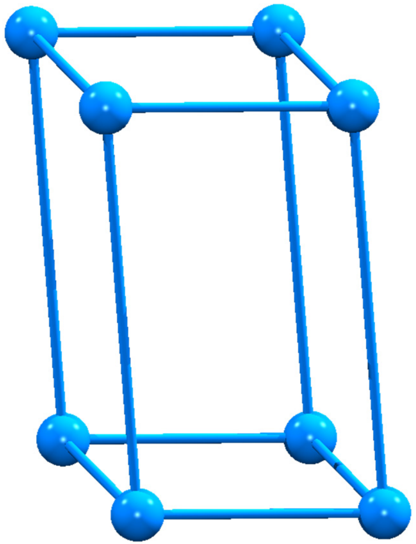


oC

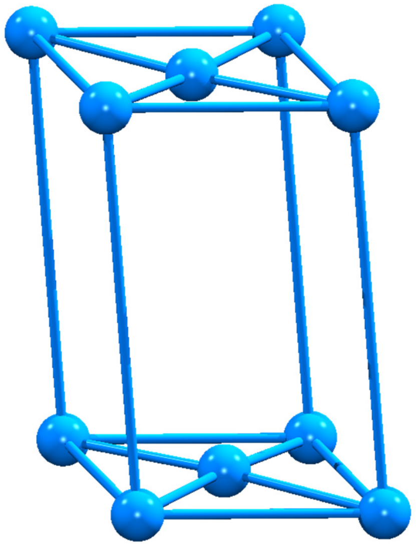


oF

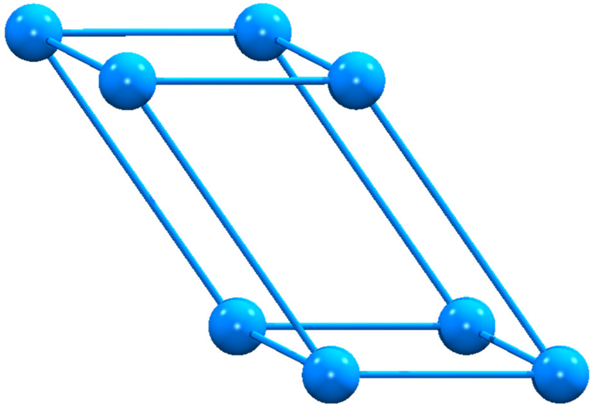
格子模型



mP



mC



aP

7.1.3 晶体具有点阵结构

1. 点阵结构：

能被某一点阵所代表的结构叫**点阵结构**

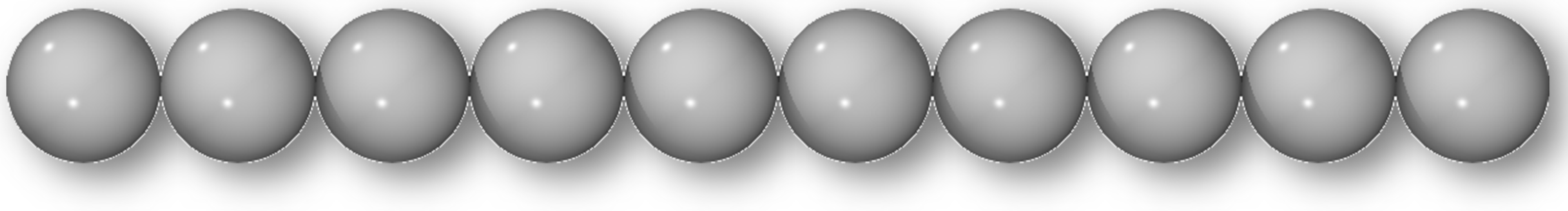
结构基元：把晶体结构抽象为点阵的过程中，点阵点所代表的内容(包括原子分子的种类，数量及在空间的排列方式)

重复周期：指在某一方向上，结构基元移动的距离——周期，也就是重复向量的方向和长短

晶体结构 = 点阵 + 结构基元

2. 从晶体点阵结构中抽象出点阵

例：等径圆球排列形成的一密置列——直线点阵

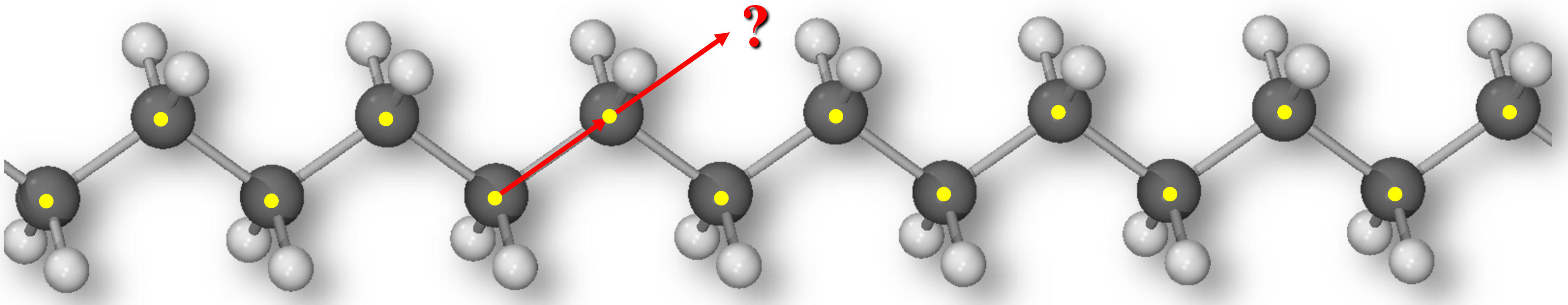


一个点阵点代表一个球，

重复周期为a　$a = 2r$

例：无限伸长的聚乙烯长链高分子，可否以[-CH_2-]单元作为结构基元

聚乙烯：$-\!\!\left[CH_2\right]\!\!-_n$

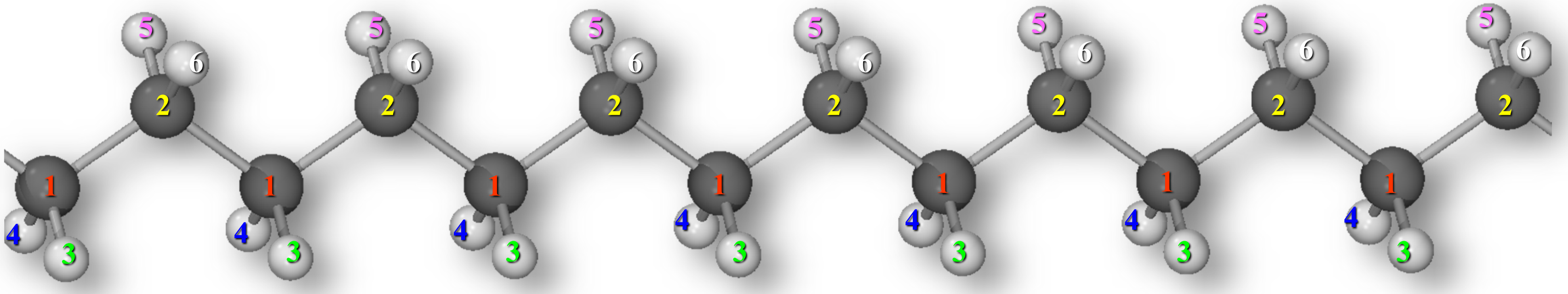


如何将具体的结构抽象成点阵形式?
如何得到结构基元的内容呢?

通过等同点来判断结构基元的方法

- 等同点：把内容相同，周围环境也相同的原子叫一套等同点
- 在一套等同点内，内容相同，周围环境也相同；在套与套之间，重复的周期一样，即方向大小一样
- 晶体的点阵结构是多套等同点的集合

例：找到聚乙烯中的等同点

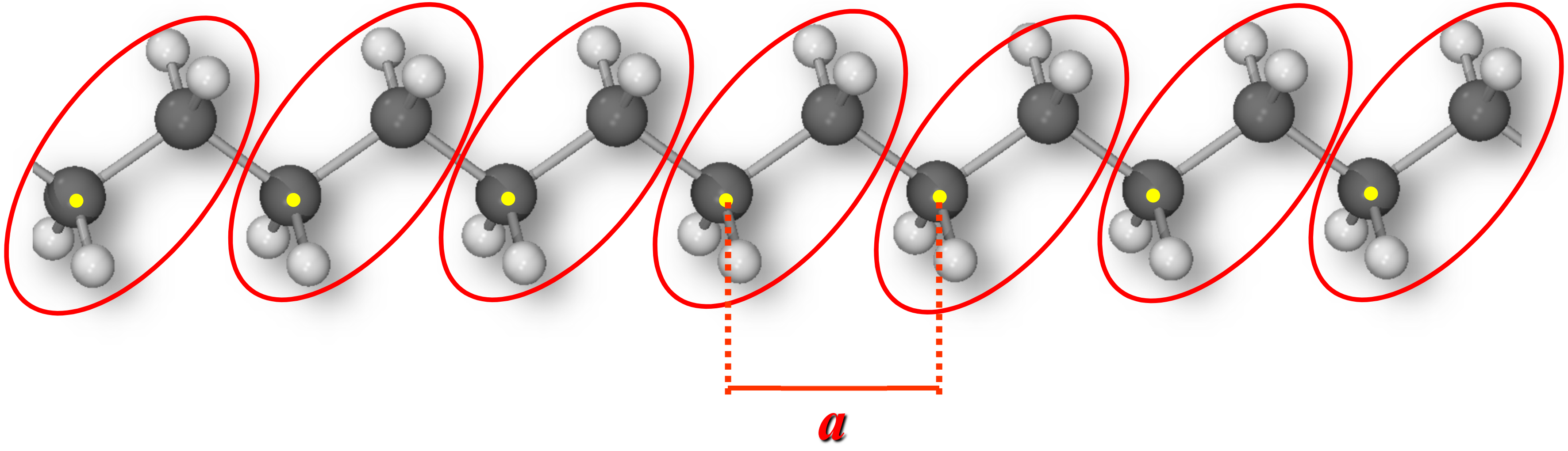


有6套等同点，2套C，4套H

判断结构基元的方法

- 找出所有等同点，指出套数和内容（每套的周期必一样）
- 把点阵点设在其中任一套等同点的位置
- 每个点阵点代表一个结构基元，**结构基元内容为各套中的一个原子**
- 结构基元的重复周期为一套点的周期

例:找出聚乙烯的结构基元，将其抽象成点阵

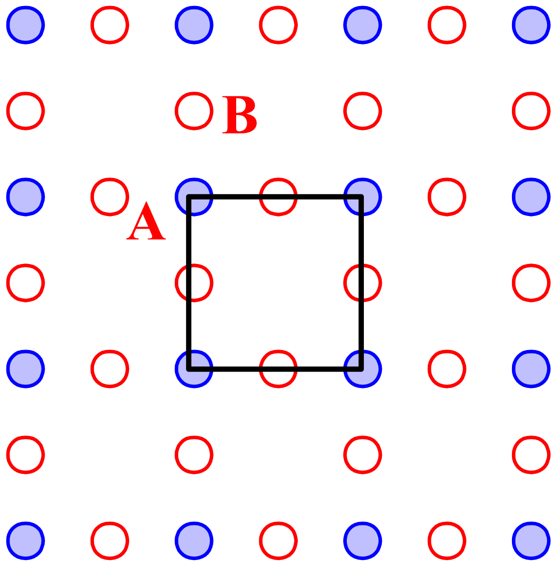


点阵点：　　把点阵点设在一套C上

每个点阵点的内容—结构基元：　　2C，4H

结构基元的重复周期：　　*a*

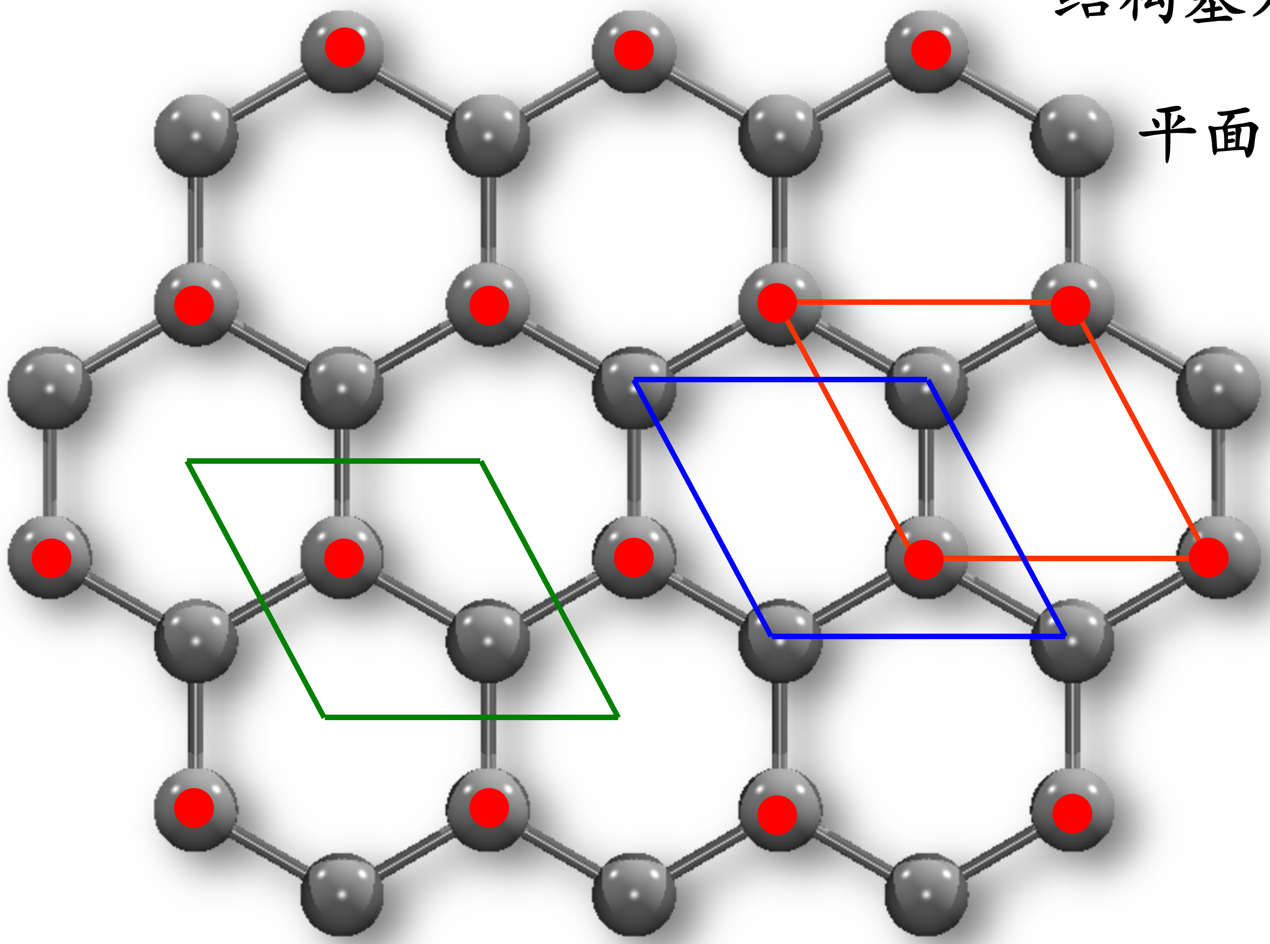
例:硫钒铜矿（Cu_3VS_2）的(100)晶面由Cu、V两种原子构成，找出其结构基元并给出其平面点阵形式



3套等同点: 2套Cu，1套V

平面正方

例：石墨晶面的点阵结构



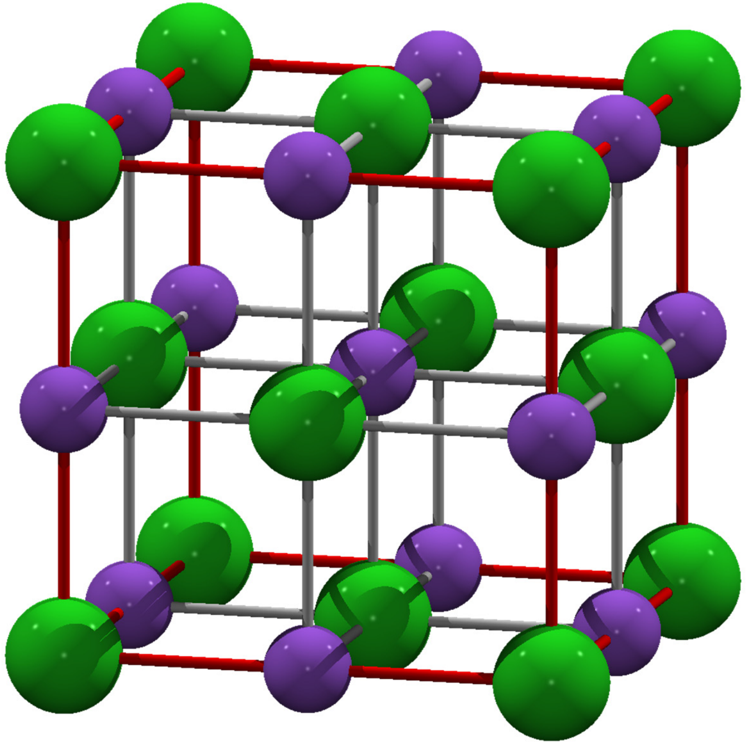
等同点套数：　2

结构基元：　2个C

平面点阵型式：

平面六方

例：NaCl



等同点套数:

$1Cl^-$, $1Na^+$

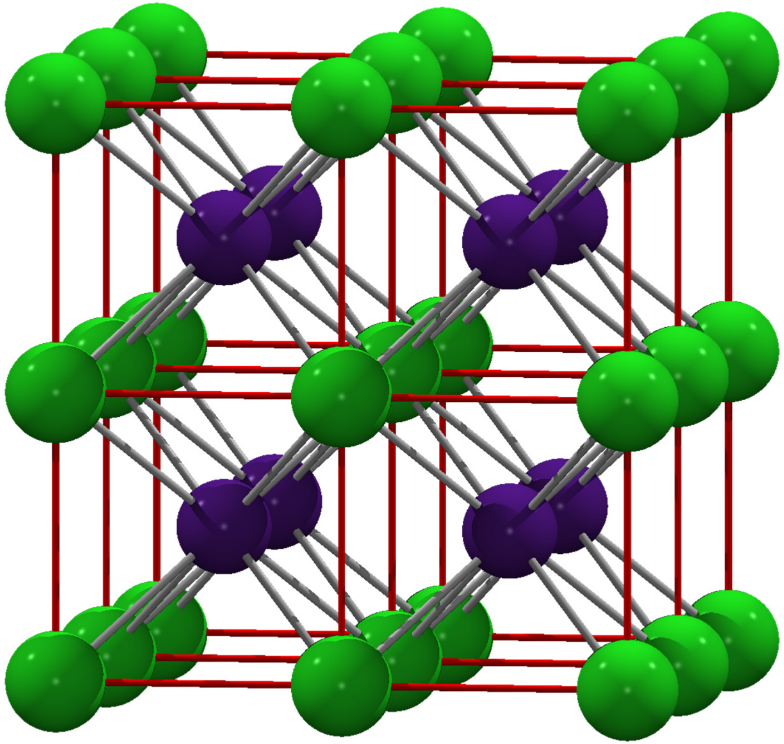
空间点阵形式:

立方F　*cF*

晶胞中原子种类、数目:

$4Cl^-$ $4Na^+$

例：CsCl



等同点套数：

$1Cl^-$, $1Cs^+$

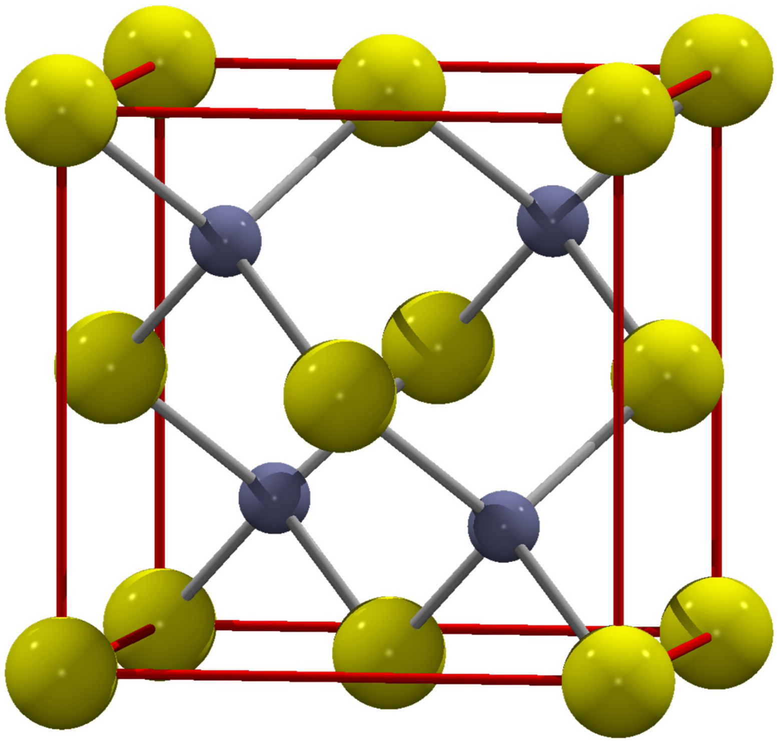
空间点阵形式：

立方P *cP*

晶胞中原子种类、数目：

$1Cl^-$ $1Cs^+$

例.立方ZnS



等同点套数：

$1S^{=}$, $1Zn^{++}$

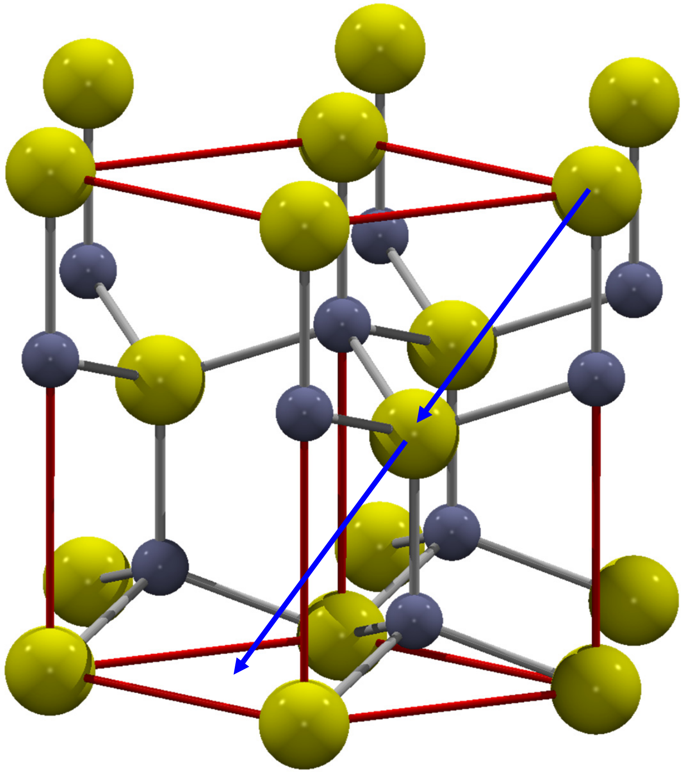
空间点阵形式：

立方F *cF*

晶胞中原子种类、数目：

$4S^{=}$, $4Zn^{++}$

例. 六方ZnS



等同点套数:

$2S^{=}$, $2Zn^{++}$

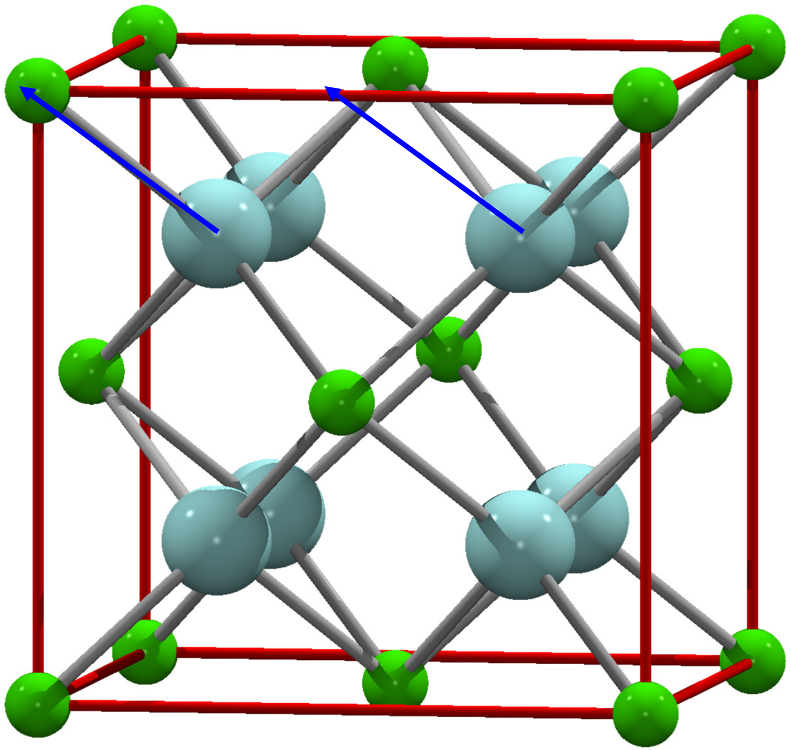
空间点阵形式:

六方P　***hP***

晶胞中原子种类、数目:

$2S^{=}$, $2Zn^{++}$

例. CaF_2



等同点套数:

$1Ca^{2+}$, $2F^{-}$

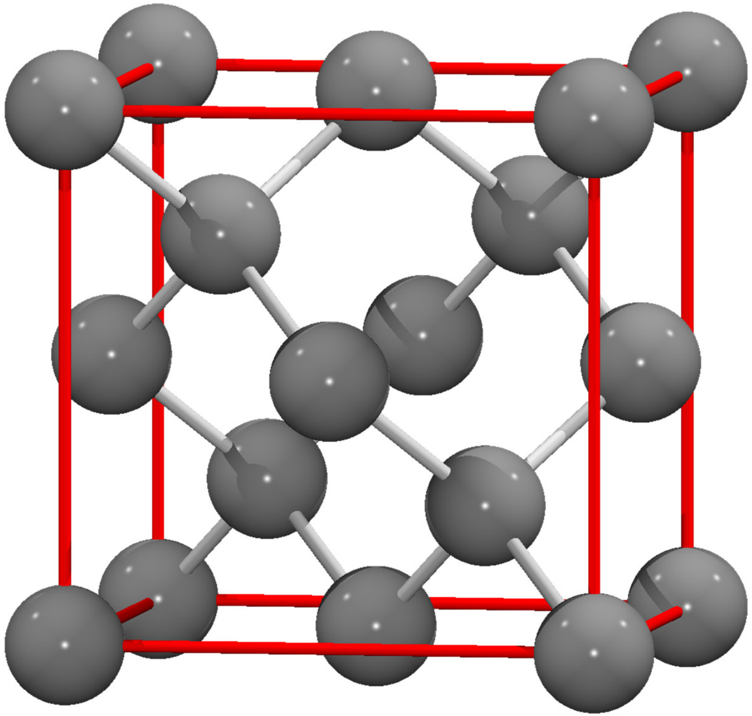
空间点阵形式:

立方F *cF*

晶胞中原子种类、数目:

$4Ca^{2+}$ $8F^{-}$

例. 金刚石



等同点套数:

2C

空间点阵形式:

立方F　*cF*

晶胞中原子种类、数目:

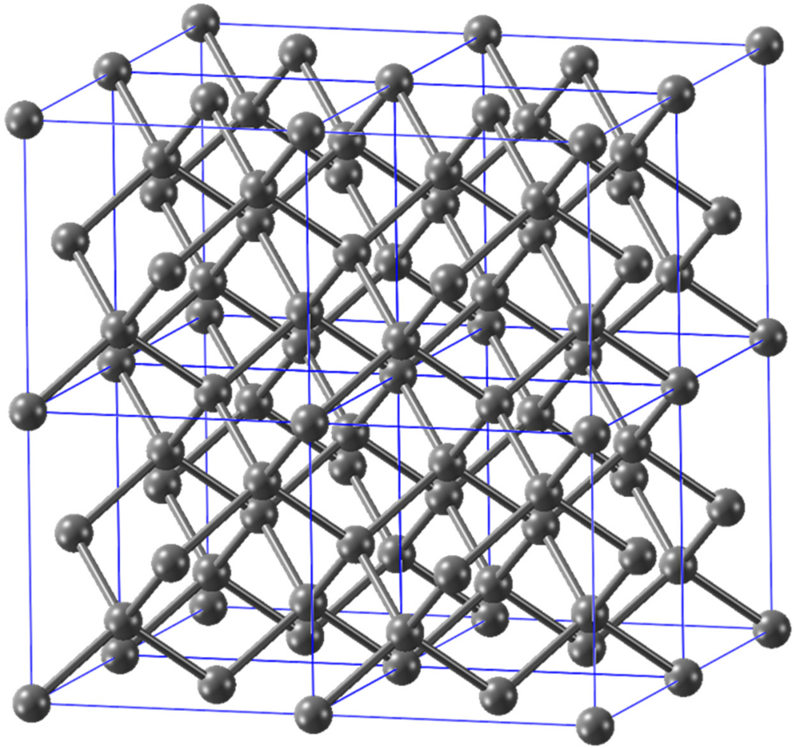
8C

3. 点阵中各要素与晶体中各要素的关系

数学抽象	晶体
点阵	点阵结构
点阵点	结构基元
直线点阵	晶棱
平面点阵	晶面
空间点阵	晶体
正当单位	正当晶胞
6种形状	6个晶族*
14种布拉威格子	14种布拉威晶格

7.1.4 晶胞

晶胞：点阵结构中划分出的平行六面体叫晶胞，它代表晶体结构的基本重复单位

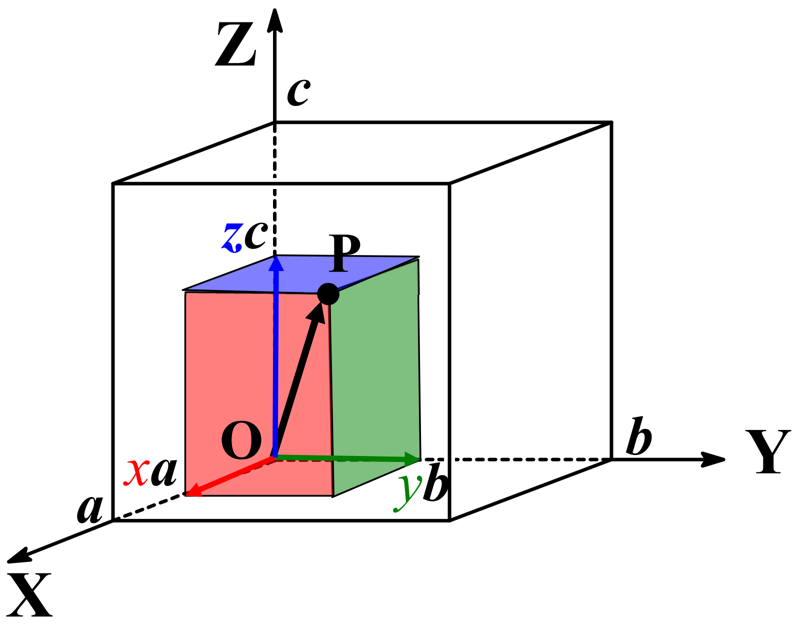


一般不加特殊说明，晶胞均指正当晶胞

晶胞的两个基本要素

- 晶胞的大小和形状：可用晶胞参数来表示，晶轴三个方向确定后，$a, b, c, \alpha, \beta, \gamma$ 描述晶胞边长、晶面夹角

- 晶胞的内容：原子的种类、数目和原子的位置(原子的分数坐标来描述)



$$\boldsymbol{OP} = x\boldsymbol{a} + y\boldsymbol{b} + z\boldsymbol{c}$$

过P作平行YZ平面，交X于$x\boldsymbol{a}$

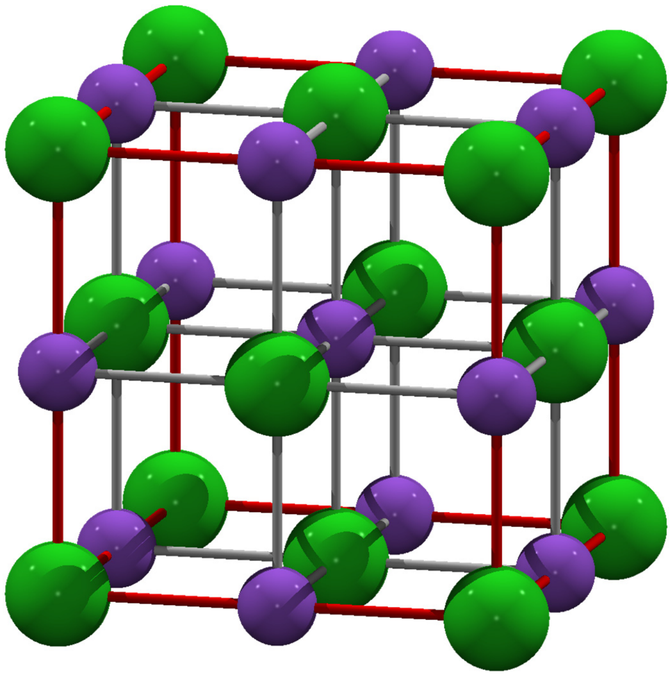
过P作平行XZ平面，交Y于$y\boldsymbol{b}$

过P作平行XY平面，交Z于$z\boldsymbol{c}$

分数坐标的标记方法：

- 凡不到一个周期的原子都必须标记分数坐标，即坐标都为分数，这样的晶胞并置形成晶体
- 晶胞内能写出分数坐标的原子的个数，一定等于该晶胞内所包括原子的个数
- 必须注意的是，欲得到原子在某晶轴上的分数坐标，应过该原子做与另两个晶轴平行的平面，这个平面在这个晶轴上所截的单位向量的分数为分数坐标
- 分数坐标与选取晶胞的原点有关

例：岩盐 NaCl



晶胞中原子数：

Cl^-：4

Na^+：4

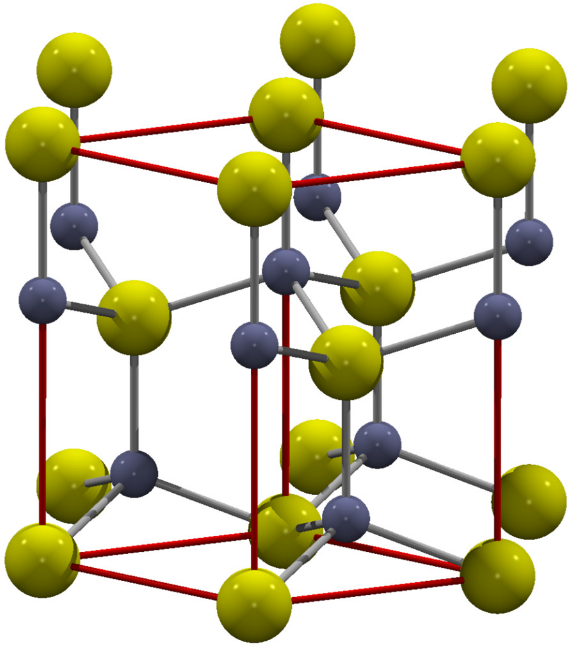
Cl^-：顶点：0,0,0;

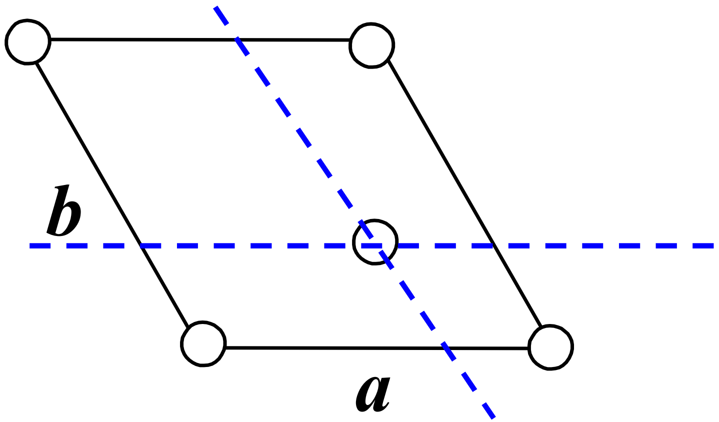
面心：1/2,1/2,0; 0,1/2,1/2; 1/2,0,1/2

Na^+：体心： 1/2,1/2,1/2

棱心： 1/2,0,0; 0,1/2,0; 0,0,1/2

例：纤锌矿 六方ZnS



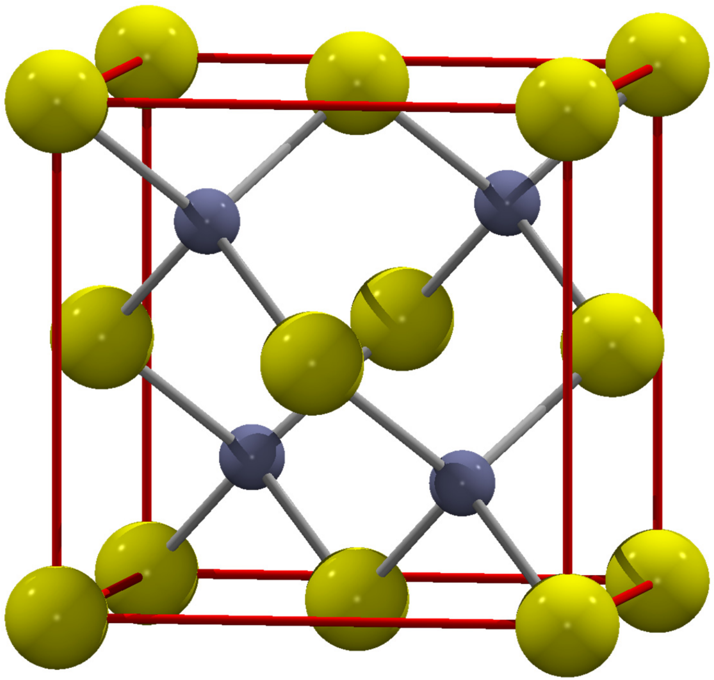


S^{2-} : 0,0,0; 2/3,1/3,1/2;

Zn^{2+}: 0,0,5/8; 2/3,1/3,1/8

晶胞中原子数：S：2；Zn: 2

例：闪锌矿 立方ZnS

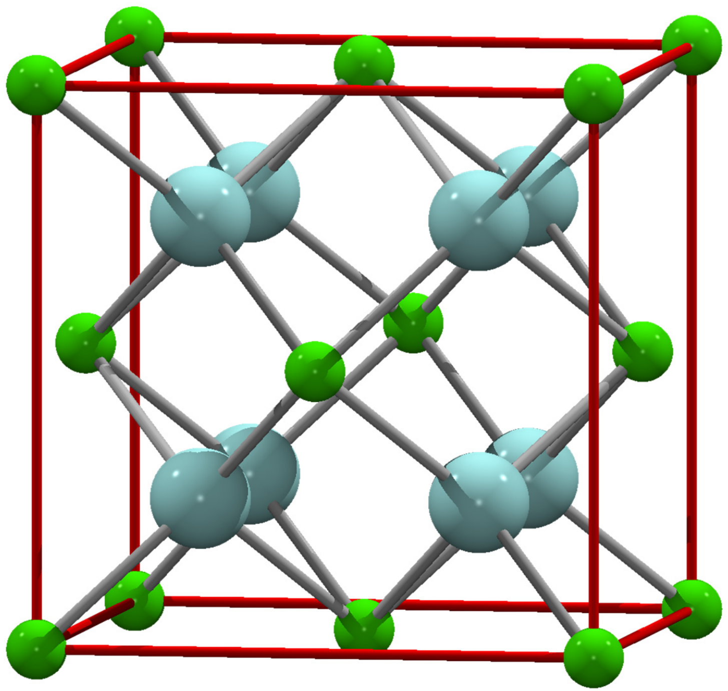


S^{2-}： 0,0,0;
1/2,1/2,0;
0,1/2,1/2;
1/2,0,1/2

Zn^{2+}: 1/4,1/4,1/4;
3/4,3/4,1/4;
3/4,1/4,3/4;
1/4,3/4,3/4;

晶胞中原子数： S：4；Zn: 4
S: 顶点+面心
Zn:交错的四个1/8小立方体体心

例：萤石 CaF_2



F占据相互交错的8个小立方体的中心

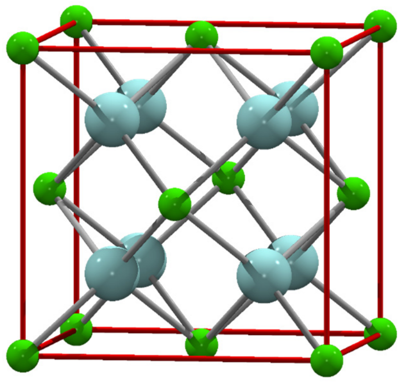
F^-:

1/4,1/4,1/4;
3/4,3/4,1/4;
3/4,1/4,3/4;
1/4,3/4,3/4;
3/4,3/4,3/4;
3/4,1/4,1/4;
1/4,3/4,1/4;
1/4,1/4,3/4;

立方晶胞特殊位置的分数坐标

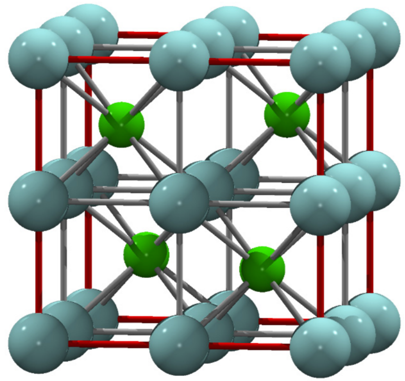
- 顶点和面心
- 体心和棱心
- 1/8小立方体的中心(交错)

看到位置直接能写出分数坐标，看到分数坐标能马上反映出位置



分数坐标变换

=



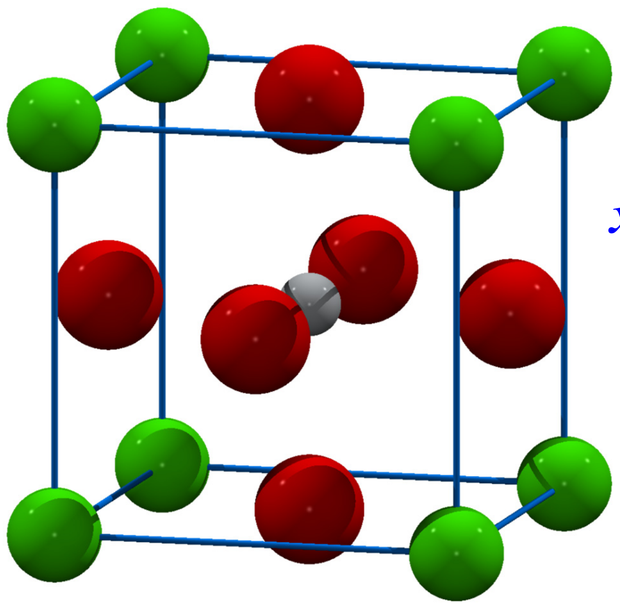
F

1/4,1/4,1/4 → 0,0,0
3/4,3/4,1/4 → 1/2,1/2,0
3/4,1/4,3/4 → 1/2,0,1/2
1/4,3/4,3/4 → 0,1/2,1/2
3/4,3/4,3/4 → 1/2,1/2,1/2
3/4,1/4,1/4 → 1/2,0,0
1/4,3/4,1/4 → 0,1/2,0
1/4,1/4,3/4 → 0,0,1/2

Ca

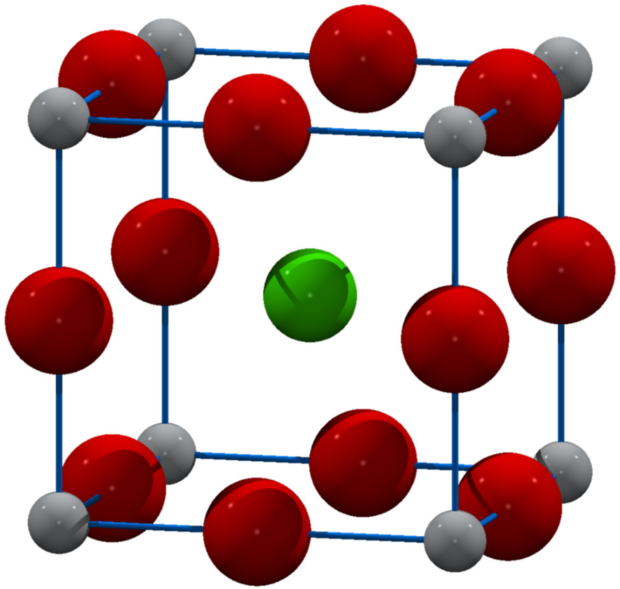
0,0,0 → 3/4,3/4,3/4 (-1/4,-1/4,-1/4)
1/2,1/2,0 → 1/4,1/4,3/4
1/2,0,1/2→1/4,3/4,1/4
0,1/2,1/2 → 3/4,1/4,1/4

例：钙钛矿 $CaTiO_3$



x, y, z均减1/2

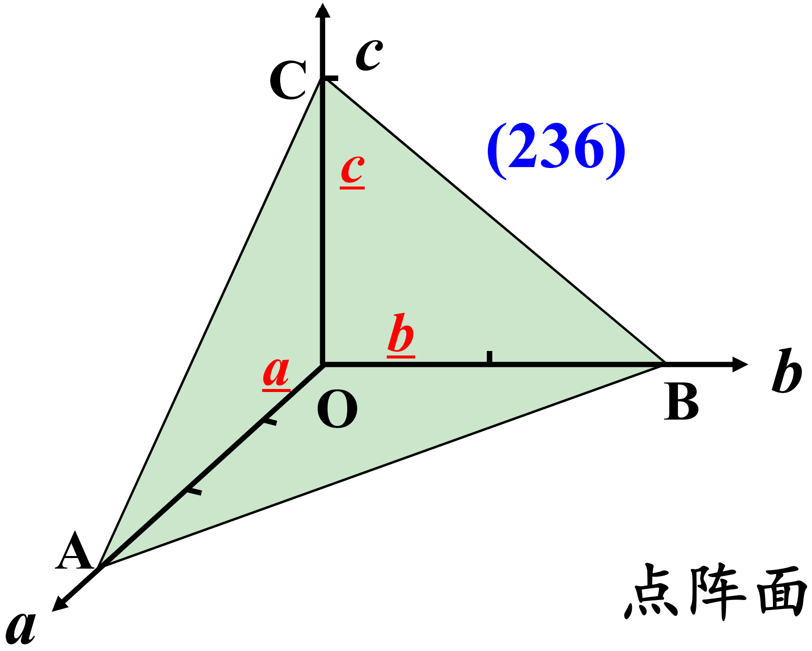
$=$



7.1.5 晶面和晶面指标

点阵面：点阵结构中平面点阵面叫 (或晶面)

有理指数定理：晶面在三个晶轴上的**倒易截数**之比可以化为一组**互质**的整数比



$OA/a = 3 \quad OB/b = 2$

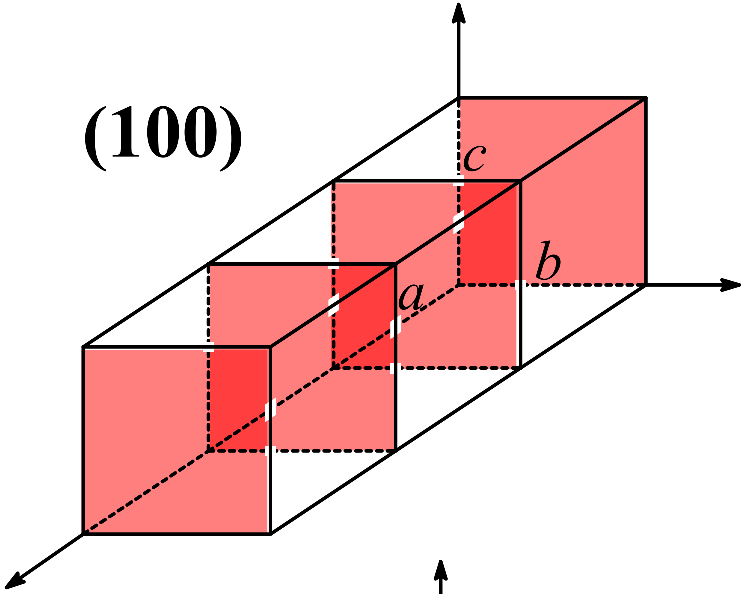
$OC/c = 1$

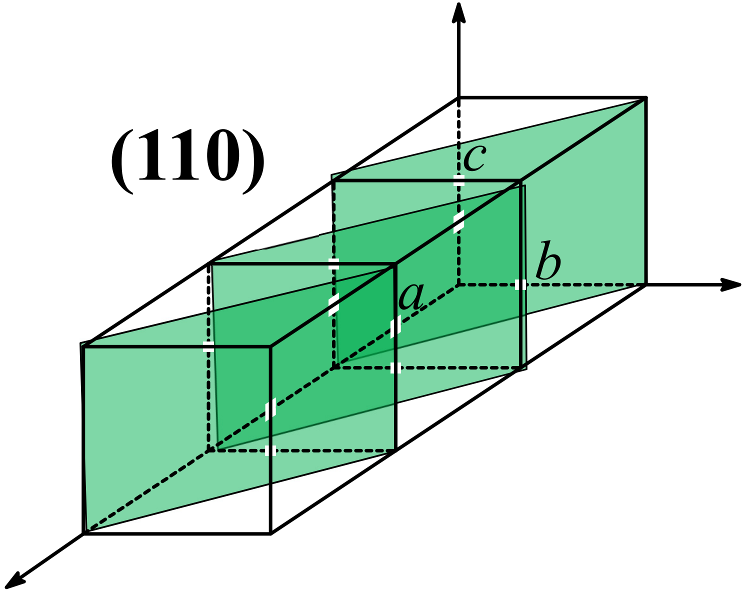
倒易截数之比

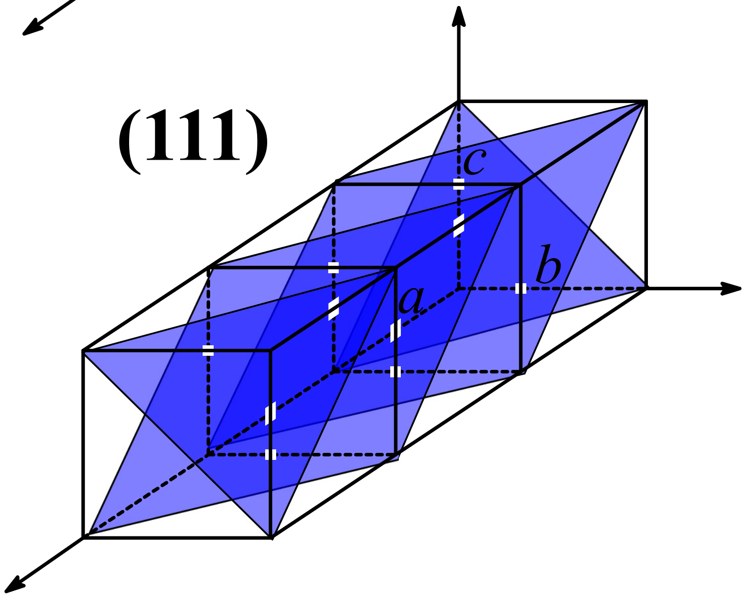
$=1/3:1/2:1 =2:3:6$

$=h^*:k^*:l^*$

点阵面指标(晶面指标)　$(h^*k^*l^*)$

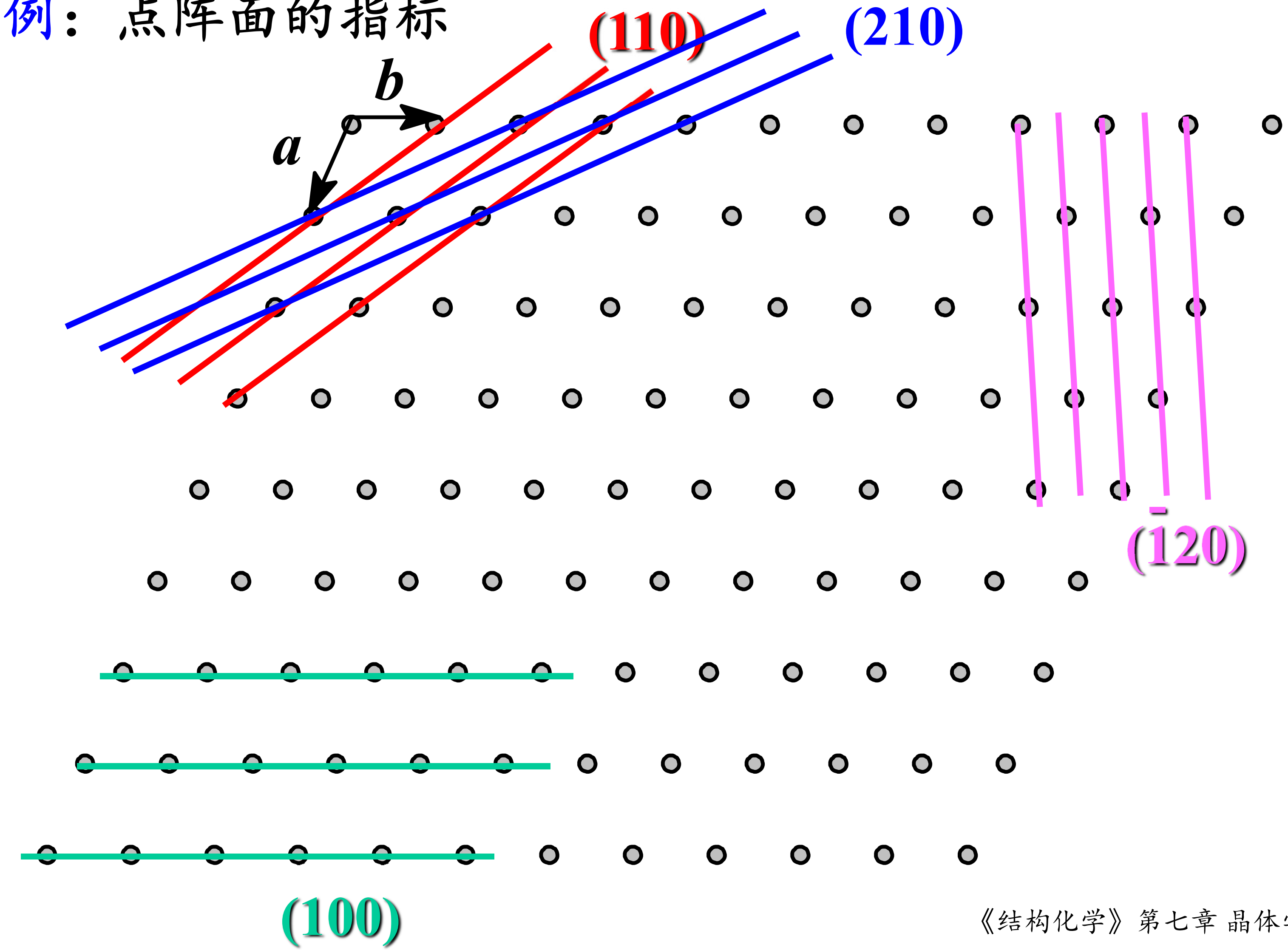






所有和$(h^*k^*l^*)$平行的晶面(平面点阵面)都用该指标表示——晶面族

例：点阵面的指标



晶面间距：任三个晶轴上截数为整数的一族晶面中，相邻晶面间的垂直距离

立方晶系：

$$d_{(h^*k^*l^*)} = \frac{a}{\sqrt{h^{*2} + k^{*2} + l^{*2}}}$$

正交晶系：

$$d_{(h^*k^*l^*)} = \frac{1}{\sqrt{(h^*/a)^2 + (k^*/b)^2 + (l^*/c)^2}}$$

四方晶系：

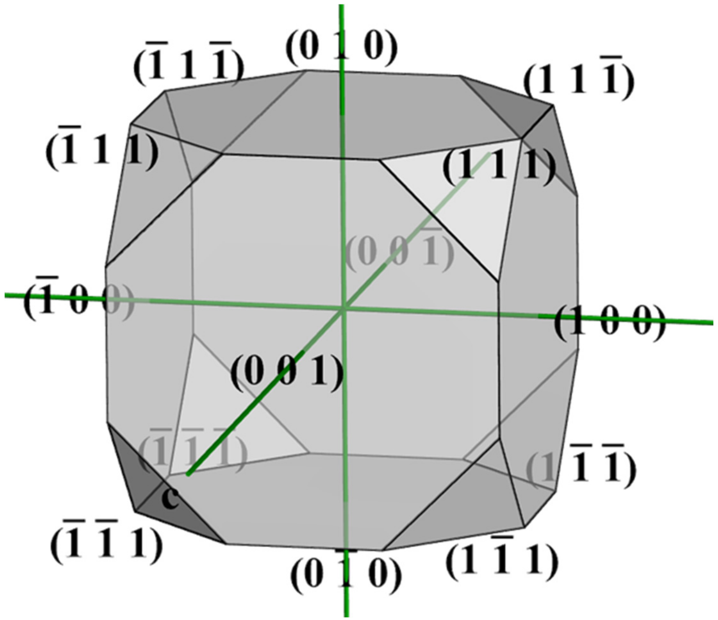
$$d_{(h^*k^*l^*)} = \frac{1}{\sqrt{(h^{*2} + k^{*2})/a^2 + (l^*/c)^2}}$$

六方晶系：

$$d_{(h^*k^*l^*)} = \frac{1}{\sqrt{\frac{4(h^{*2} + h^*k^* + k^{*2})}{3a^2} + \frac{l^{*2}}{c^2}}}$$

宏观晶体的晶面指标

对于宏观晶体的外形晶面进行标记时，习惯上把原点设在晶体的中心，根据晶体的所属晶系确定晶轴的方向，两个平行的晶面一个为 (hkl)，另一个为 $(\bar{h}\bar{k}\bar{l})$



§ 7.2 晶体的宏观对称性及32点群

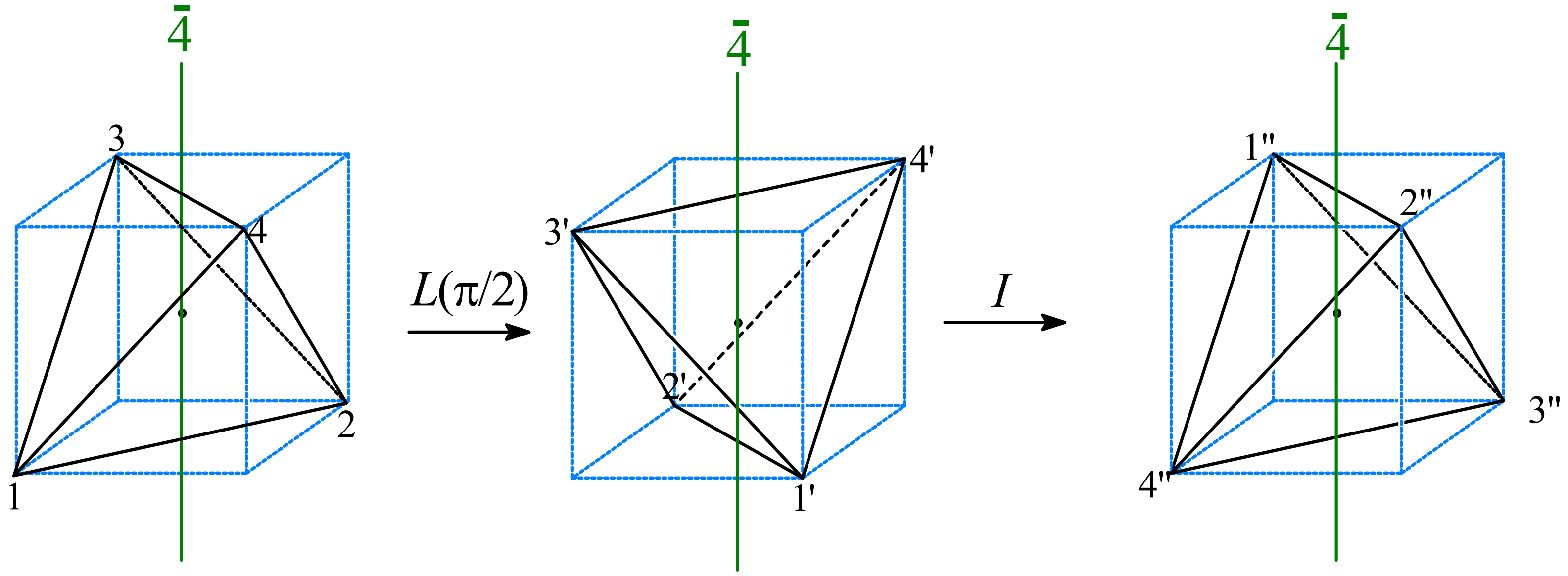
7.2.1 晶体的宏观对称元素及对称操作

1. 晶体对称性与分子对称性习惯表示的差别

分子对称性		晶体对称性	
对称元素	对称操作	对称元素	对称操作
旋转轴 C_n	旋转 $\hat{C}_n$	$\underline{n}$ 或 n	$L(\alpha=2\pi/n)$
镜面 σ	反映 $\hat{\sigma}$	m	M
对称中心 i	反演或倒反 $\hat{i}$	i	I
象转轴 S_n	旋转反映 $\hat{S}_n$	反轴 $\overline{n}$	旋转倒反 $L(\alpha)I$

2. 反轴

旋转倒反操作：先绕某轴旋转一定角度($\alpha=2\pi/n$)后，再通过轴线上中心点进行倒反，即能复原的图形。 $L(\alpha)\ I$ or $I\ L(\alpha)$，该轴为反轴 $\bar{n}$



从各反轴对应的操作可以证明：

$$\bar{1} = i = S_2$$

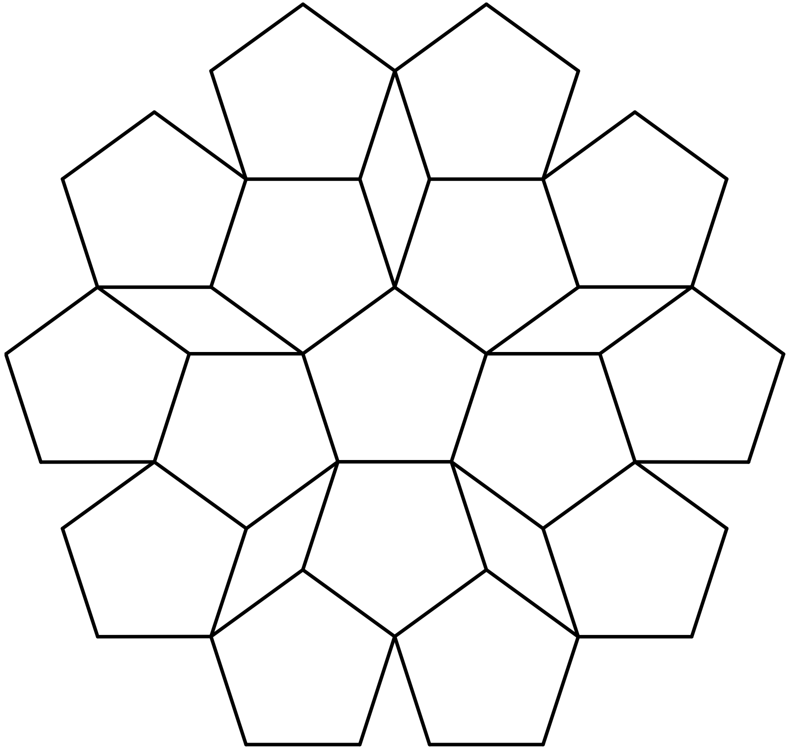
$$\bar{2} = m = S_1$$

$$\bar{3} = 3 + i = S_6$$

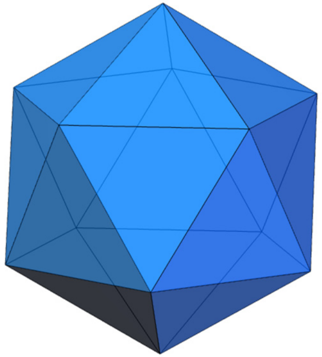
$$\bar{4} = S_4$$

$$\bar{6} = 3 + m_h = S_3$$

3. 晶体的对称性定律：晶体中对称轴的轴次n不是任意的，只可能有n=1, 2, 3, 4, 6



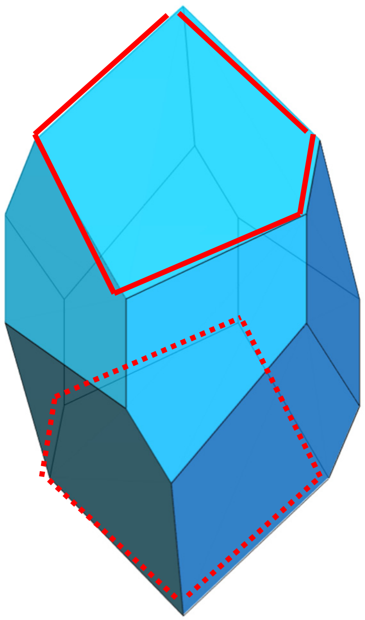
五次轴破坏了点阵的平移对称性

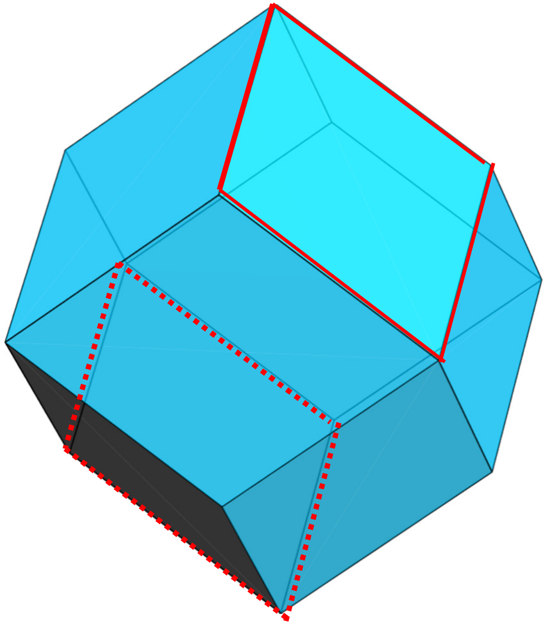


准晶体

4. 对称中心存在时，i与重心重合，每一晶面必有另一与之平行的晶面：

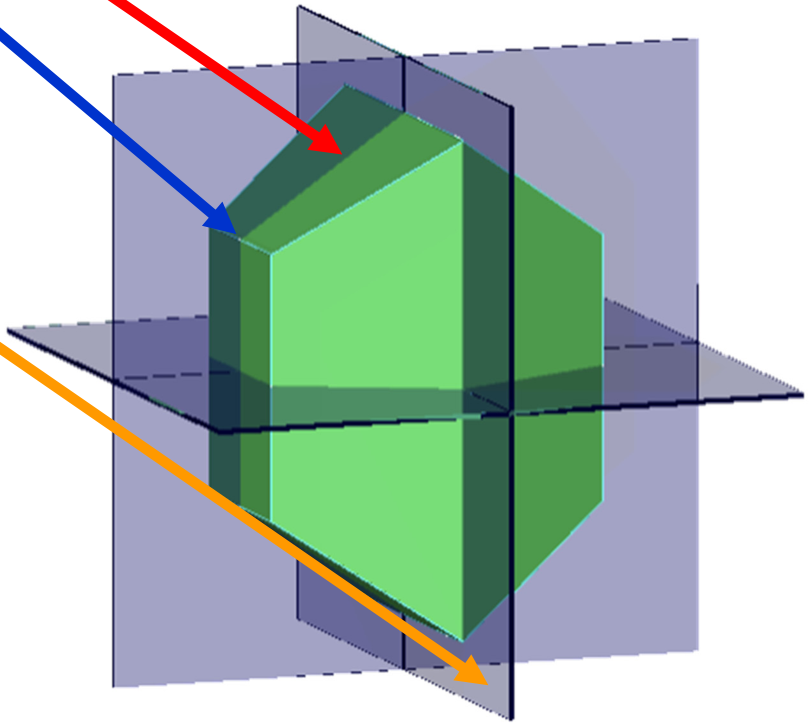
- ❑晶面无i — 晶体的晶面必双双反向平行
- ❑晶面有i — 晶体的晶面正向平行





5. 在晶体的宏观对称性中，*m*只有以下几种形式：

- ❑ 垂直晶面并等分晶面
- ❑ 垂直晶棱并过其中点
- ❑ 包含晶棱



7.2.2 晶体的七个晶系及特征对称元素

<table>
<tr><th>晶族</th><th>晶系</th><th>特征对称元素</th><th colspan="2">晶胞边角关系</th></tr>
<tr><td>c</td><td>立方晶系</td><td>四个3</td><td colspan="2">$a=b=c\ \ \alpha=\beta=\gamma=90°$</td></tr>
<tr><td rowspan="3">h</td><td>六方晶系</td><td>6 或 $\bar{6}$</td><td colspan="2">$a=b\neq c\ \ \alpha=\beta=90°\ \ \gamma=120°$</td></tr>
<tr><td rowspan="2">三方晶系</td><td rowspan="2">3 或 $\bar{3}$</td><td>六方晶胞</td><td>$a=b\neq c\ \ \alpha=\beta=90°\ \ \gamma=120°$</td></tr>
<tr><td>菱面体晶胞</td><td>$a=b=c\ \ \alpha=\beta=\gamma\neq 90°$</td></tr>
<tr><td>t</td><td>四方晶系</td><td>4 或 $\bar{4}$</td><td colspan="2">$a=b\neq c\ \ \alpha=\beta=\gamma=90°$</td></tr>
<tr><td>o</td><td>正交晶系</td><td>两个相互垂直的m
或三个相互垂直的2</td><td colspan="2">$a\neq b\neq c\ \ \alpha=\beta=\gamma=90°$</td></tr>
<tr><td>m</td><td>单斜晶系</td><td>2 或 m</td><td colspan="2">$a\neq b\neq c\ \ \alpha=\gamma=90°\ \ \neq\beta$</td></tr>
<tr><td>a</td><td>三斜晶系</td><td>无 或 i</td><td colspan="2">$a\neq b\neq c\ \ \alpha\neq\beta\neq\gamma\neq 90°$</td></tr>
</table>

7.2.3晶体的宏观对称类型(32点群)的判断

- 起点
  - 有4$\underline{3}$
    - 有3$\underline{4}$ → O
      - 有i → O_h 正八面体
      - → O
    - → T
      - i → T_h
      - $\bar{4}$ → T_d 正四面体
      - → T
    - 立方晶系
  - 无轴群
    - 有m → C_s 单斜
    - 有i → C_i 三斜
    - → C_1 三斜
  - 只有$\bar{4}$ → S_4 四方
  - 有一个$\underline{n}$
    - 有垂直$\underline{n}$的$\underline{2}$
      - m_h → D_{nh} ---> D_{2h}(正交)，D_{3h}(六方*)，D_{4h}(四方)，D_{6h}(六方)
      - m_d → D_{nd} ---> D_{2d}(四方*)，D_{3d}(三方)
      - → D_n ---> D_2(正交)，D_3(三方)，D_4(四方)，D_6(六方)
    - m_h → C_{nh} ---> C_{2h}(单斜)，C_{3h}(六方*)，C_{4h}(四方)，C_{6h}(六方)
    - m_v → C_{nv} ---> C_{2v}(正交)，C_{3v}(三方)，C_{4v}(四方)，C_{6v}(六方)
    - $\underline{3}+i$ → C_{3i} ---> C_{3i}(三方)
    - → C_n ---> C_2(单斜)，C_3(三方)，C_4(四方)，C_6(六方)

注：C_{3h}, D_{3h}群有$\bar{6}$属六方晶系

D_{2d}有$\bar{4}$属四方晶系

7.2.4 晶体32点群的国际符号

1. 点群通常采用熊夫利记号(Schöflies Symbol)

2. 点群的国际符号(Hermann-Mauguin Symbol)表示

国际符号是用晶体在某特定方向上的对称元素来表示32个点群。

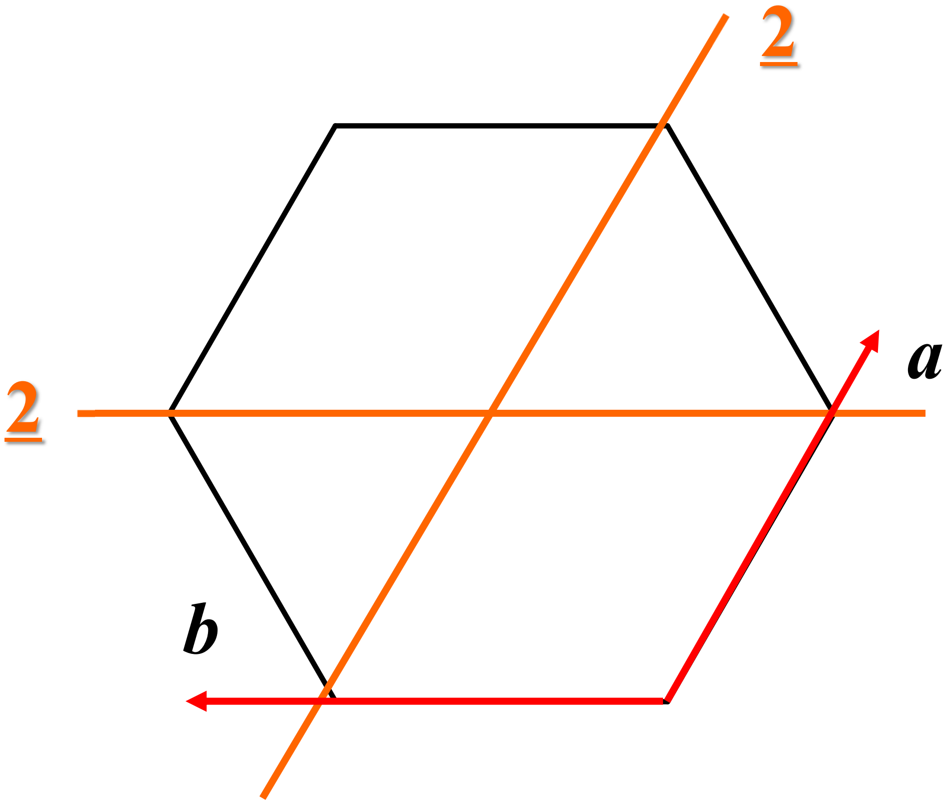
特定方向叫**位方向**

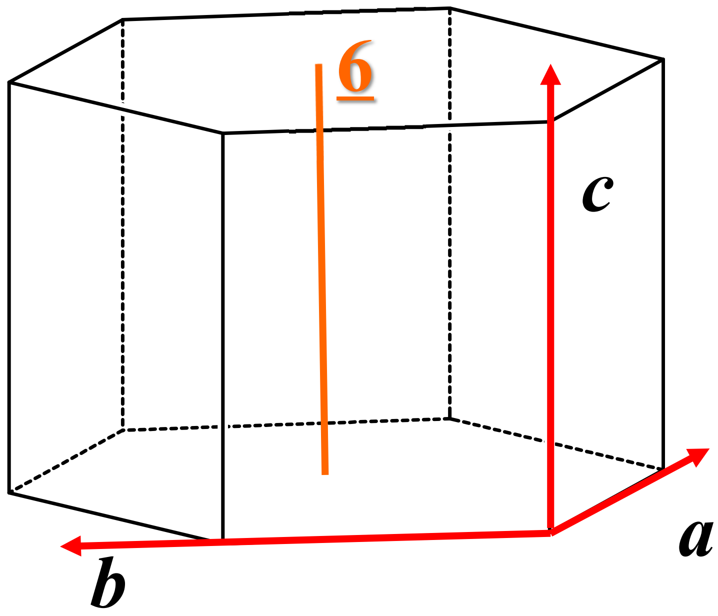
先根据晶系确定晶轴，依次找处位方向

- 在某方向出现的轴对称元素，指和该方向平行的轴(旋转轴，反轴)
- 在某方向出现的镜面指与该方向**垂直**的镜面

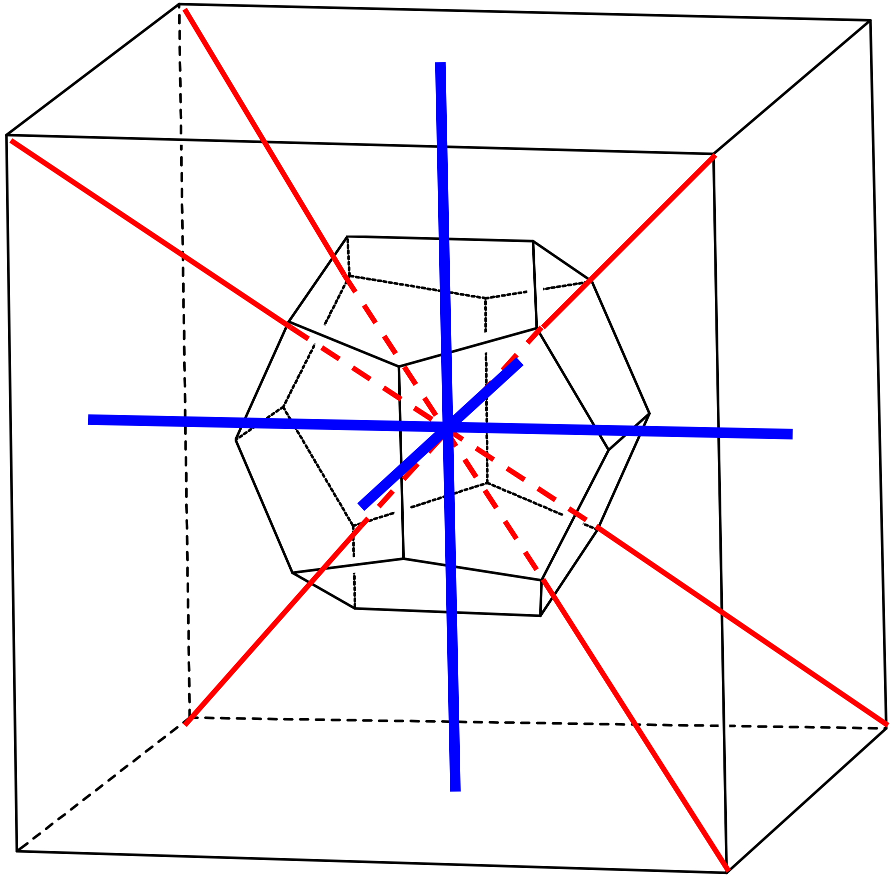
晶族	晶系	选晶轴方法	位方向
c	立方	4 个 3 // 4 条体对角线，立方体的三边即为 a, b, c	$a, a+b+c, a+b$
h	六方	c // 6(或$\bar{6}$)，a, b // 2 或⊥m 或 a, b 选⊥c 的晶棱	$c, a, 2a+b$
	三方	六方晶胞：c // 3(或$\bar{3}$)，a, b // 2 或⊥m 或 a, b 选⊥c 的晶棱	c, a
		菱面体晶胞：a, b, c 选 3 个与 $\underline{3}$(或$\bar{3}$)交成等角的晶棱	$a+b+c, a-b$
t	四方	c // 4(或$\bar{4}$)，a, b // 2 或⊥m 或 a, b 选⊥c 的晶棱	$c, a, a+b$
o	正交	a, b, c // 2 或⊥m	a, b, c
m	单斜	b // 2 (或⊥m)，a, c 选⊥c 的晶棱	b
a	三斜	a, b, c 选 3 个不共面的晶棱	a

例：某晶体宏观外形为正六棱柱，确定其晶轴





例：确定某立方晶系晶体的晶轴



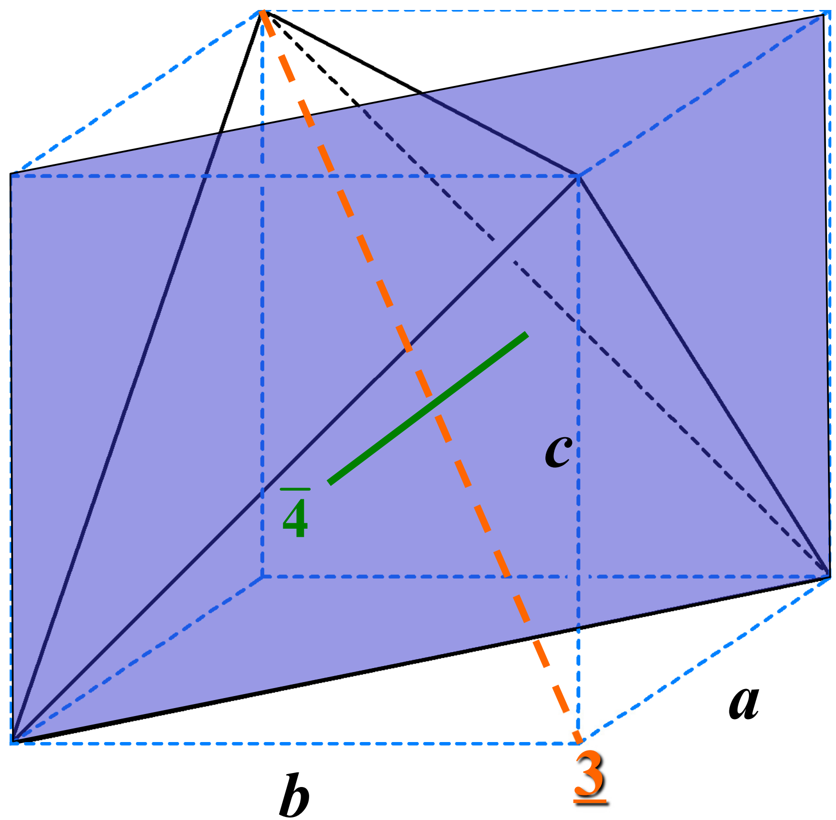
写出国际符号的步骤：

1. 找出特征对称元素，确定晶系

2. 确定晶轴方向及位方向，

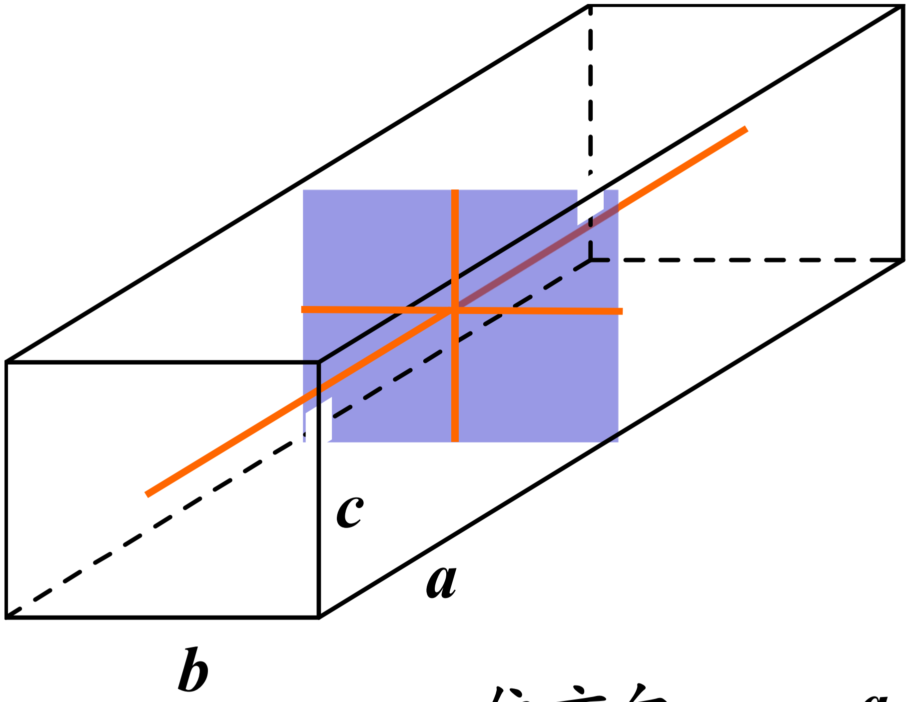
3. 写出规定方向上的对称元素

例：正四面体宏观外形的晶体，写出其所属点群的国际符号



位方向	对称元素
a	$\bar{4}$
$a+b+c$	3
$a+b$	m
T_d	$\bar{4}3m$

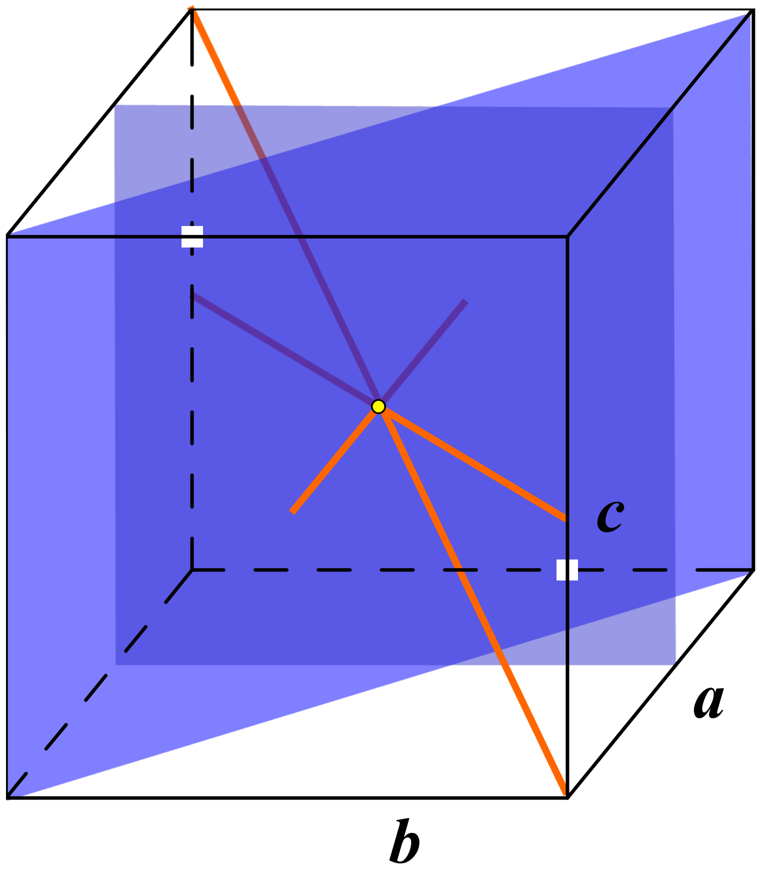
例：具有长方体（三条边不等长）外形的晶体，写出其国际符号



正交晶系 D_{2h}

位方向	a	b	c
对称元素	$\frac{2}{m}$	$\frac{2}{m}$	$\frac{2}{m}$

例：具有立方体外形的晶体，写出其国际符号



立方晶系 O_h

$$\frac{4}{m}\bar{3}\frac{2}{m}$$

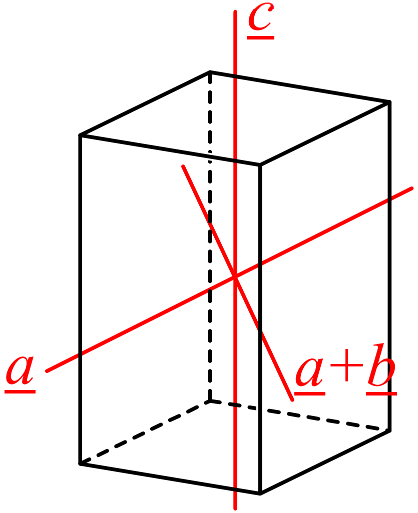
位方向	a	$a+b+c$	$a+b$
对称元素	$\frac{4}{m}$	$\bar{3}$	$\frac{2}{m}$

例：四方晶系晶体，连线对应熊夫利与国际符号

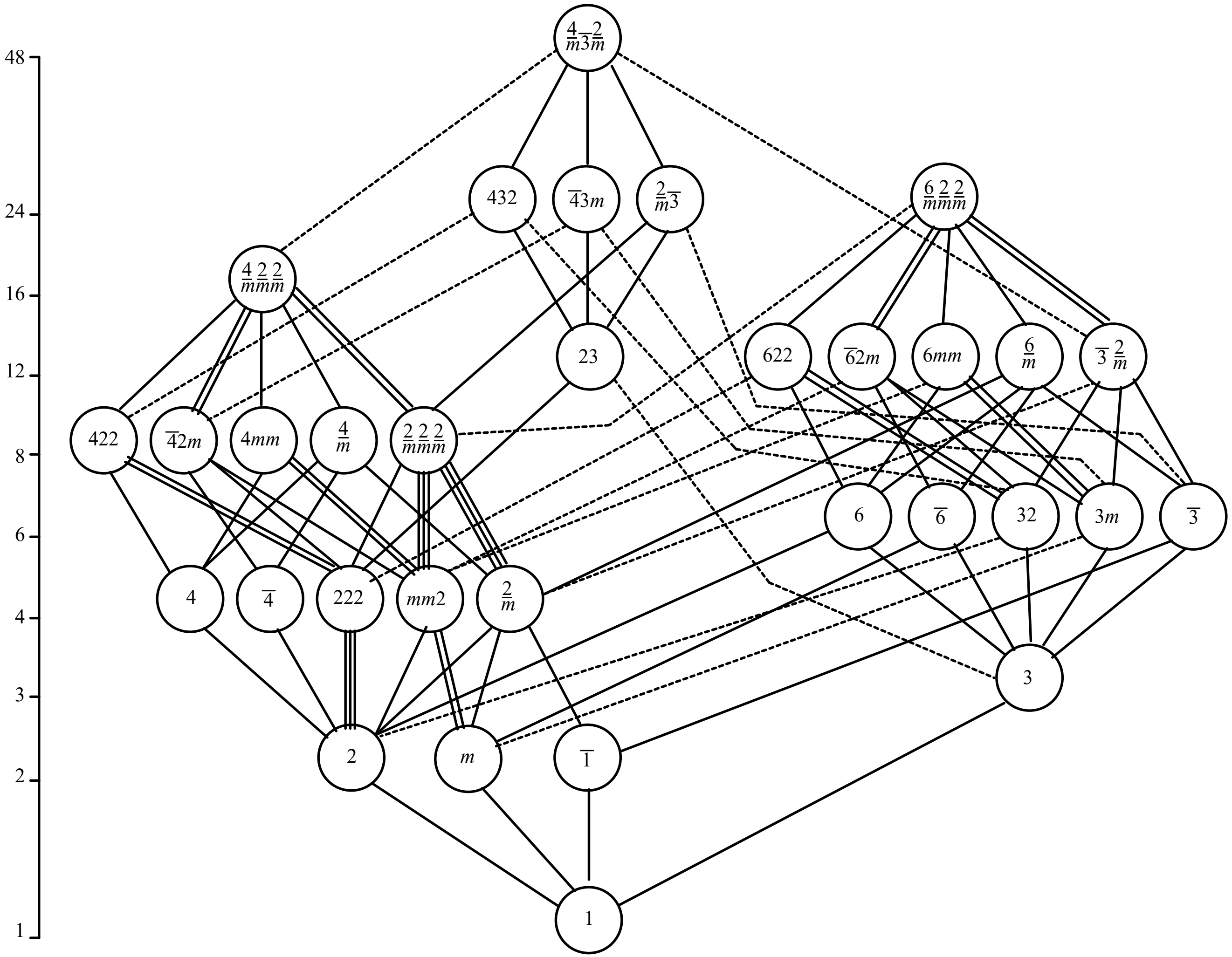
四方晶系位方向　$\underline{c}$, $\underline{a}$, $\underline{a}+\underline{b}$

C_4　　C_{4v}　　C_{4h}　　D_4　　D_{4h}　　D_{2d}

$\bar{4}2m$　　4　　$4mm$　　$4/m$　　422　　$\frac{4}{m}\frac{2}{m}\frac{2}{m}$

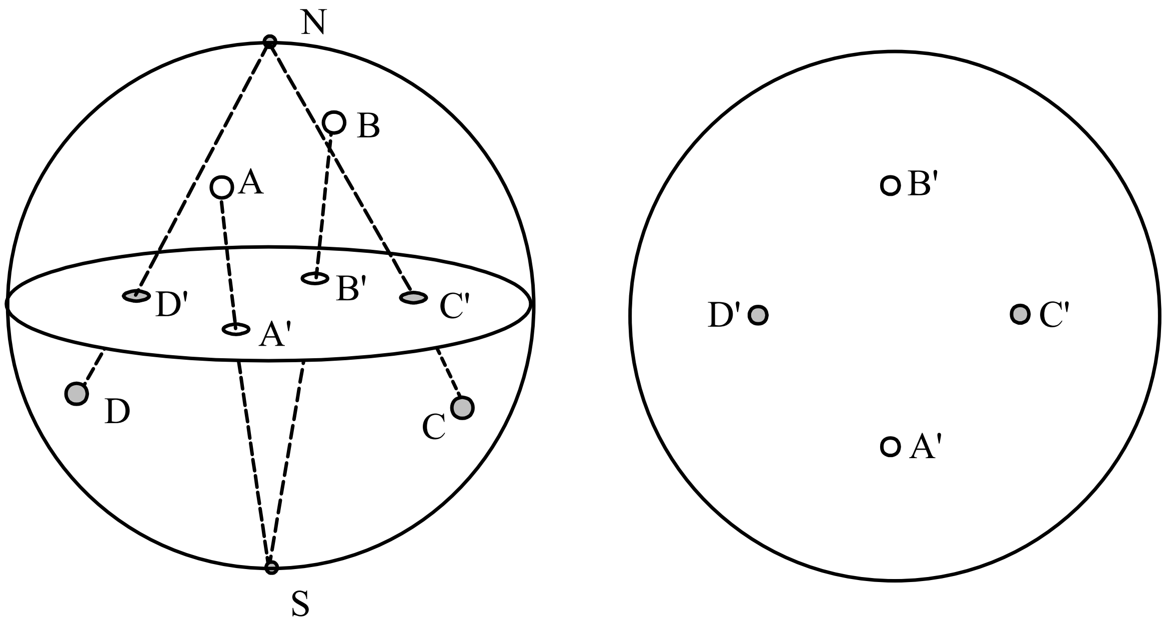


32点群关系



Maximal subgroups and minimal supergroups of the three-dimensional crystallographic point groups. Solid lines indicate maximal normal subgroups; double or triple solid lines mean that there are two or three maximal normal subgroups with the same symbol. Dashed lines refer to sets of maximal conjugate subgroups. The group orders are given on the left

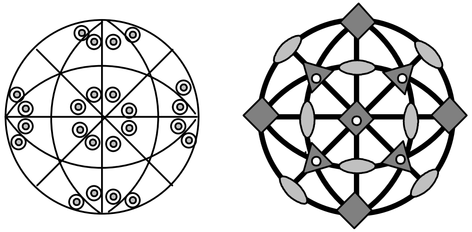
极射赤平投影*



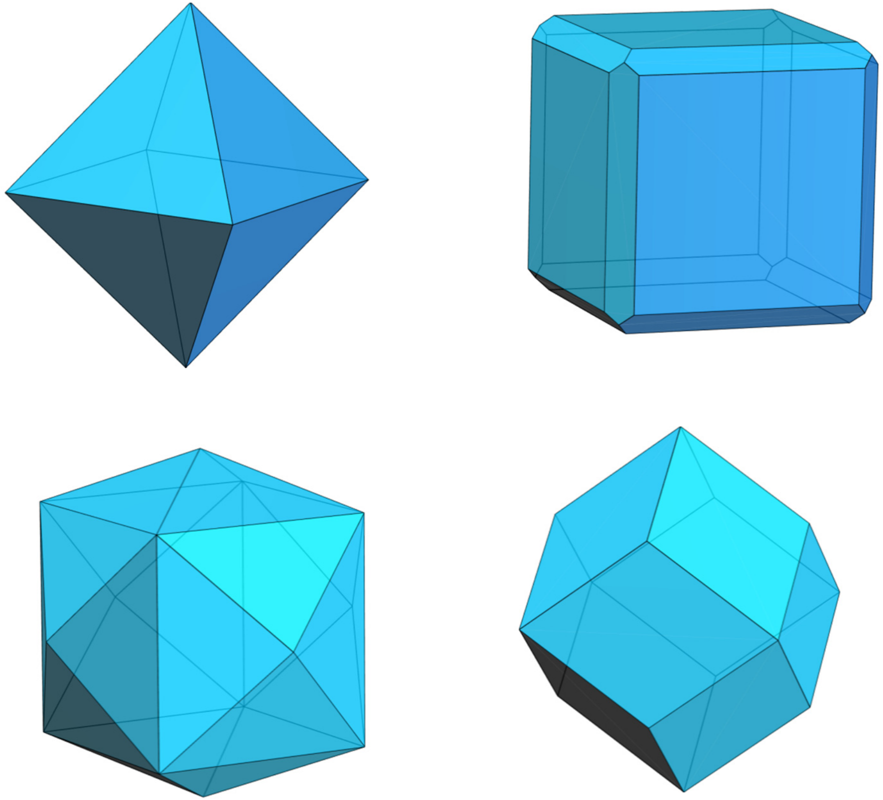
S_4群的极射赤平投影

7.2.5 晶体32点群典型晶体外型

O_h $\frac{4}{m}\bar{3}\frac{2}{m}$ $m\bar{3}m$

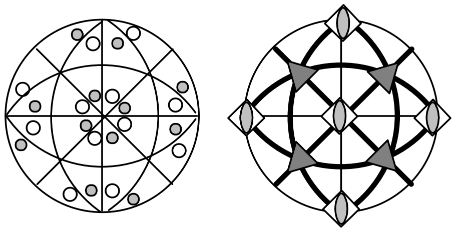


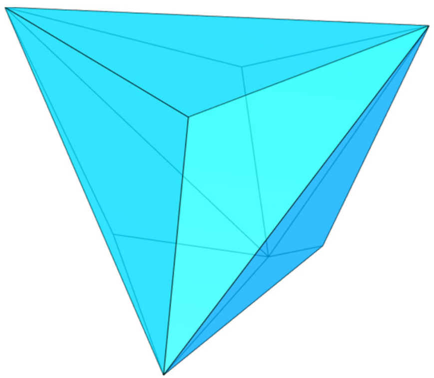
例：**CaF_2(萤石)**

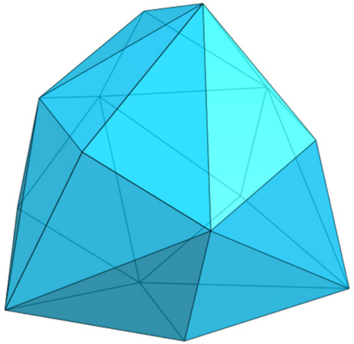


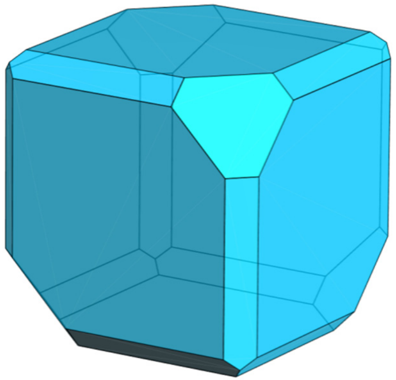
立方晶系

T_d $\bar{4}3m$



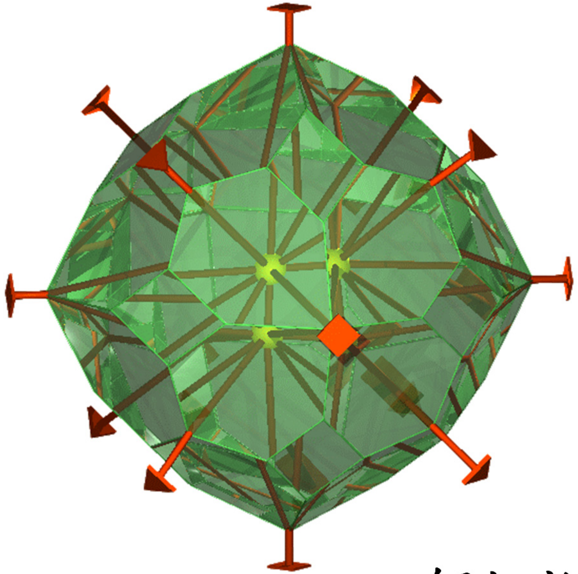


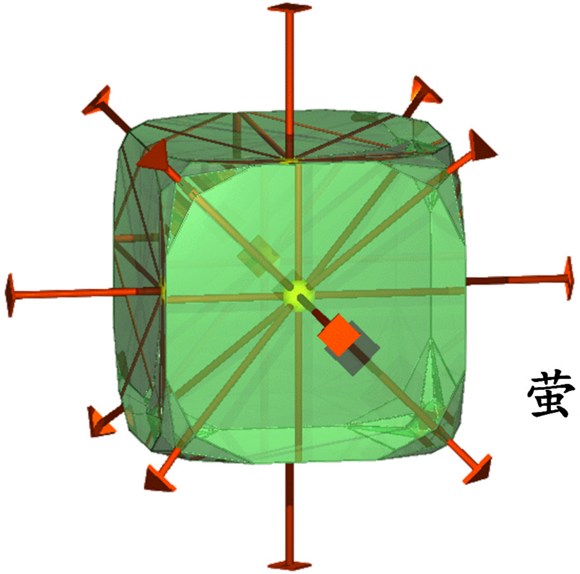




例：ZnS(闪锌矿)

立方晶系

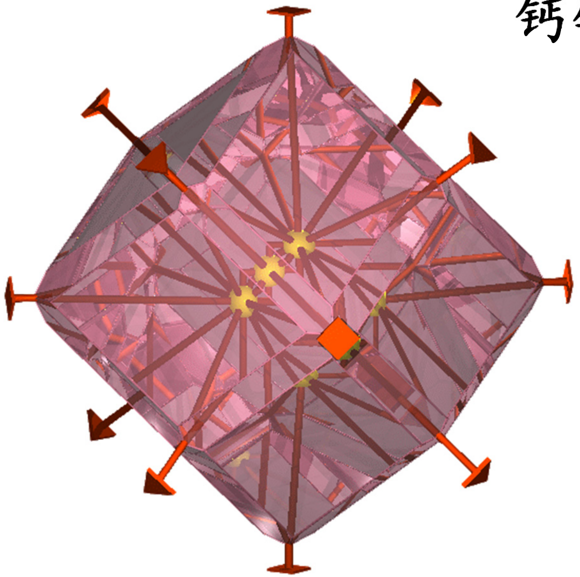


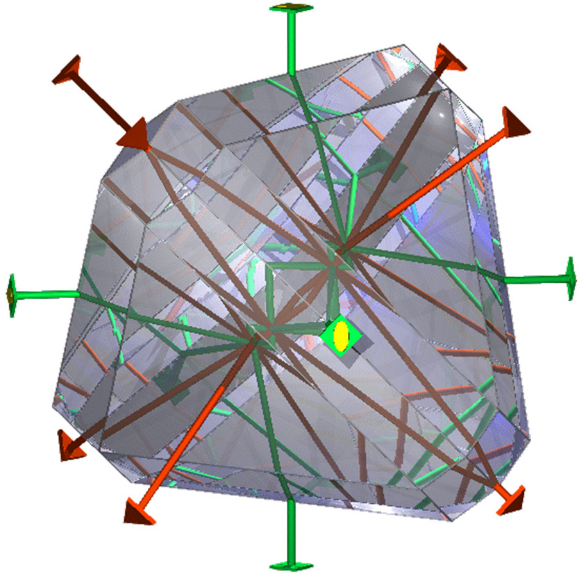


萤石

钙铝榴石

O_h

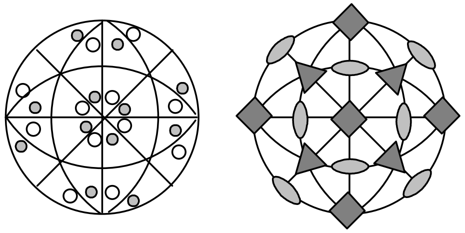


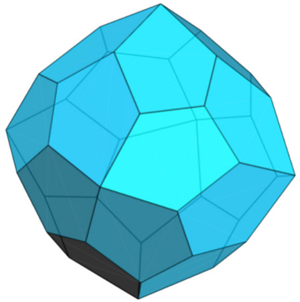


T_d

黝铜矿

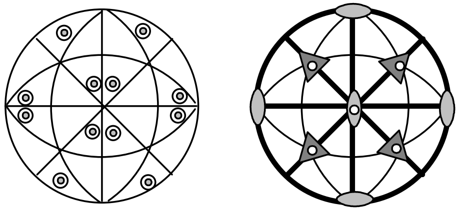
O **432**

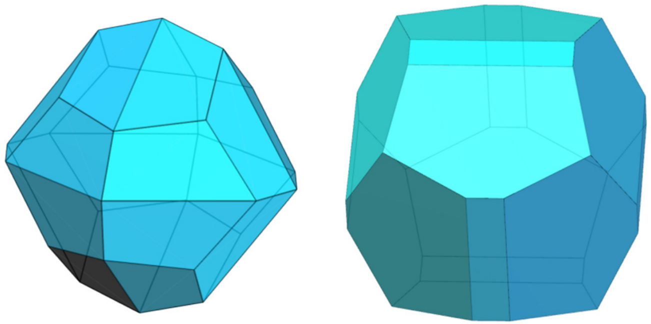




例：**NH_4Cl　β-Mn(A13)**

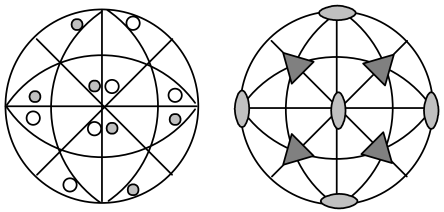
T_h $\frac{2}{m}\bar{3}$　$m\bar{3}$

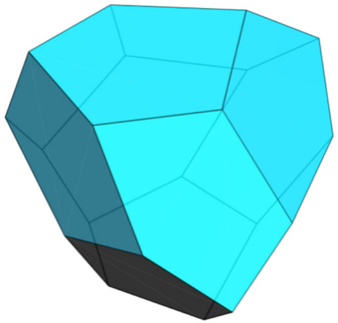




例：**FeS_2**

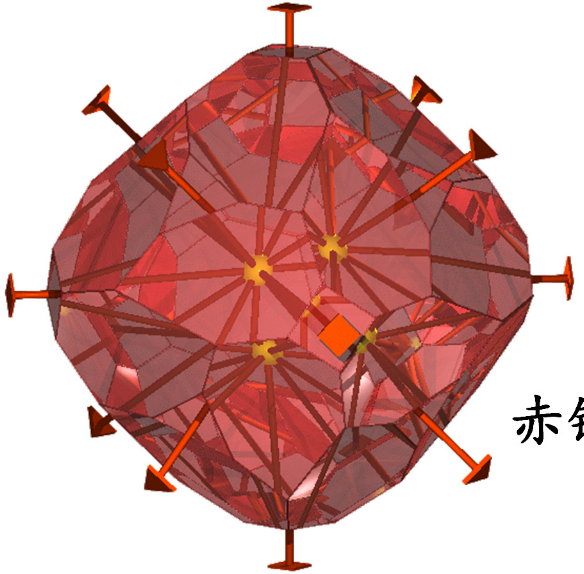
T **23**





例：**FeSi**

立方晶系

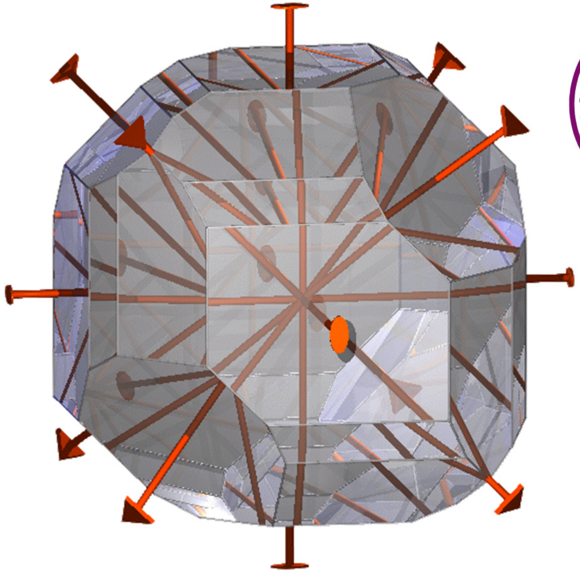


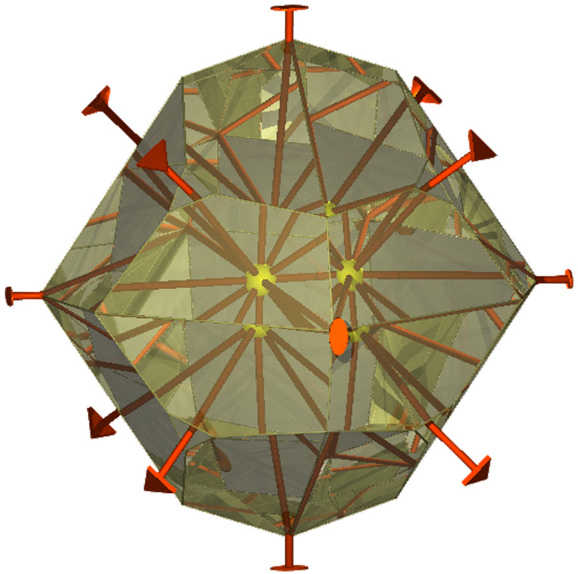
O

赤铜矿

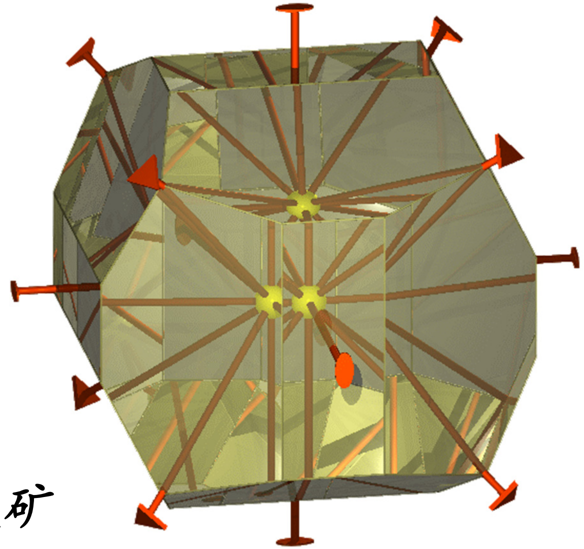
T

氯酸钠





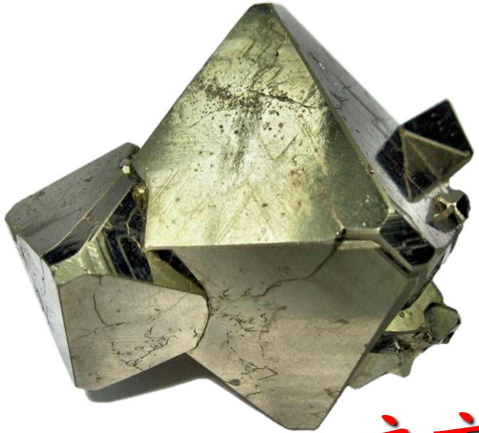
T_h



黄铁矿

CaF_2(萤石) O_h

ZnS(闪锌矿) T_d

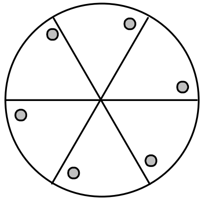
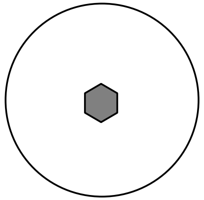
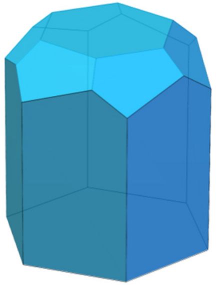


FeS_2 T_h

钻石

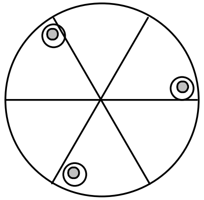
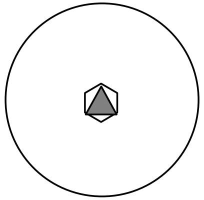
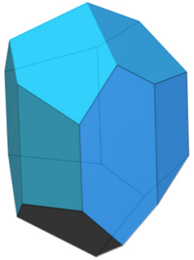
立方晶系

C_6 6

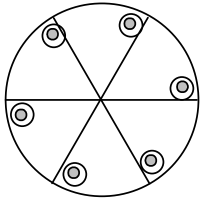
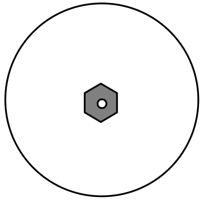
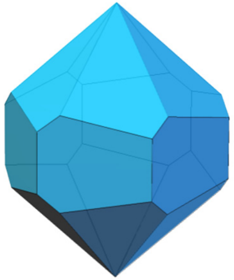
例：$KAlSiO_4$(霞石)

C_{3h} $\bar{6}$

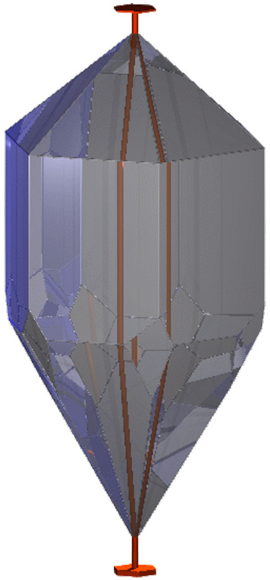
例：AgH_2PO_4

C_{6h} $\frac{6}{m}$

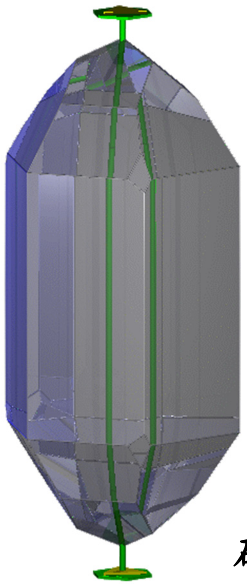
例：磷灰石$Ca_5(PO_4)_3OH$

六方晶系



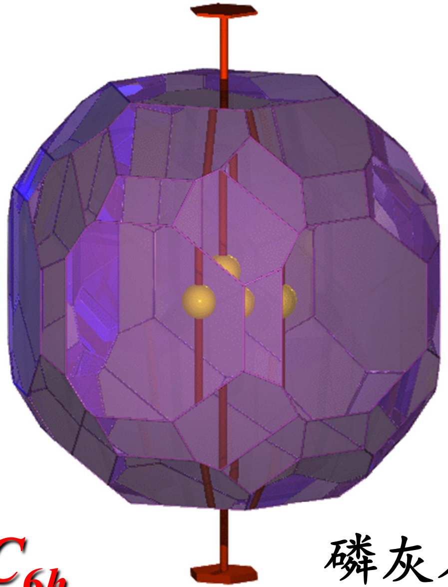
C_6

酒石酸锑锶



C_{3h}

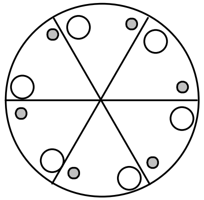
磷酸氢二银

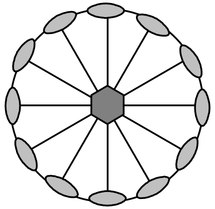


C_{6h}

磷灰石

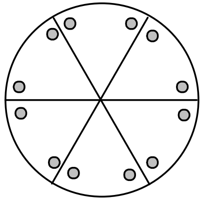
D_6 622

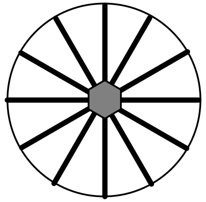




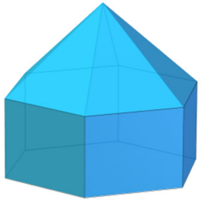
例：β-石英(SiO_2)

C_{6v} $6mm$

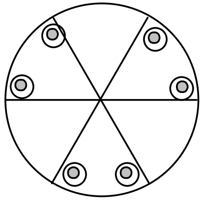


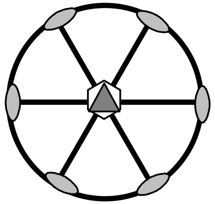


例：ZnO (红锌矿)

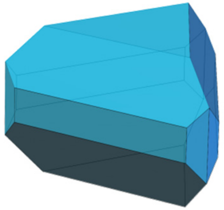


D_{3h} $\bar{6}2m$



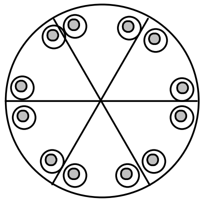


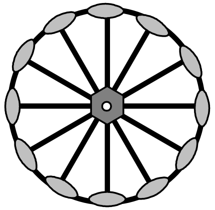
例：$BaTiSi_3O_9$
(硅酸钡钛矿)



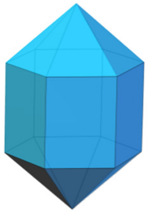
D_{6h} $\frac{6}{m}\frac{2}{m}\frac{2}{m}$

$6/mmm$

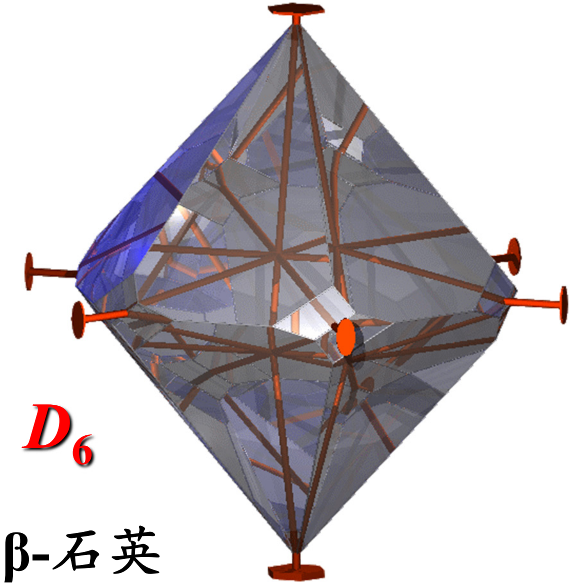




例：$Be_3Al_2(SiO_3)_6$(绿宝石)
MoS_2(辉钼矿)，石墨
Zn，冰(H_2O)



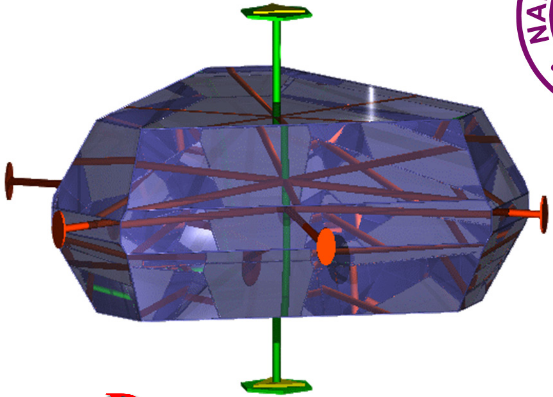
六方晶系



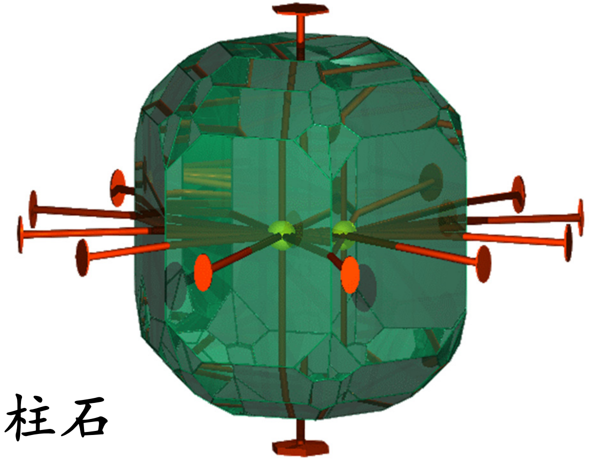
D_6

β-石英

C_{6v} 红锌矿

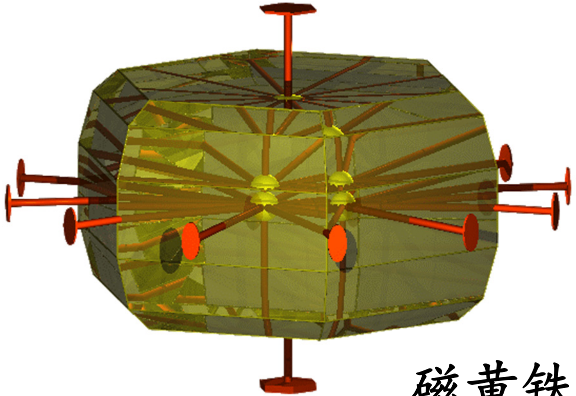


D_{3h} 矽酸钡钛矿

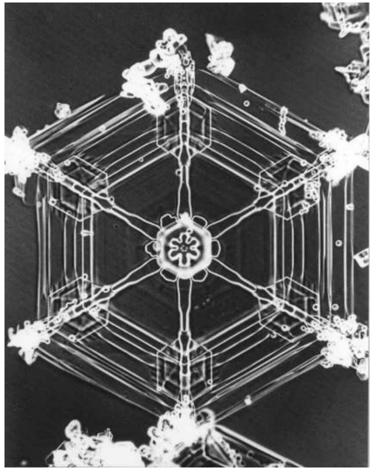


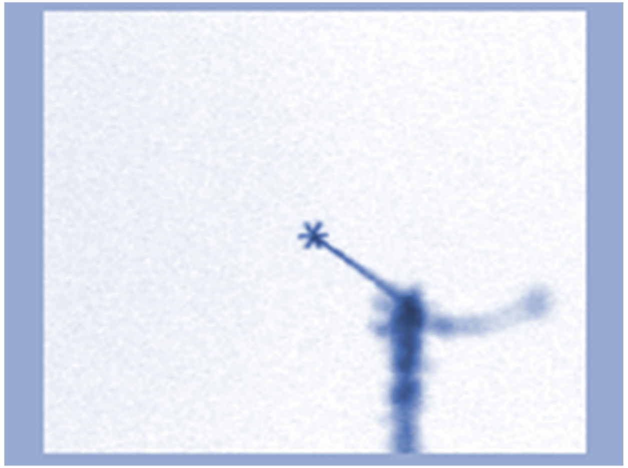
绿柱石

D_{6h}



磁黄铁矿





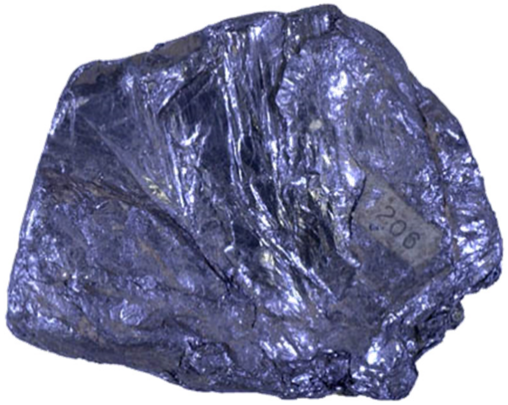
冰

石墨

磷灰石

β-石英(SiO_2)

六方晶系



辉钼矿

红锌矿

绿宝石

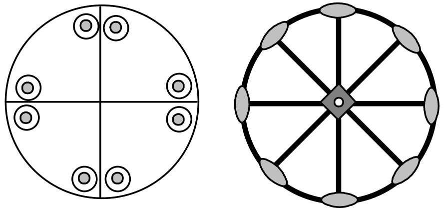
蓝锥矿(硅酸钡钛矿)

霞石

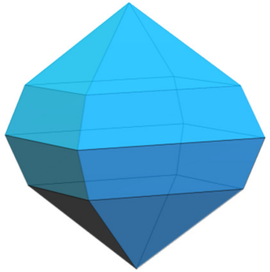
六方晶系

D_{4h} $\frac{4}{m}\frac{2}{m}\frac{2}{m}$

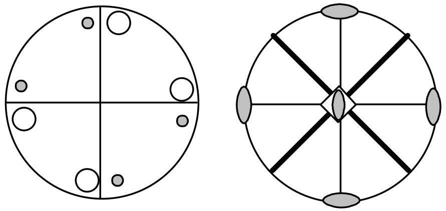
$4/mmm$

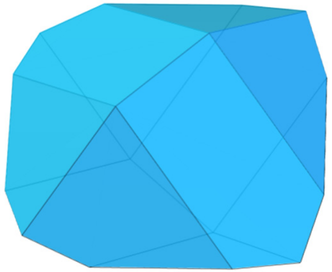


例：TiO_2(金红石)



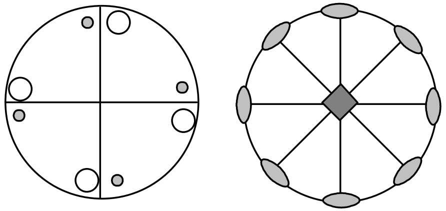
D_{2d} $\bar{4}2m$

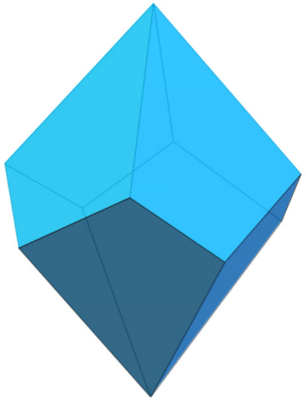




例：$CuFeS_2$(黄铜矿)

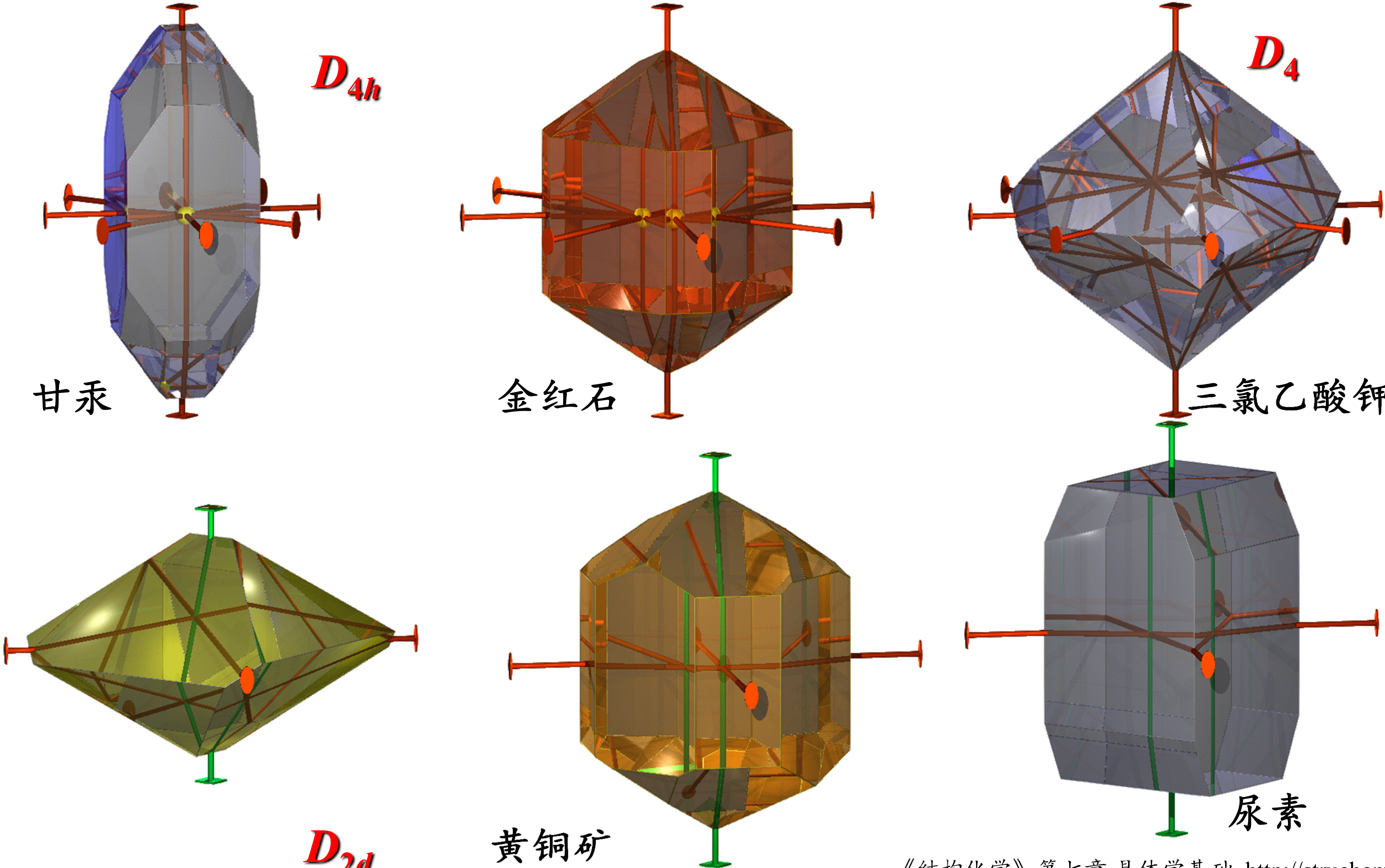
D_4 422



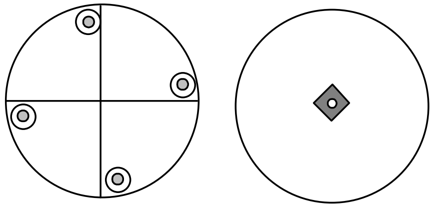


例： $NiSO_4 \cdot 6H_2O$

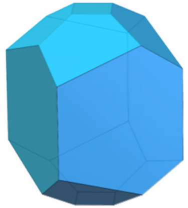
四方晶系


D4h
甘汞
金红石
D4
三氯乙酸钾
D2d
黄铜矿
尿素

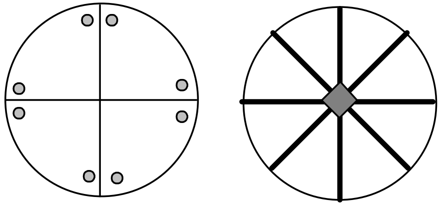
C_{4h} $\frac{4}{m}$



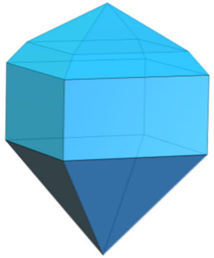
例： $CaWO_4$(白钨矿)



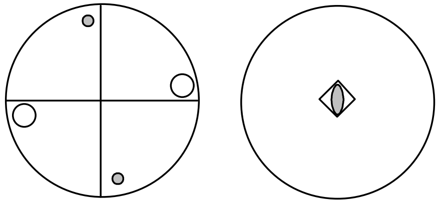
C_{4v} $4mm$



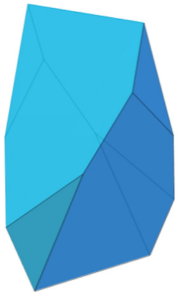
例： $BaTiO_3$



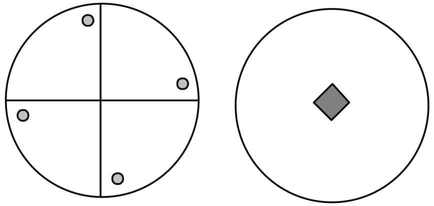
S_4 $\bar{4}$



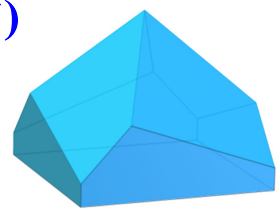
例： BPO_4



C_4 4

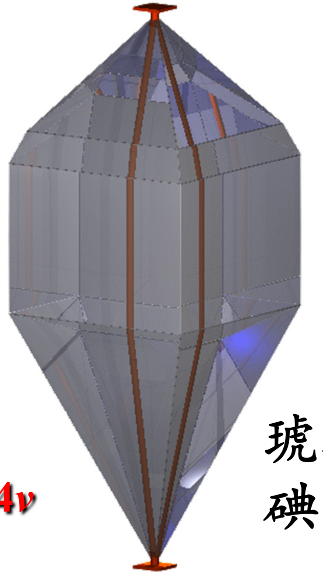


例： $PbMoO_4$(钼铅矿)

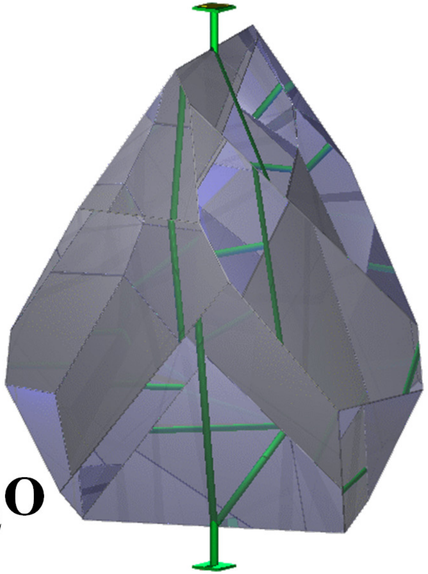


四方晶系

C_{4h} 白钨矿

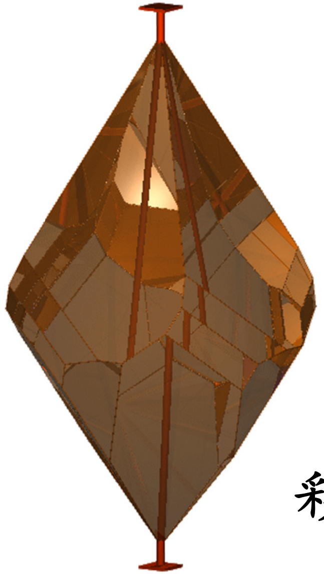


C_{4v} 琥珀酸碘亚氮



S_4

$Co_4B_2As_2O_{12} \cdot 4H_2O$



C_4 彩钼铅矿

TiO_2(金红石)

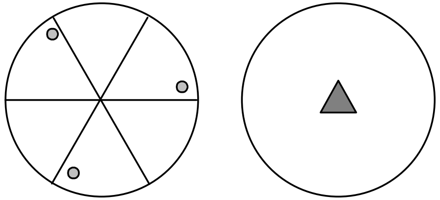
$CuFeS_2$(黄铜矿)

钼铅矿

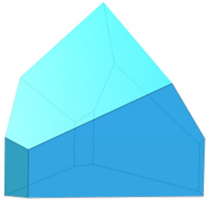
白钨矿

四方晶系

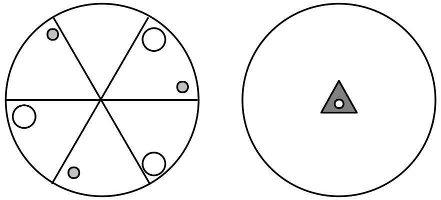
C_3 3



$Pb_9As_4S_{15}$(细硫砷铅矿)

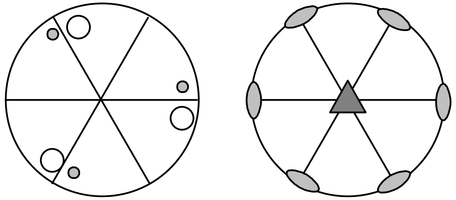


C_{3i} $\bar{3}$

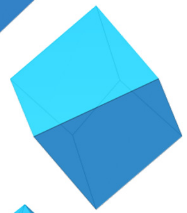


$CaMg(CO_3)_2$(白云石)
$FeTiO_3$(钛铁矿)

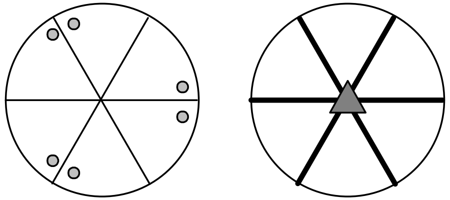
D_3 32



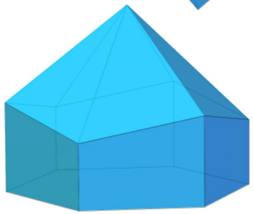
HgS(辰砂)，α-SiO_2(石英)



C_{3v} $3m$

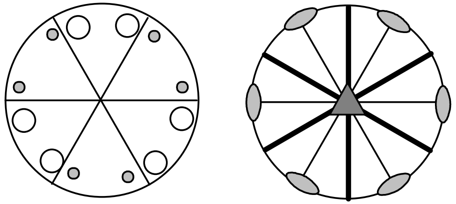


$KAl_3(SO_4)_2(OH)_6$
(明矾石)

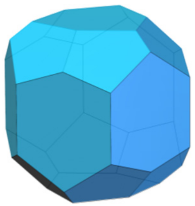


D_{3d} $\bar{3}\dfrac{2}{m}$

$\bar{3}m$

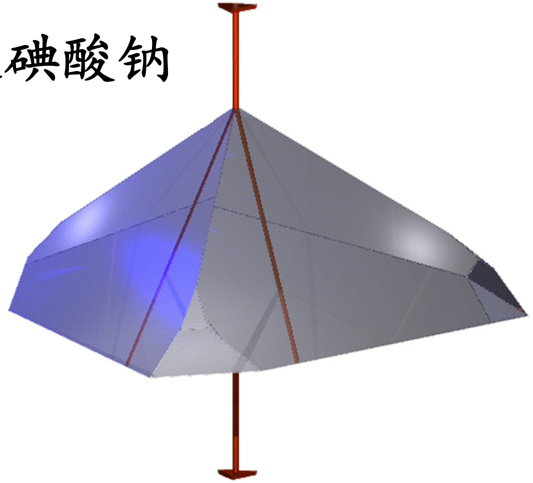


$CaCO_3$(方解石)
Al_2O_3(刚玉)



三方晶系

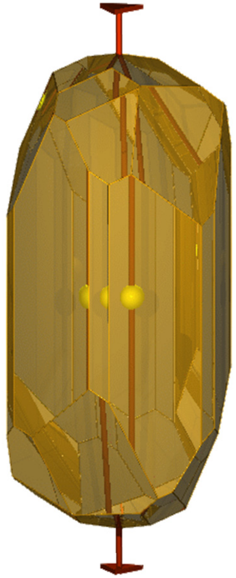
过碘酸钠

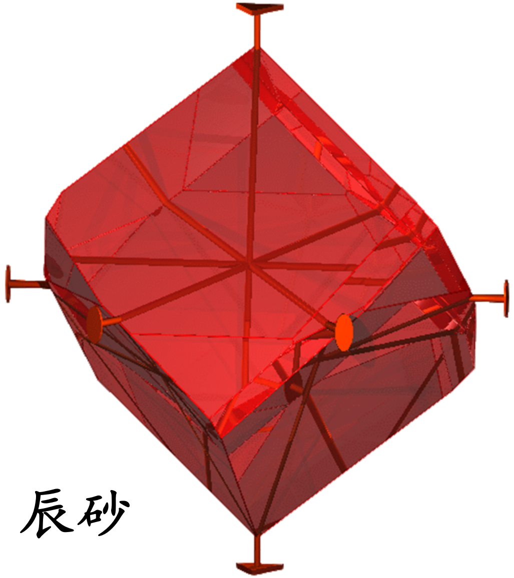


C_3

似晶石

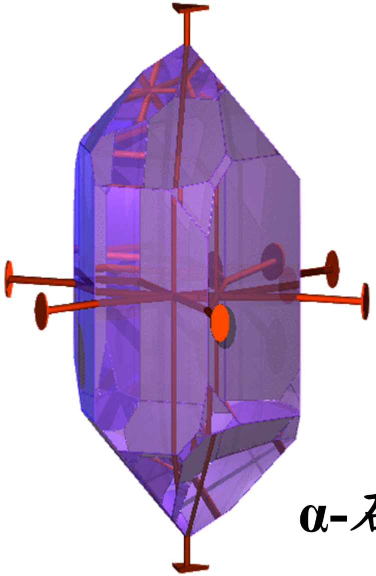
C_{3i}





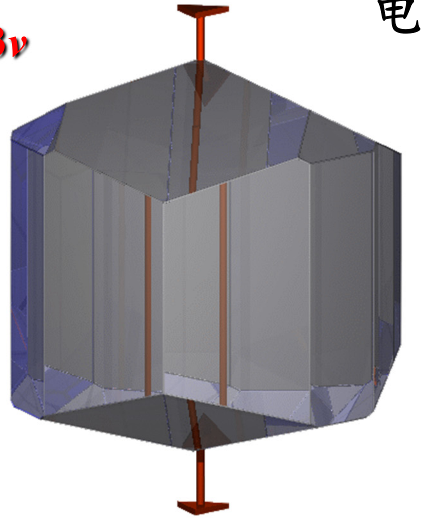
辰砂

D_3

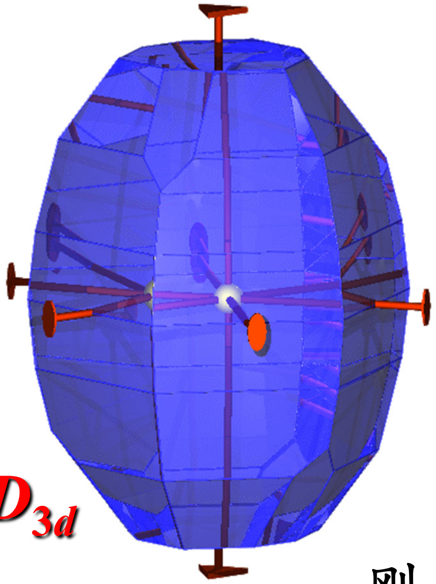


α-石英

C_{3v}

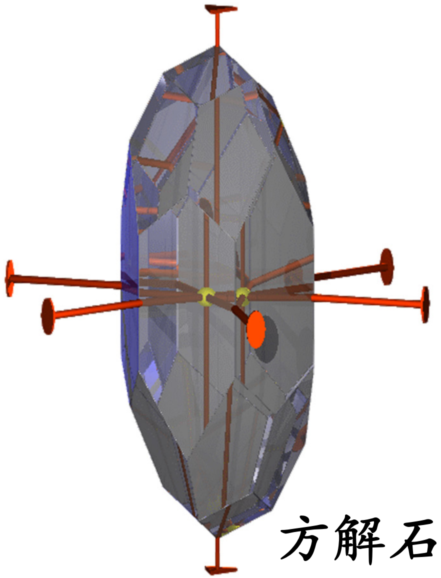


电气石

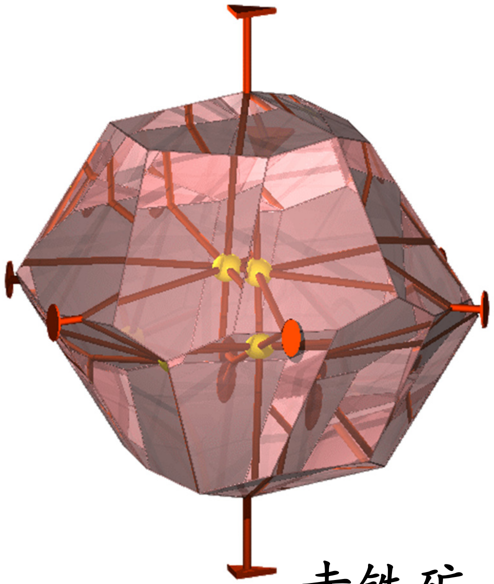


D_{3d}

刚玉



方解石



赤铁矿

$CaCO_3$(方解石)

电气石

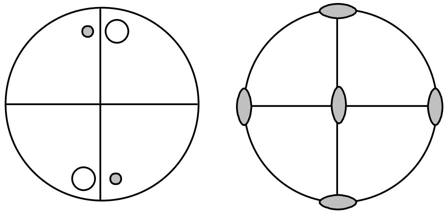
白云石

刚玉

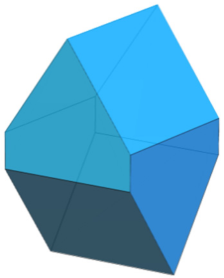
辰砂

三方晶系

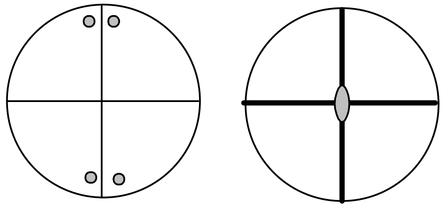
D_2 222



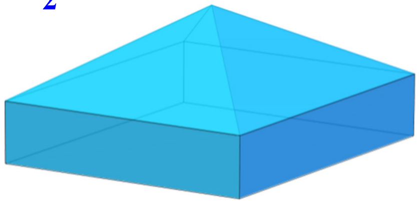
$MgSO_4 \cdot 7H_2O$(泻利盐)



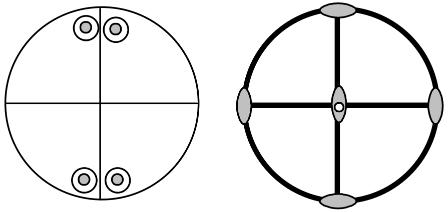
C_{2v} $2mm$ $(mm2)$



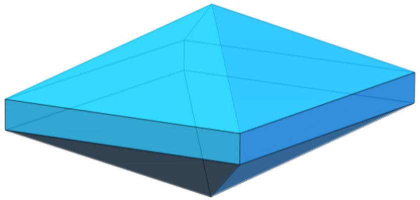
$Na_2Al_2Si_3O_{10} \cdot 2H_2O$
(钠沸石)



D_{2h} $\frac{2}{m}\frac{2}{m}\frac{2}{m}$ (mmm)

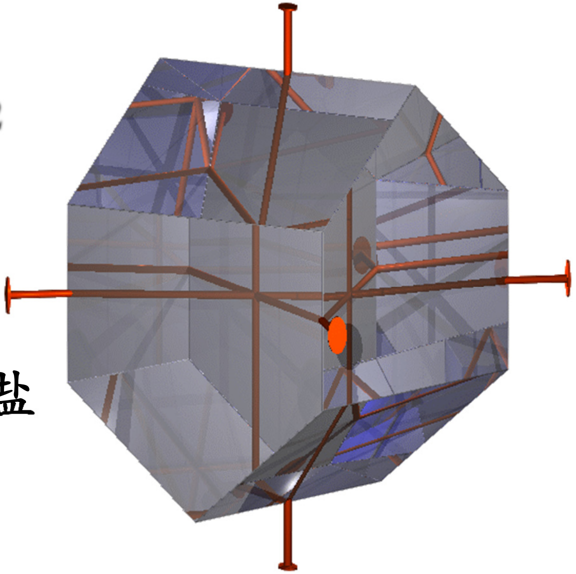


硫黄(S)



正交晶系

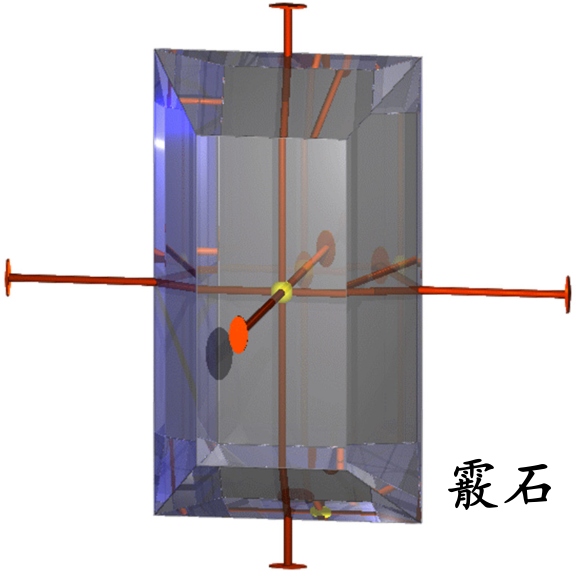
D_2



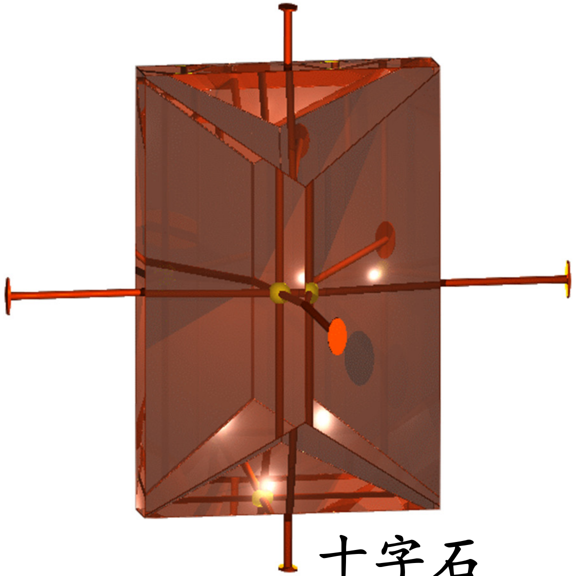
泻利盐

C_{2v}

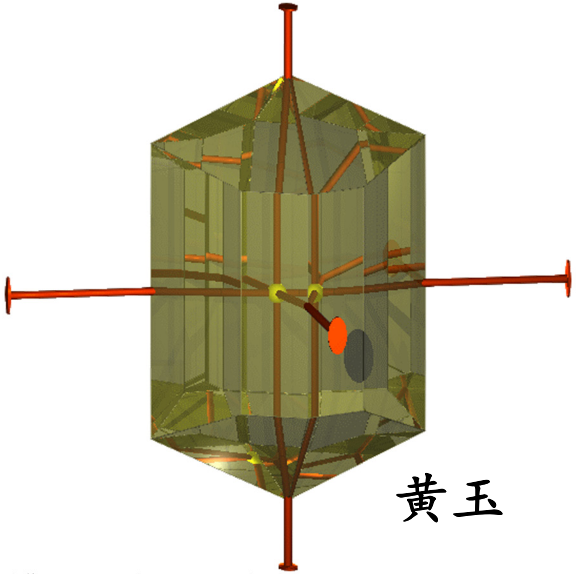
异极矿



霰石



十字石



黄玉

D_{2h}

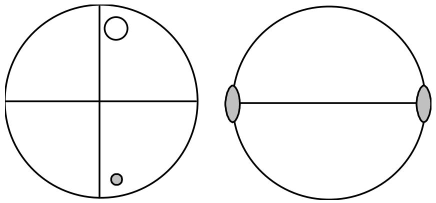
泻利盐

钠沸石

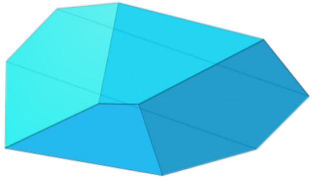
硫黄(S)

正交晶系

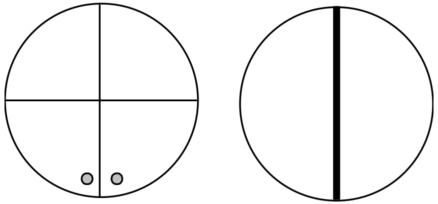
C_2 $\quad 2$



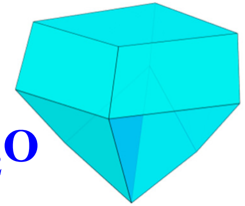
$C_4H_6O_8$(酒石酸)



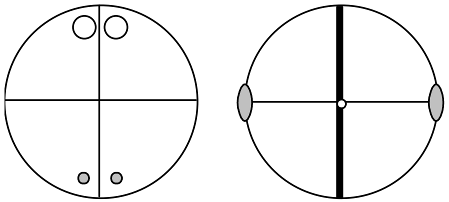
C_s $\quad m$



$Ca_2Zn_2Si_2O_7(OH)_2 \cdot H_2O$
(斜晶石)

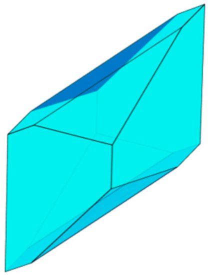


C_{2h} $\quad \frac{2}{m}$



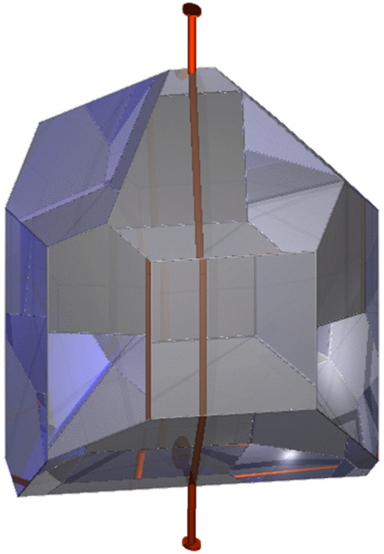
$Na_2B_4O_7 \cdot 10H_2O$(硼砂)

$CaSO_4 \cdot 2H_2O$(石膏)



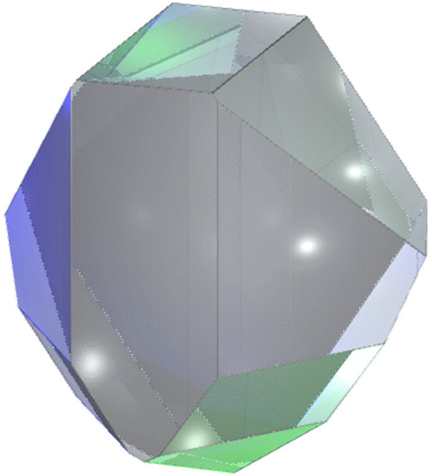
单斜晶系

C_2

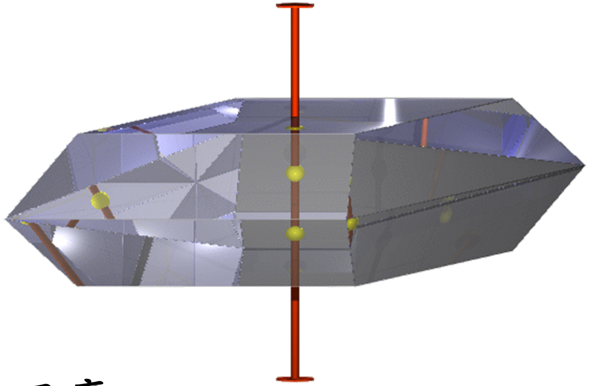


酒石酸

C_s

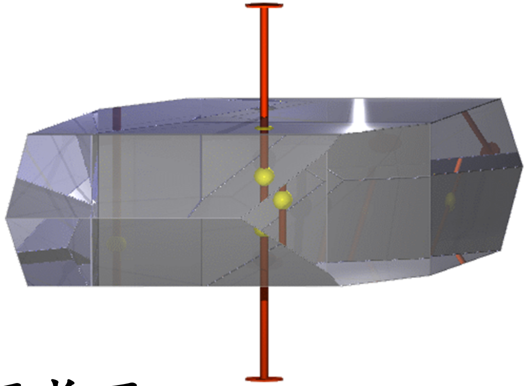


四硫酸钾

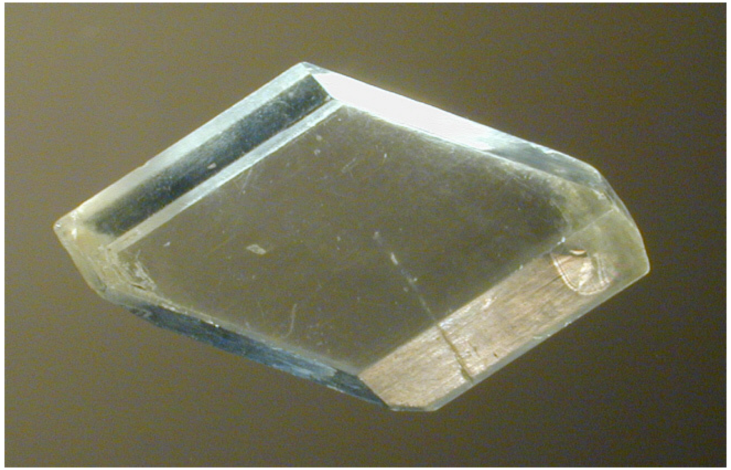


石膏

C_{2h}



正长石



石膏

硼砂

斜晶石

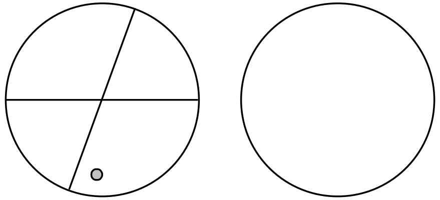
单斜晶系

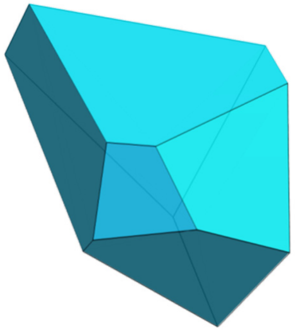
Crystal Palace

In the Naica mines of northern Mexico, near the city of Chihuahua, an underground city of giant crystals form a truly unreal landscape. Hundreds of thousands of years old, the giant selenite crystals existed for millennia in a completely closed environment; a true geode, the Naica Cuevo de los Cristales is completely covered in the transparent "macrocrystals," some of which have grown up to 12 meters in length. Discovered in 2000 by two brothers working in the Naica silver and gold mine 1,000 feet below the surface of the earth, the crystals in this cave are some of the largest ever to be found.

For hundreds of thousands of years, groundwater saturated with ***calcium sulfate*** *filtered through the many caves at Naica, warmed by heat from the magma below. As the magma cooled, water temperature inside the cave eventually stabilized at about 136° F. At this temperature minerals in the water began converting to selenite, molecules of which were laid down like tiny bricks to form crystals.*

C_1 1

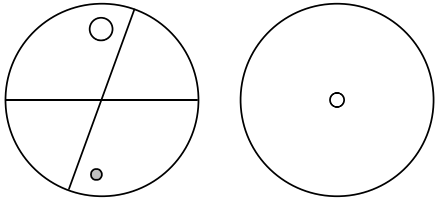




$Al_2Si_2O_5(OH)_4$(高岭石)

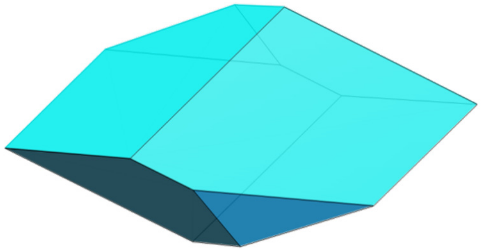
$CaS_2SO_3 \cdot 6H_2O$

C_i $\bar{1}$

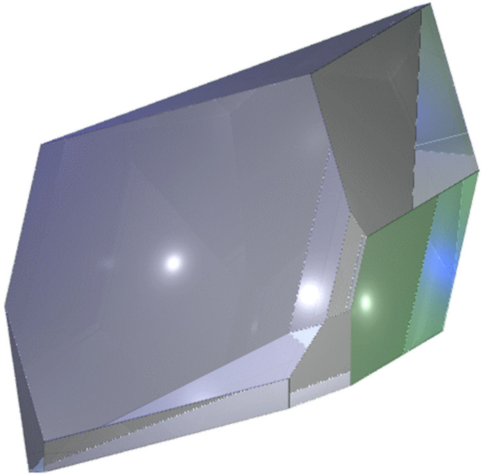


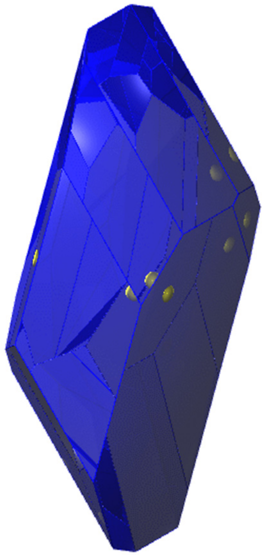
$NaAlSi_3O_8$(钠长石)

$CuSO_4 \cdot 5H_2O$(胆矾)



三斜晶系

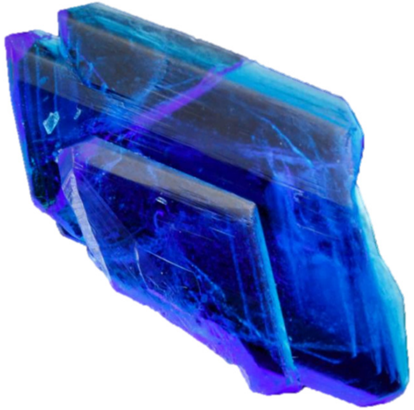




C_1 硫代硫酸钙

C_i 硫酸铜

钠长石



胆矾

高岭石

三斜晶系

§7.3 晶体微观对称性及230个空间群简介

7.3.1 微观对称元素及相应的对称操作

晶体的微观对称性是指晶体内部点阵结构的对称性

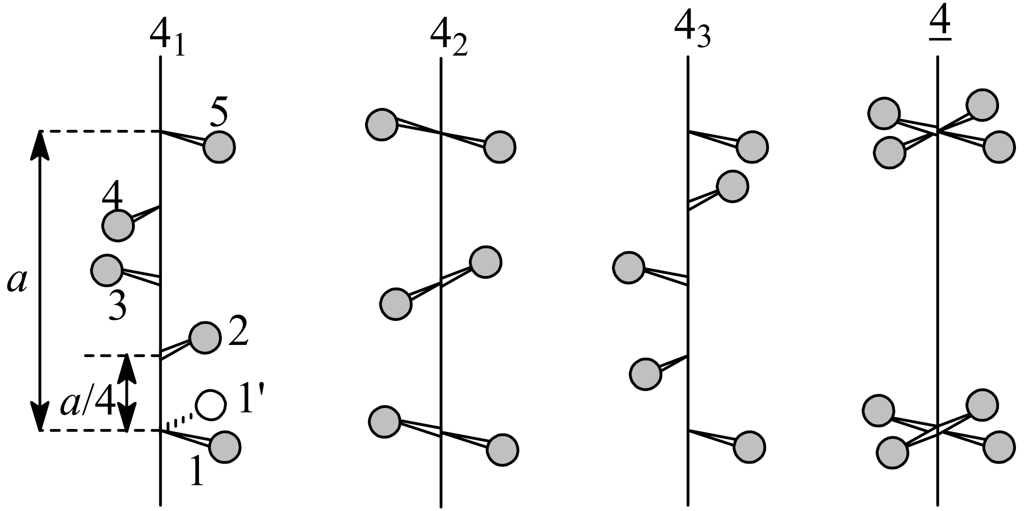
1. 四种宏观对称元素及相应的点对称操作(至少有一点不动)

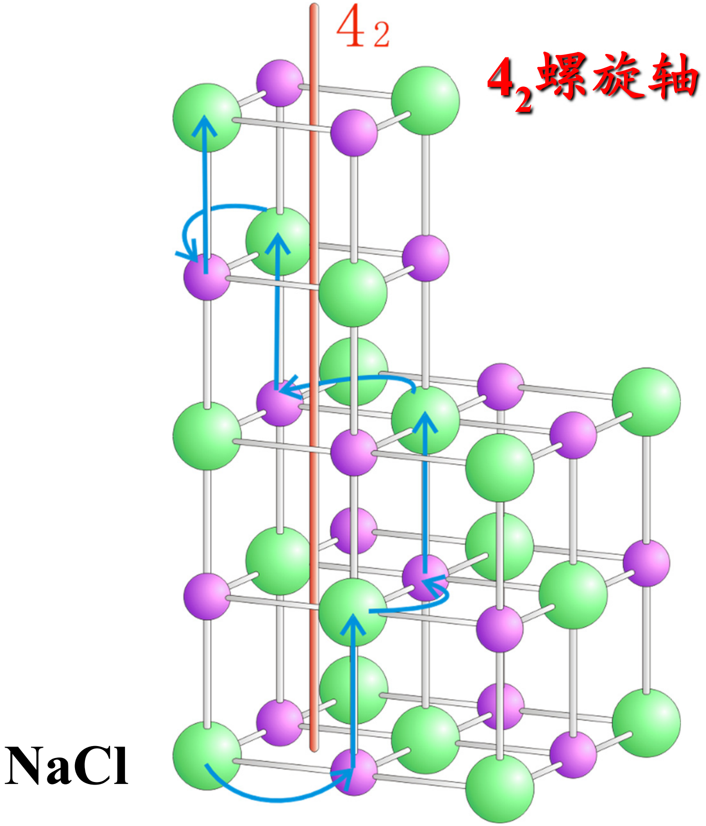
$\underline{\boldsymbol{n}}$　$\boldsymbol{m}$　$\boldsymbol{i}$　$\boldsymbol{\bar{n}}$

2. 三种微观对称元素及相应的空间对称操作

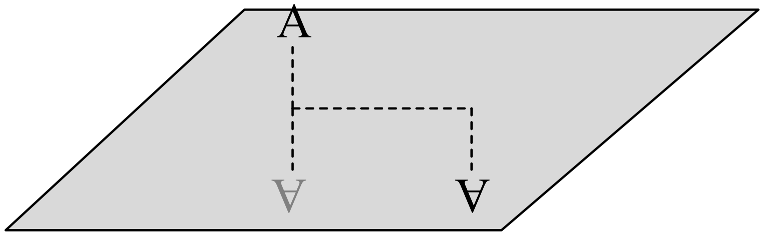
① 点阵t 和平移操作T

② 螺旋轴n_m和旋转平移操作 $L(\frac{2\pi}{n})T(\frac{m}{n}a)$

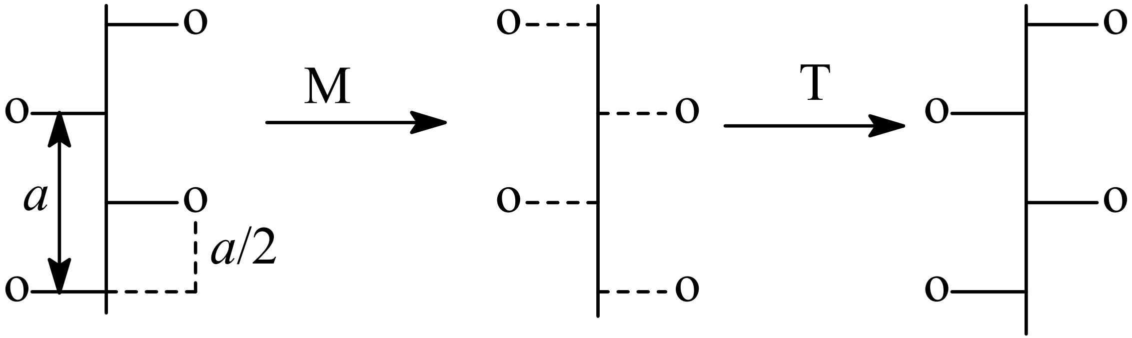


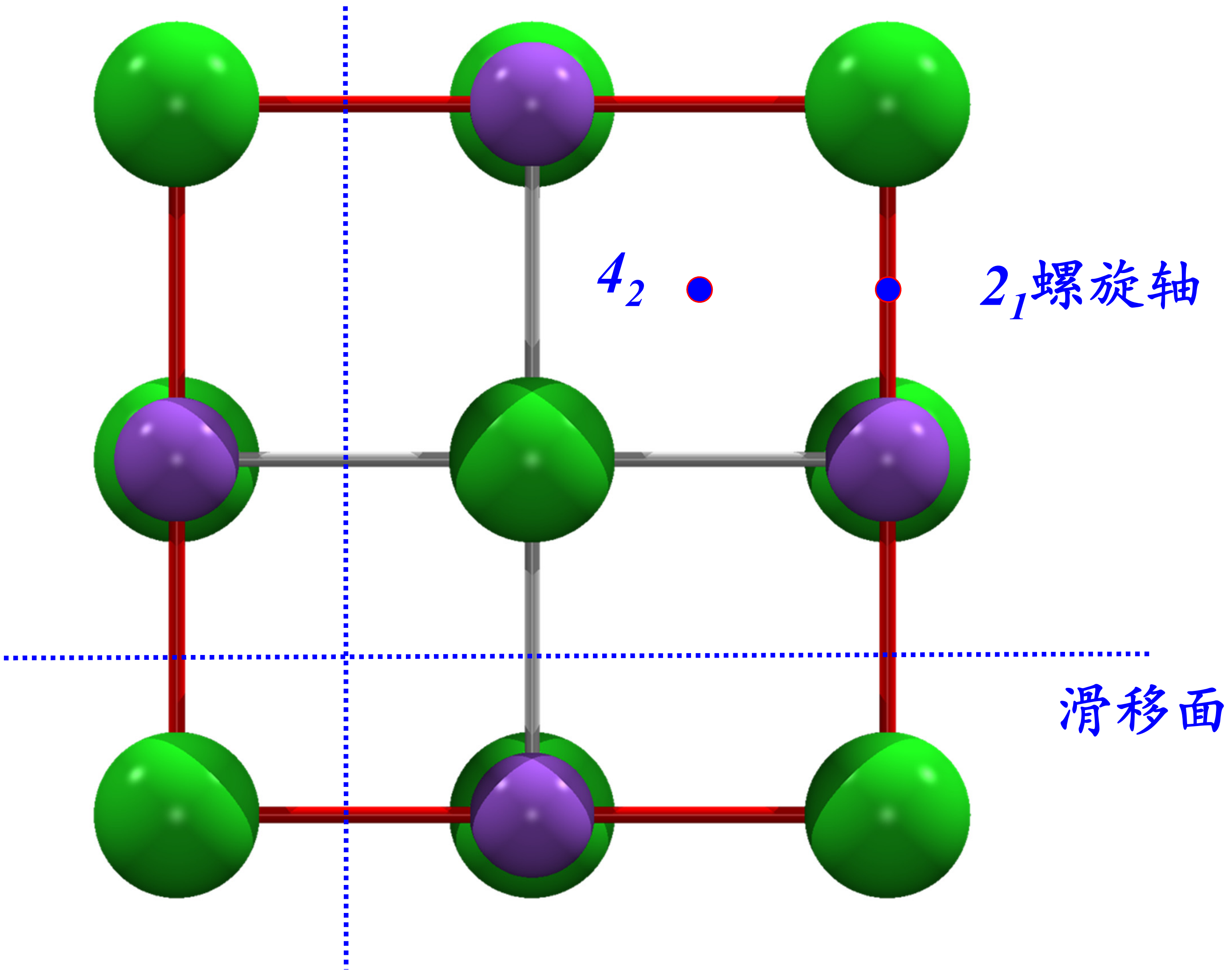


③ 滑移面(T)和滑移反映(TM)对称操作(平移，反映联合操作)

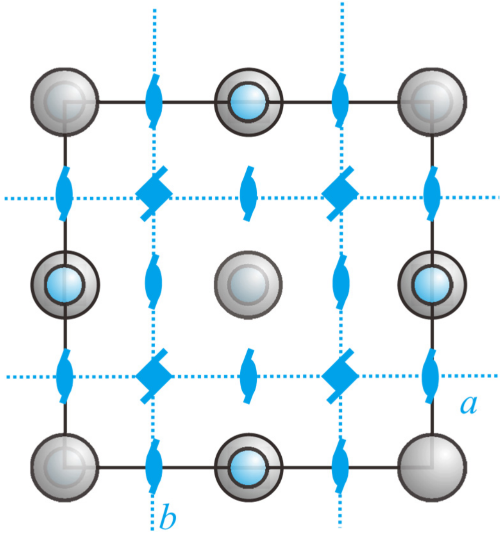


a.轴线滑移面*a*(*b*或*c*)：通过镜面反映后，再沿*a*轴(*b*或*c*)方向滑移*a*/2(*b*/2或*c*/2)



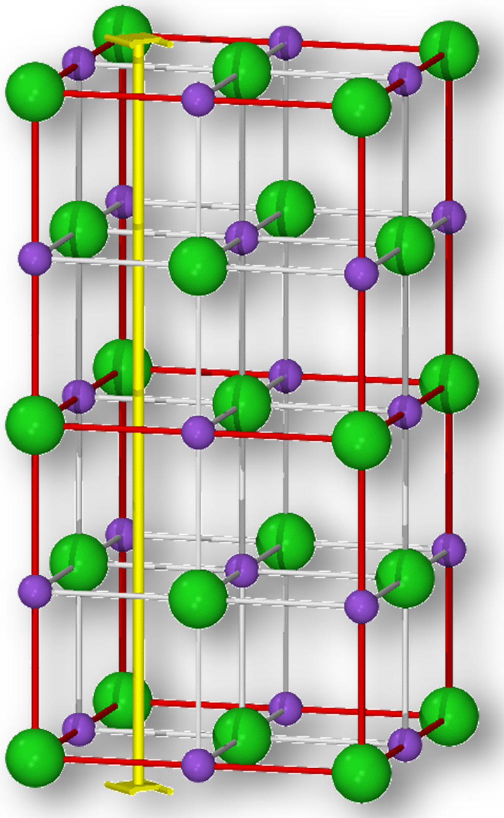


4_2
2_1螺旋轴
滑移面

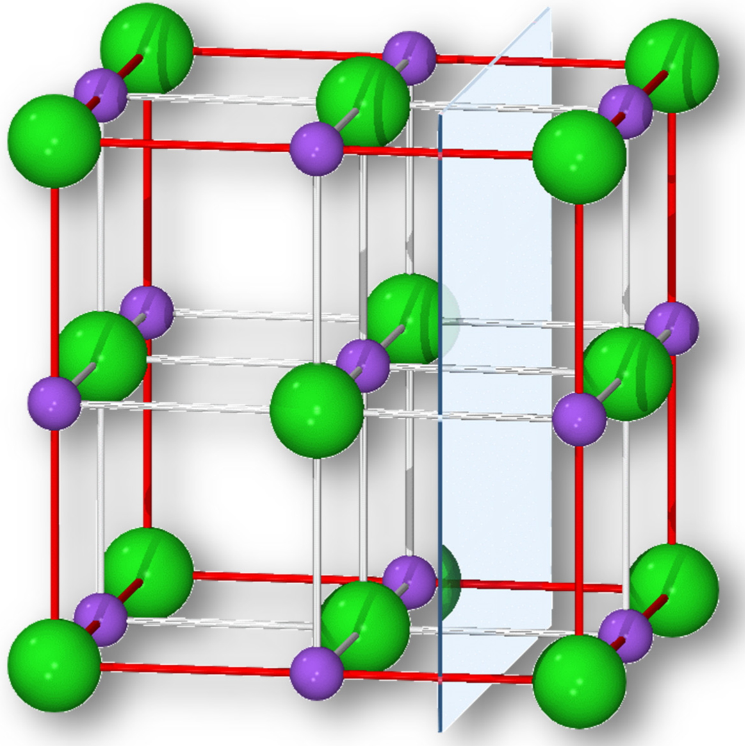


a
b

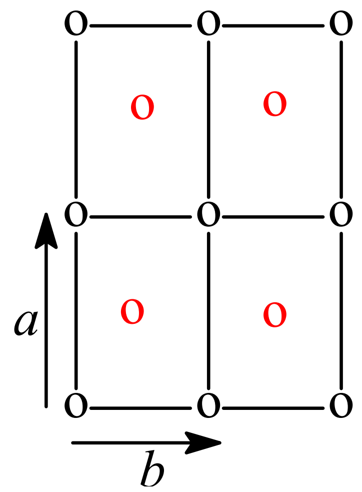
NaCl中的4_2螺旋轴



NaCl中的*c*滑移面



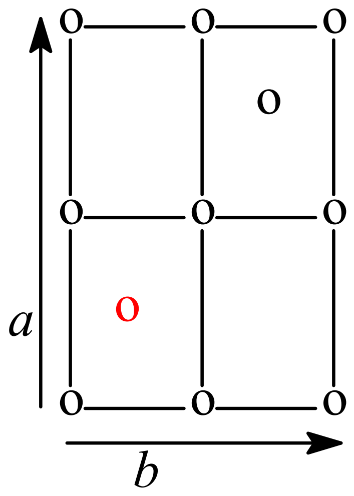
- **对角滑移面*n*：**



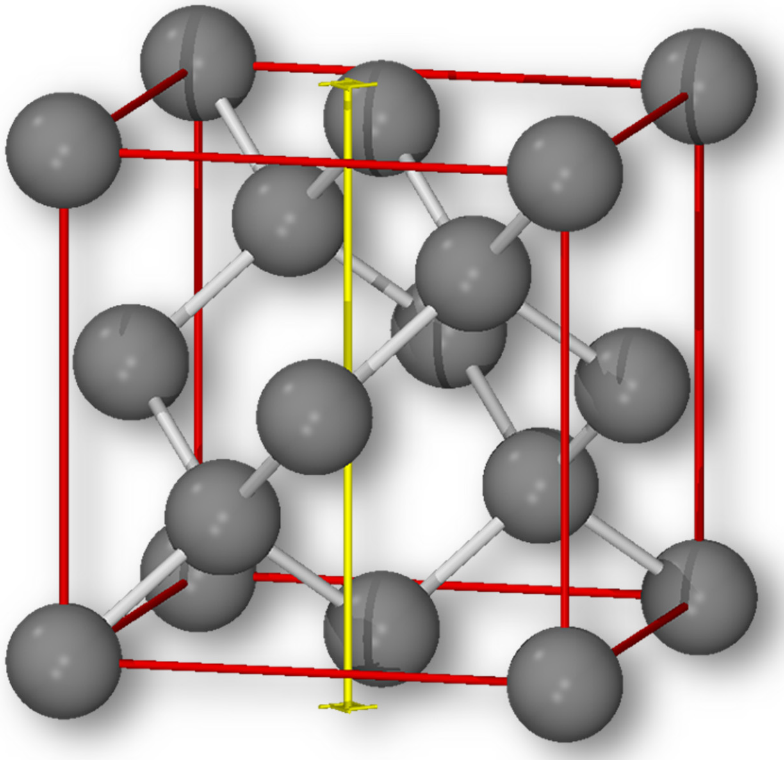
$$\left(\frac{a}{2}+\frac{b}{2}\right),\left(\frac{a}{2}+\frac{c}{2}\right),\left(\frac{b}{2}+\frac{c}{2}\right),\left(\frac{a}{2}+\frac{b}{2}+\frac{c}{2}\right)$$

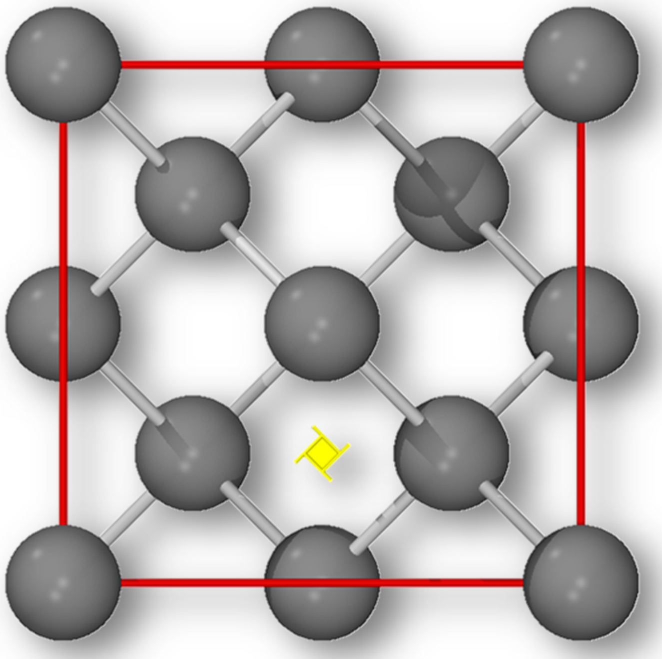
- **菱形滑移面*d*(金刚石滑移面)：**

$$\left(\frac{a}{4}\pm\frac{b}{4}\right),\left(\frac{b}{4}\pm\frac{c}{4}\right),\left(\frac{a}{4}\pm\frac{c}{4}\right)$$

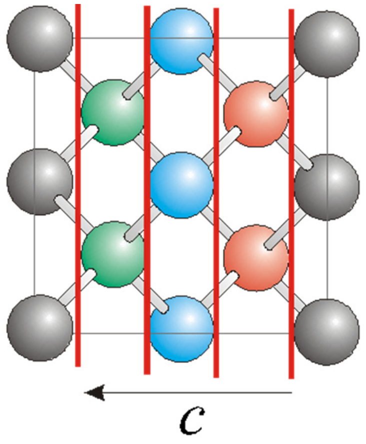


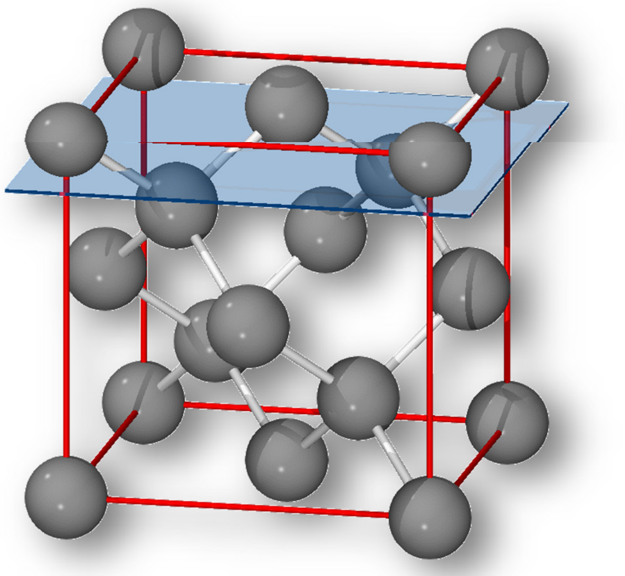
金刚石中的4_1螺旋轴

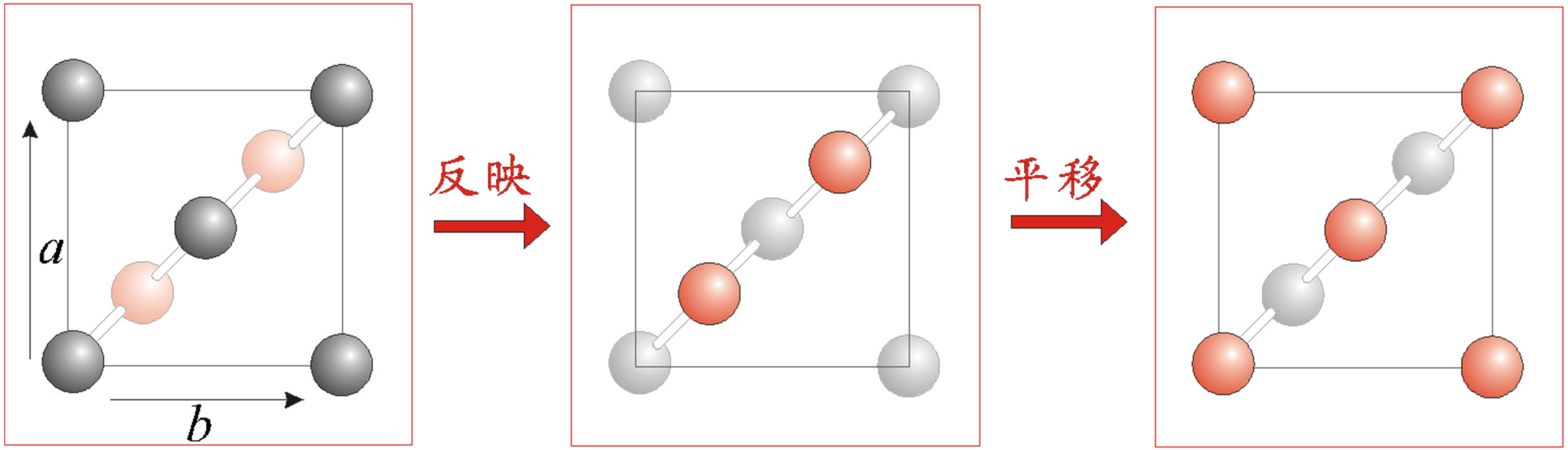




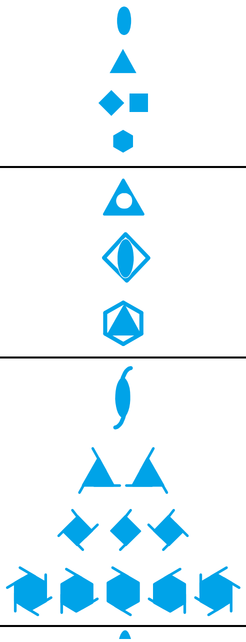
金刚石滑移面

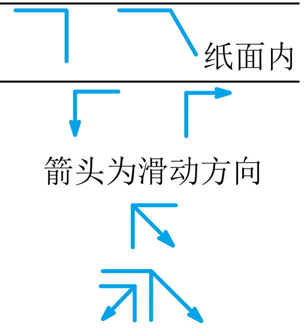






晶体结构中的对称元素

对称元素	符号	图示
	1	无
旋转轴	2	
	3	
	4	
	6	
反轴	$\bar{3}$	
	$\bar{4}$	
	$\bar{6}$	
螺旋轴	2_1	
	3_1 3_2	
	4_1 4_2 4_3	
	6_1 6_2 6_3 6_4 6_5	

轴+对称中心	$2/m$		
	$2_1/m$		
	$4/m$		
	4_2/m		
	$6/m$		
	$6_3/m$		
对称中心	$i(\bar{1})$	○	
镜面	$m(\bar{2})$	垂直纸面	
滑移面	*a b c*	纸面内滑动 离开纸面滑动	
	n		
	d		

7.3.2 230个空间群

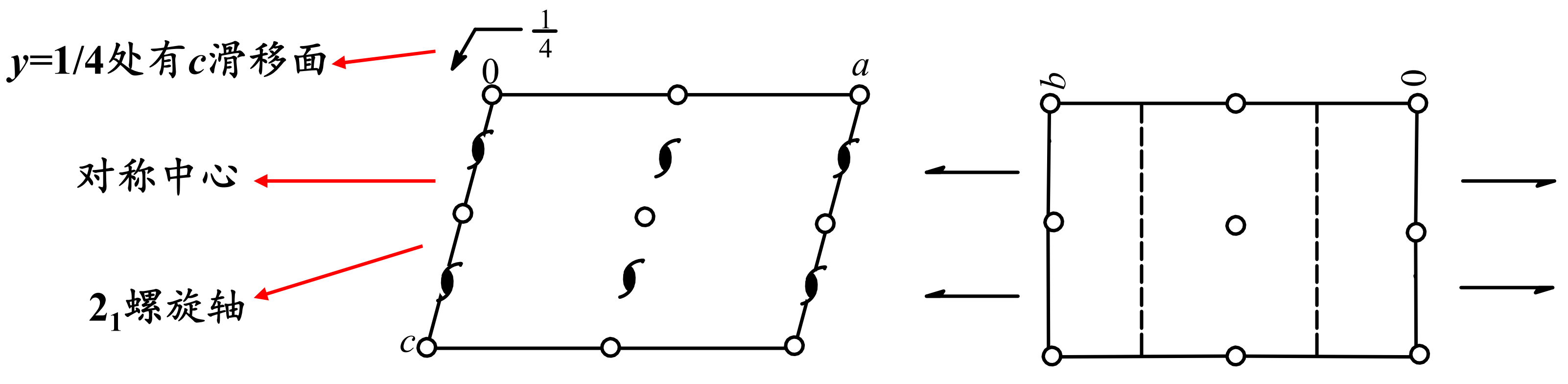
空间群符号一般用熊夫利和国际符号联合表示

$$C_{2h}-\frac{2}{m}\begin{cases} C_{2h}^{1}-P\dfrac{2}{m} \\ C_{2h}^{2}-P\dfrac{2_1}{m} \\ C_{2h}^{3}-C\dfrac{2}{m} \\ C_{2h}^{4}-P\dfrac{2}{c} \\ \boxed{C_{2h}^{5}-P\dfrac{2_1}{c}} \\ C_{2h}^{6}-C\dfrac{2}{c} \end{cases}$$

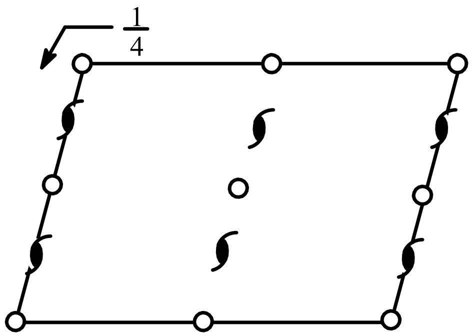
- 宏观对称点群的熊夫利符号，上角编号是统一的，宏观点群C_{2h}包括6个微观空间点群
- ***P***：该点群所属晶系中空间点阵形式，即14种中的哪一种。单斜简单
- **2_1**：单斜晶系的位方向为***b***，***b***方向上有2_1螺旋轴，和***b***方向垂直方向有*c*滑移面

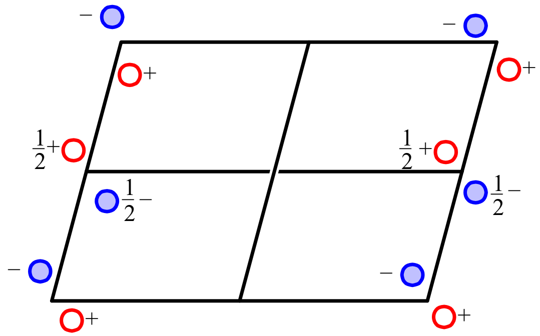
等效点系图

- **等效点**(对称等效点)：一个点经过某一指定的对称元素的操作后，与另一个点完全重合，则这两个点互为等效点。等效点可代表宏观外形的晶面，也可代表结构基元(微观)，等效点间不仅在几何上完全一致，在物理化学性质上也完全一样



$C_{2h}^{5}-P\frac{2_1}{c}$ 对称元素分布





一般等效位置　x, y, z　$\bar{x}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$

$\bar{x}, \bar{y}, \bar{z}$　$x, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$