现代结构分析方法教学大纲
(04－05年度第一学期)

第二讲

复习

一、微观结构分析基本原理

载能粒子与物质相互作用

电子与物质相互作用

分析方法的种类及功能

二、晶体结构及晶体学

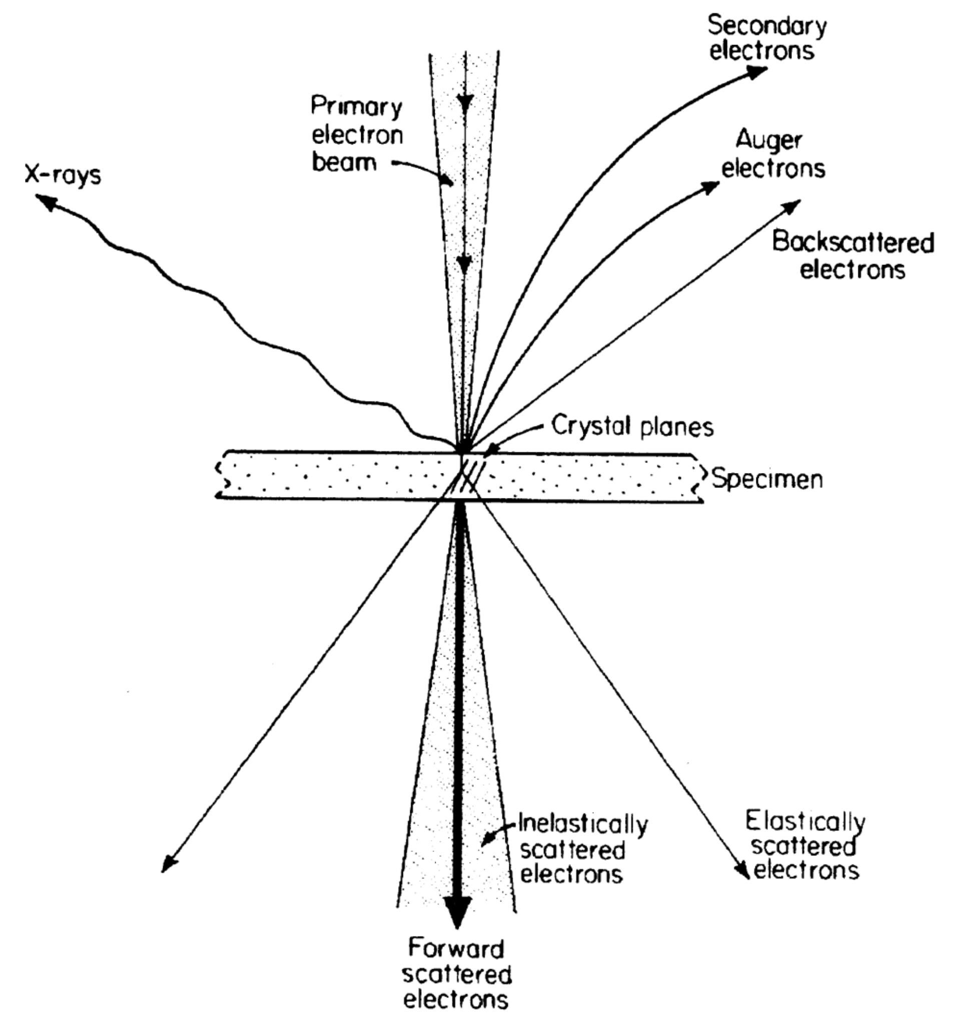
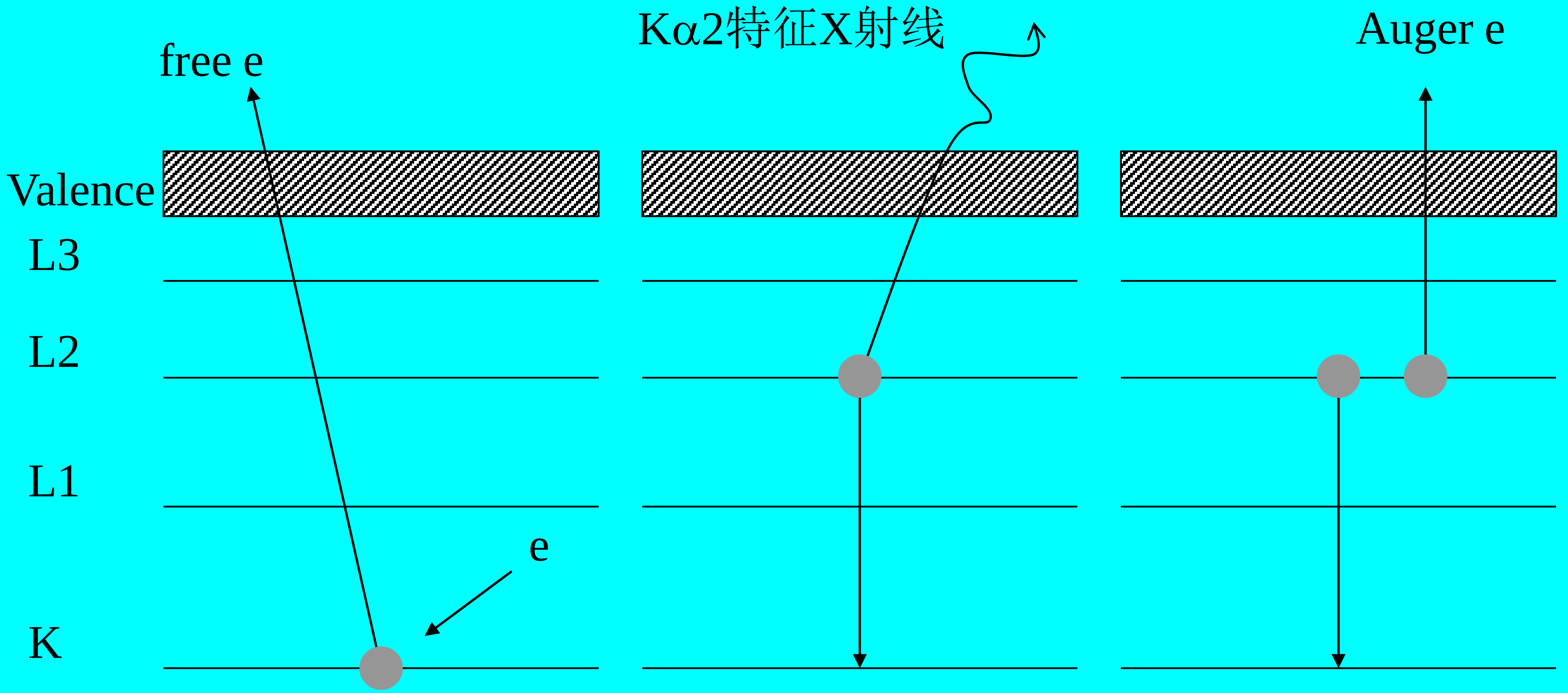


图 2-2　AEM 中电子与样品相互作用原理示意图

Energy Dispersive Analysis of X-rays (EDAX)

Wave length Dispersive Analysis of X-rays (Electron Microprobe)

Auger spectroscopy



K激发态

发射K光子（重元素）
平均自由程μm

发射俄歇电子（轻元素）
平均自由程Å,
表面几层原子

Glasses

非晶结构与晶体结构比较

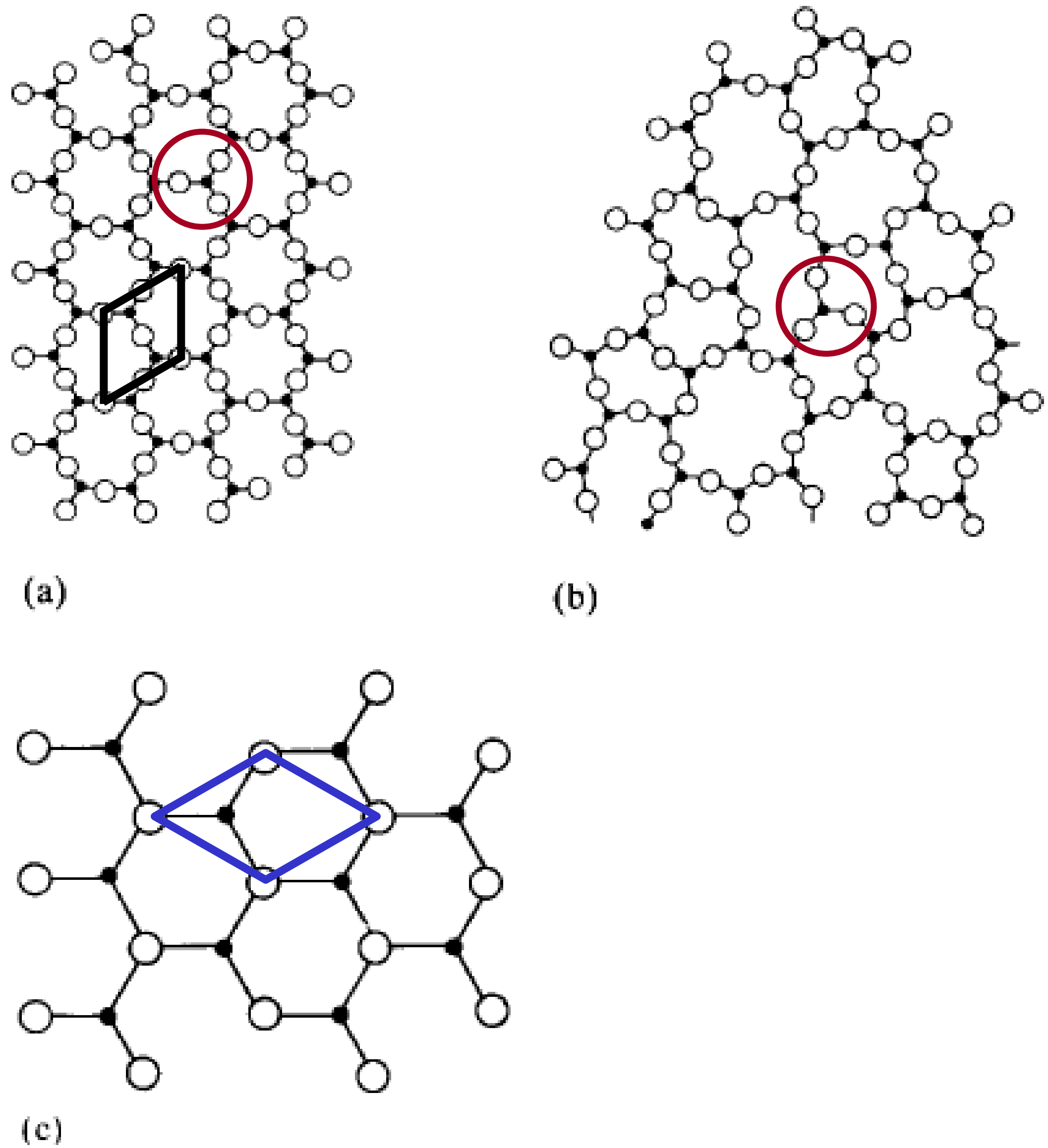


Fig. 2.13 Schematic two-dimensional representation of the structure of
(a) a hypothetical crystalline compound A_2O_3
(b) the Zachariasen model for the glassy form of the same compound and
(c) the hypothetical crystalline compound AO.

从原子排列方式看，固体物质分晶态（长程有序）和非晶态(短程有序)两种。

Glasses

基本单元的
排列特点

基本单元构成
几何格点→点阵

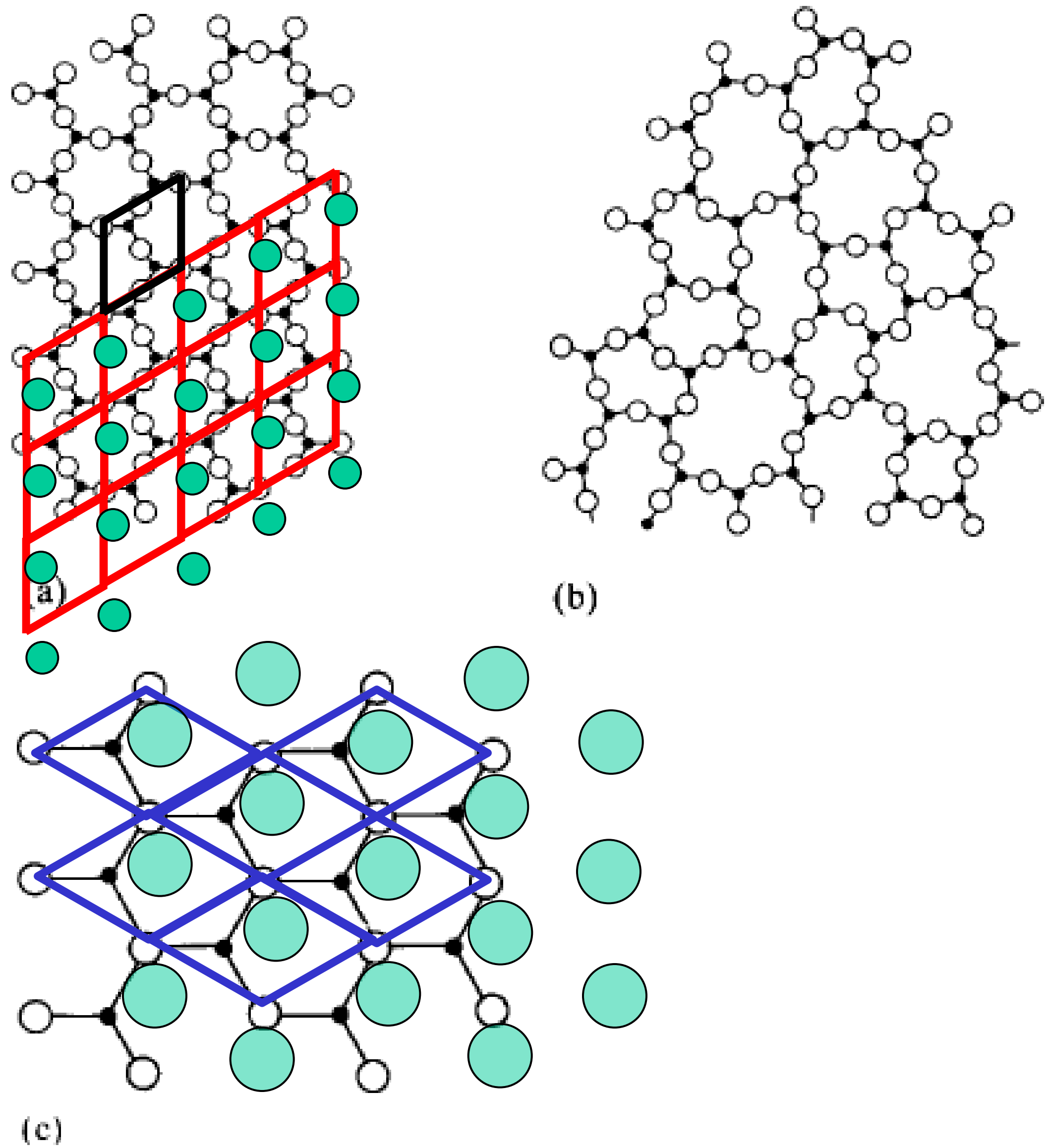


Fig. 2.13 Schematic two-dimensional representation of the structure of
(a) a hypothetical crystalline compound A_2O_3
(b) the Zachariasen model for the glassy form of the same compound and
(c) the hypothetical crystalline compound AO.

单元内的原子的排列特点

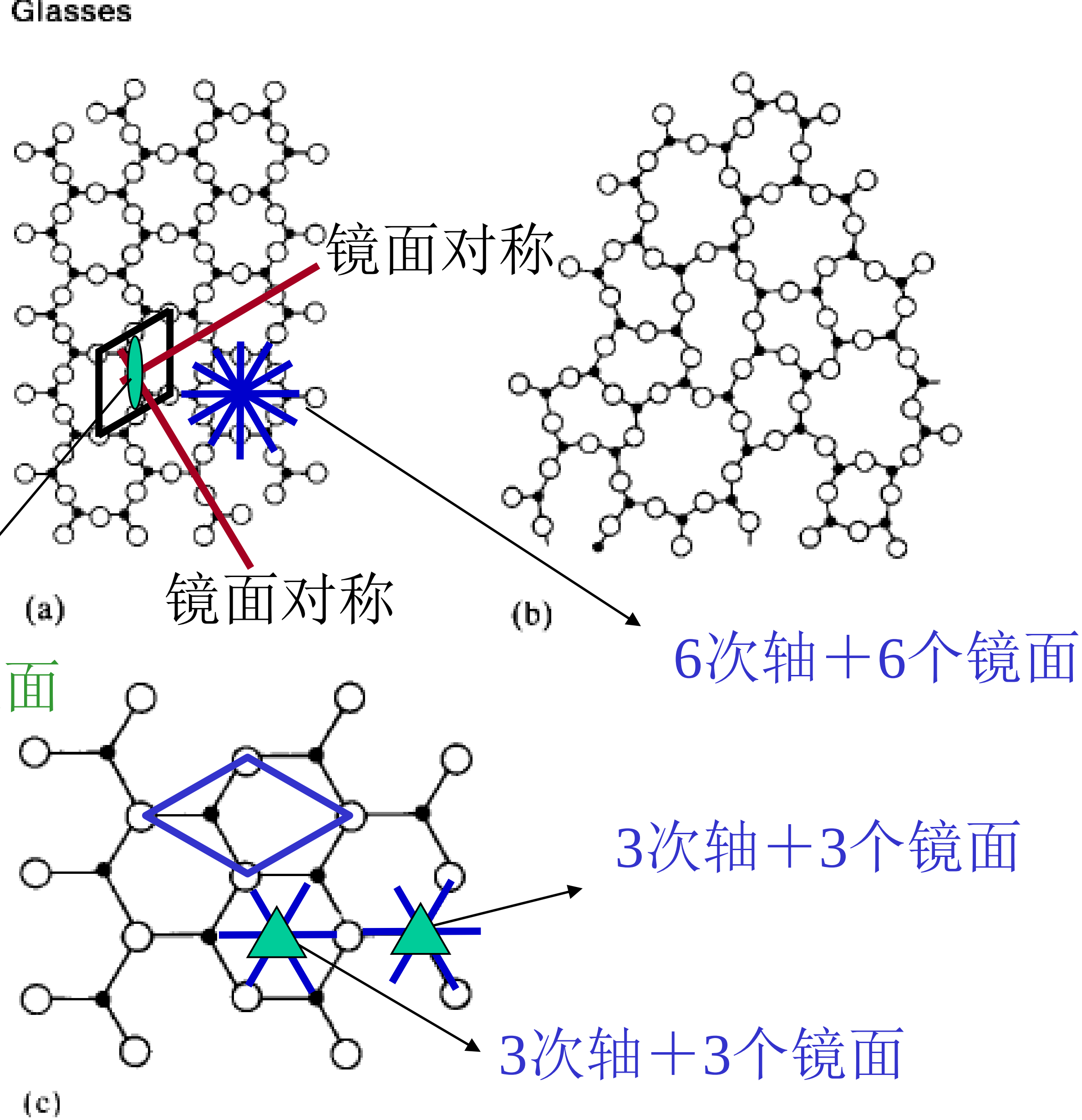


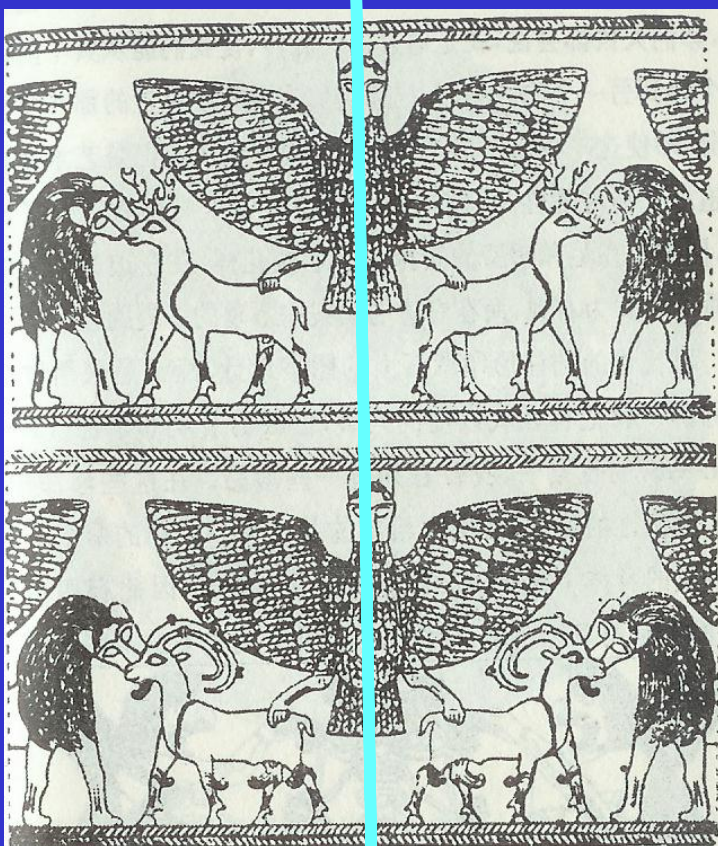
Fig. 2.13 Schematic two-dimensional representation of the structure of
(a) a hypothetical crystalline compound A_2O_3
(b) the Zachariasen model for the glassy form of the same compound and
(c) the hypothetical crystalline compound AO.

原子之间由对称性联系

人类社会中的对称性

Sumerian culture：

Mirror reflection



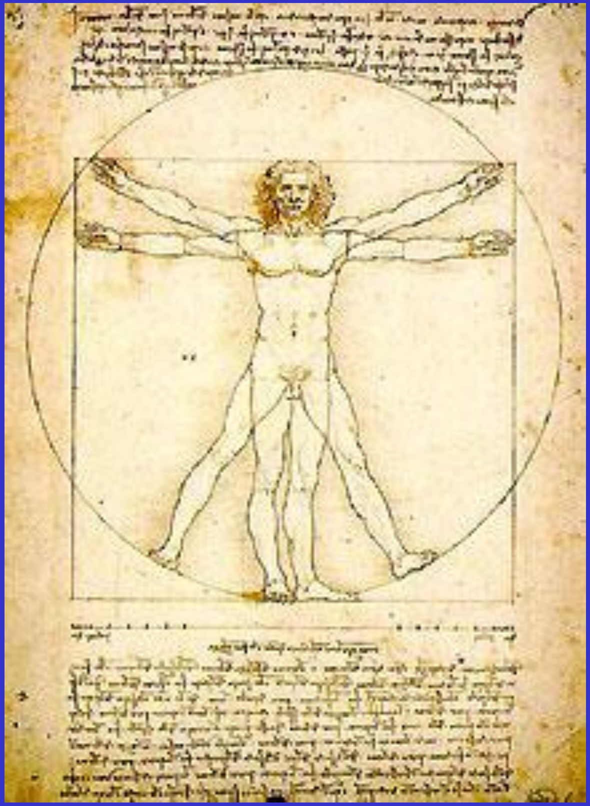
2—fold rotation

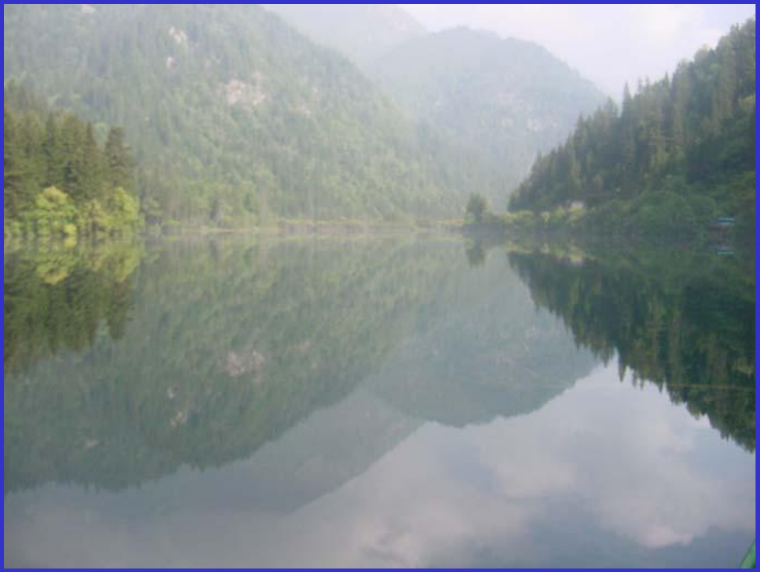
180°

人类社会中的对称性

秩序！

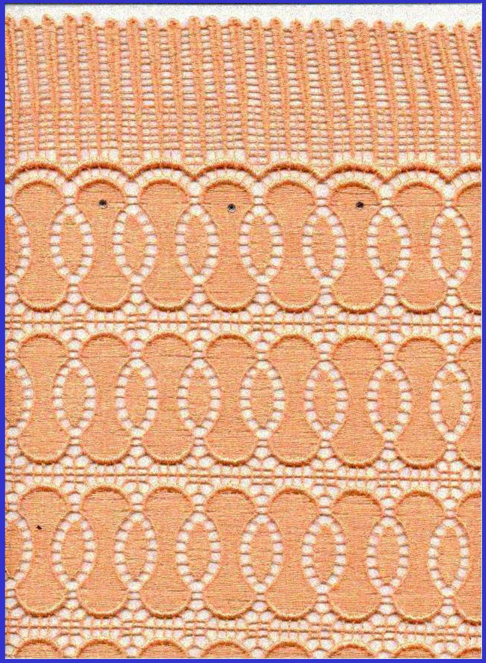
自然界中的对称性

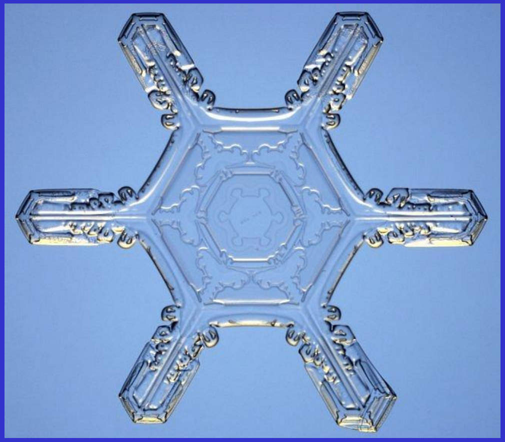




对称性的优美

对称　→静止、约束、秩序、规律、死亡
不对称→运动、松弛、任意、偶然、生命



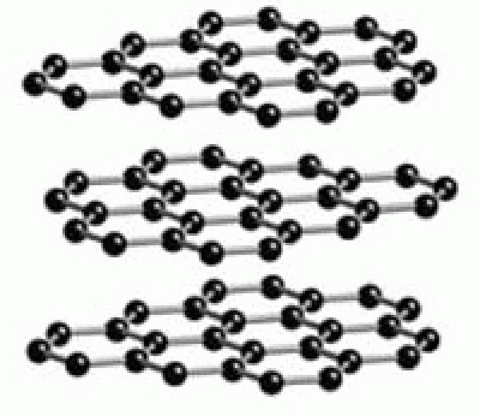


一、　晶体学基础

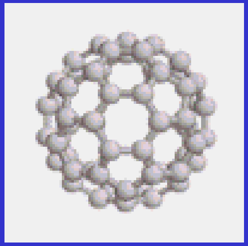
（1）　基本概念：

晶体学所描述的对象：原子排列方式（简化；理想；几何）=》周期。

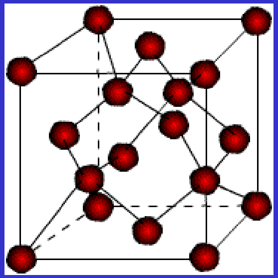
晶体结构＝结构单元（单胞）＋单胞周期平移



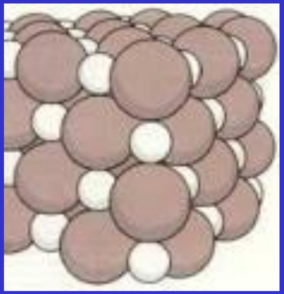
石墨



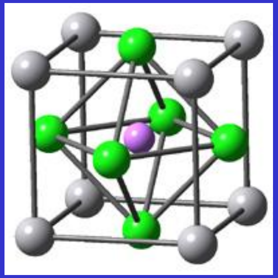
C60



金刚石



NaCl



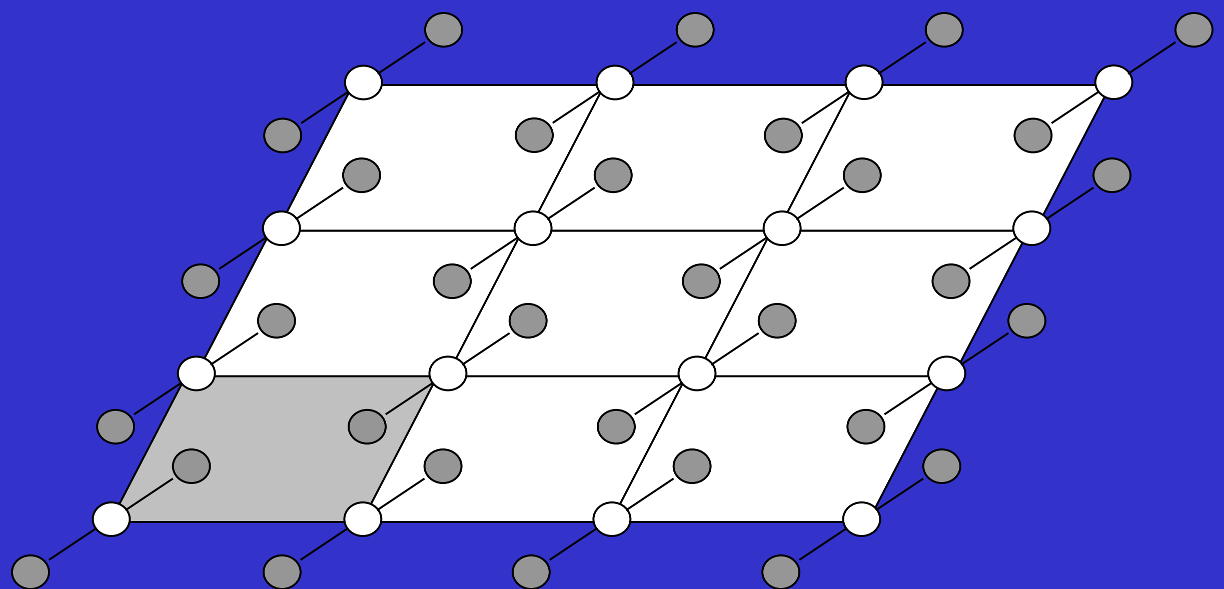
BaTiO3

一、　晶体学基础

（1）　基本概念：

晶体学所描述的对象：原子排列方式（简化；理想；几何）=》周期。

晶体结构＝结构单元（$\overbrace{\text{单胞）＋单胞周期平移}}^{\text{对称性}}$



(2)对称（宏观对称）操作

对称有两个层面含义：

文学词汇：
对称的：均匀协调的
对称性：整体的组成部分的和谐性
如人体、音乐

学术术语：几何概念
使自身复原的操作

①对称性

对称操作：

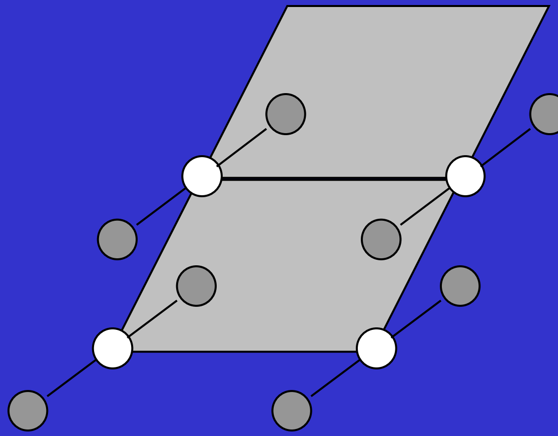
使图形保持不变（完全复原）的操作；

在对称操作中始终保持不变的轴、平面、或点称为对称元素。

原子位置由对称性操作联系。

对称操作：点对称和平移两种。

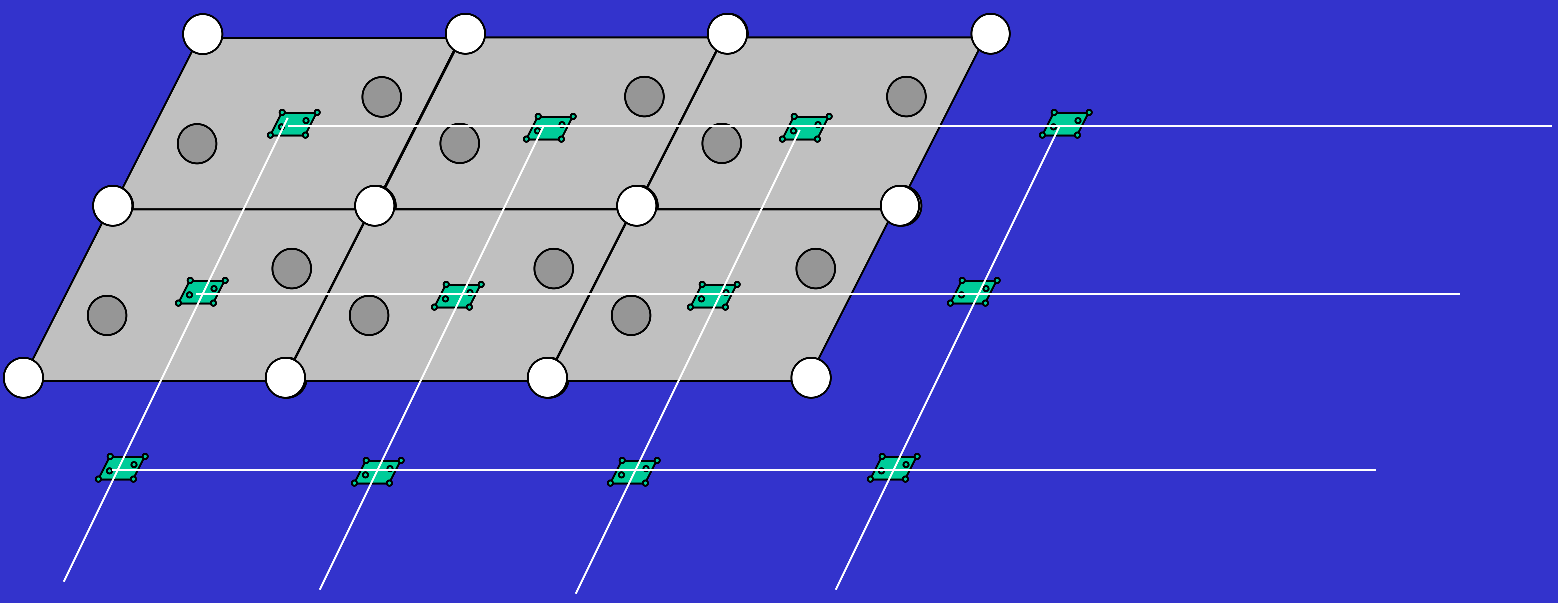
单胞位置由平移对称性联系。



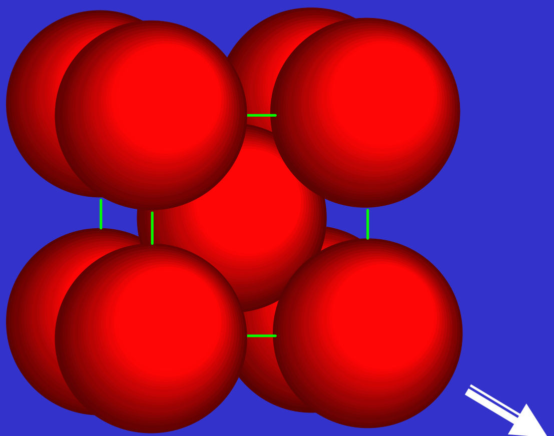
②点阵与晶体结构

阵点（几何点代替结构单元）和点阵（阵点的分布总体）

注意与晶体结构（=点阵+结构单元）的区别。

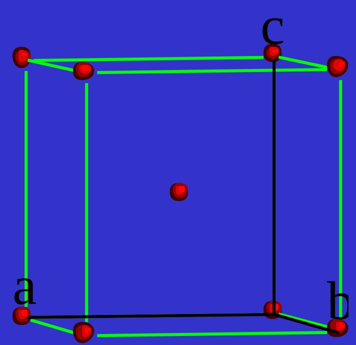


点阵与晶体结构：例子



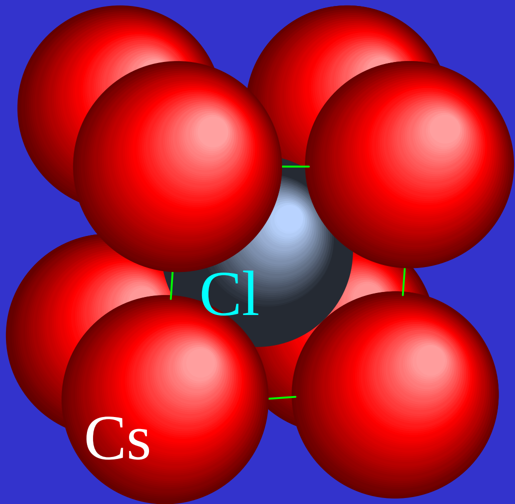
α-Fe, bcc

Steps to reach lattice
1, determine the basic unit
2, regard the unit as a point
3, the geometry of the points = lattice



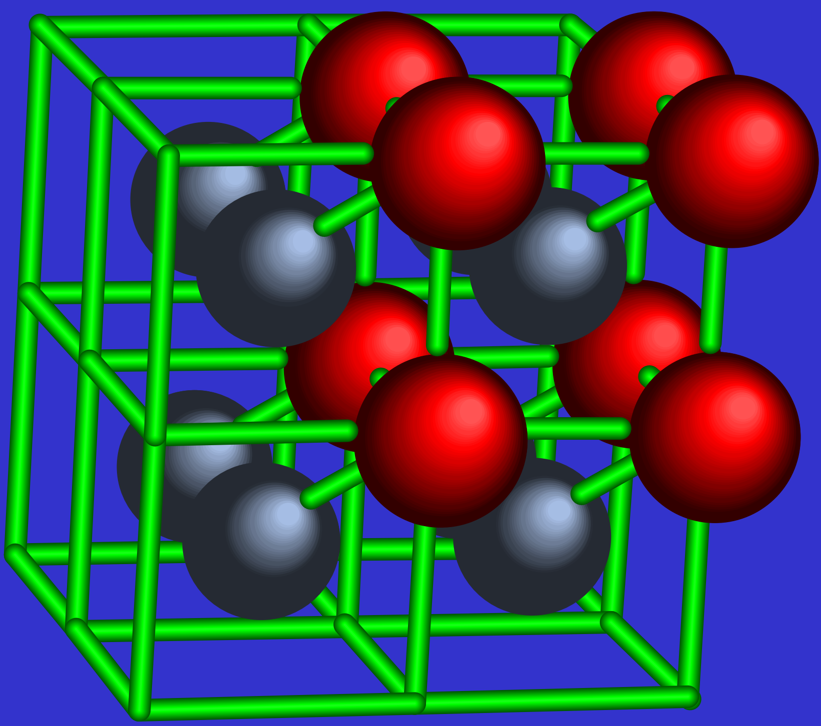
α-Fe
1, the basic unit: one Fe atom
2, regard the unit as a point
3, the geometry of the points =
Body centered cubic lattice

点阵与晶体结构：例子



Steps to reach lattice
1, determine the basic unit
2, regard the unit as a point
3, the geometry of the points = lattice

CsCl, simple cubic



CsCl
1, the basic unit: one Cs atom + one Cl
2, regard the unit Cs + Cl as a point
3, the geometry of the points =
simple cubic lattice

(2)点对称（宏观对称）操作

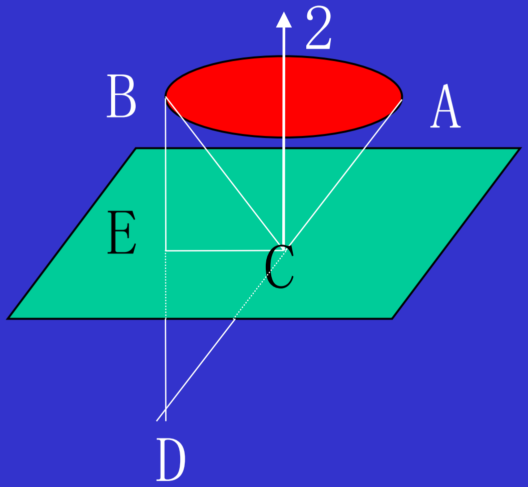
③种类：

镜面（对称面）m：B-D

旋转对称轴 n：A-B (2)

对称中心 $\bar{1}$：A-D

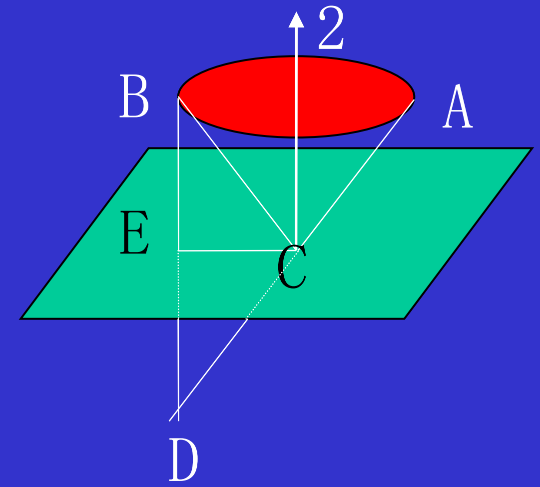
旋转反演对称轴 $\bar{n}$ ：$n+\bar{1}$, 2+m

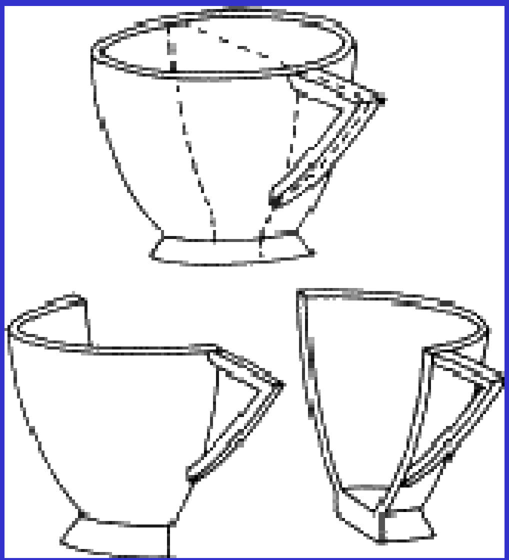


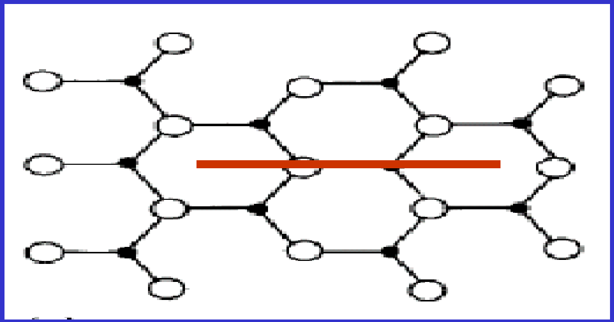
单晶外形常常呈现出点对称性

(2) 点对称（宏观对称）操作

镜面：B – D关系
等同于$2+\bar{1}$

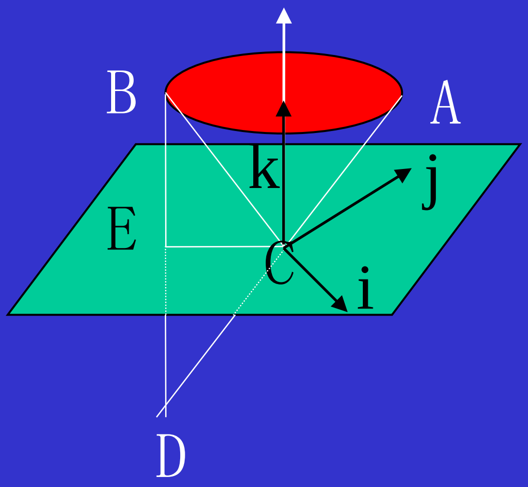






(2) 点对称（宏观对称）操作

镜面操作的数学表达



选k轴与镜面垂直

A (x, y, z) →B (-x, -y, z)→ D (-x, -y, -z)

镜面操作时，与镜面垂直的坐标变负

矩阵表达：

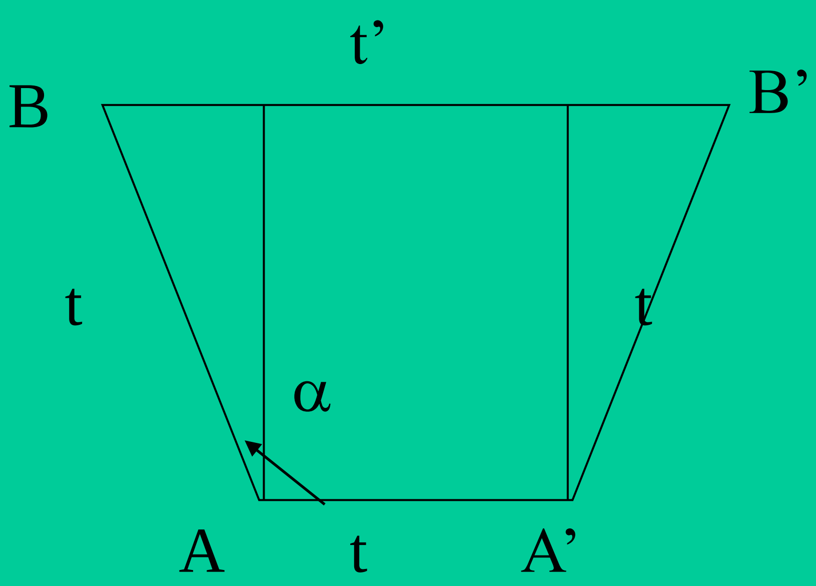
$$\begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} = Q_m \cdot \begin{bmatrix} -x \\ -y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

Q_m反映了镜面操作的实质！

轴次

轴次：1，2，3，4，6

晶体的周期性限制了可能的对称操作。



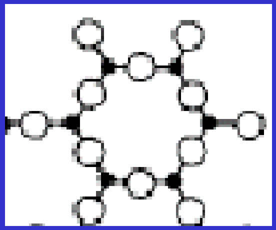
$t' = m\,t = t + 2t\,\mathrm{Sin}\,(\alpha\text{-}90)$

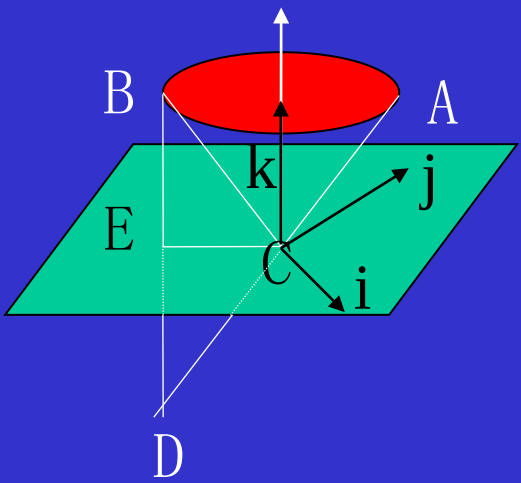
$= t - 2t\,\mathrm{Cos}\,\alpha$

$-1 \le \mathrm{Cos}\,\alpha = (1\text{-}m)/2 \le 1$

m =	-1,	0,	1,	2,	3
	360	60	90	120	180

2次轴





数学表达

选k轴与2次轴平行

A (x, y, z) →B (-x, -y, z)

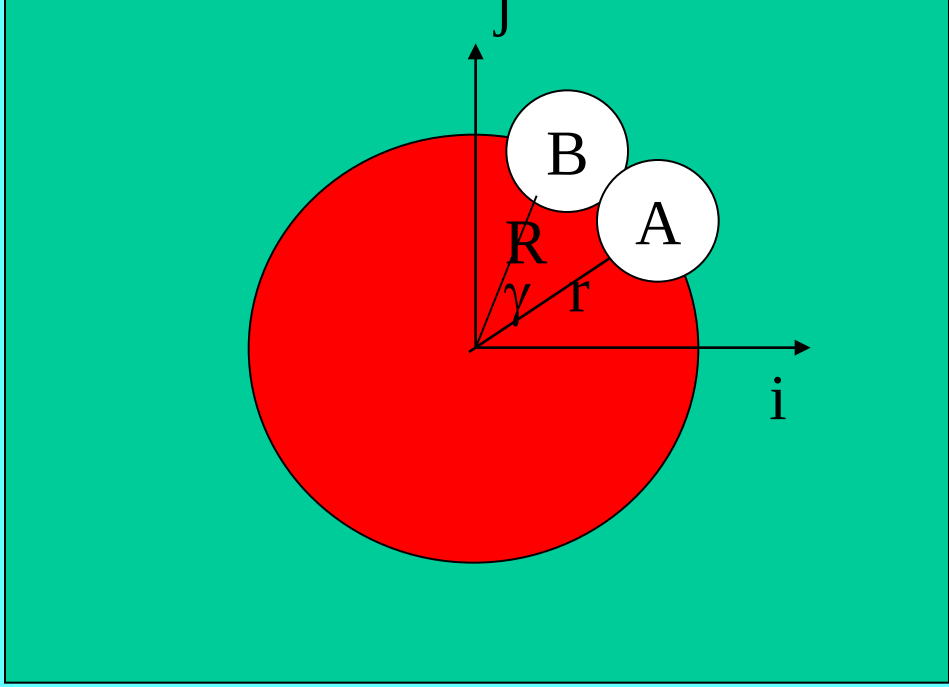
矩阵表达：

$$\begin{bmatrix} -x \\ -y \\ z \end{bmatrix} = Q_2 \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Q_2反映了2次轴操作的实质！

n次轴

数学表达



选k轴与n次轴平行

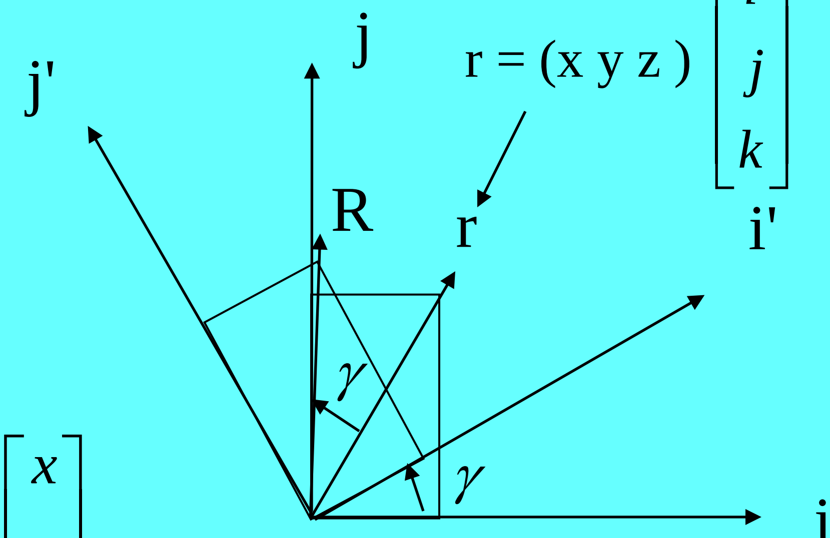
A (x, y, z) →B (X, Y, Z)

矩阵表达：

$$R = (X\ Y\ Z)\begin{bmatrix} i \\ j \\ k \end{bmatrix} = (x\ y\ z)\begin{bmatrix} i' \\ j' \\ k' \end{bmatrix}$$

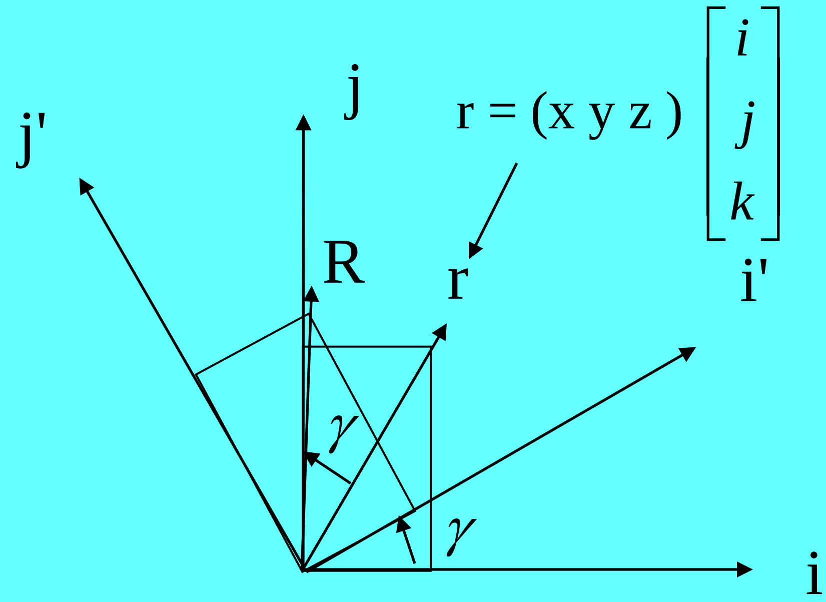
$$= (x\ y\ z)\ M_R\begin{bmatrix} i \\ j \\ k \end{bmatrix} \qquad \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = M_R^{\ t}\begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$r = (x\ y\ z)\begin{bmatrix} i \\ j \\ k \end{bmatrix}$$

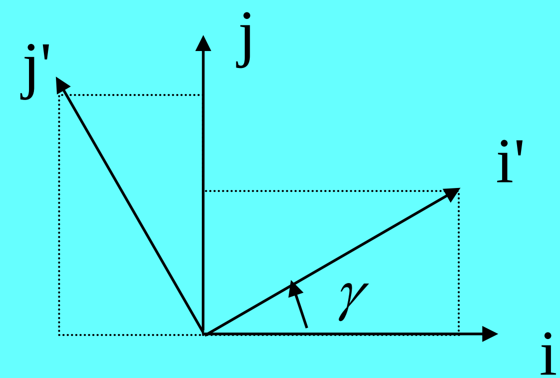


坐标系的旋转

选k轴与n次轴平行



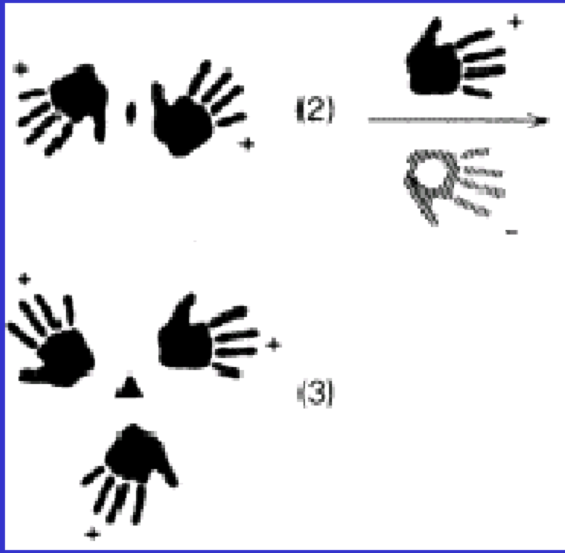
$$\begin{bmatrix} \boldsymbol{i}' \\ \boldsymbol{j}' \\ \boldsymbol{k}' \end{bmatrix} = \boldsymbol{M}_R \cdot \begin{bmatrix} \boldsymbol{i} \\ \boldsymbol{j} \\ \boldsymbol{k} \end{bmatrix}$$



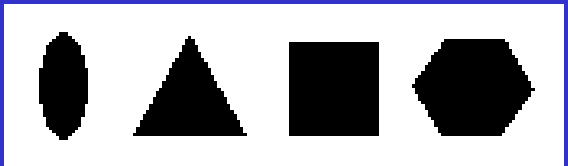
$$\begin{bmatrix} i' \\ j' \\ k' \end{bmatrix} = \begin{bmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} i \\ j \\ k \end{bmatrix}$$

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = M_R{}^t \begin{bmatrix} x \\ y \\ z \end{bmatrix} \rightarrow \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

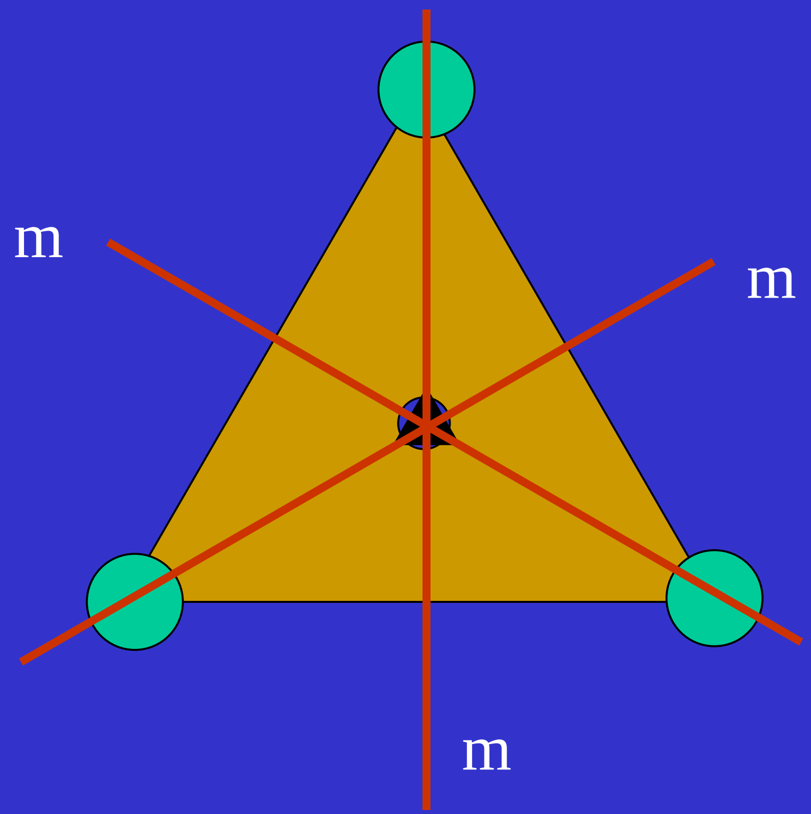
转轴实例

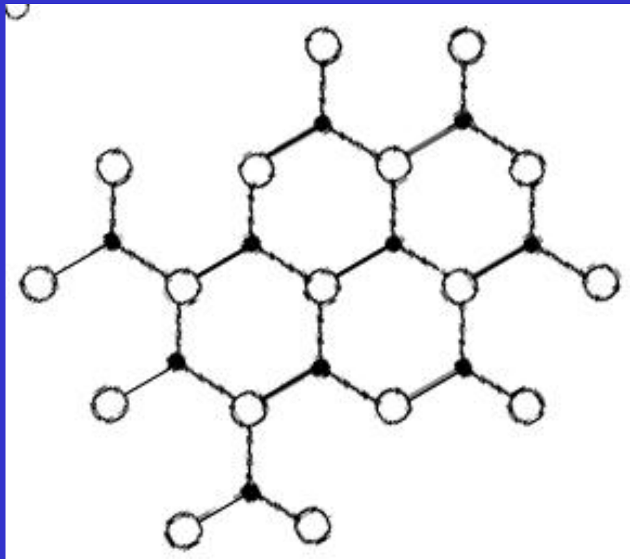


转轴符号

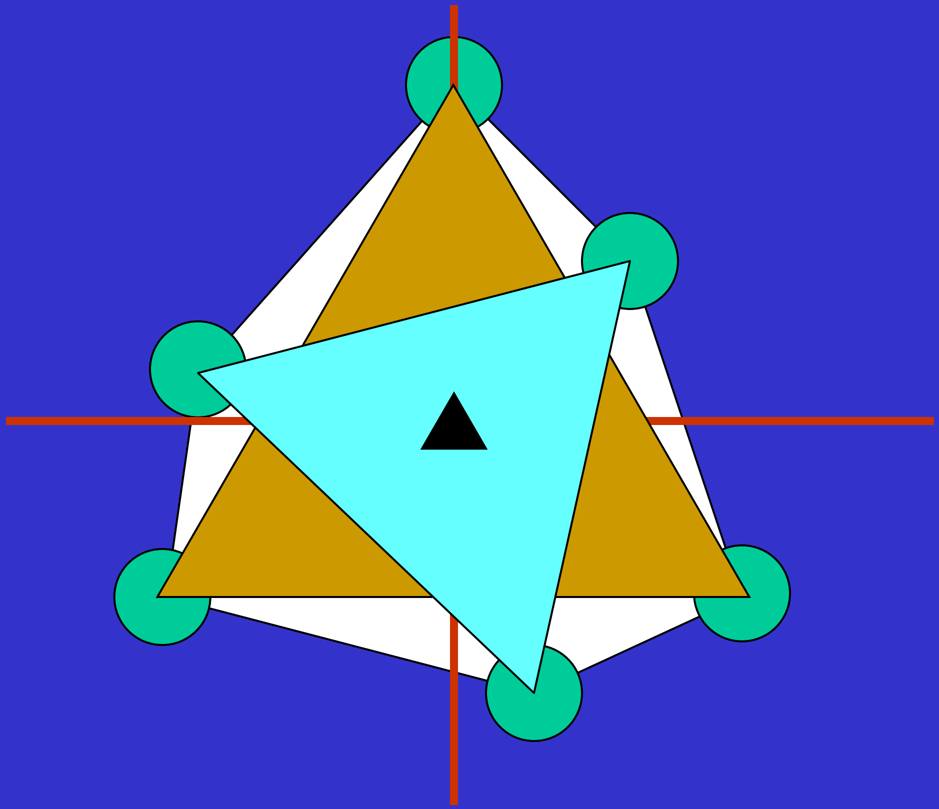


转轴实例

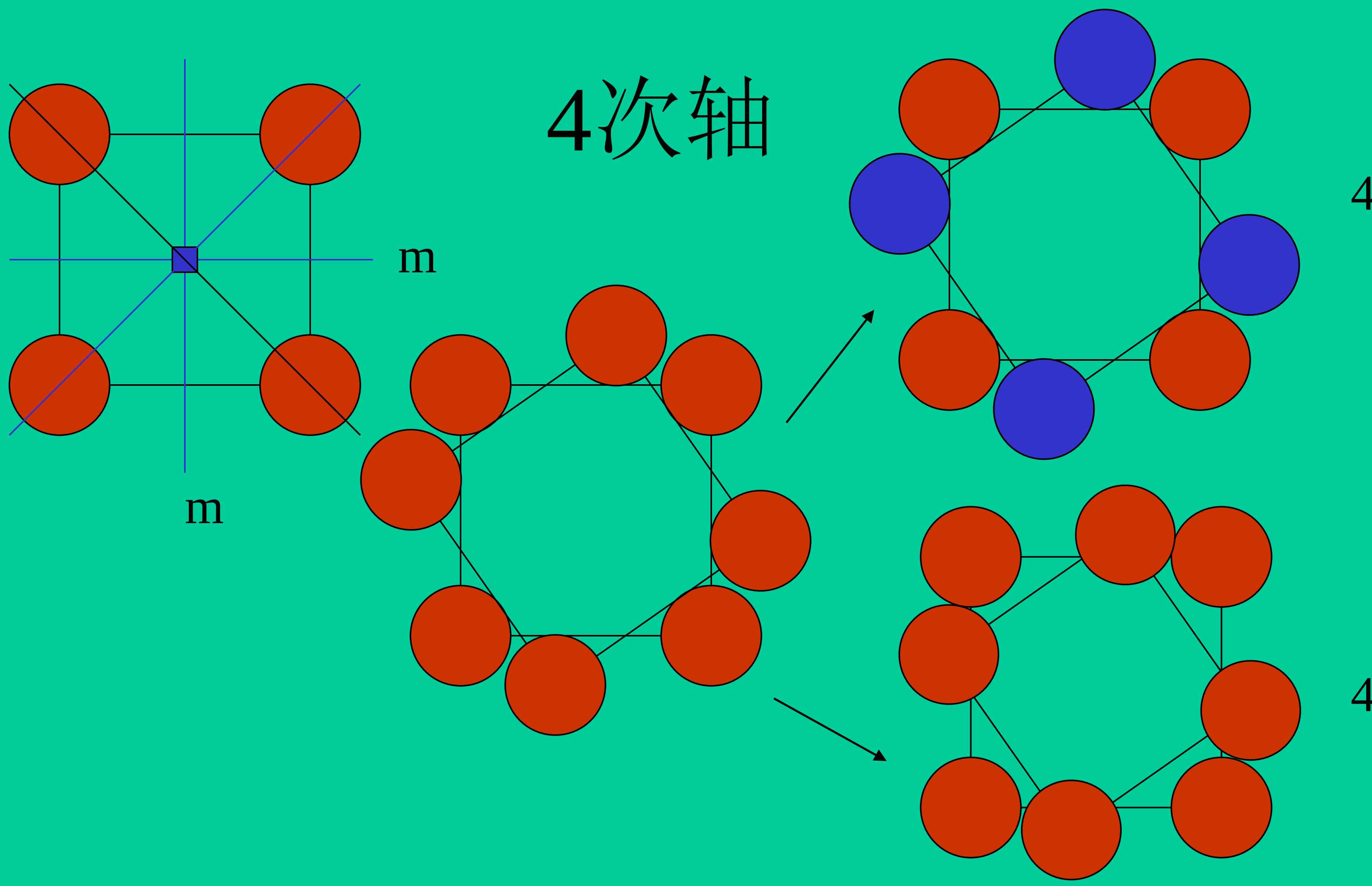




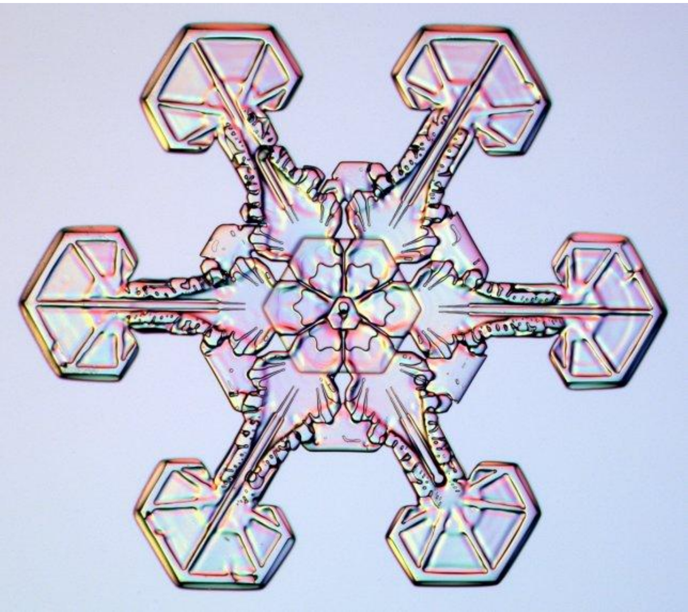
转轴实例



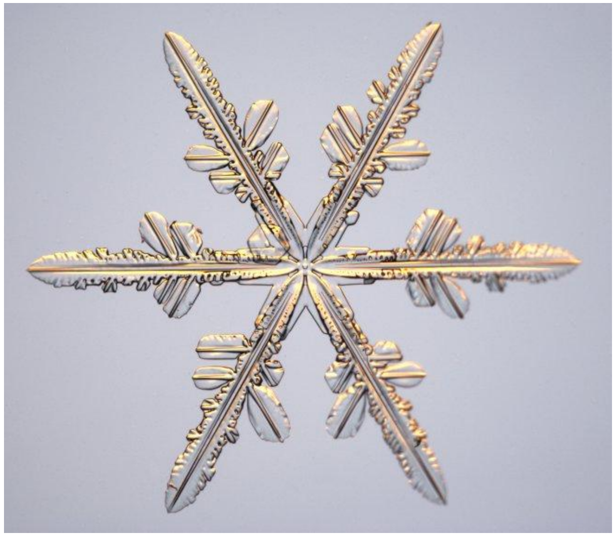
4次轴

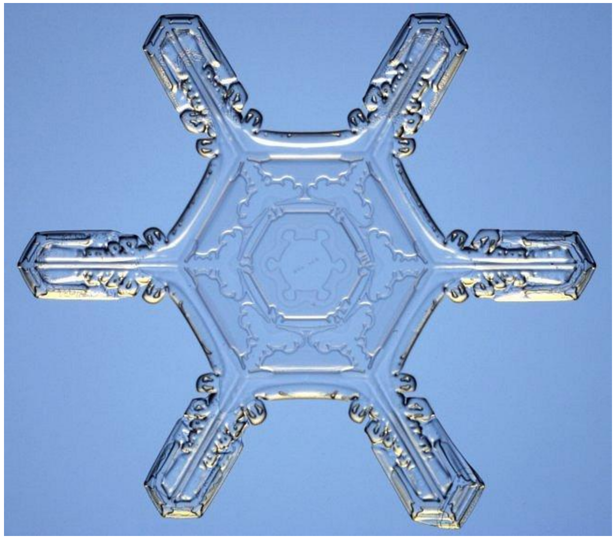


Snowflakes



对称性不变！





How about 5 fold symmetry?

It exists but only in aperiodic systems.

二维准晶模型：Penrose 拼图

5-fold: 非晶体学旋转

长程有序，但不是周期性质

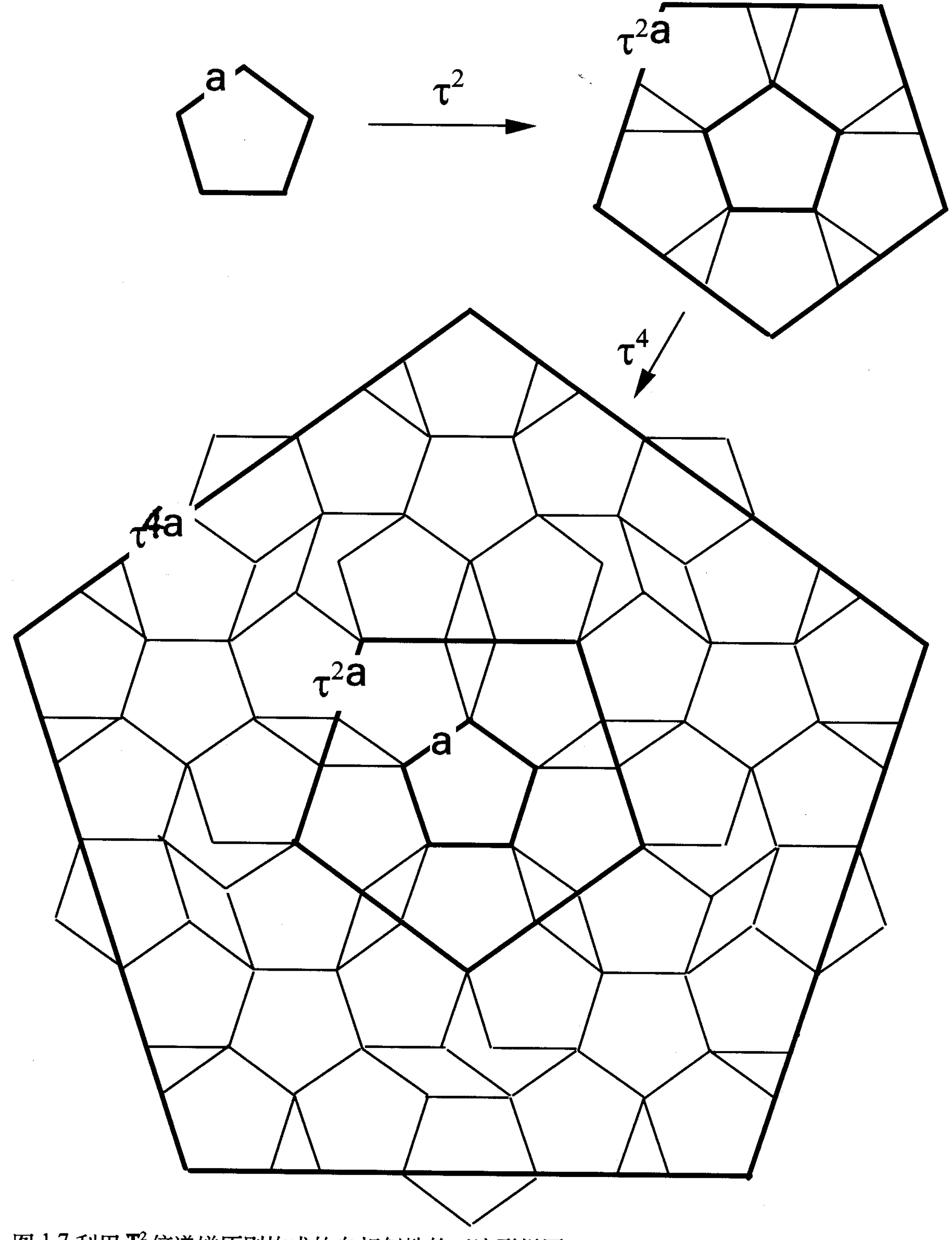
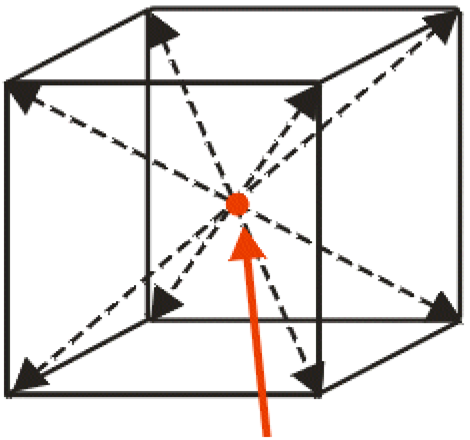


图 1.7 利用 $\mathbf{T}^2$ 倍递增原则构成的自相似性的五边形拼图。

Center of symmetry



In three-dimensions there are additional kinds of symmetry which do not arise in two dimensions. The simplest is inversion symmetry.

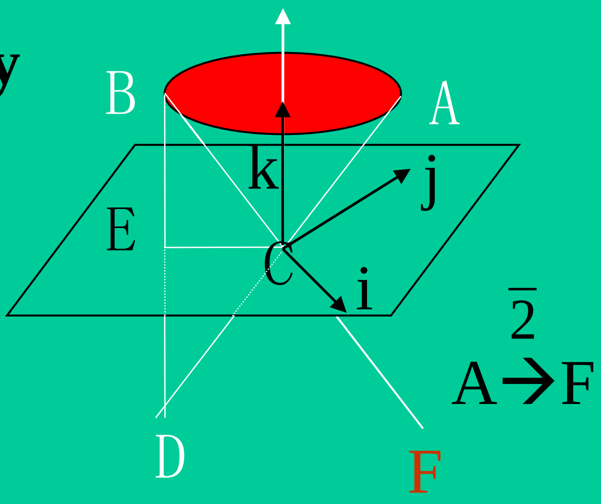
$$\begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} = Q_{inv} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

A structure possesses a centre of symmetry if it remains unchanged when every small element of the structure with coordinates (*x*,*y*,*z*) is reflected through the centre of symmetry at (0,0,0) to (-*x*,-*y*,-*z*). An operation of point inversion is to reflect each point (*x*,*y*,*z*) to (-*x*,-*y*,-*z*).

A centre of symmetry is denoted by $\bar{1}$.

Inversion axis

Additional kinds of symmetry are obtained by combining inversion with each rotation axis. These inversion axes consist of a rotation, followed by point inversion.



The operation of say an inversion tetrad is a rotation of 90°, followed by inversion through a centre. A four fold pattern of faces around the axis results, with each face inverted. The shorthand symbol to denote these axes is, $\bar{2}$ **,** $\bar{3}$ **,** $\bar{4}$ **and** $\bar{6}$**. A centre of symmetry is denoted by** $\bar{1}$ **.**

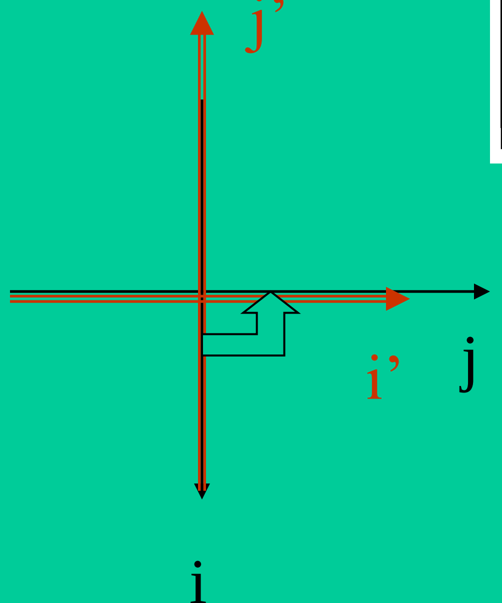
$$\begin{bmatrix} x \\ y \\ -z \end{bmatrix} = Q_2^t \cdot Q_{inv}^t \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

=m

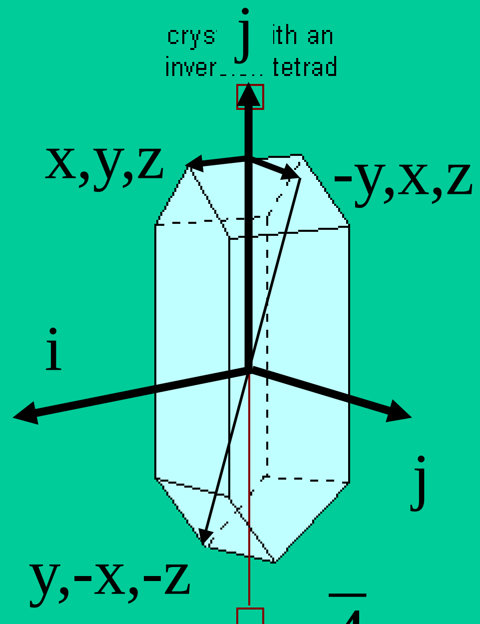
Inversion axis

$$\begin{bmatrix} y \\ -x \\ -z \end{bmatrix} = Q_4^t \cdot Q_{inv}^t \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

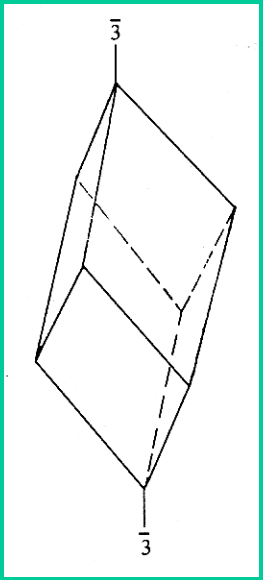
$$\begin{bmatrix} i' \\ j' \\ k' \end{bmatrix} = \begin{bmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} i \\ j \\ k \end{bmatrix}$$



$$\begin{bmatrix} i' \\ j' \\ k' \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} i \\ j \\ k \end{bmatrix}$$



$\bar{4}$



Inversion axis

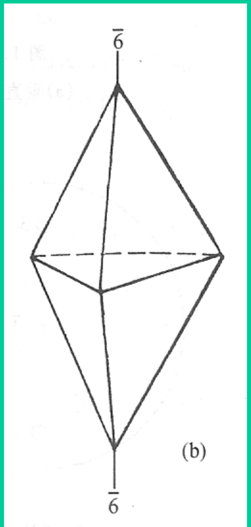


表 1.2　宏观对称元素图示

对称元素名称	符　号	图　　示	
		垂直于图面	平行于图面
对称中心	$C(=\bar{1})$	C · ∘	C · ∘
对称面	$P(=m)$	‖ // ═	◎
一次旋转轴*	$L_1(=1)$		
二次旋转轴	$L_2(=2)$	⬮	⬮—⬮
三次旋转轴	$L_3(=3)$	▲	▲—▲
四次旋转轴	$L_4(=4)$	■	■—■
六次旋转轴	$L_6(=6)$	⬢	⬢—⬢
三次旋转反演轴	$L_{\bar{3}}(=\bar{3})$		
四次旋转反演轴	$L_{\bar{4}}(=\bar{4})$		
六次旋转反演轴	$L_{\bar{6}}(=\bar{6})$		

*　对称自身.

④对称性的矩阵

A rotation matrix M_R contains only three independent variables

$\text{Cos}\theta = (a_{11} + a_{22} + a_{33} - 1)/2$

$U:V:W = a_{32} - a_{23} : a_{13} - a_{31} : a_{21} - a_{12}$

Or conversely, the elements of M_R in terms of θ/UVW are given by

$a_{11} = U^2(1-\cos\theta) + \cos\theta$

$a_{12} = UV(1-\cos\theta) - W \sin\theta$

$a_{13} = UW(1-\cos\theta) + V \sin\theta$

$a_{21} = VU(1-\cos\theta) + W \sin\theta$

$a_{22} = V^2(1-\cos\theta) + \cos\theta$

$a_{23} = VW(1-\cos\theta) - U \sin\theta$

$a_{31} = WU(1-\cos\theta) - V \sin\theta$

$a_{32} = WV(1-\cos\theta) + U \sin\theta$

$a_{33} = W^2(1-\cos\theta) + \cos\theta$

对称矩阵W特性

1、 联系等效位置

2、 tr(W)迹与坐标选取无关

3、 det(W)行列式与坐标选取无关

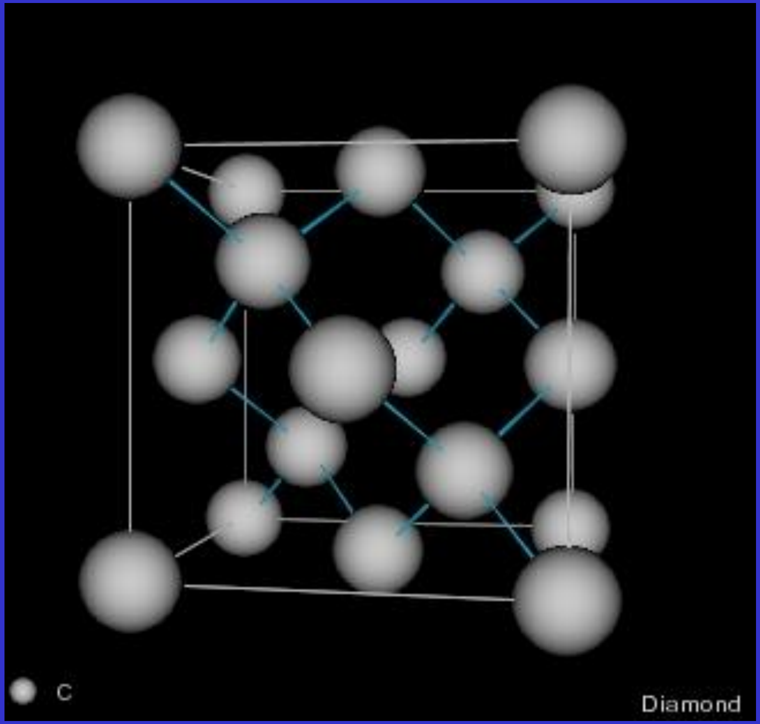
4、 由tr(W)和det(W)确定种类

det(W) = 1 纯旋转；det(W) = -1 非纯旋转；

		tr(W)						
		-3	-2	-1	0	1	2	3
Det(W)	1			2	3	4	6	1
	-1	$\bar{1}$	$\bar{6}$	$\bar{4}$	$\bar{3}$	$\bar{2}$ = m		

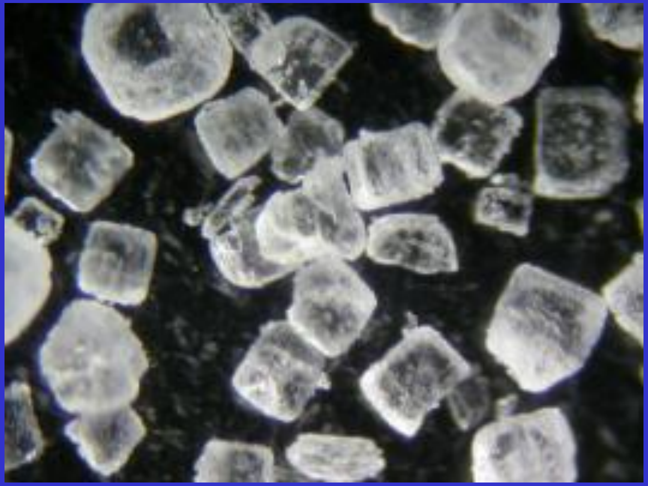
(2) 点对称（宏观对称）操作

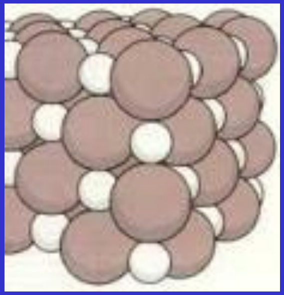
⑤实例



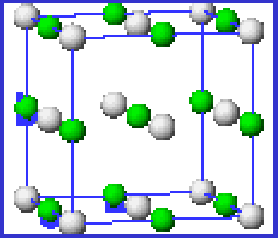
金刚石，C原子以四面体配位，面心立方点阵。

(2) 点对称（宏观对称）操作

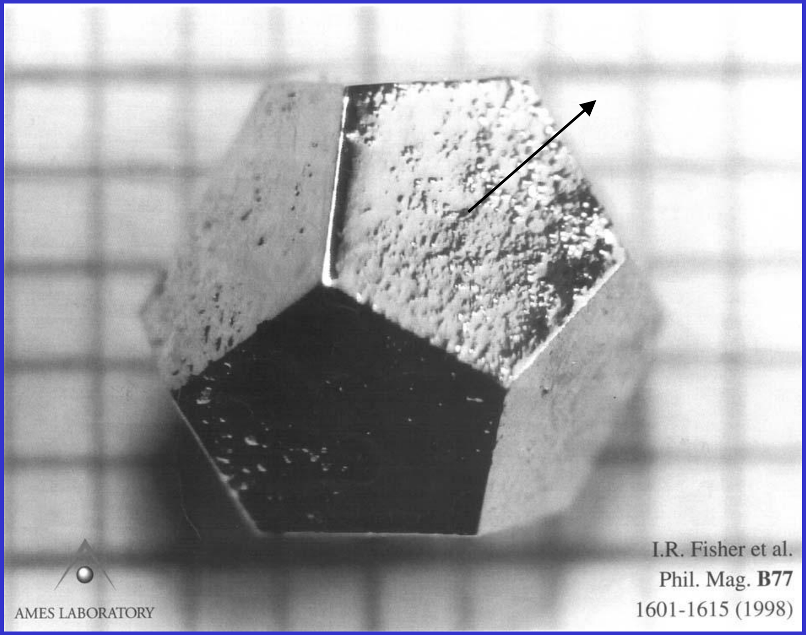


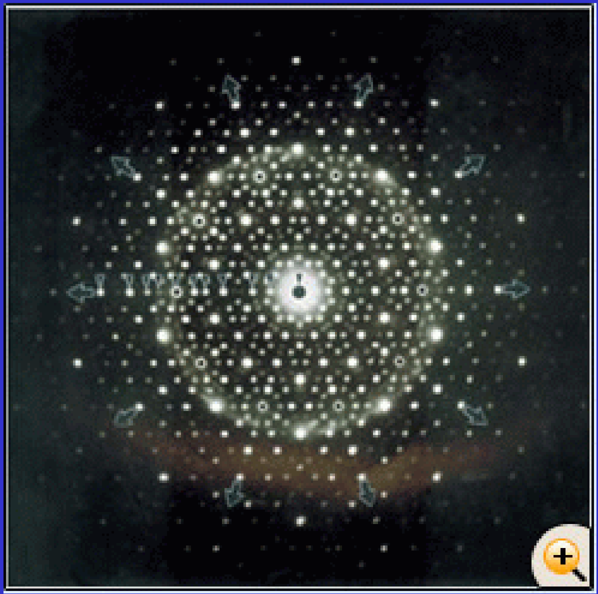


NaCl



(2) 点对称（宏观对称）操作





quasicrystal

(3) 平面点群

若干个点对称操作O_i（又称对称元素，注意与对称性区别）的组合C（集合），$O_i\,C = C$，满足：

（1） 封闭性：$O_j\,O_i\,C = O_j\,(O_i\,C) = O_j\,C$；

（2） 单位元：全同操作1；

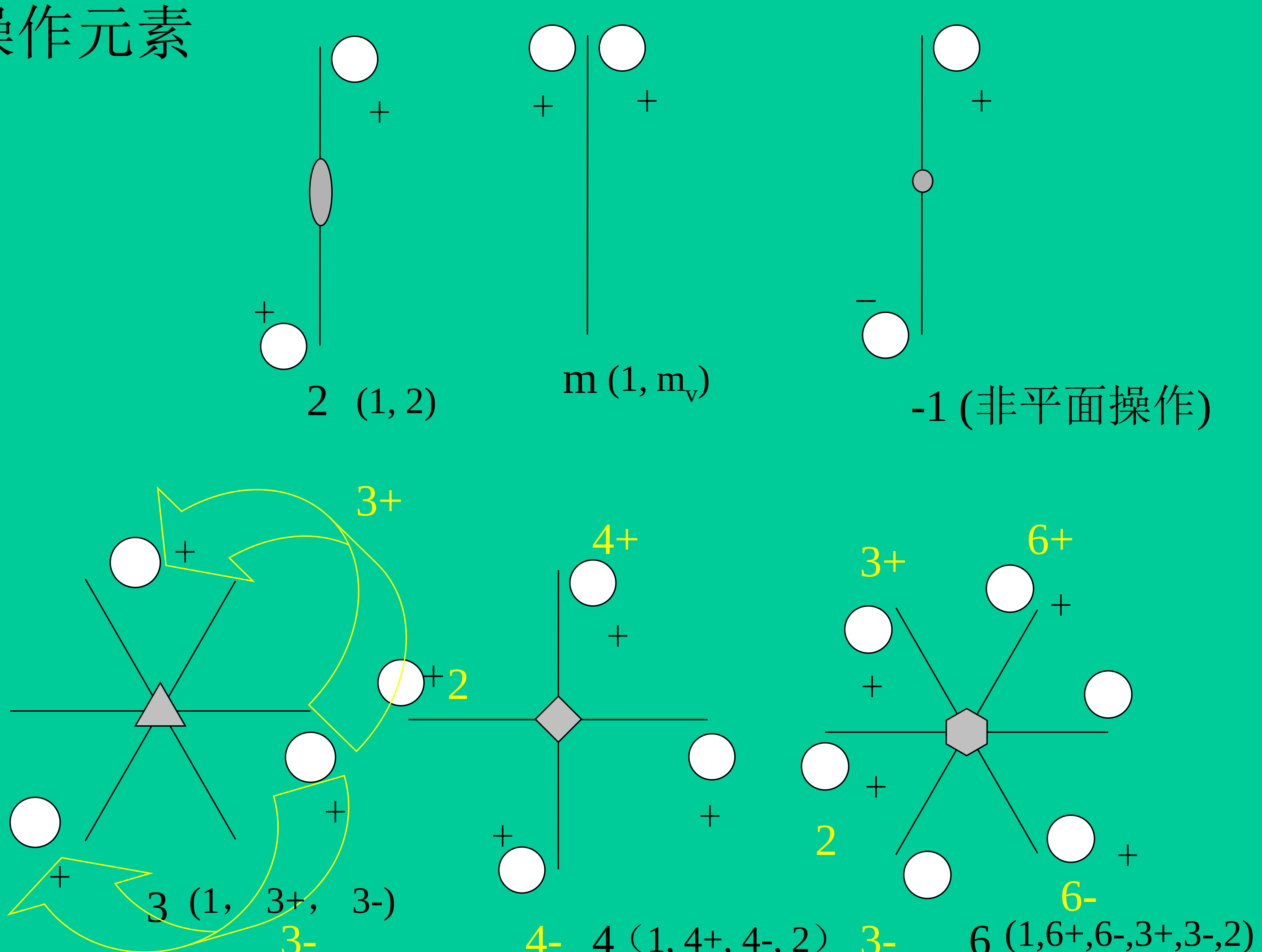
（3） 逆元：$O_i^{-1}\,C = O_i^{-1}\,O_i\,C = 1\,C = C$；

（4） 结合律：$O_i\,(O_j\,O_k) = (O_i\,O_j)O_k$

共10个

旋转轴	1 (1)	2 (1, 2)	3 （1， 3+, 3-）	4 （1, 2个4, 2）	6（1, 6+, 6-， 3+, 3-， 2）
镜面m	m（1, m_v)	2mm (1, 2, m_v, m_d)	3m (1, 2个3, 3个m_v)	4mm（1, 2个4, 2, 2个m_v, 2个m_d）	6mm（1, 6+, 6-, 3+, 3-, 2, 3个m_v, 3个m_d）

操作元素

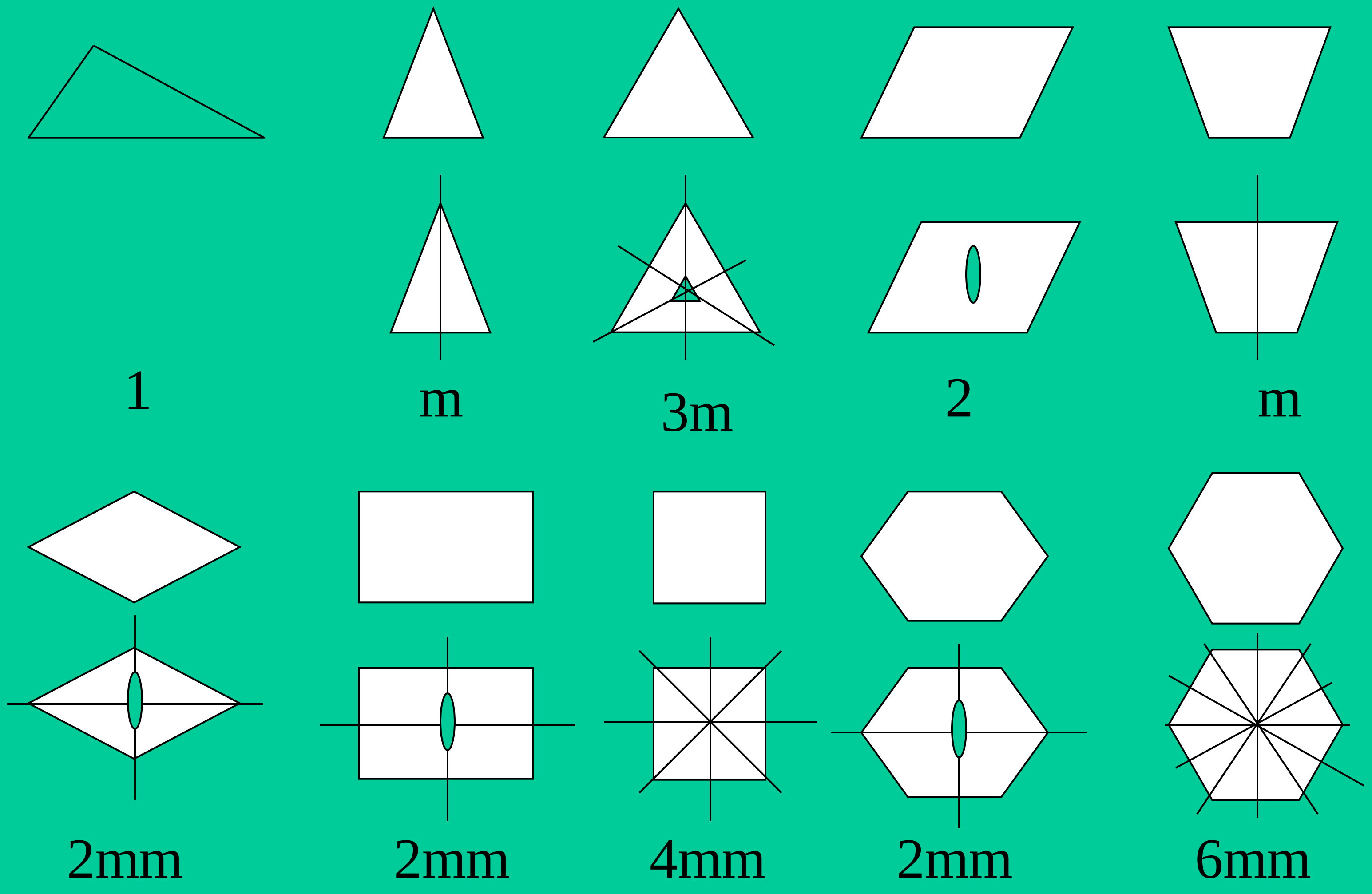


阶＝对称操作个数

高阶 = 低阶的乘积

旋转轴	1	2	3	4	6
镜面m	m 2	2mm = {2}{m} 2×2＝4	3m = {3}{m} 3×2＝6	4mm = {4}{m} 4×2＝8	6mm = {6}{m} 6×2＝12

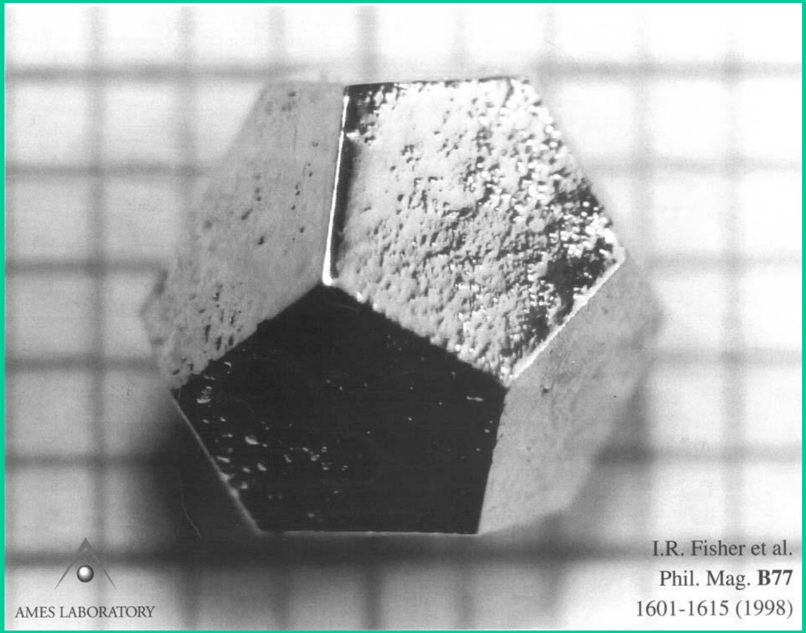
例：分析下图型的点群，找出对称性和对称操作



(4)晶体学点群

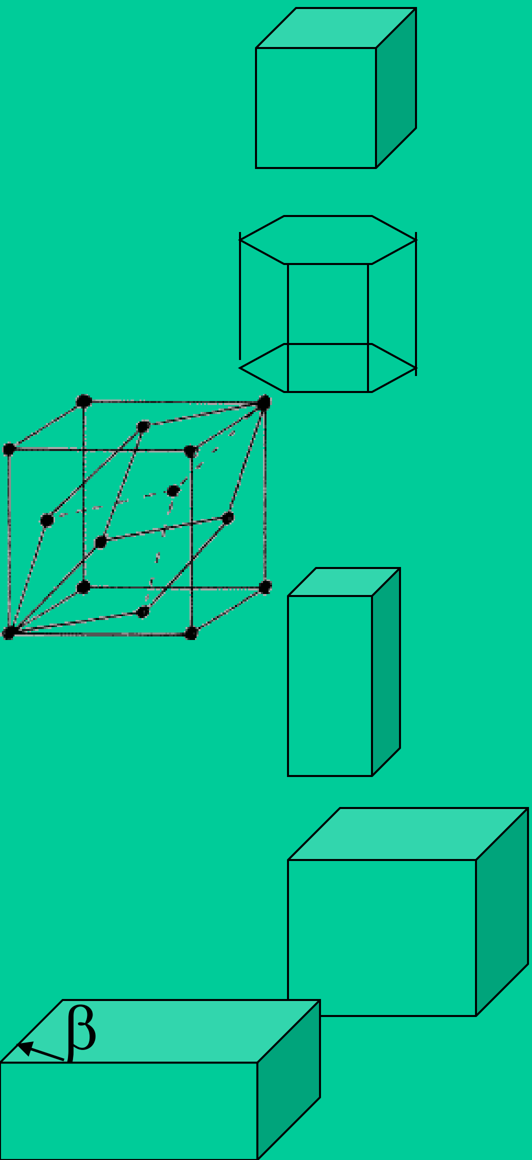
按天然晶体外表面的法线方向，分32类；与点阵平移结合，构成空间群；许多晶体的性能取决于点群。

点群国际符号：赫曼-莫吉恩（Hermann-Mauguin）



晶体学点群国际符号

数字代表对称性；三位，主导元素，



晶系	位序	代表方向
立方	1	a
	2	a + b + c
	3	a + b
六角	1	c
	2	a
	3	2a + b
三角	1	a + b + c
	2	a − b
四方	1	c
	2	a
	3	a + b
正交	1	a
	2	b
	3	c
单斜	1	b
三斜	1	

纯旋转点群：

① cos w = (cos W + cos U cos V)/(sin U sin V)

② 晶体中旋转轴的组合：多数情形下cos w绝对值大于1，只有：

222，223 （32），224（422），226（622），233（23），234（432）。加上1，2，3，4，6，共11个。

③ 纯旋转点群的子群：

	阶	子群										
1	1	1										
2	2	1	2									
3	3	1		3								
4	4	1	2		4							
6	6	1	2	3		6						
222	4	1	2				222					
32	6	1	2	3				32				
422	8	1	2		4		222					
622	12	1	2	3		6	222	32		622		
23	12	1	2	3			222				23	
432	24	1	2	3	4		222	32	422		23	432
			2	3	4	6	222	32	422	622	23	432

32种点群符号及劳厄群

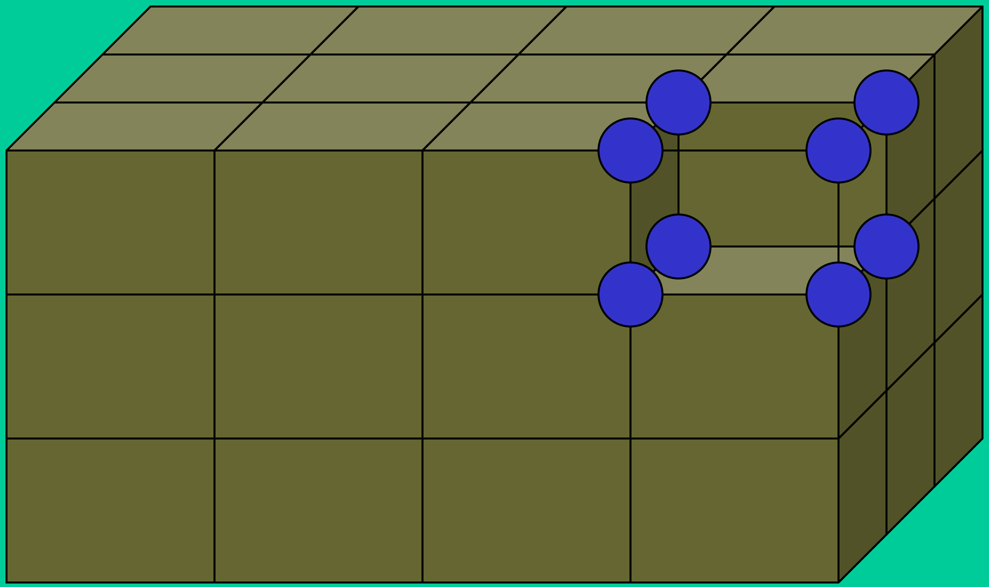
21个非旋转晶体学点群

32种点群符号及劳厄群

晶系	点群符号		主导对称元素的方向			劳 厄群
	国际符号	熊夫利	a	b	c	
三斜	1	C_1				-1
	-1	C_i				
单斜	2	C_2		2		2/m
	m	C_S		m		
	2/m	C_{2h}		2/m		
正交	222	D_2	2	2	2	mmm
	mm2	D_{2v}	m	m	2	
	mmm	D_{2h}	2/m	2/m	2/m	
四方	4	C_4	c	a	a+b	4/m
			4		[110]	
	-4	S_4	-4			
	4/m	C_{4h}	4/m			
	422	D_4	4	2	2	
	4mm	C_{4v}	4	m	m	
	-42m	D_{2d}	-4	2	2	
	4/mmm	D_{4h}	4/m	2/m	2/m	
三角	3	C_3	c	a	-	3
			3			
	-3	C_{3I}	-3			
	32	D_3	3	2		3m
	3m	C_{3v}	3	m		
	-3m	D_{3d}	-3	m		
六角	6	C_6	c	a	2a+b	6/m
			6	-	[110]	
	-6	C_{3h}	-6	-	-	
	6/m	C_{6h}	6/m	-	-	
	622	D_6	6	2	2	6/mmm
	6mm	C_{6v}	6	m	m	
	-62m	D_{3h}	-6	m	2	
	6/mmm	D_{6h}	6/m	2/m	2/m	
立方	23	T	a	a+b+c	a+b	m3
			2	3	-	
	m3	T_h	2/m	3	-	
	432	O	4	3	2	m3m
	-432	T_d	-4	3	2	
	m3m	O_h	4/m	3	2/m	

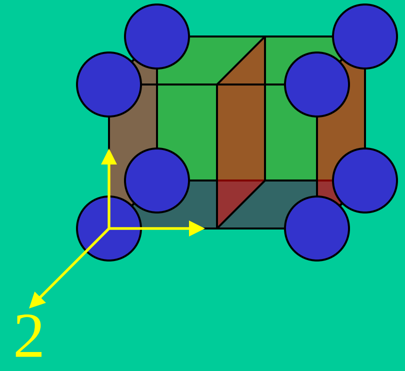
点群例：

例：



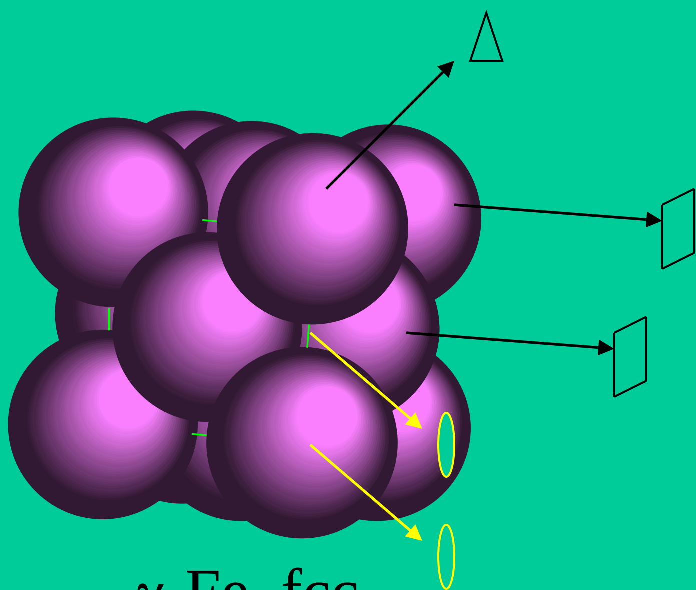
单胞(结构单元)：正交，含有一个 

点群：2/m 2/m 2/m → mmm

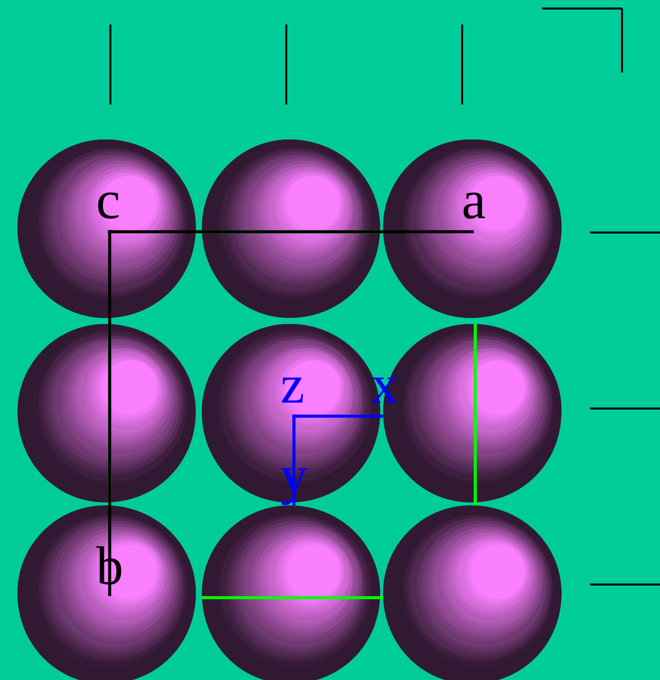


将所有对称性汇集在一点

点群例：

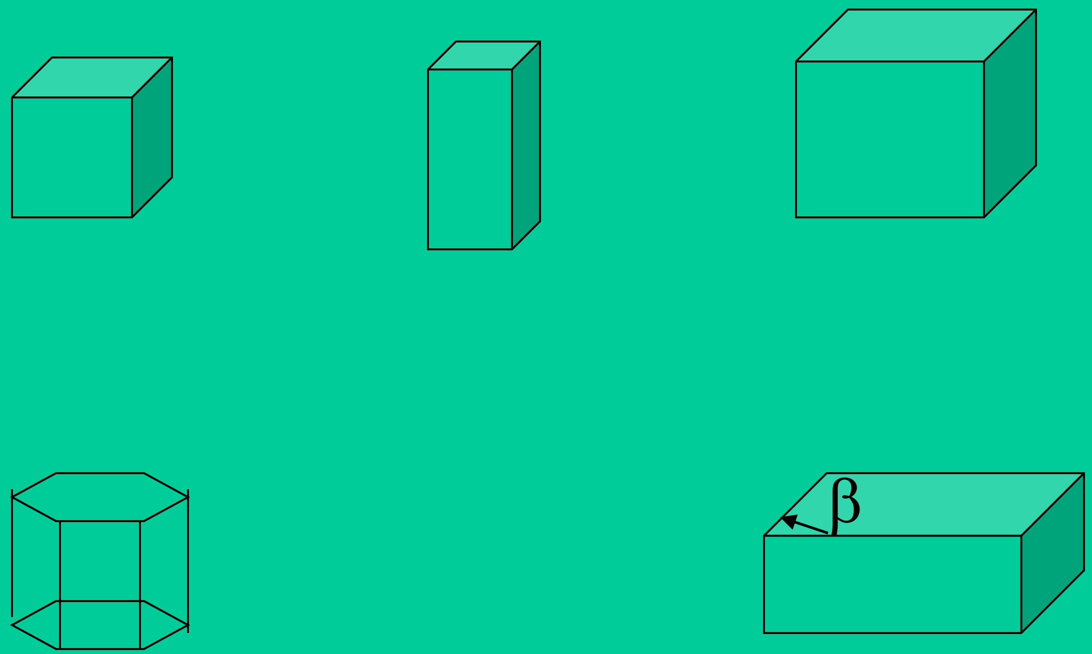


γ-Fe, fcc



4, 3, 2, m, -1→4/m 3 2/m→m3m

对称性分析举例



极赤投影图

viewing direction