

Elements of Solid State Physics

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Preface

This book consists of organized lecture notes which were used many times for a one-year graduate course on solid state physics. It deals with crystalline solids, excluding the effects of contact with another medium. The properties of solids in contact with vacuum or another material are of great scientific and technological interest, including the case where a very thin layer of material is in contact with different materials on the two sides and may in a sense be considered two-dimensional. However, these properties belong to an area of specific problems of various complexities, for which the theories presented here are the basis of treatment.

The geometrically regular arrangement of atoms makes crystalline solids, three-dimensional and infinite in extent, the most easily comprehended model of condensed matter. Understanding gained from such idealized models is essential for the treatment of condensed matter in general, such as amorphous or glassy solids and liquid crystals.

This book is to be regarded as an introduction to the subject, being limited to considerations of basic problems. Its content is organized with an attempt to follow a logical sequence. Ion lattice symmetry and its direct consequences are treated in Chapter I. Following the adiabatic approximation, the treatment is divided into two parts: the system of ions, dealt with in Chapter II, and the system of electrons, treated in Chapters III and IV. Interactions of

the two systems are considered in Chapter V. The extensive Chapter VI deals with the various properties of the solid, beginning with some general considerations in Section A and ending with Section F on structure and Section G on phase transitions.

There are a number of books on solid state physics and numerous review articles dealing with its various special topics. The bibliography lists some books which appear to be of broad interest.

As a lecturer, I have continually gained a clearer understanding of the subject from questions and discussions with students taking the course. In addition, I have benefited from discussions with many colleagues and research collaborators. It is a pleasure to acknowledge my indebtedness to all these friends.

H. Y. FAN

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CHAPTER ONE

Symmetry and the Lattice

1. SYMMETRY

The consideration of condensed matter is simplified if the substance possesses some symmetry in the spatial arrangement of ions, nuclei with firmly bound electrons. Symmetry refers to the fact that the matter appears the same from the point of view of a different coordinate system. An equivalent definition of symmetry is that the matter appears unchanged under an operation of a length-preserving, linear coordinate transformation in the fixed coordinate system. A linear transformation of Cartesian coordinates represented by a vector \mathbf{x} to those represented by \mathbf{x}' is given by

$$\mathbf{x}' = R\mathbf{x} + \mathbf{t}. \quad (1.1)$$

The transformation preserves length if the components of \mathbf{t} are real and R is a real orthogonal matrix. A real orthogonal matrix has real components, and its inverse is its transpose. In a suitably oriented coordinate system, the matrix R has the form

$$R = \begin{vmatrix} \pm 1 & 0 & 0 \\ 0 & \cos \phi & -\sin \phi \\ 0 & \sin \phi & \cos \phi \end{vmatrix}. \quad (1.2)$$

R with $+1$ represents a rotation through the angle ϕ about the x_1 axis. R with -1 represents the same rotation followed by reflection

across the x_2x_3 plane; the operation is called an improper rotation. R with $+1$ and $\phi = \pi$ is simply an inversion giving $\mathbf{x}' = -\mathbf{x}$. A symmetry operation may be represented by an operator

$$T \equiv \{R | \mathbf{t}\}, \quad (1.3)$$

which consists of an operation R followed by a translation \mathbf{t} .

Obviously, successive symmetry operations together are equivalent to some individual symmetry operation. A collection of distinct operations that are pure translations is a translation group or a group of primitive translations. A collection of operations $\{R | 0\}$ that do not involve any translation is a point group; all the rotation axes and reflection planes have a common point that remains fixed under all the transformations. A finite body can have only a point group of symmetry, and the point group usually refers to a body whose surface has the shape that gives the highest symmetry for a body of the given matter. The collection of all symmetry operations irrespective of the involvement of translation is the space group of the substance. Operations that include translation occur only for a body of infinite extent. The space group and point group of a substance apply to the bulk of a large body whose surface has negligible effects. In addition to pure translations, there are two more kinds of operations $\{R | \mathbf{t} \neq 0\}$: (1) rotation about an axis followed by a translation and (2) reflection across a plane followed by a translation. The axis is a screw axis, and the plane is a glide plane. These operations are sometimes included in the point group with their translations set to zero; it must be kept in mind, then, that the resulting "point group" contains modified transformations that are not symmetry operations.

Considerations of geometry show that there are 14 distinct translation groups, 32 point groups, and 230 space groups. There are 73 space groups that do not involve screw axes and glide planes; they are called symmorphic space groups. The number of symmorphic space groups (73) and the number of total space groups (230) are less than the product $14 \times 32 = 448$ because transformations about a point must hold about all points resulting from symmetry translations. Therefore each translation group is compatible with a limited number of point groups.

Certain substances may be considered two-dimensional or one-dimensional for the problems of interest. The number of relevant operations and consequently the number of distinct groups is therefore less than that for an actually three-dimensional substance. For the two-dimensional case, translations are limited to a plane, rota-

tion axes can only be normal to the plane, and a reflection can only be across a line in the plane; there are 5 distinct translation groups, 10 point groups, and 17 space groups. One-dimensional substances have only two space groups.

2. ELEMENTS OF GROUP THEORY

In mathematics, a group is defined as a collection of elements A, B, C, \dots having the following properties:

- (a) Any pair of elements combined in a prescribed way is also an element of the group.
- (b) One of the elements, E , is a unit element or identity:

$$EP = PE = P, \quad (1.4)$$

where P is any element of the group.

- (c) Every element P of the group must have an inverse P^{-1} that is an element of the group. In particular,

$$PP^{-1} = P^{-1}P = E. \quad (1.5)$$

- (d) The associative law holds:

$$PQR = (PQ)R = P(QR). \quad (1.6)$$

Some examples of a group are:

1. The collection of all integers with addition as combination, $E = 0$, $P = n$, $P^{-1} = -n$.
2. The collection of $\exp(j/n)$ s with multiplication as combination, where n is an integer and $j = 0, 1, \dots, n-1$.
3. The collection of vectors $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ with vector addition as combination, where n_1, n_2, n_3 are integers including zero.

Two special kinds of groups may be mentioned: Abelian and cyclic. A group is Abelian if the combination is commutative, that is, if $AB = BA$ for all the elements. In a cyclic group, all the elements are combinations of a single element. Obviously, a cyclic group must be Abelian. The three example groups given above are all Abelian. Only example 2 is a cyclic group.

The order of a group is the number of different elements in the group. A subgroup is a collection of some elements of a group that form a group by themselves; the identity element by itself is a trivial subgroup. For example, all even integers including zero constitute a subgroup of the group given above as example 1.

Coset. Let (H) be a subgroup, and let X be an element not contained in (H) . $X(H)$ and $(H)X$ are, respectively, the left coset and right coset of group (G) under its subgroup (H) . It can easily be shown that a left or right coset cannot have any element in common with (H) . Furthermore, two right cosets or two left cosets either contain the same elements or have no common elements at all.

Expansion of a group in cosets. All the various right or left cosets together contain all elements of the group. Therefore a group can be expanded as

$$(G) = (H), X(H), Y(H), \dots = [E, X, Y, \dots](H) \quad (1.7)$$

or

$$(G) = (H), (H)P, (H)Q, \dots = (H)[E, P, Q, \dots]. \quad (1.8)$$

Index of a subgroup (H) in group (G) . This is the ratio n/n_H , where n is the order of (G) and n_H is the number of elements in (H) and in each coset. The collection of elements $[E, X, Y, \dots]$ or $[E, P, Q, \dots]$ may not be a group. The two collections may not be the same.

Invariant subgroup. An invariant subgroup (H) satisfies the condition

$$(H) = X^{-1}(H)X, \quad (1.9)$$

where X is any element of the group. For such a subgroup,

$$X(H) = (H)X,$$

and expansions in right cosets and in left cosets are identical.

Factor group. An invariant subgroup and the cosets (right or left), each taken as an element, constitute the factor group:

$$(G/H) = [(H)], [X(H)], [Y(H)], \dots \quad (1.10)$$

It is easily shown that the factor group is indeed a group whose identity element is (H) . The order of the factor group (G/H) is the index of (H) in (G) .

Isomorphic groups. A group (G) is said to have an $n:1$ isomorphism with the group (g) if each element X_i of (G) corresponds to one element x_i of (g) but x_i corresponds to a collection of elements $X_{j1}, X_{j2}, \dots, X_{jn}$ of (G) . Two groups of $1:1$ isomorphism are said to be isomorphic or simply isomorphic groups. The elements of (G) that correspond to the identity element of (g) form an invariant subgroup of (G) .

Direct-product group. Consider two groups

$$(G_1) = E, A_2, A_3, \dots, A_i$$

and

$$(G_2) = E, B_2, B_3, \dots, B_j$$

such that every element of one group commutes with all the elements of the other group. The direct-product group $(G_1 \times G_2)$ is defined by

$$(G_1 \times G_2) = E, A_2, \dots, A_i, B_2, A_2 B_2, \dots, A_i B_2, \dots, A_i B_j. \quad (1.11)$$

It is easy to show that a product group is indeed a group.

Class of elements. Two elements, A and B , related by $B = X^{-1}AX$, where X is some element of the group, are said to conjugate to each other. Evidently, an element is conjugate to itself; if A is conjugate to B , then B is conjugate to A ; if A is conjugate to B and C , then B and C are conjugate to each other.

A complete set of conjugate elements is a class of the group. The class containing an element A can be obtained by taking each element of the group to form an element conjugate to A . An element belongs to only one class; a group is divided into classes that have no elements in common. The identity element forms a class by itself, and therefore no other class is a subgroup. An invariant subgroup consists of complete classes in the group, including the class of the identity element.

Symmetry and group theory. The consideration of symmetry is covered by group theory. Symmetry operations are group elements, and successive operations are elements in combination. The translation group, point group, and space group in symmetry are groups in the sense of group theory. In terms of group theory, the translation group and point group are two subgroups of the space group, and a symmorphic space group is the direct-product group of the two.

The point group is isomorphic with the factor group. The translation group is an invariant subgroup, and it is Abelian.

Group multiplication table. For a group with noncommutative combination, such as some point groups of symmetry, it is expeditious to tabulate the combination for each pair of elements. The elements of the group are listed in the top row and in the left column. The element listed at the intersection of the m th row and n th column is the combination of the m th element in the column and the n th element in the row, with the latter preceding the first.

3. PROPERTIES OF MATTER AND SYMMETRY

A physical property P expresses the relation between two measurable quantities Q_1 and Q_2 of the substance: $Q_1 = PQ_2$. Q_1 , Q_2 , and P are given by tensors. The rank of P is equal to the sum of the ranks of Q_1 and Q_2 . If P is the same for the quantities measured relative to two different sets of axes, then the transformation from one set of axes to the other is a symmetry element of the property P . The important and understandable Neumann's principle states that the symmetry of any physical property must include the symmetry elements of the point group of the substance. It should be pointed out that some properties possess certain inherent symmetries irrespective of the substance. For example, all second-rank tensor properties inherently have inversion symmetry. The symmetry possessed by a tensor reduces the number of independent components; the effect simplifies problems involving the tensor. In the transformation of x axes to x' axes with

$$x'_s = a_{sr} x_r, \quad (1.12)$$

the components of a tensor T transform according to

$$T_{i'j'...} = (a_{i'i} a_{j'j} ...) T_{ilm...} \quad (1.13)$$

The equations are written in the dummy suffix notation, and the range of each suffix is the three axes. A transformation of axes that is a symmetry element of property P gives

$$P_{ij...} = P_{i'j'...} = (a_{i'i} a_{j'j} ...) P_{ilm...}, \quad (1.14)$$

which provides a number of relations among the components of P , thereby reducing its number of independent components.

Sometimes symmetry requires some component of the property tensor to be symbolically different from itself. In such a case, the

component must be numerically zero. For example, consider the component D_{133} of a third-rank property tensor, for example, a piezoelectric modulus. A rotation of axes by π about x_3 has

$$a_{1'1} = -1, \quad a_{2'2} = -1, \quad a_{3'3} = 1, \quad \text{and} \quad a_{r's} = 0 \quad \text{for} \quad r \neq s,$$

giving

$$D_{1'3'3'} = -D_{133}.$$

For a substance that contains such a rotation of axes in its point group of symmetry, we should have

$$D_{1'3'3'} = D_{133}.$$

Therefore, D_{133} must be zero for such substances. For the same reason, all the components that have only one 1 or one 2 in the subscript must be zero.

It should be borne in mind that the symmetry of a substance pertains to the substance in a definite condition that is specified by the so-called external parameters. Usually, the symmetry considered refers to a condition fully specified by two of the three external parameters temperature, pressure, and volume per unit mass. For many properties, however, the condition of the substance involves additional external parameters. For example, isothermal magnetoresistance and the Hall effect are electrical properties of a substance with an applied magnetic field as an additional external parameter, and electro-optical effects are optical properties of a substance with an applied electric field as an additional parameter. For such cases, the following evident principle is helpful: A substance with an additional external parameter possesses only those symmetry elements that are common to the substance without the additional external parameter and the external parameter by itself.

In the foregoing discussion about the symmetry of a property, property is defined as a relation between two measurable rather than measured quantities. The definition implies that the measurements of concern do not affect the symmetry. This is not always the case. For example, electrical resistivity relates the electric field and electric current density, and the measurements may be made at a field sufficiently high to significantly affect the symmetry of the substance. Should this be the case, the effect of the field on the symmetry of resistivity has to be taken into account like that of an additional external parameter.

4. LATTICES

A lattice consists of points in a regular geometrical arrangement. It is characterized by primitive translation vectors that number 3, 2, or 1 for a three-, two-, or one-dimensional lattice, respectively. The lattice is invariant under any translation that consists of multiples of individual primitive translation vectors. The primitive translation vectors define a primitive cell. Each primitive translation vector connects two neighboring points, each has a different direction, and no more than two vectors are coplanar. There is an arbitrariness in the choice of the vectors and the resulting shape of the primitive cell. However, a primitive cell always has the dimension ascribed to one point; that is, there are only points at the corners of the cell. A lattice of points is known as a Bravais lattice. The number of different Bravais lattices is the number of different groups of translational symmetry. Each Bravais lattice has the highest point-group symmetry compatible with the particular translational symmetry, which is called the holohedral point group.

A lattice is often described in terms of a unit cell, which has a more conventional shape. A unit cell may contain more than one primitive cell. It may be primitive (P), having points only at the corners; body-centered (I), with an extra point at the center; base-centered (C), with a point at the center of the base; or face-centered (F), with a point at the center of each surface. Lattices are classified into systems according to the shape of the unit cell. There are four systems for the five possible two-dimensional lattices:

oblique (P);
 rectangular (P) and (C),
 square (P), and
 hexagonal (P);

The 14 possible three-dimensional lattices have seven systems:

triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma$, (P);
monoclinic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ \neq \gamma$, (P) and (C);
orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$, (P), (C), (I), and (F);
tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$, (P) and (I);
cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$, (P), (I), and (F);
trigonal	$a = b = c, \alpha = \beta = \gamma < 120^\circ (\neq 90^\circ)$, (P); and
hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$ (P);