

## Space Groups

### Groupes d'espace

#### Introduction

For the description or the study of properties of physical systems, symmetry is of paramount importance. The symmetry groups of crystals are the so-called space groups. Other symmetry operations, such as time reversal, are sometimes also relevant, but the most important operations are the elements of the space groups. Space group symmetry is a generalization of the property that crystals are, usually, periodic in three dimensions. This article deals with the periodicity, the other symmetry operations of crystals, the classification of the space groups, and, what is of greater relevance for the physical properties, their representations.

#### Lattice Periodicity

Ideally, the most common crystals consist of a periodic array of identical building blocks repeated in all three directions. There are other types of crystals also, but a discussion of these will be taken up at the end of this section. Real crystals always have shortcomings in their periodic order; they are finite, which implies that there is a limit to the periodicity. Repetition means that one may go from one block into another by a translation. Such a translation is given by a vector  $\mathbf{n}$ . All vectors of the translations form a lattice. That means there are three fundamental translations, with vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , such that each lattice translation  $\mathbf{n}$  is a linear combination of these three with integer coefficients, and each such combination transforms a building block into another:

$$\mathbf{n} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}, \quad \text{with integers } n_1, n_2, n_3 \quad [1]$$

The building blocks do not have an overlap, and there are no gaps between them. Each building block consists of an arrangement of atoms or molecules. It is called a unit cell. The whole structure then remains the same if it is shifted by any of the translations of the lattice. Suppose that there are  $N$  atoms in the building block at positions  $\mathbf{r}_1, \dots, \mathbf{r}_N$ . Then the position of an arbitrary atom of the crystal is given by the expression

$$\mathbf{r}_{n,j} = \mathbf{r}_j + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} \quad [2]$$

for specific values of  $j$ ,  $n_1$ ,  $n_2$ , and  $n_3$ . The vectors  $\mathbf{r}_j$  may be chosen inside the unit cell. The vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are the basis vectors.

Because the building blocks are repeated in all directions, the three fundamental vectors are independent, which also means that every point in space can be reached from a fixed point by a linear combination, not necessarily with integer coefficients. In general, the coefficients are real numbers. In particular, the position of an arbitrary atom with respect to a chosen origin can be written as

$$\mathbf{r}_{n,j} = (n_1 + \xi_1)\mathbf{a} + (n_2 + \xi_2)\mathbf{b} + (n_3 + \xi_3)\mathbf{c} \quad [3]$$

Here  $(n_1 + \xi_1)$ , etc., are real numbers. For example, for CsCl, the three basis vectors are in Cartesian coordinates  $(a, 0, 0)$ ,  $(0, a, 0)$ , and  $(0, 0, a)$ . There is a Cs atom at  $\mathbf{r}_1 = (0, 0, 0)$  and a Cl atom at  $\mathbf{r}_2 = (a/2, a/2, a/2)$ . With respect to the lattice basis, the Cl coordinates are  $\xi_1 = \xi_2 = \xi_3 = 1/2$ . The unit cell is a cube.

#### Distance-Preserving Transformations

Physical laws remain the same if positions are transformed into newer positions with the same distances. Therefore, such distance-preserving transformations are important for physics. Among them are translations, where all positions are shifted by the same translation vector. In addition, rotations around an arbitrary point and the full reflection of all points through an arbitrary point leave the distances invariant. Let  $O$  be an arbitrary point in space. Then the orthogonal group consists of all rotations leaving this point invariant and all products of such a rotation with the reflection through  $O$ . The group of three-dimensional orthogonal transformations is denoted by  $O(3)_O$ . Choosing  $O$  as origin and a basis of space consisting of three basis vectors  $\mathbf{e}_1$ ,  $\mathbf{e}_2$ ,  $\mathbf{e}_3$ , an orthogonal transformation  $R$  corresponds to a matrix via

$$R\mathbf{e}_i = \sum_{j=1}^3 R_{ij}\mathbf{e}_j \quad (i = 1, 2, 3) \quad [4]$$

For a special choice of the basis, namely, with three mutually perpendicular vectors of the same length, the matrices satisfy  $\sum_j R_{ij}R_{kj} = \delta_{ik}$  or  $RR^T = E$ , where  $T$  indicates the transpose, and  $E$  the unit matrix. Such matrices are called orthogonal. Their determinant is either  $+1$  (for rotations) or  $-1$ . If one chooses another origin, the orthogonal group around that point gives the same group of matrices, which can then be indicated by  $O(3)$ .

All distance-preserving transformations can be obtained as a combination of a translation and an orthogonal transformation around an origin  $O$ . The effect on a point  $r$  of an orthogonal transformation  $R$  together with a translation  $t$  is

$$\{R|t\}r = Rr + t \quad [5]$$

All these transformations again form a group, the Euclidean group  $E(3)$ . Its elements are called Euclidean transformations. The product of two such transformations then is the subsequent execution of the two:

$$\begin{aligned} \{R_1|t_1\}\{R_2|t_2\}r &= \{R_1|t_1\}(R_2r + t_2) \\ &= R_1R_2r + R_1t_2 + t_1 \end{aligned} \quad [6]$$

from which it follows that

$$\{R_1|t_1\}\{R_2|t_2\} = \{R_1R_2|t_1 + R_1t_2\} \quad [7]$$

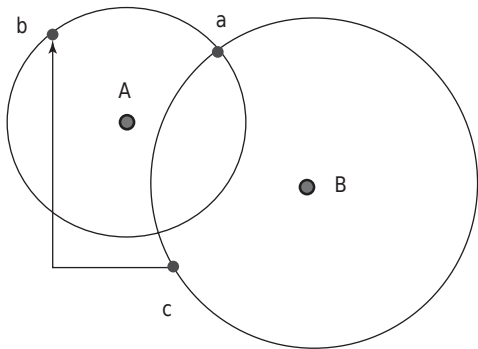
In particular,  $\{R|t\} = \{E|t\}\{R|0\}$  and  $\{R|t\}^{-1} = \{R^{-1}| -R^{-1}t\}$ .

A rotation  $R$  from  $O(3)_O$  leaves the point  $O$  invariant. A translation  $u$  transfers  $O$  to  $O + u$  and this point is left invariant by  $\{E|u\}\{R|0\}\{E| -u\}$ . This means that, the product  $\{R|u - Ru\}$  belongs to the orthogonal group  $O(3)_{O+u}$ . In other words, the translation part  $t$  of a space group element  $\{R|t\}$  may be changed by an origin shift  $u$  according to

$$t = t + (E - R)u \quad [8]$$

The combination of a translation and a rotation around  $O$  is then the same as a combination of another translation and a rotation around  $O + u$  (see Figure 1).

There is a simple matrix formulation for the action of a Euclidean transformation on a point  $r$  with co-



**Figure 1** The  $90^\circ$  rotation around  $A$  brings  $a$  to  $b$ , a  $90^\circ$  rotation around  $B$  plus a translation brings  $a$  via  $c$  to  $b$ .

ordinates  $x$ ,  $y$ , and  $z$ :

$$\{R|t\} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} & t_1 \\ R_{21} & R_{22} & R_{23} & t_2 \\ R_{31} & R_{32} & R_{33} & t_3 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix} \quad [9]$$

## Space Groups, Plane Groups, Higher Dimensions

A collection of atoms which is invariant under the translations of a three-dimensional lattice is, in general, invariant under still more Euclidean transformations. A space group is a group of Euclidean transformations that has a translation subgroup as a lattice group, with three linearly independent basis vectors. If  $\{E|a\}$  is a translation from the translation subgroup, and  $\{R|t\}$  an arbitrary element of the space group, then the following relation holds:

$$\{R|t\}\{E|a\}\{R|t\}^{-1} = \{E|Ra\} \quad [10]$$

The first consequence is that the translation subgroup is an invariant subgroup. (A subgroup  $A$  of a group  $G$  is invariant if, for each element  $a$  of  $A$  and each  $g$  from  $G$ , the element  $gag^{-1}$  is an element of  $A$ .) Because  $\{E|Ra\}$  is a translation, and therefore an element of the translation subgroup,  $Ra$  belongs to the lattice. Consequently, the lattice is invariant under  $R$ , and because all  $R$ 's form a subgroup of  $O(3)$ , this is a crystallographic point group, one of the 32 point groups. The Euclidean transformations leaving the CsCl structure invariant are the 48 elements of the cubic point group, combined with the lattice translations of the cubic lattice.

A plane group is a subgroup of the Euclidean group in two dimensions having as translation subgroup a two-dimensional lattice group. The elements  $R$  now form one of the 10 two-dimensional crystallographic point groups. The generalization to space groups in arbitrary dimensions then is straightforward. Such a group in arbitrary dimensions (including two) is also called a space group.

## The Structure of a Space Group

The translation subgroup  $A$  of a space group  $G$  is invariant. (It is also called a normal subgroup.) The orthogonal transformations  $R$  appearing in the elements  $\{R|t\}$  form a three-dimensional crystallographic point group  $K$ . All the elements of  $K$  can now be numbered:  $R_1 = E, R_2, \dots, R_N$ . All elements  $\{R_i|t\}$  in  $G$  form a set  $S_i$  for fixed  $i$ . One can multiply two such sets: the product  $S_i S_j$  is the set  $S_k$  if  $R_i R_j = R_k$ . In this

way, the sets  $S_i$  form a group, which is in fact identical to the group of all elements  $R_i$ , that is, the point group  $K$ . The group of sets  $S_i$  is called the factor group, and it is identical to (more precisely isomorphic to) the point group  $K$ . So, the space group  $G$  has an invariant subgroup  $A$  and the factor group  $G/A$  is isomorphic to the point group  $K$ .

From each set  $S_i$ , one may choose an element  $\{R_i|t_i\}$ . Then, every other element from  $S_i$  may be written as the product of the representative  $\{R_i|t_i\}$  and a lattice translation  $\{E|a\}$ . Of course, one could have chosen another representative element  $\{R_i|t'_i\}$ . Then the two translations  $t_i$  and  $t'_i$  differ by a translation  $a$  from the lattice. The translations  $t_i$  are not necessarily lattice vectors, and they are determined by  $R_i$  only up to a lattice vector. If the representatives can be chosen such that their translation part is zero, that is, when all translations  $t_i$  are lattice vectors, the group has a simple structure: each element is a product of an element of the translation subgroup and an element of the point group. Then the space group is called symmorphic.

Consider as examples the plane groups of the two-dimensional structures for which the unit cell is given in Figure 2. The unit cells are rectangles, the lattices have bases vectors  $(a, 0)$  and  $(0, b)$ . The example of Figure 2a has two different atoms in  $(0, 0)$  and  $(1/2, 1/2)$ . The point group symmetry of the lattice consists of the identity  $E$ , the two mirrors  $m_x$  and  $m_y$ , and the inversion  $-E$ . All four elements transform the position of an atom to a position that is related to the original position by a lattice vector. Thus, the plane group has a point group  $(2mm)$  with four elements. The example of Figure 2b has one molecule at the position  $(0, 0)$ . There are only two point group elements leaving the molecule invariant, and the point group is 2 with elements  $E$  and  $-E$ , although the lattice is the same. In example (c), there are molecules at  $(0, 0)$  and  $(1/2, 1/2)$ . The subgroup leaving each molecule invariant has two elements:  $\pm E$ . The transformation  $m_x$  does not leave a molecule invariant, but the Euclidean transformation  $\{m_x|(1/2, 1/2)\}$  does. The space group elements are the elements of the translation subgroup  $A$  and the cosets  $\{-E|0\}A$ ,  $\{m_x|(1/2, 1/2)\}A$ , and  $\{m_y|(1/2, 1/2)\}A$ . The point group is again  $2mm$ .

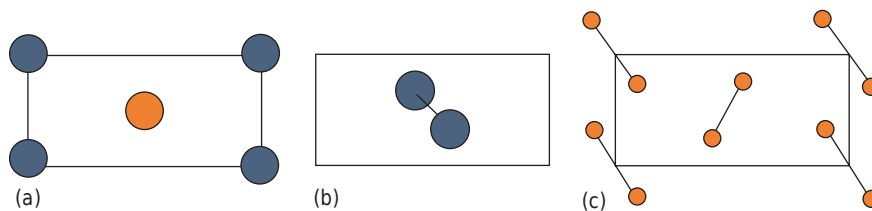


Figure 2 Three unit cells for the space groups (a)  $pmm$ , (b)  $p2$ , and (c)  $pgg$ .

## Space Group Elements

Each element of a space group is a product of an orthogonal transformation (an element of the point group  $K$ ) and a translation  $t$ , the latter not always a lattice translation. The translations  $t_i$  form a vector system for the space group. The translations satisfy

$$\begin{aligned} t_i + R_i t_j &= t_k \quad \text{up to a lattice vector } a \\ \text{if } R_i R_j &= R_k \end{aligned} \quad [11]$$

The translations  $t_i$ , however, depend on the choice of the origin. According to eqn [8] they change to  $t_i + (E - R_i)u$ , if the origin is shifted by a translation  $u$ . This makes it necessary to review the concept of a symmorphic space group. A space group is called symmorphic if there is an origin such that all representatives  $\{R_i|t_i\}$  may be chosen with  $t_i = 0$ . Then each element of  $G$  is the product of a point group element and a lattice translation. If the group is not symmorphic, then it is called nonsymmorphic.

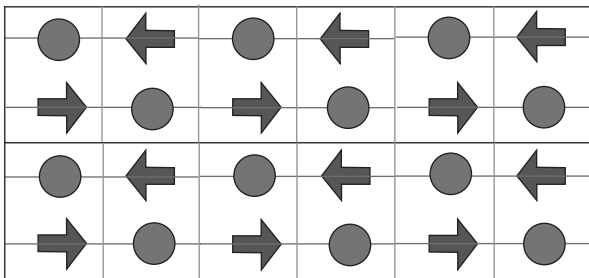
A three-dimensional rotation has an axis and a rotation angle. If one chooses an orthonormal coordinate system and the rotation angle along the  $z$ -axis, then the rotation is given by a matrix

$$\begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

When an orthogonal transformation has a determinant equal to  $-1$ , it has the same form but with an overall minus sign. Consider the case that the orthogonal transformation is combined with a translation  $t$  with coordinates  $a$ ,  $b$ , and  $c$  in the same reference system. By a shift of origin over the vector  $u$  with components  $x$ ,  $y$ , and  $z$ , the translation is transformed into the translation  $t + (1 - R)u$ , with components

$$\begin{aligned} a + x(1 - \cos \phi) + y \sin \phi, \\ b - x \sin \phi + y(1 - \cos \phi), \quad c \end{aligned}$$

By a proper choice of  $u$ , the first two components can be eliminated, but not the third. It is the case of a screw axis, a rotation combined with a translation along the rotation axis. If the rotation is over an



**Figure 3** A two-dimensional pattern with *pgm* symmetry: rectangular lattice, horizontal mirrors, and vertical glides.

angle  $\phi = 2\pi m/n$ , with  $n = 2, 3, 4$ , or  $6$ , the translation is always  $1/n$  of a lattice vector. When the determinant is  $-1$ , the origin can always be shifted such that the translation vanishes, except for the case  $n = 2$ . Then the orthogonal transformation is

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

and the first two components cannot be changed. It is a mirror operation with a translation in the mirror plane, and is called a glide operation. The plane of the mirror is the glide plane (Figure 3).

In two dimensions, the only plane group elements with intrinsic nonzero translation components are glide operations. For a rotation with a translation, the latter can always be eliminated by a shift of the origin.

## Classification

Because the orientation and the lattice constants may vary continuously, the number of space groups is infinite. However, there is good reason to identify space groups under certain conditions, for example, if they are just different orientations of the same group in space. In principle, which groups may be identified depends on the physics of the problem one wants to study by symmetry. Space groups are subgroups of the inhomogeneous affine group as well, the group of pairs of nonsingular linear transformations and translations. If a group  $G_1$  may be transformed into group  $G_2$  by a change of origin (translation) and a linear transformation of the lattice (homogeneous affine transformation), the two may be identified, or in other words considered as equivalent, because the choice of origin and basis does not change the physics. This is a definition inspired by physics. In mathematical language, the two groups are conjugated subgroups of the inhomogeneous affine group. This means that the groups  $G_1$  and  $G_2$  are considered to be equivalent if there is a nonsingular linear transformation  $S$  and a

translation  $\{E|t\}$  such that

$$G_1 = \{S|t\}G_2\{S|t\}^{-1} \quad [12]$$

With this relation, there are 219 equivalence classes of three-dimensional space groups. If the handedness of the basis is relevant, for instance, in the case of helical structures, there is a finer definition, which calls the groups equivalent if the conjugation is by an element  $\{S|t\}$  such that  $\det(S) > 0$ . Then there are 230 equivalence classes of space groups in three dimensions. With both definitions, there are 17 different plane groups in two dimensions. A theorem by Bieberbach states that conjugation in the affine group is equivalent to isomorphism.

The space groups can also be grouped into larger classes. A coarser classification uses arithmetic equivalence. Choosing an origin and a lattice basis, the point group  $K$  of a space group corresponds to a group of integer matrices  $D_1(K)$ . After a basis transformation, corresponding to an integer nonsingular matrix  $S$ , the same group is represented by an integer matrix group  $D_2(K) = SD_1(K)S^{-1}$ . Two such groups are called arithmetically equivalent. Then a space group determines an arithmetic crystal class. If one drops the condition that the conjugation matrix  $S$  has integer entries and allows real matrices, two groups conjugated by  $S$  are said to be geometrically equivalent. Arithmetic equivalence implies geometric equivalence. Space groups may be grouped into affine equivalence classes, and further into arithmetic and geometric crystal classes. In three dimensions, there are 219 affine classes, 73 arithmetic classes, and 32 geometric classes. The latter two classifications can, of course, be used for point groups as well. For each arithmetic class there is exactly one symmorphic space group. Finally, there are seven systems (triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal, and cubic) and six families (each three-dimensional system is a family, except the rhombohedral and hexagonal, which belong to the same family). The reader is referred to more specialized works on crystallography for a definition.

## Notation

Because the full explanation of the notation and nomenclature for crystallographic groups requires much more space, only a brief discussion is presented here. There are two systems, the Hermann–Mauguin symbols, recommended by the International Union for Crystallography (IUCr), and the Schoenflies symbols. The latter are based on the symbols for the 32 point groups arranged in geometric classes. For each class there is a numbering of the corresponding space

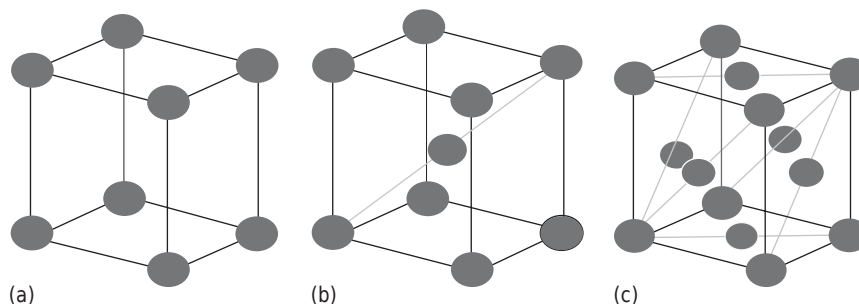
groups. An example is  $C_2^2$  with point group  $C_2$  consisting of an identity and a two-fold rotation. It is the second group with this point group. The Hermann–Mauguin symbols tend to have more information. They are based on the IUCr symbols for point groups. A second ingredient are the lattices. Lattices are considered to be equivalent if the point groups that leave them invariant (which on a lattice basis may be given by groups of integer matrices) may be represented by a change of lattice basis by the same groups of matrices. These classes are the Bravais classes. In three dimensions, there are 14 Bravais classes (Table 1). For lattices with the same point group symmetry, there is a common conventional basis on which the point group elements are simple, but one needs additional lattice vectors. For example, there are three Bravais classes for which the symmetry is the symmetry group of the cube, with 48 elements. The lattices of one Bravais class have a basis with three mutually perpendicular basis vectors of the same lengths. For the

other two, the face-centered cubic (f.c.c.) and body-centered cubic (b.c.c.), there is a sublattice of this kind, but not all lattice vectors belong to that. One needs additional vectors to obtain all the lattice translations:  $(0, 1/2, 1/2)$ ,  $(1/2, 0, 1/2)$ , and  $(1/2, 1/2, 0)$  for f.c.c. and  $(1/2, 1/2, 1/2)$  for b.c.c. (Figure 4). These additional vectors are given by capital letters in three dimensions, and lower case letters in two dimensions. The symbols of the symmetry groups of the three cubic lattices are  $Pm\bar{3}m$ ,  $Fm\bar{3}m$ , and  $Im\bar{3}m$ . These are the Hermann–Mauguin symbols for the space groups of the primitive cubic, f.c.c., and b.c.c. lattices, respectively. For each of the 73 arithmetic crystal classes, and thus for all symmorphic space groups there is such a symbol, consisting of the symbol for the point group preceded by a letter indicating the additional lattice vectors (the centering).

Finally, for nonsymmorphic space groups, the nonlattice translations for the elements appearing in the symbol for the symmorphic space group are

**Table 1** The 14 Bravais classes in three dimensions and their maximal symmorphic space groups

System	Centering translations	Maximal symmorphic space group	Basis
Triclinic	None	$P\bar{1}$	No relations
Monoclinic	None $(1/2, 0, 1/2)$	$P2/m$ $B2/m$	$\mathbf{a} \cdot \mathbf{c} = \mathbf{b} \cdot \mathbf{c} = 0$
Orthorhombic	None $(1/2, 1/2, 1/2)$ $(0, 1/2, 1/2)$ , $(1/2, 0, 1/2)$ , $(1/2, 1/2, 0)$ $(1/2, 1/2, 0)$	$Pmmm$ $Immm$ $Fmmm$ $Cmmm$	Three axes perpendicular
Tetragonal	None $(1/2, 1/2, 1/2)$	$P4/mmm$ $I4/mmm$	Three axes perpendicular $ \mathbf{a}  =  \mathbf{b} $
Rhombohedral	None	$R\bar{3}m$	$ \mathbf{a}  =  \mathbf{b}  =  \mathbf{c} $ $\angle(\mathbf{a}, \mathbf{b}) = \angle(\mathbf{b}, \mathbf{c}) = \angle(\mathbf{c}, \mathbf{a})$
Hexagonal	None	$P6/mmm$	$ \mathbf{a}  =  \mathbf{b} $ , $\mathbf{c} \perp \mathbf{a}$ , $\mathbf{c} \perp \mathbf{b}$ $\angle(\mathbf{a}, \mathbf{b}) = 2\pi/3$
Cubic	None $(0, 1/2, 1/2)$ , $(1/2, 0, 1/2)$ , $(1/2, 1/2, 0)$ $(1/2, 1/2, 1/2)$	$Pm\bar{3}m$ $Fm\bar{3}m$ $Im\bar{3}m$	All basis vectors mutually perpendicular and equal in length



**Figure 4** Unit cells for lattices from each of the three cubic Bravais classes. (a) Primitive, (b) b.c.c. with additional basis vector  $(1/2, 1/2, 1/2)$ , and (c) f.c.c. with additional  $(0, 1/2, 1/2)$ ,  $(1/2, 0, 1/2)$ , and  $(1/2, 1/2, 0)$ .

indicated by either a change of the letter or by a subindex. The symbol for a symmorphic space group with point group  $m$  may be  $Pm$ . If the mirror  $m$  becomes a glide with nonlattice translation in the third direction, the symbol is  $Pc$ . The symbol  $P2$  gives a symmorphic space group with point group 2,  $P2_1$  indicates a nonsymmorphic group with a screw axis. All space groups, their symbols and their elements can be found in the *International Tables for Crystallography, vol. A*.

### Reciprocal Lattice, Invariant Functions, Extinction Rules

A function that is invariant under translations has special properties for its Fourier transform. Suppose  $\rho(\mathbf{r})$  is such a function (e.g., a density function of a crystal). It has the property that  $\rho(\mathbf{r})$  and  $\rho(\mathbf{r} + \mathbf{a})$  are equal for every translation  $\mathbf{a}$  from the lattice. Writing down the Fourier decomposition yields

$$\begin{aligned}\rho(\mathbf{r}) &= \int \hat{\rho}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{k} \\ \rho(\mathbf{r} + \mathbf{a}) &= \int \hat{\rho}(\mathbf{k}) \exp(i\mathbf{k} \cdot (\mathbf{r} + \mathbf{a})) d\mathbf{k}\end{aligned}\quad [13]$$

from which it follows that  $\mathbf{k} \cdot \mathbf{a} = 0 \pmod{2\pi}$  for each translation vector  $\mathbf{a}$ . Therefore, for each wave vector  $\mathbf{k}$  occurring in the Fourier expansion, one has this relation. All vectors  $\mathbf{k}$  satisfying this relation form a lattice, as is easily checked. This lattice is called the reciprocal lattice for the so-called direct lattice of the vectors  $\mathbf{a}$ .

If  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  span the direct lattice, a basis for the reciprocal lattice is given by  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}^*$  defined by

$$\begin{aligned}\mathbf{a}^* &= 2\pi(\mathbf{b} \times \mathbf{c})/V, & \mathbf{b}^* &= 2\pi(\mathbf{c} \times \mathbf{a})/V, \\ \mathbf{c}^* &= 2\pi(\mathbf{a} \times \mathbf{b})/V\end{aligned}\quad [14]$$

where  $V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$  is the volume of the unit cell. Then the Fourier decomposition is

$$\rho(\mathbf{r}) = \sum_{\mathbf{k} \in \Lambda^*} \hat{\rho}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad [15]$$

where  $\Lambda^*$  is the reciprocal lattice. Each vector of the reciprocal lattice can be expressed in terms of the basis of the lattice

$$\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \in \Lambda^* \quad [16]$$

The reciprocal lattice is left invariant by the point group  $K$  as well.

Apart from translations, a lattice periodic function is generally left invariant by other distance-preserving transformations as well. Suppose  $g = \{R|\mathbf{t}\}$  is an element of the space group that leaves a function  $\rho(\mathbf{r})$  invariant. This means that  $\rho(\mathbf{r})$  and  $\rho(g^{-1}\mathbf{r})$  are

the same (the exponent  $-1$  is just for convenience). Then one has the relation

$$\rho(\mathbf{r}) = \rho(\{R|\mathbf{t}\}^{-1}\mathbf{r}) \quad [17]$$

For the Fourier components  $\hat{\rho}(\mathbf{k})$ , this implies

$$\hat{\rho}(\mathbf{k}) = \hat{\rho}(R\mathbf{k}) \exp(iR\mathbf{k} \cdot \mathbf{t}) \quad [18]$$

This is a very interesting formula. It is known that the wave vectors occurring in the Fourier decomposition belong to the reciprocal lattice. Now, consider a reciprocal lattice vector  $\mathbf{k}$  that is invariant under orthogonal transformation  $R$ . Then the expression becomes  $\hat{\rho}(\mathbf{k}) = \hat{\rho}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{t})$ . This is only possible if  $\hat{\rho}(\mathbf{k}) = 0$  or if  $\mathbf{k} \cdot \mathbf{t} = 0 \pmod{2\pi}$ . If  $\mathbf{t}$  is a translation from the lattice, this relation is trivially fulfilled. But if there is a  $\mathbf{t}$  such that the second relation is not satisfied, this means that the corresponding Fourier component  $\hat{\rho}(\mathbf{k})$  vanishes. This is an extinction rule.

An important example is the diffraction intensity. A crystal diffracts and the diffraction pattern consists of sharp Bragg peaks at the positions  $\mathbf{k}$ . The intensity of the peaks is given by the square of the absolute value of the static structure factor:

$$I(\mathbf{k}) = |F(\mathbf{k})|^2 = \left| \frac{1}{N} \sum_{j=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_j) \right|^2 \quad [19]$$

Here  $j$  runs over the  $N$  particles in the unit cell. It is the Fourier transform of the autocorrelation function, which is invariant under space group elements. Hence, the positions of the Bragg peaks are on the reciprocal lattice, and the extinction rules apply: the intensity is zero at  $\mathbf{k}$  if there is a space group element  $\{R|\mathbf{t}\}$  with  $R\mathbf{k} = \mathbf{k}$  and  $\mathbf{k} \cdot \mathbf{t} \neq 0 \pmod{2\pi}$ . Additionally, one has for arbitrary  $\mathbf{k}$  that  $I(R\mathbf{k}) = I(\mathbf{k})$ . Consequently, the diffraction has the point group in its symmetry group.

### Representations of Space Groups

Euclidean transformations act on positions in space. A quantum mechanical system in such a space has states on which the Euclidean transformations act as linear operators. For example, if the state is given by a wave function  $\psi(\mathbf{r})$ , the effect of a Euclidean transformation  $\{R|\mathbf{t}\}$  gives a new wave function  $\psi'(\mathbf{r}) = \psi(R^{-1}(\mathbf{r} - \mathbf{t}))$ . This is the action of a linear operator  $T_g$  with  $g = \{R|\mathbf{t}\}$ . Choosing a basis  $\psi_j(\mathbf{r})$  in the space of states, such a linear operator corresponds to a matrix  $D(g)$ :

$$T_g \psi_i(\mathbf{r}) = \sum_{j=1}^N D(g)_{ji} \psi_j(\mathbf{r}) \quad [20]$$

( $n$  is the dimension of the state space.) Now the matrices satisfy  $D(g_1)D(g_2) = D(g_1g_2)$ . This is called a (matrix) representation. If the dimension of the space is  $n$ , then the representation is said to be  $n$ -dimensional, and the matrices are  $n \times n$ . These representations are important for characterizing energy levels and other properties. Clearly, the space is mapped onto itself and, therefore, it is invariant under the group of transformations  $G$ . If there is no subspace (different from the origin or the whole space) that is invariant, the representation is said to be irreducible. In general, an energy level space carries an irreducible representation of the symmetry group, the dimension of the space is the level degeneracy, and there are orthogonality relations between states from the state space.

This gives a short argument why one should look at the irreducible representations of the space groups. The simplest space group is just a translation group, with three basis translations. Because the order in which translations are applied is not relevant, it is a commutative group, and according to the results of group theory the irreducible representations of commutative groups are one-dimensional, that is the matrices are just numbers. They satisfy  $D(\{E|a\})D(\{E|b\}) = D(\{E|a+b\})$ . The solution is  $D(\{E|a\}) = \exp(i\mathbf{k} \cdot \mathbf{a})$  for some vector  $\mathbf{k}$ . Two vectors  $\mathbf{k}$  and  $\mathbf{k}'$  give the same representation if  $\mathbf{k} - \mathbf{k}'$  belongs to the reciprocal lattice, because then  $\mathbf{k} \cdot \mathbf{a} = \mathbf{k}' \cdot \mathbf{a} \pmod{2\pi}$  for all lattice vectors  $\mathbf{a}$ . Therefore, the irreducible representations are characterized by a vector from the unit cell of the reciprocal lattice. A special choice of this unit cell is the Brillouin zone. It is the unit cell of the reciprocal lattice consisting of all points in reciprocal space which are closer to the origin than to any other point of the reciprocal lattice. Of course, the unit cell of a lattice is not uniquely defined. However, the choice of the Brillouin zone is very convenient when studying electrons or elementary excitations in crystals.

A wave function  $\psi(\mathbf{r})$  in a lattice periodic crystal which belongs to an irreducible representation of the lattice subgroup has a special form, the Bloch form, as follows from a group-theoretical argument. Under a translation  $\mathbf{a}$ , the function transforms to  $\psi(\mathbf{r} - \mathbf{a})$  which should be equal to  $\exp(i\mathbf{k} \cdot \mathbf{a})\psi(\mathbf{r})$  for some  $\mathbf{k}$ . Then define  $U(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})\psi(\mathbf{r})$ . It follows that

$$\begin{aligned} U(\mathbf{r} + \mathbf{a}) &= \exp(i\mathbf{k} \cdot (\mathbf{r} + \mathbf{a}))\psi(\mathbf{r} + \mathbf{a}) \\ &= \exp(i\mathbf{k} \cdot (\mathbf{r} + \mathbf{a}))\exp(-i\mathbf{k} \cdot \mathbf{a})\psi(\mathbf{r}) \\ &= U(\mathbf{r}) \end{aligned}$$

which proves that  $\psi(\mathbf{r})$  is the product of a plane wave,  $\exp(-i\mathbf{k} \cdot \mathbf{r})$  and a lattice periodic function  $U(\mathbf{r})$ . This constitutes the well-known Bloch's theorem.

Consider a state space that is invariant under a space group acting on the space by operators  $T_g$  for each element  $g$  of the space group  $G$ . Suppose, furthermore, that the representation is irreducible. The translation subgroup  $A$  is a subgroup of  $G$ . So, there is a basis formed by functions  $\psi_i$  for the space consisting of the eigenvectors of the commuting operators  $T_a$ . One has

$$T_a\psi_j = \exp(i\mathbf{k}_j \cdot \mathbf{a})\psi_j \quad [21]$$

A subspace of the space is that belonging to one particular wave vector  $\mathbf{k}$ . For each state,  $\psi$  from this space it holds that  $T_a\psi = \exp(i\mathbf{k} \cdot \mathbf{a})\psi$ . Applying  $T_g$  to any state from this space,  $\psi$  transforms to  $T_g\psi$ . How does this transform under the translations? Applying a translation  $\{E|a\}$  to the transformed vector:

$$\begin{aligned} T_aT_g\psi &= T_g(T_{g^{-1}}T_aT_g)\psi = T_gT_b\psi \\ &= \exp(-i\mathbf{k} \cdot \mathbf{b})T_g\psi \end{aligned}$$

Here  $\mathbf{b} = R^{-1}\mathbf{a}$  if  $g = \{R|t\}$ . The state  $T_g\psi$ , therefore, acquires a phase factor  $\exp(iR\mathbf{k} \cdot \mathbf{a})$  and belongs to the subspace of states transforming with a wave vector  $R\mathbf{k}$ . This means that, if there are states transforming under translations with a wave vector  $\mathbf{k}$ , then there are, in the irreducible space, states transforming with the wave vector  $R\mathbf{k}$  for every point group element. One can write the whole space as a sum of spaces each belonging to a specific  $R\mathbf{k}$ . One of these spaces is that of states transforming with  $\mathbf{k}$ .

Now define the subgroup of  $G$  consisting of all elements  $\{R|t\}$  for which  $R\mathbf{k} = \mathbf{k}$  (modulo the reciprocal lattice because  $\mathbf{k}$  and  $\mathbf{k} + \mathbf{K}$  give the same representation if  $\mathbf{K}$  belongs to the reciprocal lattice). This group is called the group of  $\mathbf{k}$ :  $G_{\mathbf{k}}$ . The subspace of states transforming with  $\mathbf{k}$  under translations is invariant under the group of  $\mathbf{k}$ . Then for an element  $g$  from the group of  $\mathbf{k}$ :

$$T_g = \exp(i\mathbf{k} \cdot \mathbf{t})D_R \quad (g = \{R|t\})$$

The operators form an irreducible representation of the group of  $\mathbf{k}$ . For a symmorphic group of  $\mathbf{k}$  the elements  $g$  can be written as a product  $\{E|t\}\{R|0\}$  of a lattice translation and a point group element. In this case, the operators  $D_R$  form an irreducible representation of the point group of the group of  $\mathbf{k}$ , denoted by  $K_{\mathbf{k}}$ . These are known, and can be labeled by a label  $\nu$ . Then a basis of the space of  $G_{\mathbf{k}}$  transforms under  $g$  as

$$T_g\psi_j = \exp(i\mathbf{k} \cdot \mathbf{t})D_{k_j}(R)\psi_k \quad [22]$$

The basis carries an irreducible representation  $\nu$  of the point group  $K$  (simply take  $\mathbf{t} = 0$  in the last formula). Here the matrices  $D(R)$  are the irreducible representation  $\nu$  of the point group  $K_{\mathbf{k}}$ . For non-symmorphic groups, the procedure is somewhat

more complicated, because not only standard representations but projective representations also occur.

Finally, a basis for the full state space can be constructed as follows. The group of  $\mathbf{k}$  is a subgroup of the space group  $G$ .  $G$  can be decomposed according to

$$G = G_{\mathbf{k}} + g_2 G_{\mathbf{k}} + \cdots + g_s G_{\mathbf{k}}$$

where the space group elements  $g_i$  have homogeneous parts  $R_i$  for which  $R_i \mathbf{k} = \mathbf{k}_i$ . Then the basis is defined as

$$\Psi_{ij} = T_{gi} \psi_j \quad [23]$$

The dimension of the representation is  $sd$ , where  $s$  is the number of points  $\mathbf{k}_i$ , and  $d$  the dimension of the point group representation  $D(K_{\mathbf{k}})$ . The irreducible representation carried by the state space then is characterised by the so-called “star” of  $\mathbf{k}$  (all vectors  $\mathbf{k}_i$ ), and an irreducible representation of the point group  $K_{\mathbf{k}}$ . This means that electronic states and phonons can be characterized by  $\mathbf{k}$ ,  $\nu$ . Their transformation properties under space group transformations follows from this characterization.

## Aperiodic Crystals

Apart from crystals with three-dimensional lattice periodicity, there are materials with a diffraction pattern with sharp Bragg peaks on positions

$$\mathbf{k} = \sum_{i=1}^n h_i \mathbf{a}_i^* \quad (\text{integer } h_i) \quad [24]$$

When  $n=3$ , the structure is periodic. If  $n>3$ , the structure is aperiodic, but it is still considered as crystal, because there is long-range order. Examples are modulated phases and quasicrystals. They may be described as intersections of physical space with a higher-dimensional lattice periodic structure. The symmetry of such structures is a space group in  $n$  dimensions, and in this case the theory of space groups in arbitrary dimensions can be used.

*See also:* Crystal Structure; Electron–Phonon Interactions and the Response of Polarons; Group Theory; Insulators,

Electronic States of; Lattice Dynamics: Vibrational Modes; Periodicity and Lattices; Point Groups; Quantum Mechanics: Foundations; Quasicrystals; Scattering, Elastic (General).

**PACS:** 61.50.Ah; 02.30. – a

## Further Reading

- Cornwell JF (1997) *Group Theory in Physics*. San Diego: Academic Press.
- Hahn Th. (ed.) (1992) *Space-Group Symmetry*. In: International Tables for Crystallography. vol. A, Dordrecht: Kluwer.
- Hahn T and Wondratschek H (1994) *Symmetry of Crystals: Introduction to International Tables for Crystallography*. vol. A. Sofia, Bulgaria: Heron Press.
- Janssen T (1973) *Crystallographic Groups*. North-Holland: Amsterdam.
- Janssen T, Janner A, Looijenga-Vos A, and de Wolff PM (1999) *Incommensurate and commensurate modulated structures*. In: Wilson AJC and Prince E, *International Tables for Crystallography*, vol. C, *Mathematical, physical and chemical tables*. ch. 9.8, Dordrecht: Kluwer.

## Nomenclature

$a, b, c$	lattice basis vectors
$a^*, b^*, c^*$	reciprocal lattice basis vectors
$A$	translation subgroup of a space group
$D(R)$	matrix representation
$\exp(-i\mathbf{k} \cdot \mathbf{r})U(\mathbf{r})$	Bloch form of a wave function
$E(3)$	Euclidean group
$F(\mathbf{k})$	structure factor
$G$	space group
$K$	point group
$\mathbf{n}$	lattice translation vector
$O(3)$	orthogonal group in three dimensions
$r_j$	position of an atom in the unit cell
$R$	orthogonal transformation
$\{R t\}$	space group element
$T_g$	linear operator for group element $g$ :
$\hat{\rho}(\mathbf{k})$	Fourier component of $\rho(\mathbf{r})$
$\rho(\mathbf{r})$	density function
$\psi_i$	basis of a state space
$\psi(\mathbf{r})$	wave function

## Specific Heat

**N E Phillips and R A Fisher**, University of California at Berkeley, Berkeley, CA, USA

© 2005, Elsevier Ltd. All Rights Reserved.

## Introduction

The specific heat of a substance is the amount of heat required to raise the temperature by one degree.

When heat is introduced under certain specified conditions, it is a well-defined thermodynamic property that gives a measure of the increases in the entropy, the energy, and the enthalpy with increasing temperature. It is related to other thermodynamic properties, for example, the thermal expansion, which is a measure of the pressure dependence of the entropy. Specific-heat data make an important contribution to