

I. Symmetry and Crystal Physics

All crystals have translational periodicity and most possess other symmetry elements as well. A *symmetry* operation relates one part of an object to another. After performing the symmetry operation, the object is indistinguishable from its original appearance, both in form and orientation. We live in a three-dimensional world*, and as a consequence there are three principal types of symmetry operators: two-dimensional mirror planes, one-dimensional rotation axes, and zero-dimensional inversion centers. Consider a set of orthogonal axes X, Y, Z . A mirror plane at $Y=0$ takes any point at (x, y, z) and transforms it to $(x, -y, z)$, changing the sign of the y -coordinate. The mirror plane is a symmetry element of the object if it appears identical, before and after the mirror operator is applied. Two-fold rotation axes occur in many crystals. If the axis is coincident with Z , then a point at (x, y, z) is rotated 180° about Z to $(-x, -y, z)$, changing the sign of two of the coordinates. An inversion center at the origin of the coordinate system transforms (x, y, z) to $(-x, -y, -z)$. The three symmetry operations are illustrated in Fig. 1.

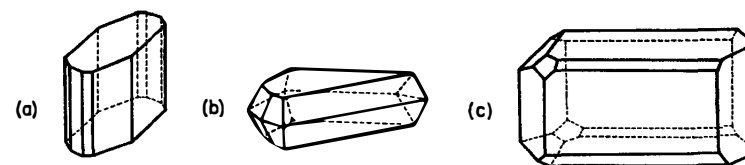


Fig. 1a-c. Crystals illustrating the three principal types of symmetry elements: inversion, reflection and rotation. Chalcanthite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), (a) crystals show a center of symmetry only, while hilgardite ($\text{Ca}_8\text{B}_{18}\text{O}_{33}\text{Cl}_4 \cdot 4\text{H}_2\text{O}$), (b) has mirror symmetry, and sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), (c) has a single two-fold rotation axis

* The reason *why* our world has three space dimensions was discussed at a recent meeting of the American Physical Society [1]. It can be proved that for dimensionality $n=3$, and only for $n=3$, *any* ordered sequence of n -dimensional hypersurfaces with given intrinsic geometries and with given normal separations becomes, in the limit of infinitesimal separations, an $(n+1)$ -dimensional manifold with a unique metric. For $n \leq 3$, *any* such ordered sequence becomes in the limit an $(n+1)$ -dimensional manifold with metric—but when $n < 3$ the resulting metric is not unique. Furthermore, $n \geq 3$, every sequence, which becomes in the limit an $(n+1)$ -dimensional manifold with metric, has a unique metric; but for $n > 3$, some sequences do not become a manifold with metric at all.

1. Crystal Classes

A point group is a self-consistent set of symmetry elements operating around a point. There are an infinite number of point groups, but only thirty-two are consistent with the translational periodicity found in crystals. The thirty-two crystal classes govern the physical properties of crystals.

Hermann-Mauguin symbols are used in describing symmetry elements and point groups. Numbers denote rotation axes: a three-fold symmetry axis with rotation of $360^\circ/3 = 120^\circ$ is simply 3. A mirror plane is m and its orientation can be inferred from the point group symbol.

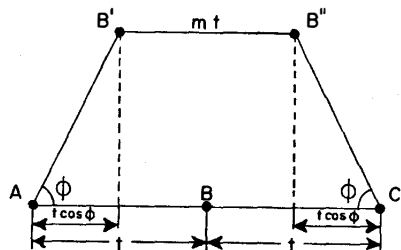


Fig. 2. A one-dimensional chain with rotation axes normal to the paper. The only allowed values of Φ are those corresponding to 1-, 2-, 3-, 4-, and 6-fold symmetry axes

$3/m$ means the three-fold axis is perpendicular to the mirror plane. In class $3m$, the three-fold axis lies *in* the mirror plane. Inversion symmetry does not appear explicitly as a symbol, though many of the groups are centric. The reason for this is that the symbol lists only the independent symmetry elements. As an example, consider the monoclinic class $2/m$ which contains a two-fold axis along Y , a mirror plane perpendicular to Y , and a center of symmetry at the origin. The two-fold axis carries a point (x, y, z) to $(-x, y, -z)$. Operating on $(-x, y, -z)$ with the mirror plane takes it to $(-x, -y, -z)$. Thus consecutive operations of 2 and m take the point from (x, y, z) to $(-x, -y, -z)$, the same as the inversion operation.

The thirty-two crystal classes can be derived geometrically by answering the following questions. Which types of rotational symmetry are consistent with translational periodicity? Which combinations of intersecting rotation axes are possible? How are the various types of rotational symmetry combined with mirror and inversion symmetry?

Using Fig. 2, it is easy to show that only five types of rotational symmetry are consistent with translation. Imagine a one-dimensional

array of lattice points, each with identical surroundings, separated by distance t . Let a rotation axis with angle $\Phi = 360^\circ/n$ be normal to the line, with one such axis passing through each lattice point. Operating on Point B with the rotation axis through A , takes B to B' . Operating on B with the axis through C takes B to B'' . Points B' and B'' define a line parallel to $A-B-C$ which will have the same repeat distance as ABC . The distance between B' and B'' is thus mt where m is an integer. By geometry, $mt = 2t - 2t \cos \Phi$. Letting m be any integer leads to five allowed values for $\Phi = 360^\circ$, 60° , 90° , 120° , and 180° . These correspond to the identity Operator 1, and the four rotation Operators 6, 4, 3, and 2. Other types of rotation axes (5, 7, 8, etc.) do not occur in crystals, though they have been found in molecules.

To derive the permissible combinations of intersecting rotation axes, we make use of Euler's construction [2]. The proof rests on spherical trigonometry and contains two important results. The first is that two intersecting rotation axes always generate a third. This means that rotation axes never come in pairs. Point groups contain either *one* rotation axis or *more than two*. The five crystal classes containing a single rotation axis are labeled simply 1, 2, 3, 4, and 6. The second result of Euler's construction is an equation relating the angles between the intersecting rotation axes. If OA and OB are two axes intersecting at Point O , then the angle between the two axes, AOB , is given by:

$$\cos(AOB) = \frac{\cos(\Phi_3/2) + \cos(\Phi_1/2)\cos(\Phi_2/2)}{\sin(\Phi_1/2)\sin(\Phi_2/2)},$$

where Φ_1 , Φ_2 , and Φ_3 are the rotation angles of the three intersecting axes. To illustrate, consider the combination of two three-fold axes and one two-fold axis. The cosine of the angle between the two three-fold axes will be given by

$$\cos(AOB) = \frac{\cos(180^\circ/2) + \cos(120^\circ/2)\cos(120^\circ/2)}{\sin(120^\circ/2)\sin(120^\circ/2)} = 1/3.$$

Angle AOB is 70.5° , the supplement of the tetrahedral angle. The angle between the two-fold axis and either of the three-fold axes is 54.7° . These angles correspond to angles between two body diagonals of a cube, and between the body-diagonal and a cube edge. Hence the 332 symmetry combination is identified with the cubic system. Not all combinations of symmetry elements are permitted. The axial combination 643, for example, leads to impossible cosine values. Six-fold axes and four-fold axes never occur together in crystals. The permissible axial combinations are 222, 322, 422, 622, 332, and 432. All other combinations of 1, 2, 3, 4, and 6 satisfying Euler's equation are equivalent to one of these.

The six permissible combinations lead to point groups 222, 32, 422, 622, 23, and 432, respectively. These six crystal classes together with the five classes containing a single rotation axis (1, 2, 3, 4, and 6) are called the eleven enantiomorphic crystal classes because right- and left-handed crystals occur in these classes. They contain no symmetry elements which transform a right-hand to a left-hand. Inversion and mirror operations change handedness but rotation operations do not.

All crystal structures are referred to one of the seven crystal systems: cubic, hexagonal, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic. Rhombohedral crystals are a subdivision of the trigonal system. Each system is defined by its minimum symmetry. The minimum axial symmetry for the cubic system is four three-fold axes. The uniaxial systems hexagonal, tetragonal and trigonal have a single six-, four-, and three-fold axis, respectively. Orthorhombic has three perpendicular two-fold axes, and monoclinic a single two-fold axis. Triclinic crystals possess no rotational symmetry higher than 1.

Restrictions on cell dimensions follow from the minimum symmetry requirements. For instance, an orthorhombic unit cell has three perpendicular axes, but there is no relation between the cell edges, a , b , and c . This follows from 222 point symmetry. From Euler's construction, three intersecting two-fold axes must intersect at right-angles to form a closed group, hence orthorhombic axes are perpendicular to one another. There is no relation between the cell dimensions a , b , and c because two-fold symmetry never transforms one axis to another, it only reverses the signs of axes. Therefore, a would never be transformed to b giving an equivalence between the two. This is not true in crystal systems of higher than orthorhombic symmetry. In the trigonal system a three-fold axis parallel to c carries a to b , and since a unit cell is left unchanged by its symmetry elements, a must be equal to b in length.

Of the eleven axial point groups, one contains only the identity operator (1), four are based on a single rotation axis (2, 3, 4, 6) and six contain three or more intersecting symmetry axes (222, 32, 422, 622, 23, 432). The remaining 21 crystal classes are obtained by combining the eleven axial classes with inversion and mirror symmetry. Consider first the combinations with a center of symmetry. Adding a center to the identity operator 1 gives $\bar{1}$, a centric triclinic class.

There are two ways of adding a center to the classes with a single rotation axis. Consider the combination of a center with a single two-fold rotation axis. The inversion center must lie on the axis, otherwise more lines and more points are generated. The inversion and rotation operations may be applied *consecutively* or *concurrently*. Four equivalent points are generated under *consecutive* application. A two-fold axis parallel to Y takes a point at (x, y, z) to $(-x, y, -z)$. Operation on (x, y, z)

and $(-x, y, -z)$ with the inversion operator at the origin takes them to $(-x, -y, -z)$ and $(x, -y, z)$, respectively, giving a total of four equivalent points. A mirror at $Y=0$ relates (x, y, z) to $(x, -y, z)$, which also relates $(-x, -y, -z)$ to $(-x, y, -z)$. Thus the point group contains a center, a two-fold rotation axis along Y , and a mirror plane perpendicular to the two-fold axis. This is the monoclinic point group $2/m$. Applying the inversion center and the two-fold axis along Y *concurrently* gives a different result, taking (x, y, z) to (x, \bar{y}, z) . This is point group $\bar{2}=m$, also monoclinic but with only two equivalent points rather than four. Combining inversion symmetry with a single 3-, 4-, or 6-fold axis gives classes $\bar{3}$, $\frac{4}{m}$, $\frac{6}{m}$ when applied consecutively and $\bar{3}$, $\bar{4}$, $\bar{6}=\frac{3}{m}$ when applied

concurrently. Thus eight new point groups are obtained from inversion by combining single rotation axes with inversion symmetry rotation.

Combining mirror symmetry with a single rotation axis in consecutive sequence leads to several more groups. There are only two orientations of the mirror plane which will *not* generate additional rotation axes: 1. the mirror is perpendicular to the axis, 2. the axis lies in the mirror plane. Case (1) gives nothing new: $\frac{1}{m}=m$, $\frac{2}{m}, \frac{3}{m}=\bar{6}$, $\frac{4}{m}, \frac{6}{m}$ are classes

previously generated by rotation-inversion combinations. Placing the mirror in the parallel position (2) gives $1m=m$, $2m=mm$, $3m, 4m=4mm$, and $6m=6mm$. The latter four are new, giving a total of 23 point groups.

The remaining nine are derived by combining mirror planes with the axial combinations 222, 32, 422, 622, 23, and 432. Six are obtained by placing a mirror perpendicular to the leading symmetry axis in each case: $\frac{2}{m}22=\frac{2}{m}\frac{2}{m}\frac{2}{m}=mmm$, $\frac{3}{m}2=\frac{3}{m}m2=\bar{6}m2$, $\frac{4}{m}22=\frac{4}{m}\frac{2}{m}\frac{2}{m}=\frac{4}{m}mm$, $\frac{6}{m}22=\frac{6}{m}\frac{2}{m}\frac{2}{m}=\frac{6}{m}mm$, $\frac{2}{m}3=\frac{2}{m}\bar{3}=m3$, $\frac{4}{m}32=\frac{4}{m}\bar{3}\frac{2}{m}=m3m$. The last three classes are derived by adding parallel planes to the combinations 222, 322, and 23, yielding $\bar{4}2m$, $\bar{3}\frac{2}{m}=\bar{3}m$ and $\bar{4}3m$, respectively.

2. Space Groups

The full microscopic symmetry of a crystal structure is given by the space group; all crystal structures belong to one of the 230 space groups. A complete listing of the space groups, together with equipoint positions and symmetry drawings, is given in the *International Tables for X-ray*

Table 1. Symbols and direction used to designate space groups

Lattice type	Lattice point positions	Symbol	
Primitive	0, 0, 0	<i>P</i>	
(100)-face centered	0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$	<i>A</i>	
(010)-face centered	0, 0, 0; $\frac{1}{2}$, 0, $\frac{1}{2}$	<i>B</i>	
(001)-face centered	0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0	<i>C</i>	
Body-centered	0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$	<i>I</i>	
Face-centered	0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0	<i>F</i>	
Rhombohedral	0, 0, 0; $\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{3}$; $\frac{2}{3}$, $\frac{2}{3}$, $\frac{2}{3}$	<i>R</i>	
Symbol	Symmetry operation		
<i>m</i>	reflection (mirror plane)		
<i>a, b, c</i>	axial glide planes		
<i>n</i>	diagonal glide plane, or net plane		
<i>d</i>	diamond glide plane		
1	identity (monad)		
$\bar{1}$	center of symmetry (inversion)		
2, 3, 4, 6	rotation axes (diad, triad, tetrad and hexad)		
$\bar{3}, \bar{4}, \bar{6}$	inversion axes		
$\left. \begin{matrix} 2_1, 3_1, 3_2, 4_1 \\ 4_2, 4_3, 6_1, 6_2 \\ 6_3, 6_4, 6_5 \end{matrix} \right\}$	screw axes		
Order of position of symbols in point groups and space groups			
Crystal system	Primary position	Secondary position	Tertiary position
Triclinic	—	—	—
Monoclinic	[010]	—	—
Orthorhombic	[100]	[010]	[001]
Trigonal	[001]	$\langle 100 \rangle^a$	$\langle 210 \rangle^a$
Tetragonal	[001]	$\langle 100 \rangle^a$	$\langle 110 \rangle^a$
Hexagonal	[001]	$\langle 100 \rangle^a$	$\langle 210 \rangle^a$
Cubic	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 110 \rangle^a$

^a These directions are not symmetry axes in all classes within the system.

Crystallography, Volume I [3]. A few examples and an explanation of the Hermann-Mauguin symbols are presented here.

All space group symbols begin with a capital letter giving the lattice type using the code symbols in Table 1. The second symbol corresponds to the primary symmetry direction. Symmetry element symbols and the orientations for various crystal systems are also given in Table 1. The crystal system is not stated explicitly in the space group symbol but is easily deduced from the symmetry elements. If secondary and tertiary symmetry elements are present, they appear in third and fourth positions.

To illustrate, consider the space group of fluoroapatite, $P6_3/m$. The lattice is primitive and the crystal system must be hexagonal since a six-fold axis is present. The single symbol, $6_3/m$, refers to the [001] direction the *Z*-axis. Fluorapatite does not contain the secondary and tertiary symmetry directions found in some hexagonal crystals. The 6_3 in $P6_3/m$ is a screw axis parallel to [001]. A 6_3 screw consists of a 60° rotation accompanied by a translation along [001] of $\frac{1}{6}c$, or half the unit cell. The */m* in $P6_3/m$ means a mirror plane perpendicular to the 6_3 axis. The mirror is therefore perpendicular to [001].

Rutile belongs to $P \frac{4_2}{m} \frac{2_1}{n} \frac{2}{m}$. Again the lattice is primitive, but this

time the symmetry is tetragonal because of the four-fold axis. Cubic crystals sometimes have four-fold symmetry also, but rutile is not cubic because three-fold symmetry does not appear in the symbol. All cubic crystals contain four three-fold axes along the $\langle 111 \rangle$ directions. As indicated in Table 1, $4_2/m$ refers to the primary symmetry direction [001]. The four-fold screw axis, 4_2 (90° rotation accompanied by translation of $2c/4$), is parallel to *Z* and perpendicular to a mirror plane *m*. Rutile possesses secondary and tertiary symmetry directions along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, respectively. Parallel to [100] is a 2_1 axis, 180° rotation plus translation of $\frac{1}{2}a$. The screw axis is perpendicular to a net plane denoted by *n*. A net plane operation consists of reflection—across (100) in this case—followed by a diagonal translation parallel to the mirror. The translation vector is $(b+c)/2$ for a net plane perpendicular to [100]. The tertiary direction in rutile is [110], which is parallel to a two-fold axis and perpendicular to a mirror plane. In tetragonal crystals, the [100] and [010] directions are equivalent, as are [110] and $[\bar{1}10]$. It is therefore unnecessary to specify the symmetry properties of [010] and $[\bar{1}10]$ in the space group symbol.

Orthoferrites belong to $P \frac{2_1}{b} \frac{2_1}{n} \frac{2_1}{m}$ which has a primitive lattice.

The three-fold axes in the symbol indicate the crystal is orthorhombic with symmetry directions along [100], [010], and [001]. The 2_1 screw axis along [100] is perpendicular to a *b*-axial glide plane. The symmetry operation accompanying *b* is reflection across (100) followed by translation of $\frac{1}{2}b$ along [010].

Sanidine is in $C2/m$, a *C*-centered lattice with a two-fold axis parallel to [010] and a mirror parallel to (010). Monoclinic crystals such as sanidine have a single two-fold axis of some sort.

Calcite is rhombohedral as the space group symbol $R \bar{3} \frac{2}{c}$ indicates.

When referred to hexagonal axes, rhombohedral crystals contain three lattice points in the unit cell with the coordinates listed in Table 1. When

referred to rhombohedral axes, rhombohedral crystals are primitive. Calcite has a three-fold inversion axis (120° rotation accompanied by inversion) parallel to the primary direction, $[001]$, in the hexagonal system. It also contains two-fold axes perpendicular to c -glide planes in the secondary directions $\langle 100 \rangle$.

Space groups are useful in describing crystal structures because they contain the full microscopic symmetry. Crystal classes (point groups) give the macroscopic symmetry important in crystal morphology and physical properties. Property measurements are insensitive to the tiny translations which differentiate space groups and crystal classes. Thus, a crystal with a two-fold axis has the same tensor symmetry as one with a two-fold screw axis. To convert space groups to crystal classes, change screw axes to ordinary rotation axes, glide planes to mirrors, and drop the lattice symbol. For rutile, the space group symbol $P \frac{4_2}{m} \frac{2_1}{n} \frac{2}{m}$ converts to point group $\frac{4}{m} \frac{2}{m} \frac{2}{m} = \frac{4}{m} mm$.

3. Symmetry Distribution of Crystals

Inorganic materials seldom possess large unit cells because the chemical formulae are simple compared to organic molecules. Unit cell volumes for many organic crystals are around 10000 \AA^3 , and proteins are ten to a hundred times bigger. Tipula iridescent virus crystallizes in a face-centered cubic array with a 3580 \AA cell dimension, and a cell volume of nearly 46 billion Å^3 ! Most inorganic cell volumes are in the range $10\text{--}1000 \text{ \AA}^3$. The smallest are metallic elements and the largest are polytypic compounds. Unit cell dimensions for the polytypes of silicon carbide and the hexagonal ferrites are as large as 1500 \AA .

Materials with simple chemical formulae tend to have higher symmetry than those which do not. This is borne out by Table 2 which lists the percentage distribution among the seven crystal systems. Two-thirds of the inorganic materials have higher than orthorhombic symmetry whereas 85% of the organic materials do not. The distribution is strongly influenced by the many examples of simple structure types, as the following statistics clearly indicate. For inorganic materials the leading space group populations are $Fm\bar{3}m$ (9%), $Pnma$ (7%), and six between 3 and 5%: $Fd\bar{3}m$, $P2_1/c$, $P6_3/mmc$, $Pm\bar{3}m$, $R\bar{3}m$, and $C2/c$. A number of fairly complicated minerals crystallize in $P2_1/c$ and $C2/c$, but the others consist mostly of close-packed structures. Rocksalt and face-centered cubic are in $Fm\bar{3}m$, hexagonal close-packed in $P6_3/mmc$, spinels in $Fd\bar{3}m$, perovskites in $Pm\bar{3}m$, and several deformed close-packed structures in $Pnma$ and $R\bar{3}m$.

Table 2. Distribution of crystalline materials among the seven crystal systems in percent. The percentages are based on 5572 inorganic compounds, 3217 organic, and 224 proteins tabulated in *Crystal Data* (No. 1) [4]

	Inorganic	Organic	Proteins	Total
Triclinic	2	6	2	4
Monoclinic	14	49	35	27
Orthorhombic	18	30	43	23
Trigonal	12	4	6	9
Tetragonal	14	6	6	11
Hexagonal	11	2	2	7
Cubic	30	4	5	20

Thus the preponderance of cubic inorganic materials can be traced to a few important structure-types. In regard to low symmetry crystals, the lack of triclinic crystals has several possible causes. One reason may be that there are only two triclinic space groups and if the space groups were populated approximately equally less than 1% would be triclinic. We know, however, that the space groups are not populated equally because some structures are more common than others. Another possible reason is that crystallographers do not choose their problems at random. They analyze the easiest structures first, while the really difficult ones (often triclinic) are set aside. This is less true now than in the past because most of the easy structures have already been reported, and because automated diffractometers and computers make the analysis easier. The triclinic percentage has nearly doubled in the last ten years but is still small. A third possible reason is the most interesting. Since complicated formulae tend to produce low symmetry, the number of triclinic crystals may be intrinsically small because of the scarcity of complicated inorganic compounds. Ternary and quaternary compounds are less common than binary compounds.

About 80% of inorganic structures and 60% of organic structures are centric, possibly because some of the important interatomic forces are central forces. Ionic forces depend on interatomic distance but not on angle. Covalent bonds depend on angle and therefore the percentage of acentric crystals is higher in organic solids. In biochemicals, inversion symmetry and mirror planes of all types are practically nonexistent, because most living systems—from people on down—have a handedness. The handedness arises from the replication process in which helices wind and unwind, transmitting genetic code. Helices possess screw-axis symmetry so that most crystals of biological origin belong to space groups containing screw axes. Among proteins, all the populous space groups contain screw axes: $P2_12_12_1$ (34%), $P2_1$ (23%), $C2$ (11%), and $P2_12_12$ (7%). Screw axes are also common in the crystals of simpler organic ma-

terials but many of these also possess mirror and inversion symmetry. Such crystals are often composed of zig-zag chains and aromatic rings which have mirror as well as screw-symmetry. Chain hydrocarbons and the benzene ring are examples. The most common space groups among organic compounds are: $P2_1/c$ (26%), $P2_12_12_1$ (13%), $P2_1$ (8%), and $C2/c$ (7%).

There are 230 space groups including eleven enantiomorphous pairs. Enantiomorphous space groups can be distinguished by anomalous dispersion but this experiment is seldom performed. CRYSTAL DATA (No. 1) [4] tabulates the distribution of structures among the 219 generic space groups, and MACKAY [5] has examined the probability distribution. If M_t is the number of different space groups which occur in the tables at least t times, then $1/M_t$ is found to vary almost linearly with t . The number of space groups not yet observed, agrees with statistical estimates indicating that their absence is due to chance and not to intrinsic impossibility for physical reasons.

4. Bond Length Calculations

The result of crystal structure determinations are published in Acta Crystallographica, Zeitschrift für Kristallographie and occasionally, in other journals such as American Mineralogist and the Journal of Metals. Collected reviews of crystal structure determination are published in a series of books by the International Union of Crystallography and by Wyckoff; efforts are being made to bring these abreast with the current literature.

Many structure analysis papers do not present a complete tabulation of interatomic distances and bond angles because they are readily calculated from the atomic coordinates and lattice parameters. To derive the general formulae, consider a triclinic crystal with unit cell dimensions (in Angstroms) a, b, c and interaxial angles, α, β, γ (Fig. 3). The problem is to find the interatomic distance between atoms located at (x_1, y_1, z_1) and (x_2, y_2, z_2) . Atomic coordinates are expressed in cell fractions and are therefore dimensionless quantities. Vectors from the origin of 0 to Atoms 1 and 2 are given by $\mathbf{r}_1 = x_1 \mathbf{a} + y_1 \mathbf{b} + z_1 \mathbf{c}$ and $\mathbf{r}_2 = x_2 \mathbf{a} + y_2 \mathbf{b} + z_2 \mathbf{c}$. The difference between these two vectors $\mathbf{r}_1 - \mathbf{r}_2 = (x_1 - x_2) \mathbf{a} + (y_1 - y_2) \mathbf{b} + (z_1 - z_2) \mathbf{c}$ points between the atoms as shown in Fig. 3. The magnitude $|\mathbf{r}_1 - \mathbf{r}_2|$ is the interatomic distance d_{12} , in angstroms

$$d_{12}^2 = |\mathbf{r}_2 - \mathbf{r}_1|^2 = (x_1 - x_2)^2 a^2 + (y_1 - y_2)^2 b^2 + (z_1 - z_2)^2 c^2 + 2(x_1 - x_2)(y_1 - y_2)ab \cos \gamma + 2(y_1 - y_2)(z_1 - z_2)bc \cos \alpha + 2(z_1 - z_2)(x_1 - x_2)ca \cos \beta. \quad (1)$$

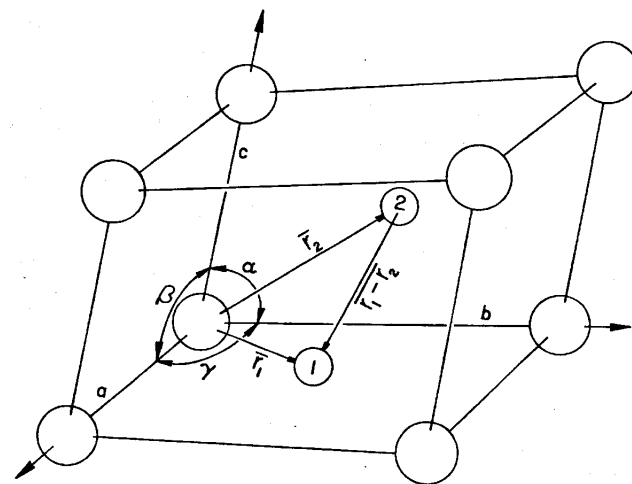


Fig. 3. A triclinic unit cell defined by the lattice vectors a, b, c pointing out from the origin to the origins of neighboring cells. The distance between two atoms in the cell is given by the magnitude of vector $\mathbf{r}_1 - \mathbf{r}_2$

Bond angles are obtained from the law of cosines. If Θ is the angle subtended at Atom 2 by bonds to Atoms 1 and 3, then

$$\cos \Theta = \frac{d_{12}^2 + d_{32}^2 - d_{13}^2}{2d_{12}d_{32}}.$$

To illustrate the use of the interatomic distance formula, the Si-O distance in quartz is determined from crystallographic data. Quartz is trigonal, with $a = b = 4.913 \text{ \AA}$, $c = 5.403 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. Neighboring silicon and oxygen atoms are located at $(0.465, 0, 0)$ and $(0.415, 0.272, 0.120)$, respectively. From the interatomic distance formula

$$d_{\text{Si-O}}^2 = (0.465 - 0.415)^2 (4.913)^2 + (-0.272)^2 (4.913)^2 + (-0.120)^2 (5.403)^2 + 2(0.465 - 0.415)(-0.272)(4.913)(4.913)(\cos 120^\circ) + 0 + 0,$$

so $d_{\text{Si-O}} = 1.61 \text{ \AA}$.

5. Density

The density of a crystal is intimately related to chemical composition and crystal structure through the relation

$$\rho = \frac{MZ}{N_0 V}.$$

The density $\rho(\text{g/cm}^3)$ is determined by the molecular weight M , the number of molecules per unit cell Z , Avogadro's number N_0 , and the unit cell volume V measured in cm^3 . For a triclinic crystal, V is $abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{\frac{1}{2}}$, where a, b, c are the cell dimensions and α, β, γ are the interaxial angles. Unit cell volumes for higher symmetry crystals are easily deduced from the triclinic formula.

The most important factor affecting density is molecular weight because atomic weights vary over a wider range than do atomic volumes. Among difluorides, densities increase with cation atomic weight: BeF_2 1.99, MgF_2 3.14, CaF_2 3.18, SrF_2 4.24, BaF_2 4.89, PbF_2 8.24. The densities of MgF_2 and CaF_2 are nearly the same because the fluorite structure is more open than the rutile arrangement.

As a rule, oxides with close-packed oxygen arrays have larger densities than those which do not. Thus the densities of corundum, spinel, chrysoberyl and olivine lie in the range 3.3–4.0, considerably larger than those of quartz, beryl and feldspar which are near 2.7 g/cm^3 . The differences in densities of these minerals are useful in separating them by flotation methods.

Among polymorphs, high-pressure phases tend to be denser than low-pressure phases because of the importance of the PV term in the free energy when P is large. Kyanite, the stable high-pressure form of Al_2SiO_5 , has a density of 3.63, compared to 3.15 for andalusite. For the same reason, low-temperature polymorphs are often denser than high-temperature forms. When T is very small, the PV term dominates the TS term in the free energy function. As an example, quartz ($\rho = 2.65$) is denser than its high-temperature polymorph cristobalite ($\rho = 2.32$).

Precise density measurements have been used to infer the presence of interstitials and vacancies in crystals, though the effects seldom exceed 1%. Exceptions to this include crystals which have suffered severe radiation damage such as metamict zircon whose density is 20% lower than well-crystallized zircon, and semi-metals such as TiO with large numbers of vacancies.

6. Physical Properties

A change in external environment elicits a response from a material, and physical properties express the relationship between response and applied force. Properties can be classified as equilibrium, steady-state, hysteretic, or irreversible [6].

Irreversible properties are defined in terms of a specific test which invariably leaves the material in a permanently altered condition. The tests are qualitative in nature, providing a scale of numbers to rank various materials in regard to the property it purports to measure. MOH's

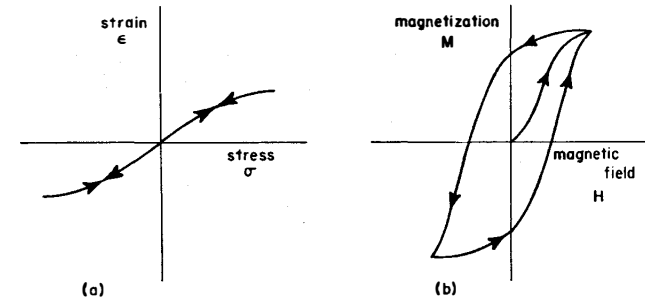


Fig. 4a and b. Relationships between intensive and extensive parameters for (a) an equilibrium property, and (b) a hysteretic property. Steady-state properties show reversible behavior like equilibrium properties

hardness scale is a scratch test which assigns a hardness number on a scale from zero to ten. Other hardness tests, including those of VICKERS and BRINNELL, give quite a different scale including occasional changes in ranking. Since the tests are only relative and do not rest upon firm theoretical understanding, the results should not be applied to situations significantly different from those of the test. For example, predictions based on mechanical failure tests under uniaxial stress may give poor agreement with failure rates under biaxial or triaxial stress. Such tests are often of prime importance to an engineer and must be carefully designed to measure the quantity of interest.

Irreversible properties can be correlated with crystal symmetry, even though there are no precise definitions. Tensile strength depends on direction, as do friction, elongation at rupture, ductility, and tarnishing rates. Atomic mechanisms explaining the orientational effects can sometimes be identified.

Equilibrium properties, steady-state properties, and hysteretic properties relate intensive and extensive parameters such as stress and strain, or temperature and entropy. Intensive parameters are changes in the environment which produce a response in the material, as measured by an extensive parameter. Stress produces strain, magnetic fields cause magnetization, electric field gradients result in current flow. *Equilibrium properties* are derived from reversible incremental changes in a material which is in thermal equilibrium with its surroundings. A mechanical stress is applied in incremental steps, allowing the body to establish equilibrium at each stage. Stress-strain measurements give the curve shown in Fig. 4a. Decreasing the stress retraces the curve, demonstrating reversibility. The elastic coefficients relating stress and

strain constitute an equilibrium property of the material. Such properties can be formulated as tensors and matrices, and are subject to certain thermodynamic and symmetry restrictions.

Steady-state properties can also be written as tensors but the thermodynamic relations are more complex. Most transport properties are measured under steady-state conditions: a gradient in an intensive variable is established across the body, including some quantity to flow. A gradient in electric potential causes charge to flow. The steady state property relating potential gradient (electric field) to charge flow (electric current) is electric resistivity. Parameter gradients and flow distinguish steady state properties from equilibrium effects. The system is not changing with time, but it is not in equilibrium with its surroundings.

Systems exhibiting hysteresis make it impossible to define a unique functional relationship between extensive and intensive variables. Consider the relationship between magnetization M and magnetic field H in a ferromagnetic material. Beginning from the demagnetized state and slowly increasing the field, the magnetization traces out the initial magnetization curve (Fig. 4 b). On reaching some arbitrary value, the field is slowly reversed but the curve does not retrace itself. Rather it follows a different path leading to remanent magnetization at zero field. Cycling the field between $\pm H$ gives a hysteresis loop. Such behavior is caused by metastable domain configurations. Ferroelectric and ferroelastic crystals show hysteresis loops similar to ferromagnets.

7. Symmetry of Physical Properties

In determining the effect of symmetry on physical properties, there are four symmetries to be considered: 1. the symmetry of the material, 2. the symmetry of the external forces, 3. the symmetry of resulting change or displacement, and 4. the symmetry of the physical property relating displacement to external force. Here we are using the terms *force* and *displacement* in the general sense to include electric, magnetic, and thermal quantities as well as mechanical effects.

All materials—whether crystalline or not—show some kind of symmetry. Single crystals belong to one of the 32 crystal classes as discussed previously. Ferromagnetic, ferrimagnetic and antiferromagnetic crystals exhibit long-range magnetic order. Additional symmetry groups involving time reversal operators are used to describe magnetic structures.

Amorphous materials, glasses, and liquids have spherical symmetry, $\frac{\infty}{m} \infty$. Liquid crystals and liquids made up of the enantiomorphic

molecules exhibit somewhat lower symmetry. Ceramics, metals, rocks and other polycrystalline solids made up of grains with random orientation have spherical symmetry. Effects found in platy or fibrous materials with aligned crystallites conform to cylindrical symmetry, $\frac{\infty}{m} m$. A rectangular plank cut from a large tree has orthorhombic symmetry because of the difference in properties associated with the longitudinal, tangential and radial directions. Thus wood has nine independent elastic constants just as orthorhombic crystals do.

The physical forces of importance in materials science are mechanical stress, electric field, magnetic field and temperature. Tensile stresses possess cylindrical symmetry $\left(\frac{\infty}{m} m\right)$ while shear stresses have orthorhombic symmetry (mmm). Both are centric because a balance of forces is required to prevent translational or rotational motion. Electric fields can be represented by a vector with polar cylindrical symmetry, ∞m . Moving electric charges produce magnetic fields so that a current loop can be used as the symmetry representation. Magnetic fields have axial cylindrical symmetry, point group $\frac{\infty}{m} m'$. Temperature is a scalar quantity with spherical symmetry $\frac{\infty}{m} \infty$.

When a polycrystalline solid is hot-pressed it adopts the cylindrical symmetry of the compressive stress. Poled ferroelectric ceramics are cooled through the Curie temperature in the presence of an electric field to influence the domain structure. The resulting symmetry is ∞m with the ∞ -fold rotation axis parallel to the applied field. Magnetically-poled ceramics have symmetry $\frac{\infty}{m} m'$. When subjected to two forces, a ceramic retains the symmetry elements common to both. An electrically-poled, hot-pressed ceramic has symmetry ∞m when field and stress are parallel and $mm2$ when perpendicular.

The same principle applies to the symmetry of any change or displacement: a crystal under an external influence will exhibit only those symmetry elements that are common to the crystal without the influence and the influence without the crystal. As an illustration, when a tensile stress is applied along the $[111]$ direction of a cubic crystal belonging to $m3m$, the symmetry of the strained crystal is $\bar{3}m$, the highest group common to $m3m$ $\left(= \frac{4}{m} \bar{3} \frac{2}{m}\right)$ and cylindrical symmetry about $[111]$. This principle is true regardless of the size of the force or its effect on the material. The displacement may be permanent (plastic flow), semi-permanent (domain change) or reversible (elastic). In the latter case, the

symmetry of the crystal reverts to its original class when the force is removed, but when the external forces produce permanent changes, the crystal retains the symmetry of the displacement after the force is removed.

8. Tensors

Equilibrium and steady-state properties of materials can be formulated in tensor notation [7]. Tensors are defined in terms of transformations from one orthogonal axial system to another. Let x_1, x_2, x_3 be the old axes and x'_1, x'_2, x'_3 be the new set. The set of nine numbers, a_{ij} ($i, j = 1, 2, 3$), represents the cosines of the angles between the new axes x'_i and the old axes x_j . The axes transform according to the equations $x'_i = a_{ij}x_j$ where summation is automatically understood for repeated subscripts.

A zero-rank tensor is unchanged by the transformation from old to new axes. Scalar properties such as density are zero-rank tensors. The transformation law for a first-rank tensor is the same as that for the coordinates. Force, electric field, and other vector quantities are first-rank tensors. The components of electric field for instance, transform as $E'_i = a_{ij}E_j$. The transformation law for a second-rank tensor is the same as that for the product of two coordinates. Electric susceptibility is second rank tensor whose components transform as $\kappa'_{ij} = a_{ik}a_{jl}\kappa_{kl}$. Additional important examples of tensors are given in Table 3. A tensor of rank n has n subscripts and transforms as the products of n coordinates.

The tensors just described are polar tensors. The transformation law for a *polar tensor* is unaffected by handedness. It is the same regardless

Table 3. Defining relations for several important tensor properties

Extensive quantities	Tensor	Intensive quantities
Entropy S	Zero-rank polar	Temperature T
Electric polarization P_i	First-rank polar	Electric field E_i
Magnetization M_i	First-rank axial	Magnetic field H_i
Strain ϵ_{ij}	Second-rank polar	Stress σ_{ij}
Properties	Defining relation	Tensor
Electric susceptibility κ_{ij}	$P_i = \kappa_{ij}E_j$	Second-rank polar
Magnetic susceptibility χ_{ij}	$M_i = \chi_{ij}H_j$	Second-rank polar
Magnetoelectric effect α_{ij}	$M_i = \alpha_{ij}E_j$	Second-rank axial
Magnetoelastic effect Q_{ijk}	$M_i = Q_{ijk}\sigma_{jk}$	Third-rank axial
Piezoelectric effect d_{ijk}	$P_i = d_{ijk}\sigma_{jk}$	Third-rank polar
Elastic compliance s_{ijkl}	$\epsilon_{ij} = s_{ijkl}\sigma_{kl}$	Fourth-rank polar

of whether the old and new axes are both of the same handedness or not. For an *axial tensor*, a change in handedness introduces a minus sign to the transformation law. Magnetic field is an axial first-rank tensor whose components transform as $H'_i = \pm a_{ij}H_j$. The positive sign applies if the old and new axial systems are both right-handed or both left-handed. If the transformation is from right to left, or from left to right, the negative sign is required.

Symmetry relations between property coefficients are easily derived using the direct inspection method. The principle of the method is to transform the reference axes by the symmetry elements of the point group, eliminating certain coefficients and establishing relations between others.

Pyroelectric coefficients (p_i) relate electric polarization components (P_i) to temperature change (ΔT).

$$P_i = p_i \Delta T.$$

Using the direct inspection method, we can demonstrate that centric crystals are non-pyroelectric, that is, $p_i = 0$ for crystals possessing a center of symmetry. Acting on the reference axes (x_1, x_2, x_3), the center carries $x_1 \rightarrow -x_1$, $x_2 \rightarrow -x_2$, and $x_3 \rightarrow -x_3$. Tensor components transform like the corresponding coordinate products. Therefore p_1 transforms like x_1 , so that $p_1 \rightarrow -p_1$ under inversion. Neumann's principle states that a physical property contains the symmetry of the point group of the crystal. This means that the property is unchanged after applying the symmetry element. Hence $p_1 \rightarrow -p_1 = p_1$. This is possible only if $p_1 = 0$. Applying the same argument to the other two pyroelectric coefficients eliminates p_2 and p_3 , causing the pyroelectric effect to disappear in centric crystals.

Electrical conductivity in pyrite (cubic class $m\bar{3}$) will be used to illustrate second rank tensors. Conductivity coefficients provide a linear relation between current density components J_i and electric field components E_j :

$$J_i = \sigma_{ij}E_j.$$

Class $m\bar{3}$ has mirror planes perpendicular to x_1, x_2 , and x_3 , and three-fold axes along $[111]$ and the other body-diagonals. Rotation of 120° about $[111]$ carries $x_1 \rightarrow x_2, x_2 \rightarrow x_3, x_3 \rightarrow x_1$. This operation results in $\sigma_{11} = \sigma_{22} = \sigma_{33}$. The mirror plane perpendicular to x_1 transforms $x_1 \rightarrow -x_1, x_2 \rightarrow x_2, x_3 \rightarrow x_3$ so that $\sigma_{12} \rightarrow -\sigma_{12} = \sigma_{12} = 0$. By the same argument, $\sigma_{13} = \sigma_{31} = \sigma_{21} = 0$. The mirror plane perpendicular to x_2 results in $\sigma_{23} = \sigma_{32} = 0$. Thus $J_1 = \sigma_{11}E_1, J_2 = \sigma_{11}E_2$, and $J_3 = \sigma_{11}E_3$, and pyrite has the same conductivity in all directions.

As an example of a third rank tensor, consider the piezoelectric effect in orthorhombic class 222. In the direct piezoelectric effect, the piezoelectric coefficients (d_{ijk}) relate the components of electric polarization (P_i) to the stress tensor (σ_{jk}): $P_i = d_{ijk} \sigma_{jk}$. The direct inspection method provides a convenient method of eliminating coefficients. Tensor coefficients transform like the corresponding coordinate products, so that d_{ijk} behaves like $x_i x_j x_k$ under the symmetry operators of the group.

Table 4. Tensor properties for the 32 crystal classes [8]. Zero means the effect is absent. Other numbers indicate the number of non-zero coefficients, and the number of independent non-zero coefficients is given in parentheses. Third- and fourth-rank tensors are referred to the shortened two-subscript matrix notation

Crystal class	Tensor rank				Example
	1	2	3	4	
1 = C_1	3 (3)	9 (6)	18 (18)	36 (21)	Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})$
$\bar{1} = C_i$	0	9 (6)	0	36 (21)	Copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
2 = C_2	1 (1)	5 (4)	8 (8)	20 (13)	Sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
$m = C_s$	2 (2)	5 (4)	10 (10)	20 (13)	Potassium nitrite KNO_2
$2/m = C_{2h}$	0	5 (4)	0	20 (13)	Orthoclase KAlSi_3O_8
222 = D_2	0	3 (3)	3 (3)	12 (9)	Iodic acid HIO_3
$mm2 = C_{2v}$	1 (1)	3 (3)	5 (5)	12 (9)	Sodium nitrite NaNO_2
$mmm = D_{2h}$	0	3 (3)	0	12 (9)	Forsterite Mg_2SiO_4
3 = C_3	1 (1)	3 (2)	13 (6)	24 (7)	Nickel tellurate Ni_3TeO_6
$\bar{3} = C_{3i}$	0	3 (2)	0	24 (7)	Ilmenite FeTiO_3
32 = D_3	0	3 (2)	5 (2)	18 (6)	Low-quartz SiO_2
$3m = C_{3v}$	1 (1)	3 (2)	8 (4)	18 (6)	Lithium niobate LiNbO_3
$\bar{3}m = D_{3d}$	0	3 (2)	0	18 (6)	Corundum Al_2O_3
4 = C_4	1 (1)	3 (2)	7 (4)	16 (7)	Iodosuccinimide $\text{C}_4\text{H}_4\text{INO}_2$
$\bar{4} = S_4$	0	3 (2)	7 (4)	16 (7)	Boron phosphate BPO_4
$4/m = C_{4h}$	0	3 (2)	0	16 (7)	Scheelite CaWO_4
422 = D_4	0	3 (2)	2 (1)	12 (6)	Nickel sulfate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
$4mm = C_{4v}$	1 (1)	3 (2)	5 (3)	12 (6)	Barium titanate BaTiO_3
$\bar{4}2m = D_{2d}$	0	3 (2)	3 (2)	12 (6)	Potassium dihydrogen phosphate KH_2PO_4
$4/mmm = D_{4h}$	0	3 (2)	0	12 (6)	Rutile TiO_2
6 = C_6	1 (1)	3 (2)	7 (4)	12 (5)	Nepheline $\text{NaAlSi}_3\text{O}_8$
$\bar{6} = C_{3h}$	0	3 (2)	6 (2)	12 (5)	Lead germanate $\text{Pb}_5\text{Ge}_3\text{O}_{11}$
$6/m = C_{6h}$	0	3 (2)	0	12 (5)	Apatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$
622 = D_6	0	3 (2)	2 (1)	12 (5)	High-quartz SiO_2
$6mm = C_{6v}$	1 (1)	3 (2)	5 (3)	12 (5)	Zincite ZnO
$\bar{6}m2 = D_{3h}$	0	3 (2)	3 (1)	12 (5)	Benitoite $\text{BaTiSi}_3\text{O}_9$
$6/mmm = D_{6h}$	0	3 (2)	0	12 (5)	Beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
23 = T	0	3 (1)	3 (1)	12 (3)	Sodium chlorate NaClO_3
$m\bar{3} = T_h$	0	3 (1)	0	12 (3)	Pyrite FeS_2
432 = O	0	3 (1)	0	12 (3)	Manganese β -Mn
$\bar{4}3m = T_d$	0	3 (1)	3 (1)	12 (3)	Zincblende ZnS
$m\bar{3}m = O_h$	0	3 (1)	0	12 (3)	Rocksalt NaCl

Point group 222 contains two-fold axes parallel to x_1 , x_2 , and x_3 . The two-fold operator parallel to x_1 transforms $x_1 \rightarrow x_1$, $x_2 \rightarrow -x_2$, $x_3 \rightarrow -x_3$, or more compactly $1 \rightarrow 1$, $2 \rightarrow -2$, $3 \rightarrow -3$. Piezoelectric coefficients transform as follows: $d_{111} \rightarrow d_{111}$, $d_{112} \rightarrow -d_{112}$, $d_{113} \rightarrow -d_{113}$, $d_{121} \rightarrow -d_{121}$, $d_{122} \rightarrow d_{122}$, etc. Coefficients which transform into themselves such as d_{111} and d_{122} are unaffected by the symmetry operator, but the others disappear because they are transformed into their negatives. If $d_{ijk} = -d_{ijk}$ then $d_{ijk} = 0$. The two-fold axis along x_1 eliminates d_{222} , d_{333} and all coefficients with an odd number of 2's and an even number of 3's in the subscript, or *vice versa*. The two-fold axes along x_2 or x_3 eliminate the remaining terms with repeated indices, so the only non-zero coefficients are $d_{123} = d_{132}$, $d_{231} = d_{213}$, and $d_{312} = d_{321}$. Therefore the piezoelectric effect in epsom salt and other crystals belonging to 222 are characterized by three independent coefficients, d_{123} , d_{231} , and d_{312} .

A shortened matrix notation is often used to describe tensor properties of third-rank or higher. In this notation, the tensile stress components σ_{11} , σ_{22} , and σ_{33} are shortened to σ_1 , σ_2 , and σ_3 , respectively. Shear stresses about the three major axes (σ_{23} , σ_{31} , σ_{12}) are abbreviated to σ_4 , σ_5 and σ_6 . For class 222, the piezoelectric polarization along x_1 is given by $P_1 = d_{132} \sigma_{32} + d_{123} \sigma_{23} = 2d_{123} \sigma_{23}$. In matrix notation this is $P_1 = d_{14} \sigma_4$. Thus $d_{14} = 2d_{123}$, and in a similar way, $d_{25} = 2d_{231}$ and $d_{36} = 2d_{312}$. All other piezoelectric coefficients are zero in this class.

The number of independent coefficients of a tensor property increases rapidly with rank. For a crystal belonging to triclinic point group 1, three coefficients are required to specify a first-rank tensor property. A symmetric second-rank tensor requires six, a third-rank tensor nine, and a symmetric fourth-rank tensor 21. Crystallographic symmetry reduces the number of independent coefficients in keeping with Neumann's Principle: The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal. The number of non-zero coefficients and the number of independent coefficients for various polar tensors are listed in Table 4.

9. Magnetic Symmetry

A geometric representation of a physical quantity is helpful in determining the effect of symmetry. In picturing magnetic structures, atomic moments are often visualized as arrows. This is misleading because an arrow is a polar vector, not an axial vector. Magnetization arises from moving electric charge so that a current loop is a more meaningful symbol. It is helpful, however, to retain the arrow indicating

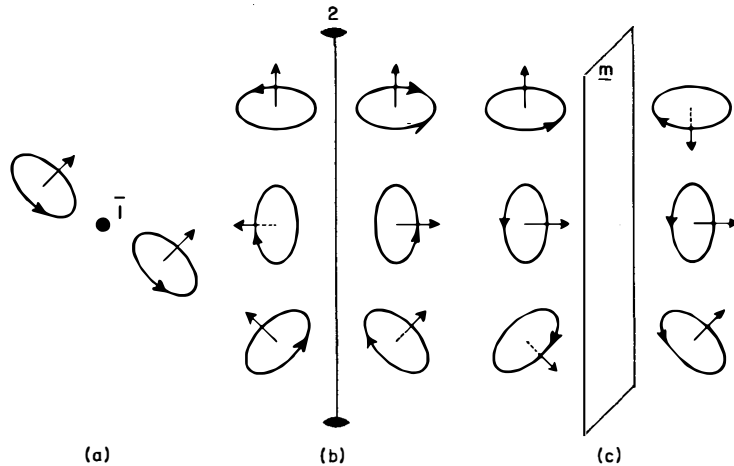


Fig. 5a-c. Transformations of an axial vector under (a) inversion, (b) rotation, and (c) reflection operations

the magnetization direction as an aid in visualizing the orientation of the current loop.

The transformations of a current loop under various symmetry operations are shown in Fig. 5. An inversion center (Fig. 5a) leaves the moment unaltered, regardless of orientation. Rotation axes and mirror planes interact with axial vectors in a more complicated way. A two-fold axis reverses atomic moments oriented perpendicular to the axis, but does not effect the parallel components (Fig. 5b). The reverse is true for mirror symmetry (Fig. 5c): magnetic moments perpendicular to the mirror are reversed by the reflection operation, whereas parallel components are unaffected. In studying the configurations focus on the current loop rather than the magnetization vector. The symmetry element acts on the loop, moving it to a new position and sometimes changing the direction of current flow. The magnetization vector follows later and is determined by the current direction using the right-hand rule. With the fingers of the right-hand parallel to current, the thumb gives the magnetization direction.

Time reversal, a nonspatial operation, is used in describing magnetic structures [9]. Reversing time reverses the direction of current flow, reversing the direction of magnetization. Consider two identical magnetic atoms whose positions are related by a two-fold rotation axis. The magnetic moments associated with the atoms may also obey the rotational operation, or they may not, depending on the orientation of the

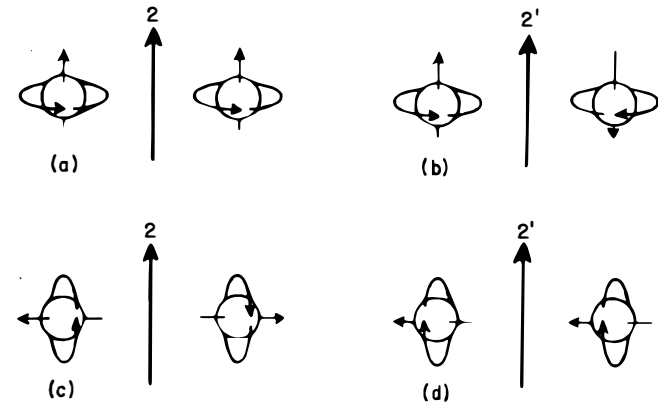


Fig. 6a-d. Spin configurations (a) and (c) possess two-fold symmetry, while in (b) and (d) the rotational symmetry is accompanied by time reversal

moments. If both spins are parallel to the two-fold axis (Fig. 6a), the two-fold axis is retained. If they are collinear with the two-fold axis and antiparallel to one another (Fig. 6b), the two-fold axis is *almost* retained. In this case, reversing the spin retains the symmetry element. Spin reversal is accomplished by time reversal, so that the two moments in Fig. 6b are related by a two-fold axis accompanied by time reversal, designated $2'$. The spins need not be parallel or antiparallel to the symmetry axis to maintain 2 or $2'$ as symmetry operators. The spin configurations shown in Fig. 6c and 6d also possess two-fold axes.

Magnetic properties are governed by magnetic point groups, just as non-magnetic properties are subject to Neumann's law and crystallographic point symmetry. Introduction of a time reversal operator increases the number of classes, adding 90 additional magnetic point groups. To illustrate, we derive the magnetic point groups associated with crystallographic point group mmm (full symbol $\frac{2}{m} \frac{2}{m} \frac{2}{m}$). This is an orthorhombic class with mirror planes perpendicular to the three orthogonal axes. Point group mmm also contains an inversion center and three two-fold axes perpendicular to the reflection planes. Ordinary non-magnetic crystals belonging to mmm also contain time reversal symmetry, although this is seldom discussed. Two atoms related by a mirror plane m are also related by m' (reflection plus time reversal). Reversing time reverses spin directions, but since spin-up and spin-down electron densities are identical in non-magnetic crystals, both m and m' are

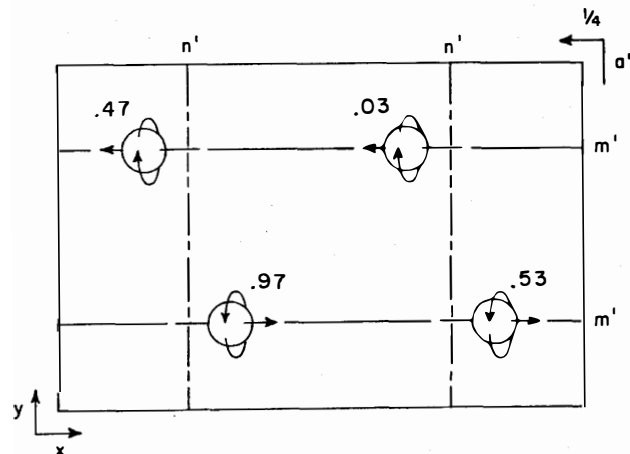


Fig. 7. Spin arrangement in antiferromagnetic lithiophilite, LiMnPO_4 . Only the magnetic manganese ions are shown. Cell heights are given in fractional coordinates and the positions of symmetry elements indicated

symmetry operators. This is not true in materials with long-range magnetic order. One symmetry operator may be obeyed, but not both.

To find the magnetic point groups associated with mmm , we look for subgroups of index two. All three mirrors may be ordinary reflection planes with no time reversal planes m' . The symbol for this group is mmm , the same as the crystallographic point group. Different magnetic groups are derived by replacing one or more of the mirror planes by m' . All three reflection operators are accompanied by time reversal in $m'm'm'$, while only $m'mm$ has only one, and $m'm'm$ two. Other orientations ($mm'm$, $mm'm'$, etc.) are possible but do not generate new groups. Thus there are four magnetic groups (mmm , $m'mm$, $m'm'm$, and $m'm'm'$) associated with crystallographic group mmm . A complete list of magnetic point groups is given by BIRSS [9].

Magnetic structures are generally determined by neutron diffraction. A free neutron has a magnetic moment which interacts with the magnetic moments of the atoms in a crystal. If the moments in the crystal are ordered, the incident neutrons are scattered at well-defined angles. Analysis of the intensities gives the magnetic structure.

The ordered spin array in lithiophilite (Fig. 7) is typical. Lithiophilite (LiMnPO_4) is paramagnetic above 35 °K, and antiferromagnetic below the transition. The structure is an olivine derivative, with four manganese atoms in the unit cell. The other atoms are unimportant in

describing the magnetic structure because the unpaired spins are associated with the 3d states of manganese. Lithiophilite belongs to crystallographic space group $Pnma$. The positions of the atoms obey these symmetry elements, but the spins do not. Time reversal operators are associated with all three planes making the magnetic space group $Pn'm'a$, and the magnetic point group $m'm'm'$. The salts LiFePO_4 and LiNiPO_4 are isostructural crystallographically but not magnetically. The relative spin arrangement in LiFePO_4 is the same as LiMnPO_4 but the spin direction is b rather than c . This changes the magnetic space group to $Pnmd$ and the point group to mmm' . In LiNiPO_4 spins are collinear with c and the space group is $Pnm'a$, magnetic point group $mm'm$. All three compounds are magnetoelectric.

References for Chapter I

1. CHRISTODOULOU, D.: Bull. Am. Phys. Soc. **17**, 139 (1972).
2. BUEGER, M.J.: Elementary crystallography. New York: John Wiley and Sons 1956.
3. International tables for X-ray crystallography, Vol.1. Symmetry groups. Birmingham: Kynoch Press 1952.
4. NOWACKI, W.: Crystal data, systematic tables. American Crystallographic Association Monograph, No.6, 1967.
5. MACKAY, A.L.: Acta Cryst. **22**, 329 (1967).
6. KOERBER, G.G.: Properties of solids. Englewood Cliffs, N.J.: Prentice-Hall, Inc. 1962.
7. NYE, J.F.: Physical properties of crystals. London: Oxford University Press 1957.
8. NEWNHAM, R.E., ROY, R.: In: HANNAY, N.B. (Ed.): Treatise on solid state chemistry, Vol. 1. New York: Plenum Press 1973.
9. BIRSS, R.R.: Symmetry and magnetism. Amsterdam: North Holland Publishing Co. 1964.