Symmetry

Any understanding of the properties of solids relies heavily on structural characterization and benefits from analysis of chemical bonding and electronic structure. The techniques of structure determination such as diffraction, magnetic resonance, and spectroscopy, as well as methods of electronic structure calculations make considerable use of symmetry. The most widely studied solids are idealized crystalline structures, but non-crystalline solids have also been examined using these same techniques. Here, we will concentrate on crystalline solids which consist of atoms repeated periodically in three dimensions. Single crystals have uniform compositions and reveal their symmetry macroscopically and microscopically, by forming faceted shapes with planar faces at precise angles with one another as well as diffracting X-rays. The results of a crystal structure determination by diffraction are reported using the minimum information needed to draw or build a 3-d model of its structure.

READING: A.K. Cheetham and P. Day, *Solid State Chemistry*, Vol. 1, "Techniques", pp. 52-57;
H.F. Franzen, *Physical Chemistry of Solids*, pp. 17-77.

(10) Crystalline Structures: Crystalline symmetry involves two components: (1) *translational symmetry*, which is described by a lattice of repeating unit cells; and (2) *rotational symmetry*, which is specified by a point group arising from the presence of rotation axes and reflection planes in the pattern of atoms throughout the crystal. Combining these two symmetry components leads to *space groups*. Examples of crystalline structures include the 2-d projections of graphene and $CeNiC_2$.[17] Graphene displays hexagonal symmetry in the middle of every 6-membered ring of C atoms. Also, the site of each C atom has trigonal symmetry, and the unit cell is a parallelogram with equal sides and interior angles of 120° and 60°. The unit cell of any crystal is typically placed so that its corners have the highest rotational symmetry. The structure of $CeNiC_2$ displays only rectangular symmetry in projection, and clearly has reflection planes, but there are additional reflections coupled with displacements that are parallel to the planes and not vectors of the lattice. These operations are called *glide reflections*.

An important reference for structure determination and analysis of crystals is the *International Tables of Crystallography*, *Volume A*, which contains all the information concerning the symmetry characteristics of crystals. The short-term goal of this subsection is to learn how to extract and comprehend information from these tables.

Brief Tutorial on Group Theory: Translations and rotations are symmetry operations of a structure when they keep the structure *invariant*. All properties of the structure also do not change by these operations. This set of symmetry operations forms a mathematical *group*, which has the following features:

- A *group* is a set of operations that satisfy four criteria: (i) the set is closed with respect to some combination (addition, matrix multiplication, etc.); (ii) the set contains an identity operation; (iii) the combination is associative; (iv) the set contains the inverse of every operation. The properties of a group are completely contained within its *multiplication table*. If the combination is also commutative, then the group is *Abelian*.
- The set of operations can be separated into different *classes* by a similarity transformation: if A, B, X all belong to the group, then A and B are in the same class if $X^{-1}AX = B$. The identity operation is in a class by itself.
- A *representation* of the group is typically a set of square matrices, one for each operation and the size of the matrices are set by the number of basis functions, e.g., 3×3 matrices are needed when operating on the spatial coordinates (x, y, z). Irreducible representations (IR) involve basis functions that are orthogonal to, i.e., inequivalent with, basis functions for all other IRs. The *degeneracy* of an IR = number of basis functions

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[17] O.I. Bodak, E.P. Marusin, *Dop. Akad. Nauk Ukr. RSR, Ser. A* **1979**, *A41*, 1048-1050.

needed = dimension of the square matrices of the IR. A general reducible representation is built up from IRs. The IRs of an Abelian group are all 1-dimensional

- The *number of irreducible representations* = *number of classes* in a group. For an Abelian group, the number of IRs = the number of group members.
- The fundamental properties of a group are summarized in a *character table* (character = trace of a matrix), which lists the characters for each IR by class. The character of every operation in a single class is the same value. In a typical character table, rows are labeled by IRs, columns are labeled by classes.

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(11) To specify a crystal structure completely, three pieces of information are needed: (1) the space group; (2) the unit cell constants specifying its size and shape; and (3) the fractional coordinates of a set of distinct atoms called the asymmetric unit. All of this information taken together leads to the spatial arrangement of atoms in a crystal and allows evaluation of bond distances and angles, as illustrated for K_2PtCl_4.[18]

Translational symmetry of a crystal is specified by its *Bravais lattice*, which is a quasi-infinite set of points that occur at the ends of all vectors $[mnp] = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$. The basis vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ are linearly independent (not coplanar), the coefficients m, n, p are integers or certain rational fractions (½, ⅓, or ⅔), and the oriented surroundings of every lattice point are identical. The corresponding *unit cell* is a parallelepiped formed by the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, and contains the fundamental block of atoms that repeats periodically throughout space. The lengths of the sides of the unit cell are a, b, c; the angles between adjacent vectors are α (between $\boldsymbol{b}$ and $\boldsymbol{c}$), β (between $\boldsymbol{a}$ and $\boldsymbol{c}$), γ (between $\boldsymbol{a}$ and $\boldsymbol{b}$); and the collection of the three distances and angles are the *lattice parameters*. Although there are many different ways to assign basis vectors for a lattice, the distances a, b, c usually correspond to the shortest periodicities along each dimension and α, β, γ range from 90° to 120°. Once defined, the unit cell specifies a coordinate system for the crystalline space so that every point can be expressed by its fractional coordinates (u, v, w), which also represents the vector $u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$. If any angle between the different unit cell vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ is not 90°, then the coordinate system is oblique, and distance calculations between points must take this characteristic into account.

All Bravais lattices have *inversion symmetry*, i.e., for every lattice vector $[mnp] = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$, there is also $[\bar{m}\bar{n}\bar{p}] = -m\boldsymbol{a} - n\boldsymbol{b} - p\boldsymbol{c}$. In usual crystallographic notation, negative values are indicated by placing the negative sign above the symbol so that $\bar{x} = -x$. The vector sum, $[mnp] + [\bar{m}\bar{n}\bar{p}] = \mathbf{0}$, is the identity vector of the lattice. Therefore, a Bravais lattice is a mathematical group under vector addition.

(12) Bravais Lattices: What rotational symmetries are compatible with Bravais lattices? In the construction to answer this question, any rotational symmetry of the lattice passes through each lattice point. Consider a 1-d sublattice of points each separated by the minimum distance a. Now, at a lattice point designated "**1**", consider a counterclockwise rotation by angle α, which creates a new lattice point $\mathbf{1'}$. If this rotation is a symmetry operation of the lattice, then there must also be the corresponding clockwise (inverse) rotation. By applying the clockwise rotation at the neighboring lattice point **2**, the new lattice point $\mathbf{2'}$ is created, which creates a segment $\mathbf{1'}\cdots\mathbf{2'}$ that is parallel to the original line. For this new segment to be part of a 2-d lattice, the distance between points $\mathbf{1'}$ and $\mathbf{2'}$ must be an integer multiple of a. Using straightforward geometry, the allowed values of the angle α must satisfy the following relation:

$$1 + 2\cos\alpha = \text{integer}.$$

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[18] R.H.B. Mais, P.G. Owston, A.M. Wood, *Acta Cryst. Sect. B* **1972**, *28*, 393-399.

The only solutions are cos α = –1, –½, 0, ½, and 1. As a result, the values of α are limited to 180°, 120°, 90°, 60°, 0°, so that the rotational symmetries compatible with a lattice include just C_1, C_2, C_3, C_4, and C_6 and the corresponding improper rotations. In 3-d, these rotational symmetries together with translational periodicity can be combined to create *seven crystal systems*:

Crystal System	**Lattice Symmetry**		**Unit Cell Shape**	**Lattice Types (# Points)**
Triclinic	$\mathcal{C}_i$ - C_1 only		$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	*P* (1)
Monoclinic	$\mathcal{C}_{2h}$ - one C_2 axis (‖ ***b***)		$a \neq b \neq c$; $\alpha = \gamma = 90°$, $\beta \neq 90°$	*P* (1); *C* (2)
Orthorhombic	$\mathcal{D}_{2h}$ - three ⊥ C_2 axes		$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	*P* (1); *I* (2); *F* (4); *C* or *A* (2)
Tetragonal	$\mathcal{D}_{4h}$ - one C_4 axis (‖ ***c***)		$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	*P* (1); *I* (2)
Cubic	$\mathcal{O}_h$ - four C_3 axes		$a = b = c$; $\alpha = \beta = \gamma = 90°$	*P* (1); *I* (2); *F* (4)
Trigonal	$\mathcal{D}_{3d}$ - one C_3 axis	(‖ [111])	$a = b = c$; $\alpha = \beta = \gamma$	*R* (3)
		(‖ ***c***)	$a = b \neq c$; $\alpha = \beta = 90°$, $\gamma = 120°$	*P* (1)
Hexagonal	$\mathcal{D}_{6h}$ - one C_6 axis (‖ ***c***)		$a = b \neq c$; $\alpha = \beta = 90°$, $\gamma = 120°$	*P* (1)

The seven crystal systems lead to seven geometrically distinct unit cell shapes. The rotational symmetry of a crystal system restricts the relative lengths and angles of the unit cell. In the table, the symbol "≠" means that there is no restriction for the two quantities to be equal to one another, i.e., they may be equal, but not for any symmetry constraints. For example, the three sides of the unit cell of an orthorhombic unit cell are not restricted to being equal, but they are for a cubic unit cell. Some important features of the different unit cell shapes include:

(i) the trigonal system offers two unit cell shapes, one of which is identical to the shape of the hexagonal unit cell, so that these two lattices are the same;

(ii) the cubic cell and one of the trigonal unit cells are closely related to each other by having equal sides and equal angles; and

(iii) the orthorhombic, tetragonal, and cubic unit cell shapes have mutually perpendicular lattice vectors.

(13) The different shapes listed in the table can be *primitive unit cells*, which contain just one lattice point typically placed at the cell corners (8 unit cells meet at each corner and each unit cell has 8 corners). Primitive unit cells are the fundamental blocks of atoms that repeat periodically by the lattice vectors $[mnp] = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$ for any integers *m*, *n*, *p*. The lattices generated by these unit cell shapes, except for one of the trigonal system unit cells, are designated as *P* for *primitive* lattices.

Now, for a given crystal system, *are there any other Bravais lattices with distinct primitive unit cells that are compatible with the rotational symmetry of the system*? The answer is yes, because rotational symmetry axes of a lattice intersect not only the corners, but also the body- and face-centers of unit cells. Thus, new *centered lattices* arise when additional lattice points are placed at these centers in the unit cell shapes described above without destroying any rotational symmetry of the crystal system. As a result, the unit cell shape is retained because restrictions on the lattice parameters *a*, *b*, *c*; α, β, γ remain unchanged, but the number of lattice points assigned to this cell is now greater than one. Possible centered 3-d lattices include:

Body-centered (I) lattices contain 2 lattice points per unit cell, one at the corners [0 0 0] and one at the center [½ ½ ½] of each cell. Orthorhombic, tetragonal, and cubic systems allow I-centering.

Face-centered (F) lattices contain 4 lattice points per unit cell, one at the corners [0 0 0] and three at the centers of each set of parallel faces, i.e., [½ ½ 0], [½ 0 ½], and [0 ½ ½] of each cell. Orthorhombic and cubic systems allow F-centering.

Base-centered (A, B, C) lattices contain 2 lattice points per unit cell, one at the corners [0 0 0] and one at the centers of one set of parallel faces. The letter specifies which set of parallel faces contains lattice points: A-centered at [0 ½ ½] (***bc***-sides); B-centered at [½ 0 ½] (***ac***-sides); and C-centered at [½ ½ 0] (***ab***-sides). Monoclinic and orthorhombic systems allow base-centering.

Rhombohedral (R) lattices occur for the trigonal system and correspond to the primitive cell with equal unit cell lengths and angles ($a = b = c$ and $\alpha = \beta = \gamma$). When this cell is propagated throughout 3-d space, a cell containing 3 lattice points with lattice parameters $a' = b' \neq c'$ and $\alpha' = \beta' = 90°$, $\gamma' = 120°$ emerges. In addition to lattice points at the corners [0 0 0], there are two points at [⅔ ⅓ ⅓] and [⅓ ⅔ ⅔] inside this cell.

(14) As the table shows, not all centering options are possible for each crystal class because any centering must maintain the rotational symmetry of the system. In fact, there are no centered triclinic or hexagonal lattices. Within the cubic system, only face- (F) and body-centered (I) cubic lattices are allowed. Base-centering of a cubic cell destroys the cubic rotational symmetry because the three sets of parallel faces are no longer equivalent. Now, for every centered lattice, a primitive unit cell containing 1 lattice point can be identified. For the centered cubic lattices, the primitive cells have trigonal symmetry: $a_1 = a_2 = a_3$ and $\alpha_1 = \alpha_2 = \alpha_3$. If a = side of the centered cubic cell, then $a_1 = \sqrt{2}a/2$ and $\alpha_1 = 60°$ for the F-centered cell and $a_1 = \sqrt{3}a/2$ and $\alpha_1 = 109.5°$ for the I-centered cell. Furthermore, the volumes of the centered cells are integer multiples of these primitive cells by factors corresponding to the number of lattice points in the centered cell. Thus, an I-centered cell is 2× the volume of its primitive cell; a F-centered cell is 4× the volume of its primitive cell. By considering all primitive and possible centered lattices, there are 14 Bravais lattices in 7 crystal classes that account for all translational periodicities of crystalline solids.

(15) <u>Crystallographic Point Groups</u>: Rotational symmetries of molecules are identified by *point groups*, which contain all proper and improper rotations that keep a molecule invariant with respect to a fixed point in space. A *proper rotation* of order n is a counterclockwise rotation by angle $2\pi/n$ in the plane oriented perpendicular to its axis. When the rotation is carried out n times in succession, the outcome is the identity operation. An *improper rotation* is the combination of a proper rotation with either a reflection in the plane perpendicular to the rotation axis or with inversion. The different types of improper rotations create the fundamental difference between two symbolisms of point groups:

(a) *Schönflies notation*. A proper rotation by angle $2\pi/n$ is denoted as C_n, i.e., C_2, C_3, C_4, C_6, and $C_1 = E$, the identity. Improper rotations are *roto-reflections* $S_n = \sigma_h \cdot C_n$, which are n-fold proper rotations followed by reflection in the plane perpendicular to the rotation axis. Roto-reflections in crystals can include S_3, S_4, or S_6. The symbols S_1 and S_2 are not used. Instead, S_1 is a reflection σ and S_2 is the inversion i. Mirror planes perpendicular to the principal rotation axis of a point group are denoted by σ_h; mirror planes parallel to the principal axis are denoted by either σ_v or σ_d, depending on their orientations.

(b) *International* (*Hermann-Mauguin*) *notation*. A proper rotation by angle $2\pi/n$ is simply designated as n, i.e., 2, 3, 4, 6, with 1 = the identity. Improper rotations are *roto-inversions* $\bar{n} = \bar{1} \cdot n$, which are n-fold proper rotations followed by inversion = $\bar{1}$ (read "bar 1" or "1 bar"), and include $\bar{3}$, $\bar{4}$, and $\bar{6}$. The symbol $\bar{2}$ is not used and denotes a reflection. Reflections perpendicular to an n-fold principal axis are symbolized by n/m (read "n over m"), e.g., $2/m$; reflections parallel to a principal axis are simply denoted by m.

There are four distinct types of point groups, and the different notations are equivalent but prioritize different operations in their point group symbols:

(i) *Nonaxial* groups have no rotation or reflection symmetry. They are $\mathcal{C}_1 = 1$ and $\mathcal{C}_i = \bar{1}$.

(ii) *Uniaxial* groups have one n-fold symmetry axis. Schönflies symbols are $\mathcal{C}_n$, $\mathcal{C}_{nh}$, $\mathcal{C}_{nv}$, $\mathcal{C}_s$, or $\mathcal{S}_{2n}$. International symbols are n, n/m, nmm or nm, m, or $\bar{n}$. Examples include $\mathcal{C}_4 = 4$ (4-fold proper rotation), $\mathcal{C}_{2h} = 2/m$ (2-fold proper rotation with a perpendicular reflection), and $\mathcal{C}_{3v} = 3m$ (3-fold proper rotation with parallel reflections).

(iii) *Dihedral* groups have 2-fold axes perpendicular to a principal n-fold axis. Schönflies symbols are $\mathcal{D}_n$, $\mathcal{D}_{nh}$, or $\mathcal{D}_{nd}$. International symbols are $n22$ or $n2$, n/mmm, $\bar{n}2m$ or $\bar{n}m2$, or $\bar{n}m$. Examples include $\mathcal{D}_3 = 32$ (3-fold proper rotation with perpendicular 2-fold rotations), $\mathcal{D}_{4h} = 4/mmm$ (4-fold proper rotation with perpendicular and parallel reflections), and $\mathcal{D}_{3d} = \bar{3}m$ (3-fold improper rotation with perpendicular 2-fold rotations and parallel reflections).

(iv) *Polyhedral* groups have multiple n-fold rotations. They include the tetrahedral groups $\mathcal{T} = 23$, $\mathcal{T}_h = m\bar{3}$, $\mathcal{T}_d = \bar{4}3m$, the octahedral groups $\mathcal{O} = 432$, $\mathcal{O}_h = m\bar{3}m$, and the icosahedral groups $\mathcal{I} = 235$, $\mathcal{I}_h = m\bar{3}5$.

To illustrate how the two notations realize identical point groups, consider $\mathcal{D}_{2d} = \bar{4}2m$. The Schönflies symbol $\mathcal{D}_{2d}$ conveys the following information: a 2-fold proper rotation as the principal axis; two perpendicular 2-fold proper rotations; and reflections parallel to the first (principal) 2-fold axis and bisecting the other two 2-fold axes. These operations generate a total of 8 operations for this group. On the other hand, the International notation $\bar{4}2m$ indicates: a 4-fold improper rotation; two perpendicular 2-fold proper rotations; and two reflections parallel to the $\bar{4}$ axis and bisecting the 2-fold axes. These operations also generate a total of 8 operations of the group that are identical to the operations specified by $\mathcal{D}_{2d}$.

Every rotation except the identity and inversion is oriented by its axis. The axis for a reflection plane is perpendicular to the plane. The Schönflies symbol for any point group emphasizes the principal axis of an object and is well suited to describe the symmetry of gas- or solution-phase molecules, which are in constant motion. The corresponding International symbol includes symmetry-related information for directions in addition to the principal axis. Therefore, these symbols are ideal for crystals. In particular, the symbol $\bar{4}2m$ immediately identifies the "tetragonal" system by "$\bar{4}$". For a crystal, the $\bar{4}$-axis is along ***c***, 2-fold axes are along the equivalent ***a***- and ***b***-axes, and the reflections m are perpendicular to the ***a***+***b***- and ***a***–***b***-directions. It is possible that the orientations of the 2-fold axes and diagonal reflection planes could be switched in a crystal. The resulting International symbol is $\bar{4}m2$, but the Schönflies symbol remains $\mathcal{D}_{2d}$.

(16) The rotations compatible with translational periodicity generate 32 *crystallographic point groups* among the 7 crystal classes. For each crystallographic point group, the table includes (i) its Schönflies and International symbols; (ii) the unit cell directions corresponding to the sequence of rotation axes in the International symbol; (iii) the order of the group, which equals the number of symmetry operations; and (iv) some important characteristics:

Crystal System	Notation		Unit Cell Directions	Order	Characteristics
Triclinic	C_i	$\bar{1}$		2	Centrosymmetric
	C_1	1		1	Polar, Chiral
	There are no special directions, so only one symbol is needed.				
Monoclinic	C_{2h}	$2/m$	[010]	4	Centrosymmetric
	C_2	2		2	Polar, Chiral
	C_s	m		2	Polar
	One symbol for the single 2-fold axis along $\boldsymbol{b}$. Some older literature may assign this axis to $\boldsymbol{c}$.				
Orthorhombic	D_{2h}	mmm	[100][010][001]	8	Centrosymmetric
	D_2	222		4	Chiral
	C_{2v}	$mm2$, $m2m$, $2mm$		4	Polar
	Three symbols for each of the mutually perpendicular 2-fold axes along $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, respectively.				
Tetragonal	D_{4h}	$4/mmm$	[001]{100}{110}	16	Centrosymmetric
	D_4	422		8	Chiral
	C_{4v}	$4mm$		8	Polar
	D_{2d}	$\bar{4}2m$, $\bar{4}m2$		8	
	C_{4h}	$4/m$	[001]	8	Centrosymmetric
	S_4	$\bar{4}$		4	
	C_4	4		4	Polar, Chiral
	1st symbol for the 4-fold axis along $\boldsymbol{c}$; 2nd symbol for 2-fold axes along equivalent $\boldsymbol{a}$ and $\boldsymbol{b}$ {100} = [100] and [010]; 3rd symbol for 2-fold axes along equivalent $\boldsymbol{a}+\boldsymbol{b}$ and $\boldsymbol{a}-\boldsymbol{b}$ {110} = [110] and [$1\bar{1}0$]. Point groups below the dashed line have no symmetry axes perpendicular to $\boldsymbol{c}$.				
Trigonal	D_{3d}	$\bar{3}m$, $\bar{3}m1$, $\bar{3}1m$	[001]{100}{210}	12	Centrosymmetric
	D_3	32, 321, 312		6	Chiral
	C_{3v}	$3m$, $3m1$, $31m$		6	Polar
	S_6	$\bar{3}$	[001]	6	Centrosymmetric
	C_3	3		3	Polar, Chiral
	1st symbol for the 3-fold axis along $\boldsymbol{c}$; 2nd symbol for axes along equivalent $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{a}+\boldsymbol{b}$ {100} = [100], [010], and [110]; 3rd symbol for axes along equivalent $2\boldsymbol{a}+\boldsymbol{b}$, $\boldsymbol{a}+2\boldsymbol{b}$, and $\boldsymbol{a}-\boldsymbol{b}$ {210} = [210], [120], and [$1\bar{1}0$]. For point groups above the dashed line, the 2-fold axes have one of two possible orientations. The symbols $\bar{3}m$, 32, and $3m$ are used for rhombohedral lattices. Point groups below the dashed line have no symmetry axes perpendicular to $\boldsymbol{c}$.				

Table continued on the next page…

Crystal System	Notation		Unit Cell Directions	Order	Characteristics
Hexagonal	$\mathcal{D}_{6h}$	$6/mmm$	[001]{100}{210}	24	Centrosymmetric
	$\mathcal{D}_6$	622		12	Chiral
	$\mathcal{C}_{6v}$	$6mm$		12	Polar
	$\mathcal{D}_{3h}$	$\bar{6}2m$, $\bar{6}m2$		12	
	$\mathcal{C}_{6h}$	$6/m$	[001]	12	Centrosymmetric
	$\mathcal{C}_{3h}$	$\bar{6}$		6	
	$\mathcal{C}_6$	6		6	Polar, Chiral

1st symbol for the 6- or $\bar{6}$-fold axis along $\boldsymbol{c}$; 2nd symbol for axes along equivalent $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{a}+\boldsymbol{b}$ {100} = [100], [010], and [110]; 3rd symbol for axes along equivalent $2\boldsymbol{a}+\boldsymbol{b}$, $\boldsymbol{a}+2\boldsymbol{b}$, and $\boldsymbol{a}-\boldsymbol{b}$ {210} = [210], [120], and [$1\bar{1}0$]. Point groups below the dashed line have no symmetry axes perpendicular to $\boldsymbol{c}$.

Crystal System	Notation		Unit Cell Directions	Order	Characteristics
Cubic	$\mathcal{O}_h$	$m\bar{3}m$	{100}{111}{110}	48	Centrosymmetric
	$\mathcal{O}$	432		24	Chiral
	$\mathcal{T}_d$	$\bar{4}3m$		24	
	$\mathcal{T}_h$	$\bar{m}3$	{100}{111}	24	Centrosymmetric
	$\mathcal{T}$	23		12	Chiral

1st symbol for axes along equivalent $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ {100} = [100], [010], and [001]; 2nd symbol for 3-fold axes along equivalent body-diagonals {111} = [111], [$11\bar{1}$], [$1\bar{1}1$], and [$\bar{1}11$]; 3rd symbol for 2-fold axes along equivalent face-diagonals {110} = [110], [101], [011], [$1\bar{1}0$], [$10\bar{1}$], and [$01\bar{1}$]. Point groups below the dashed line have no symmetry axes along the face-diagonals of a cube.

Two physical significances of these point groups are that as a single crystalline domain grows, its shape will adopt one of these point symmetries and its physical properties will conform to the same point symmetry. Some additional information about these point groups include:

Subgroups: The different chemical structures that arise during a phase transition often follow a *group-subgroup relationship*. Common examples of group-subgroup relationships for molecules include:

(a) $\mathcal{I}_h$ (icosahedron) → $\mathcal{T}_h$ (highest order subgroup allowed in 3-d crystals);

(b) $\mathcal{O}_h$ (octahedron) → $\mathcal{D}_{4h}$ or $\mathcal{D}_{3d}$ (distortions of an octahedral complex either along trans-ligand directions or opposite faces); and

(c) $\mathcal{T}_d$ (tetrahedron) → $\mathcal{D}_{2d}$ or $\mathcal{C}_{3v}$.

In the table for each crystal system, the point groups are listed from highest order to lower order subgroups. The highest order point group in each crystal system is called the *holohedral* symmetry and represents the symmetry of the Bravais lattice.

Characteristics: Of the 32 crystallographic point groups, 11 are *centrosymmetric* because they include inversion symmetry and the remaining 21 groups without inversion are *noncentrosymmetric*. The 11 centrosymmetric groups are significant for diffraction experiments because coherent diffraction patterns of any crystal always appear centrosymmetric about an origin point, which coincides with the undiffracted beam of X-rays, neutrons, or electrons incident on the specimen. This characteristic of diffraction patterns occurs whether or not the overall crystal structure has inversion symmetry. These point groups constitute the 11 possible *Laue classes* observed by diffraction experiments.

Noncentrosymmetric point groups can be assigned to molecules that are *chiral* or *polar*. Chiral point groups do not contain any improper rotations, which include inversion, reflection planes, and all other roto-inversions (or roto-reflections). Polar point groups have no unique center and a single symmetry axis. The groups of pure rotations $\mathcal{C}_1$, $\mathcal{C}_2$, $\mathcal{C}_3$, $\mathcal{C}_4$, and $\mathcal{C}_6$ are both chiral and polar, whereas the groups $\mathcal{D}_{2d}$, $\mathcal{S}_4$, $\mathcal{D}_{3h}$, $\mathcal{C}_{3h}$, and $\mathcal{T}_d$ are neither chiral nor polar because they contain even-order roto-inversions $\bar{4}$ or $\bar{6}$.

(17) If crystalline structures are noncentrosymmetric, then some interesting and useful properties can emerge. The Venn diagram summarizes four important characteristics derived from the lack of an inversion symmetry in crystals:[19,20]

Enantiomorphic (*Chiral*) crystals can rotate plane-polarized light by equal and opposite amounts, called optical activity. There are 11 chiral point groups: 1, 2, 3, 4, 6, 222, 422, 32, 622, 23, and 432. Chiral structures like α-SiO_2 (*R*-quartz and *L*-quartz) have left-handed and right-handed versions. With respect to symmetry operations, there are no roto-inversions ($\bar{n}$) or roto-reflections (S_n) in the point group, but only proper rotations. The remaining 21 crystallographic point groups are *achiral*.

Polar (*Pyroelectric*) crystals exhibit dipole moments by allowing for separation of the centers of positive and negative charges under an applied electric field. There are 10 polar point groups: 1, 2, 3, 4, 6, m, $mm2$, $4mm$, $3m$, and $6mm$. Polar structures, like the distorted perovskite-type structures of $BaTiO_3$ and $LiNbO_3$, have a single symmetry axis and no unique origin point. The 5 crystallographic point groups 1, 2, 3, 4, and 6 are both chiral and polar. Polar space groups can allow or enhance properties such as pyroelectricity and ferroelectricity.

Piezoelectric crystals generate an electric charge in response to mechanical stress such as compression. Of the 21 noncentrosymmetric crystallographic point groups, only the cubic point group 432 does not allow piezoelectricity. A similar restriction occurs for *second harmonic generation* (SHG), which is a nonlinear optical process when two photons with the same frequency generate a new photon with twice the frequency (frequency-doubling).

Circular Dichroism is the differential absorption of left- and right-handed (circularly) polarized light. Materials adopting one of the 15 point groups 1, 2, 3, 4, 6, 222, 422, 32, 622, 23, 432, $\bar{4}$, m, $mm2$, and $\bar{4}2m$ are capable of this behavior.

(18) Space groups are sets of symmetry operations formed by the product of two subsets: (1) the Bravais lattice, which describes translational symmetry; and (2) *essential symmetry operations*, which describe rotational symmetry of the entire crystalline structure. The set of essential symmetry operations either is identical to or resembles one of the 32 crystallographic point groups. These combinations of translational and rotational symmetry operations generate 230 3-d space groups, which are the possible ways to describe the symmetry of crystal structures. The types of symmetry operations allowed in space groups include:

(a) Bravais lattice translations. This set is a subgroup of every space group.

(b) Proper rotations 1, 2, 3, 4, 6 or improper rotations $\bar{1}$, m, $\bar{3}$, $\bar{4}$, $\bar{6}$.

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[19] P.S. Halasyamani, K.R. Poeppelmeier, *Chem. Mater.* **1998**, *10*, 2753-2769.
[20] K.M. Ok, E.O. Chi, P.S. Halasyamani, *Chem. Soc. Rev.* **2006**, *35*, 710-717.

(c) *Screw rotations* are n-fold proper rotations followed by displacements that are fractions m/n ($m < n$) of the lattice vector directed parallel to the rotation axis. There are 11 possible screw rotations (n_m) in crystals, designated as 2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5.

(d) *Glide reflections* are reflections followed by a displacement that is one-half a lattice vector directed parallel to the plane. There are 3 types of glide reflections, designated as axial (a, b, c), diagonal (n), or diamond (d) glides. The letter of an axial glide identifies the displacement direction.

The notation for a space group involves combining the lattice type (primitive or centered: *P*, *I*, *F*, *A*, *B*, *C*, or *R*) with symbols related to the crystallographic point group, such as $I4/mmm$ and $P4_2/mnm$. If the set of essential symmetry operations is exactly one of the crystallographic point groups, then the space group is *symmorphic*, and the point group symbol appears unchanged in the space group symbol, as for $I4/mmm$. If the set of essential symmetry operations is not a group, then the space group is *nonsymmorphic*, and the space group symbol will include a screw rotation, a glide plane, or both, such as $P4_2/mnm$, which contains a 4_2 screw rotation with respect to the ***c***-axis and diagonal n-glide planes perpendicular to the ***a***- and ***b***-axes. Of the 230 3-d space groups, 73 are symmorphic and 157 are nonsymmorphic.

The *point group of the space group* describes the symmetry characteristics of all macroscopic properties of a crystal. It is determined from the second part of the space group symbol by replacing all screw rotations n_m by their proper rotations n and glide planes by mirrors "m". Thus, the point group of $P4_2/mnm$ is $4/mmm$ (4_2 is replaced by 4; n is replaced by m) or $\mathcal{D}_{4h}$. Therefore, the symmorphic space group $I4/mmm$ belongs to the tetragonal crystal class, involves a body-centered lattice, and has overall point symmetry $\mathcal{D}_{4h}$. The nonsymmorphic space group $P4_2/mnm$ also belongs to the tetragonal crystal class, involves a primitive lattice, and also has overall point symmetry $\mathcal{D}_{4h}$.

The standard symbols of the 230 3-d space groups are listed below, separated by their crystal classes and crystallographic point groups. Symmorphic groups are designated in red.

Triclinic System (2 space groups)

1 ($\mathcal{C}_1$)	$P1$
$\bar{1}$ ($\mathcal{C}_i$)	$P\bar{1}$

- No special symmetry other than possible inversion centers.
- $P\bar{1}$ is among the most populous space groups for crystals that have been characterized.

Monoclinic System (13 space groups)

2 ($\mathcal{C}_2$)	$P2$	$P2_1$	$C2$			
m ($\mathcal{C}_s$)	Pm	Pc	Cm	Cc		
$2/m$ ($\mathcal{C}_{2h}$)	$P2/m$	$P2_1/m$	$P2/c$	$P2_1/c$	$C2/m$	$C2/c$

- Standard convention assigns the 2-fold axis parallel to ***b***.
- $P2_1/c$ is among the most populous space groups for crystals that have been studied because it describes the pattern for effective packing of ellipsoids, which roughly model many molecular structures.

Orthorhombic System (59 space groups)

222 ($\mathcal{D}_2$)	$P222$	$P222_1$	$P2_12_12$	$P2_12_12_1$	$C222$	$C222_1$	$F222$
	$I222$	$I2_12_12_1$					
$mm2$ ($\mathcal{C}_{2v}$)	$Pmm2$	$Pmc2_1$	$Pcc2$	$Pma2$	$Pca2_1$	$Pnc2$	$Pmn2_1$
	$Pba2$	$Pna2_1$	$Pnn2$	$Cmm2$	$Cmc2_1$	$Ccc2$	$Amm2$
	$Aem2$	$Ama2$	$Aea2$	$Fmm2$	$Fdd2$	$Imm2$	$Iba2$
	$Ima2$						

mmm ($\mathcal{D}_{2h}$)	$Pmmm$	$Pnnn$*	$Pccm$	$Pban$*	$Pmma$	$Pnna$	$Pmna$
	$Pcca$	$Pbam$	$Pccn$	$Pbcm$	$Pnnm$	$Pmmn$*	$Pbcn$
	$Pbca$	$Pnma$	$Cmmm$	$Cmcm$	$Cmce$	$Cccm$	$Cmme$
	$Ccce$*	$Fmmm$	$Fddd$*	$Immm$	$Ibam$	$Ibca$	$Imma$

- Assignments of ***a***-, ***b***-, and ***c***-axes can be arbitrary, which leads to other equivalent space group symbols, e.g., $Pm2m$ and $P2mm$ for $Pmm2$.
- A standard orientation of axes is right-handed, so that the direction of ***a*** × ***b*** matches the ***c***-direction; a left-handed orientation would have the direction of ***a*** × ***b*** along the –***c***-direction.
- The symbol "e" in some space groups stands for axial glide reflections along two different directions, e.g., $Ccce$ means that a-glides and b-glides occur with respect to the ***c***-axis.
- The 5 starred space groups have 2 origin settings (see slide **#24**).

Tetragonal System (68 space groups)

4 ($\mathcal{C}_4$)	$P4$	$P4_1$	$P4_2$	$P4_3$	$I4$	$I4_1$	
$\bar{4}$ ($\mathcal{S}_4$)	$P\bar{4}$	$I\bar{4}$					
$4/m$ ($\mathcal{C}_{4h}$)	$P4/m$	$P4_2/m$	$P4/n$*	$P4_2/n$*	$I4/m$	$I4_1/a$*	
422 ($\mathcal{D}_4$)	$P422$	$P42_12$	$P4_122$	$P4_12_12$	$P4_222$	$P4_22_12$	$P4_322$
	$P4_32_12$	$I422$	$I4_122$				
$4mm$ ($\mathcal{C}_{4v}$)	$P4mm$	$P4bm$	$P4_2cm$	$P4_2nm$	$P4cc$	$P4nc$	$P4_2mc$
	$P4_2bc$	$I4mm$	$I4cm$	$I4_1md$	$I4_1cd$		
$\bar{4}2m$ ($\mathcal{D}_{2d}$)	$P\bar{4}2m$	$P\bar{4}2c$	$P\bar{4}2_1m$	$P\bar{4}2_1c$	$P\bar{4}m2$	$P\bar{4}c2$	$P\bar{4}b2$
	$P\bar{4}n2$	$I\bar{4}2m$	$I\bar{4}2d$	$I\bar{4}m2$	$I\bar{4}c2$		
$4/mmm$ ($\mathcal{D}_{4h}$)	$P4/mmm$	$P4/mcc$	$P4/nbm$*	$P4/nnc$*	$P4/mbm$	$P4/mnc$	$P4/nmm$*
	$P4/ncc$*	$P4_2/mmc$	$P4_2/mcm$	$P4_2/nbc$*	$P4_2/nnm$*	$P4_2/mbc$	$P4_2/mnm$
	$P4_2/nmc$*	$P4_2/ncm$*	$I4/mmm$	$I4/mcm$	$I4_1/amd$*	$I4_1/acd$*	

- The 4- or $\bar{4}$-axis is parallel to ***c***.
- Space groups with the point group $\mathcal{D}_{2d}$ have two distinct settings according to the orientations of the 2-fold axes and vertical mirror planes with respect to lattice vectors in the ***ab***-plane.
- The 13 starred space groups have 2 origin settings (see slide **#24**).

Trigonal System (25 space groups)

3 ($\mathcal{C}_3$)	$P3$	$P3_1$	$P3_2$	$R3$			
$\bar{3}$ ($\mathcal{S}_6$)	$P\bar{3}$	$R\bar{3}$					
32 ($\mathcal{D}_3$)	$P321$	$P3_121$	$P3_221$	$P312$	$P3_112$	$P3_212$	$R32$
$3m$ ($\mathcal{C}_{3v}$)	$P3m1$	$P3c1$	$P31m$	$P31c$	$R3m$	$R3c$	
$\bar{3}m$ ($\mathcal{D}_{3d}$)	$P\bar{3}m1$	$P\bar{3}c1$	$P\bar{3}1m$	$P\bar{3}1c$	$R\bar{3}m$	$R\bar{3}c$	

- The 3- or $\bar{3}$-axis **i**s parallel to ***c***.
- Space groups with the point groups $\mathcal{D}_{3d}$ and $\mathcal{C}_{3v}$ have two distinct settings according to the orientations of the vertical mirror planes with respect to lattice vectors in the ***ab***-plane.

Hexagonal System (27 space groups)

6 ($\mathcal{C}_6$)	$P6$	$P6_1$	$P6_2$	$P6_3$	$P6_4$	$P6_5$
$\bar{6}$ ($\mathcal{C}_{3h}$)	$P\bar{6}$					
$6/m$ ($\mathcal{C}_{6h}$)	$P6/m$	$P6_3/m$				
622 ($\mathcal{D}_6$)	$P622$	$P6_122$	$P6_222$	$P6_322$	$P6_422$	$P6_522$
$\bar{6}m2$ ($\mathcal{D}_{3h}$)	$P\bar{6}m2$	$P\bar{6}c2$	$P\bar{6}2m$	$P\bar{6}2c$		
$6/mmm$ ($\mathcal{D}_{6h}$)	$P6/mmm$	$P6/mcc$	$P6_3/mcm$	$P6_3/mmc$		

- The ***c***-axis as parallel to the 6- or $\bar{6}$-axis.
- Space groups with the point group $\mathcal{D}_{3h}$ have two distinct settings according to the orientations of the 2-fold axes and the vertical mirror planes with respect to lattice vectors in the ***ab***-plane.
- Hexagonally closed packed (*hcp*) metals adopt the space group $P6_3/mmc$.

Cubic System (36 space groups)							
23 ($\mathcal{T}$)	$P23$	$P2_13$	$F23$	$I23$	$I2_13$		
$m\bar{3}$ ($\mathcal{T}_h$)	$Pm\bar{3}$	$Pn\bar{3}$*	$Pa\bar{3}$	$Fm\bar{3}$	$Fd\bar{3}$*	$Im\bar{3}$	$Ia\bar{3}$
$\bar{4}3m$ ($\mathcal{T}_d$)	$P\bar{4}3m$	$P\bar{4}3n$	$F\bar{4}3m$	$F\bar{4}3c$	$I\bar{4}3m$	$I\bar{4}3d$	
432 ($\mathcal{O}$)	$P432$	$P4_132$	$P4_232$	$P4_332$	$F432$	$F4_132$	$I432$
	$I4_132$						
$m\bar{3}m$ ($\mathcal{O}_h$)	$Pm\bar{3}m$	$Pn\bar{3}n$*	$Pm\bar{3}n$	$Pn\bar{3}m$*	$Fm\bar{3}m$	$Fm\bar{3}c$	$Fd\bar{3}m$*
	$Fd\bar{3}c$*	$Im\bar{3}m$	$Ia\bar{3}d$				

- The 6 starred space groups have 2 origin settings.
- Cubic closed packed (*ccp*) metals adopt the space group $Fm\bar{3}m$.
- Body-centered cubic (*bcc*) metals adopt the space group $Im\bar{3}m$.
- The diamond structure (C, Si, Ge, and Sn) adopts the space group $Fd\bar{3}m$.
- The 6 starred space groups have 2 origin settings (see slide **#24**).

The characteristics of the crystallographic point groups influence the characteristics of the corresponding space groups. Among the 230 3-d space groups, 92 are centrosymmetric and 138 are noncentrosymmetric. Among the 138 noncentrosymmetric space groups, there are 65 chiral groups and 68 polar groups. As mentioned above, these symmetry characteristics influence the properties of crystals adopting these space groups, e.g., chiral crystals can rotate plane polarized light and polar crystals can exhibit spontaneous electrical polarization (ferroelectricity).

(19) *Screw Rotations:* The general symbol for a screw rotation is n_m, which means a proper rotation by $2\pi/n$ followed by a displacement of m/n units along the lattice vector parallel to the rotation axis. Neither the rotation nor the displacement is a symmetry operation, but the combination is. The subscript m is any one of the nonzero integers less than n. For example, there are three possible fourfold screw rotations 4_1, 4_2, and 4_3. For tetragonal crystals, the rotation axis is parallel to $\boldsymbol{c}$. The 4_1 operation is a C_4 rotation (ccw rotation by $2\pi/4 = 90°$) followed by displacement of $\boldsymbol{c}/4$. Doing the 4_1 operation a second time, denoted by 4_1^2, completes a $C_2 = C_4^2$ ccw rotation by 180° and a net displacement of $2\boldsymbol{c}/4 = \boldsymbol{c}/2$. Four consecutive 4_1 operations yield a shift by the lattice translation $\boldsymbol{c}$. The 4_3 operation is a C_4 rotation followed by displacement of $3\boldsymbol{c}/4$. It turns out that 4_1 and 4_3 screw rotations are enantiomorphic because they are related to each other by a mirror plane parallel to the rotation axis. The 4_1 operation is a right-handed screw whereas the 4_3 operation is a left-handed screw. Lastly, the 4_2 operation is a C_4 rotation followed by displacement by $2\boldsymbol{c}/4 = \boldsymbol{c}/2$. In a space group symbol, the screw rotation is placed in the position that corresponds to the direction(s) of the rotation axis/axes.

(20) *Glide Reflections:* Three distinct types of glide reflections differ according to the displacement after reflection. Axial glides (*a*, *b*, or *c*) involve displacements parallel to one of the unit cell sides. For example, an *a*-glide is a reflection followed by a displacement of $\boldsymbol{a}/2$, so the lattice vector $\boldsymbol{a}$ must be parallel to the mirror plane. Diagonal glides (*n*) involve displacements along a face-diagonal direction of the unit cell. Lastly, diamond glides (*d*) resemble diagonal glides but occur only for face- and body-centered lattices.

In a space group symbol, the orientation of the mirror plane is specified by its position in the space group symbol. For example, in $Pmmm$, there are three sets of parallel mirror planes each perpendicular to the unit cell vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$. On the other hand, the space group $Pnma$ contains two glide reflections among the set of essential symmetry operations. There are axial a-glide planes oriented perpendicular to the $\boldsymbol{c}$-axis and diagonal *n*-glide planes oriented perpendicular to the $\boldsymbol{a}$-axis. The displacement of the *n*-glides proceeds along the face-diagonal vector $(\boldsymbol{b}+\boldsymbol{c})/2$.

(21) The International Tables of Crystallography, Volume 1 comprehensively summarizes the information about space groups that is useful for structure determination and analysis. Each of the 230 3-d space groups gets at least 2 pages. On the first page you typically find:

(a) the space group symbol in both International and Schönflies notations.
(b) the point group of the space group.
(c) the crystal system.
(d) a graphical display of symmetry operations in the unit cell.
(e) a listing of essential symmetry operations and lattice origin.

Also on this page, there is often information about certain types of subgroups and supergroups. On the second page you find:

(f) a list of generators, which are the symmetry operations that, when combined, create the entire space group.
(g) various positions separated by their equivalences, called Wyckoff sites. Each Wyckoff site is designated by a number and a letter. The number is the site multiplicity, which equals the number of different positions in one unit cell. They are listed in reverse alphabetically from top-to-bottom according to decreasing order of the point group symmetry for the sites.
(h) conditions for observable intensities of peaks in diffraction experiments.
(i) symmetry of certain 2-d projections (2-d plane groups).

The information for the various Wyckoff positions is the most important aspect of this table concerning structure and stoichiometry. The *general* site is listed first, followed by sites that fall on any rotation axes or reflection planes. These latter sites are called *special positions*. The list ends with the Wyckoff "*a*" site, which has the highest point symmetry of any site in the crystal. For symmorphic space groups, the point symmetry of the "*a*" site is the point group of the space group; for nonsymmorphic space groups, the corresponding point symmetry is a subgroup of the point group of the space group. The point symmetry of all general sites is completely asymmetric, i.e., $1 = C_1$, because no symmetry elements intersect these positions. As a result, the multiplicity of any general position is the highest in the unit cell and equals the product of the order of the point group of the space group with the number of lattice points per unit cell.

(22) As an example of using the International Tables for structure analysis, consider K_2PtCl_4. The relevant information, which would be given in any published report of its crystal structure, includes

Space group: $P4/mmm$;
Lattice constants: a = 7.028(3) Å, c = 4.144(1) Å;
Asymmetric unit: Pt(1a) = (0, 0, 0); K(2e) = (0, ½, ½); and Cl(4j) = (0.2324(1), 0.2324(1), 0).

The crystal structure is tetragonal, and the unit cell shape is a = b = 7.028(3) Å, c = 4.144(1) Å, with angles α = β = γ = 90°. The asymmetric unit identifies the atoms and their fractional coordinates in one unit cell that will generate the entire crystal structure when every space group operation is applied to each atomic site. Therefore, only the first position of any specific Wyckoff site is given. In K_2PtCl_4, all atoms lie on special positions of $P4/mmm$. The coordinates for the Pt and K atoms are fixed, but the $4j$ Cl sites (x, x, 0) allow one free parameter, which has an experimental uncertainty. Therefore, one unit cell of K_2PtCl_4 contains

1 Pt atom at (0, 0, 0),

2 K atoms at (0, ½, ½) and (½, 0, ½), and

4 Cl atoms at (0.2324(1), 0.2324(1), 0), (–0.2324, –0.2324, 0), (–0.2324, 0.2324, 0), and (0.2324, –0.2324, 0).

The empirical formula K_2PtCl_4 is the chemical formula of one unit cell.

The point symmetries of each site are $4/mmm = \mathcal{D}_{4h}$ for Pt, $mmm. = \mathcal{D}_{2h}$ for K, and $m.2m = \mathcal{C}_{2v}$ for Cl. Why do the International point group symbols for the 2*e* and 4*j* sites contain a "."? The point group for a given Wyckoff site is assigned by identifying the rotation axes and reflection planes that intersect at the site. For the K atom at the location (0, ½, ½), the intersecting symmetry elements include the reflection plane perpendicular to ***c*** (the first "*m*" in $4/mmm$) and the planes perpendicular to the ***a***- and ***b***-axes (the second "*m*" in $4/mmm$). No operations oriented with respect to the diagonal directions (the third "*m*" in $4/mmm$) intersect this site, and this is indicated by the "." at the end of the symbol "$mmm.$". Likewise, the point group $m.2m$ of the Cl atom at $(x, x, 0)$ arises from the reflection plane perpendicular to ***c*** (the first "*m*"), the mirror plane perpendicular to ***a***+***b*** (the last "*m*"), and the resulting 2-fold rotation with an axis along ***a***+***b*** (the "2"). This point symmetry contains no elements with axes parallel to ***a*** and ***b***, so the "." occurs at the second position: "$m.2m$".

All other atoms of the ideal crystal structure are generated by adding the primitive lattice vectors $m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$ (m, n, p = integers) to the sites listed above. To obtain details of the complete crystal structure, the unit cell parameters provide the length scales and angles so that local environments can be determined. In the structure of K_2PtCl_4, each Pt atom is square planar coordinated by Cl atoms with 4 Pt–Cl distances of 2.310(1) Å. Each K atom is surrounded by 8 Cl atoms in a distorted square prism ("cube") with a K–Cl distance of 3.240(1) Å. Furthermore, the structure consists of two different atomic (001) planes, i.e., planes perpendicular to ***c***: (i) at z = 0 are planes of $[PtCl_4]^{2-}$ square-planar complexes; (ii) at z = ½ are square nets of K^+ ions.

(23) PROBLEM: A compound of Cr and O adopts the space group $P4_2/mnm$ and has the asymmetric unit, Cr at (0, 0, 0) and O at (0.302, 0.302, 0).

- What is the empirical formula of this compound?

  We must compare the coordinates of the sites in the asymmetric unit to expressions in the listing of Wyckoff sites. The Cr site of (0, 0, 0) is the origin, so it will be at or near the bottom of the list: it is site 2*a*. The O site of (0.302, 0.302, 0) has $x = y$ and $z = 0$, so we must search for the coordinate "$x, x, 0$", which is seen for site 4*f*.

  Therefore, the unit cell is Cr_2O_4, so the empirical formula is $\mathbf{CrO_2}$.

- What are the point symmetries for each atom?

  Cr = 2*a*, point symmetry is $m.mm = \boldsymbol{\mathcal{D}_{2h}}$;
  O = 4*f*, point symmetry is $m.2m = \boldsymbol{\mathcal{C}_{2v}}$.

The structure of CrO_2 belongs to the rutile-type with Pearson symbol *tP*6.[21] The space group $P4_2/mnm$ is nonsymmorphic. Therefore, the point symmetry at lattice points (Wyckoff site 2*a*) is just $m.mm = \mathcal{D}_{2h}$. Drawing the structure over several unit cells shows that each Cr atom is coordinated by a distorted octahedron of O atoms and each O atom is coordinated by a nearly trigonal plane of Cr atoms.

[21] J.K. Burdett, G.J. Miller, J.W. Richardson, J.V. Smith, *J. Am. Chem. Soc.* **1988**, *110*, 8064-8071.

- The lattice parameters of CrO_2 are $a = 4.416$ Å and $c = 2.916$ Å. What is the density (in g/cm^3)? For a unit cell with lattice constants a, b, c; α, β, γ, the volume is

$$V_{\text{cell}} = abc\sqrt{1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma}.$$

The density of any crystalline solid is evaluated by determining the mass of atoms in one unit cell (in g) and the volume of one unit cell (in cm^3):

Mass of Cr_2O_4 = (2·52.00 g/mol + 4·16.00 g/mol) / (6.022 × 10^{23} atoms/mol) = 2.7898 × 10^{-22} g.
Volume of one unit cell = $a \times a \times c$ = (4.416 Å)^2(2.916 Å) · (1 cm/10^8 Å)^3 = 5.6865 × 10^{-23} cm^3.

Density = Mass of Cr_2O_4 / Volume of one unit cell
= (2.7898 × 10^{-22} g) / (5.6865 × 10^{-23} cm^3) = **4.906 g/cm^3**.

Is this answer a reasonable value? The room temperature densities of water and liquid mercury are, respectively, 1.00 g/cm^3 and 13.5 g/cm^3. Therefore, most solids will have densities within this range, so the calculated density of CrO_2 is reasonable.

PRACTICE PROBLEM: The crystal structure of a compound of W, V, and O also adopts the space group $P4_2/mnm$ and has the asymmetric unit, W at (0, 0, 0), V at (0, 0, 0.33), and two O sites, one at (0.29, 0.29, 0) and the other at (0.31, 0.31, 0.33). What is the empirical formula?

W occupies the 2*a* sites (0, 0, 0), V occupies the 4*e* sites (0, 0, *z*), one set of O occupies the 4*f* sites (*x*, *x*, 0), and the other set of O occupies the 8*j* sites (*x*, *x*, *z*). Thus, the stoichiometry of one unit cell is $W_2V_4O_{4+8} = W_2V_4O_{12}$, which gives the empirical formula $\mathbf{WV_2O_6}$.

(24) Among the 68 *nonsymmorphic*, *centrosymmetric* space groups, the highest point symmetry usually includes inversion and occurs at the origin (0, 0, 0). However, 24 of these types of space groups have two "origin settings" in the International Tables because there are two distinct ways to place the origin: one with the overall highest point symmetry; the other with the highest point symmetry including inversion. One important example is $Fd\bar{3}m$, which is the space group of diamond-type structures. The first origin setting is noncentrosymmetric $\mathcal{T}_d = \bar{4}3m$ (order = 24); the second origin setting is centrosymmetric $\mathcal{D}_{3d} = \bar{3}m$ (order = 12). In a structure description of silicon, Si atoms occupy the Wyckoff 8*a* sites. However, depending on which origin setting you use, the coordinates are not necessarily (0, 0, 0). If you are not careful to assign the correct origin setting, the structural depiction of diamond-type Si will be very different!

(25) Group-Subgroup Relationships: An important section of the International Tables for each space group lists certain maximal subgroups and minimal supergroups. These groups, which are derived by either removing or adding operations to the given space group, can be especially useful for analyzing solid-solid phase transitions during temperature or pressure changes. In particular, a maximal subgroup $\mathcal{G}$ of a group $\mathcal{G}_0$ generally arises by removing a single class of operations from $\mathcal{G}_0$. For example, if inversion or a reflection is removed, the resulting maximal subgroups $\mathcal{G}$ have one-half the number of operations of $\mathcal{G}_0$. Since space groups consist of translations and rotations, maximal subgroups belong to two major types:

Type I: *Translation-equivalent* (*Translationengleiche*) subgroups retain all translations but lower the order of the point group of the space group. This action may or may not retain the crystal system. An example occurs for $CaCl_2$.[22] High-temperature $CaCl_2$ is tetragonal, rutile-type with space group $P4_2/mnm$. As temperature decreases, $CaCl_2$ becomes orthorhombic, space group *Pnnm*, by "losing" the 4_2 and diagonal *m* operations. Translational periodicity does not change although the lengths of ***a*** and ***b*** become unequal as the crystal system changes. The 3-fold coordination of

[22] C.J. Howard, B.J. Kennedy, C. Curfs, *Phys. Rev. B* **2005**, *72*, 214114.

Cl atoms by Ca in high-temperature $CaCl_2$ is planar, and it is slightly pyramidal in the low-temperature form. During the transition, the Ca atoms remain octahedrally coordinated by Cl.

Type II: *Class-equivalent* (*Klassengleiche*) subgroups preserve the point group of the space group while some lattice translations are lost and belong to one of three subdivisions:

(IIa) These subgroups arise by removing all lattice centering translations. One example occurs during atomic ordering in β-CuZn as temperature drops. According to neutron diffraction experiments, high-temperature CuZn is a BCC-packing of completely disordered Cu and Zn atoms with space group $Im\overline{3}m$. Low-temperature CuZn has ordered Cu and Zn atoms in space group $Pm\overline{3}m$.

(IIb) These subgroups arise by losing lattice periodicities along specific directions. For example, at low pressure, the space group of $YbGa_2$ is $P6_3/mmc$ with its unit cell containing "Yb_2Ga_4" and 2 Yb planes along $\boldsymbol{c}$. $YbGa_2$ transforms on increasing pressure to space group $P6/mmm$ with a unit cell containing "$YbGa_2$" and 1 Yb plane along $\boldsymbol{c}$.[23] During the transformation from high pressure to low pressure, one-half of the lattice translations along $\boldsymbol{c}$ are lost.

(IIc) These subgroups resemble those of type IIb, for which some lattice translations are lost, but the space group remains unchanged. For example, the space group for rutile-type structures, $P4_2/mnm$, has only Type IIc maximal subgroups, such as the trirutile structure of WV_2O_6. By ordering W and V, only 3-fold multiples of the rutile-type $\boldsymbol{c}$-axis are retained.

Understanding group-subgroup relationships is important when analyzing *second-order* or continuous symmetry-breaking phase transitions in the solid state using Landau theory. These transformations occur along a single pathway by either losing translations to class-equivalent subgroups, or rotations to translation-equivalent subgroups. However, it is often experimentally challenging to completely ascertain second-order transitions, because proving that changes in thermodynamic or structural parameters are unequivocally continuous is extremely difficult. Nevertheless, the theoretical underpinnings of Landau theory have been useful to understand numerous solid-solid phase transitions.

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