SOLID STATE

PHYSICS

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PREFACE

THE purpose of this book is to introduce the reader to the study of the physical properties of crystalline solids. It is based on notes which I used for lectures in the Physics Department of the University of British Columbia, Canada, and in the Electrical Engineering Department of the University of Minnesota.

My aim has been to write an introductory text suitable for senior undergraduate and beginning graduate courses on the solid state in physics, engineering, chemistry, and metallurgy. Also, I have attempted to make it suitable for self study by scientists in industrial laboratories interested in the physical properties of solids. The widely varying background of the anticipated groups of readers has affected the organization and presentation of the subject matter. The general level of presentation has been kept elementary, with emphasis on the physical reasoning underlying the interpretation of the physical properties of solids. I have made an effort, however, to remain as rigorous and up-to-date as possible within the limits imposed by the level of presentation. The first eight chapters deal with subjects which, at least in an introductory text, can be discussed without reference to the details of the electronic structure of solids. Prerequisite for understanding this part of the book is an elementary knowledge of statistical thermodynamics and of the quantized harmonic oscillator. Chapters 9 through 20 deal with the electronic properties of solids and require familiarity with the elements of wave mechanics, although in a number of chapters no explicit use of wave mechanics is made. As a consequence of the organization of the material outlined above, the degree of difficulty tends to increase as one progresses through the book. This in itself does not compel the reader to follow the order in which the various subjects are discussed. In fact, the chapters are organized in groups which could be taken up in any order suitable to serve the particular needs of the instructor or reader.

To some extent, my own interest and taste have determined the choice of

material; however, with the possible exception of Chapter 17, the material is basic to a great variety of subjects in the field of solid state.

I am indebted to W. Opechowski for constructive criticism during the preparation of Chapters 10 and 11, and to A. H. Morrish for his comments on other parts of the manuscript. I also wish to acknowledge the cooperation of numerous publishers who kindly permitted me to reproduce illustrations. I am grateful to F. L. Vogel, W. G. Pfann, H. E. Corey, and E. E. Thomas for a micrograph of a lineage boundary in germanium. Finally, I wish to thank my wife for typing the manuscript and for her encouragement.

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Chapter 1

THE CRYSTALLINE STATE

1-1. The crystalline state of solids

The elements and their chemical compounds generally occur in three states of aggregation: the solid state, the liquid state, and the gaseous state. In solids and liquids the distance between neighboring atoms is of the order of a few Angstroms, i.e., they contain 10^{22}–10^{23} atoms per cm^3. This may be compared with a density of about 2.7×10^{19} molecules per cm^3 in a gas at room temperature under one atmosphere, corresponding to an average distance of approximately 30 Å between molecules.

In crystalline solids the atoms are stacked in a regular manner, forming a three-dimensional pattern which may be obtained by a three-dimensional

(a)   (b)
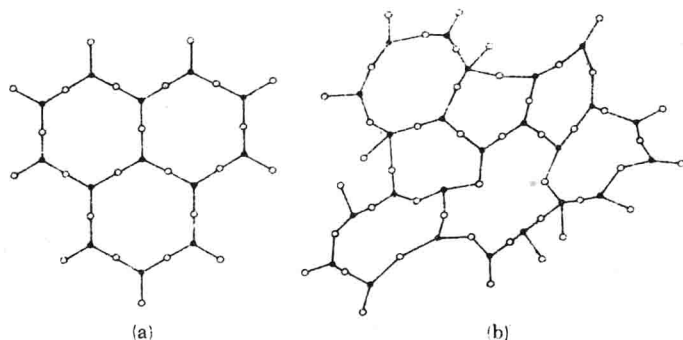
Fig. 1-1. Schematic illustration of the difference between a crystal (a) and a glass (b). [After W. H. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932)]

repetition of a certain pattern unit; two-dimensional examples are given in Fig. 1-1a and Fig. 1-3. When the periodicity of the pattern extends throughout a certain piece of material, one speaks of a single crystal. In polycrystalline materials the periodicity of structure is interrupted at so-called grain boundaries; the size of the grains in which the structure is periodic may vary from macroscopic dimensions to several Angstroms. When the size of the grains or crystallites becomes comparable to the size of the pattern unit, one can no longer speak of crystals, since the essential feature of a crystal is its periodicity of structure; one then speaks of

"amorphous" substances. For most solids the crystalline state is the natural one since the energy of the ordered atomic arrangement is lower than that of an irregular packing of atoms. However, when the atoms are not given an opportunity to arrange themselves properly, by inhibiting their mobility, amorphous material may be formed; an example is amorphous carbon formed as a decomposition product at low temperatures. Certain polymers are composed of very large and irregular molecules and in such cases a crystalline packing is not easily obtained. In other cases, the solid state may correspond to a supercooled liquid in which the molecular arrangement of the liquid state is frozen in; because of rapid cooling and a high viscosity of the liquid, crystals may not have had time to grow and a glassy material results (see Fig. 1-1b). Upon annealing, such glassy substances may crystallize (devitrify), as is well known to any experimentalist who has worked with quartz. In this book we shall be concerned essentially with solids which are generally regarded as crystalline.

Although one usually thinks of a solid as an arrangement of atoms in which the atoms occupy fixed positions relative to each other, this is not necessarily the case. Of course, in any crystal the atoms carry out a vibrational motion about their equilibrium position; this topic will be taken up in Chapter 2. However, in certain solids particular groups of atoms may have rotational freedom to some extent. For example, in KCN, which has the well-known NaCl structure (see Fig. 5-1), the CN^- ion is rotating even at room temperature;[1] neither the carbon nor the nitrogen atoms occupy fixed positions in the lattice, but are spread over a number of possible positions. Similarly, long-chain molecules may rotate about the longitudinal axis and disk-shaped ionic groups such as NO_3^- may rotate in the plane of the disk. The three-dimensional regularity is, however, maintained in such crystals. One might perhaps say that such crystals are partly melted. At sufficiently low temperatures the rotations are inhibited.

In another class of crystals, there is only two- or one-dimensional regularity,[2] viz., in the "liquid crystals." Such substances actually flow and will rise in a capillary tube. Normal crystals exhibit flow only under influence of external forces (see Chapter 3). A few hundred examples of liquid crystals are known, most of them being organic compounds, such as ammonium oleate $C_{17}H_{33}COONH_4$. They will not be discussed in this volume.

Although we shall assume in the present chapter that the crystals under consideration are "perfect," the reader will have ample opportunity in the

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[1] See, for example, C. W. Bunn, *Chemical Crystallography*, Oxford, New York, 1946, pp. 329–331.

[2] J. D. Bernal and W. A. Wooster, *Ann. Repts. Chem. Soc.*, **28**, 262 (1932); J. T. Randall, *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids and Gases*, Chapman and Hall, London, 1934; W. Voigt, *Physik. Z.*, **17**, 76, 153 (1917).

remainder of this book to realize that a large number of properties of solids are determined by lattice imperfections such as impurities, vacant lattice sites, atoms in positions where they "should not be" according to the crystal structure, etc. However, since we shall be mainly concerned
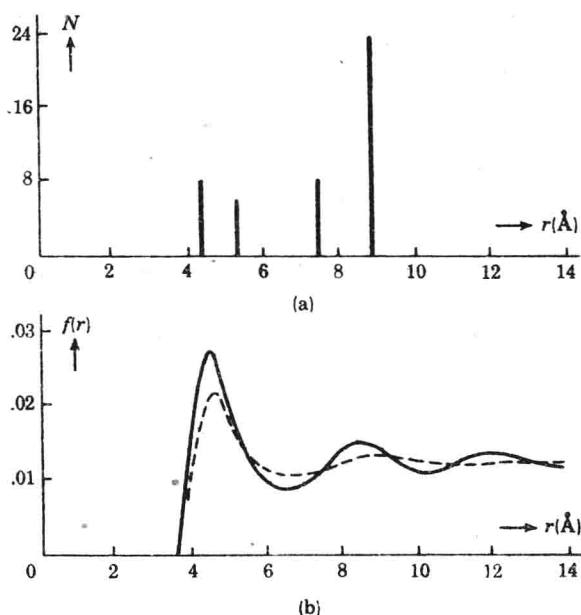
Fig. 1-2. The number of K atoms in metallic potassium is represented in (a) as function of the radial distance from a given K atom (20°C); in (b) the fully drawn and dashed curves represent the density of K atoms $f(r)$ in the liquid at 70°C and 395°C, respectively. [After Thomas and Gingrich, ref. 3]

in this chapter with crystal structures and their determination, such defects may be neglected temporarily.

In liquids, the atoms or molecules are in continual motion, and a crystalline structure is therefore absent. On the other hand, this should not lead one to believe that the arrangement of atoms is completely random. Even in liquids there is a certain amount of order, but it extends over a relatively short distance. To illustrate the difference between the "long-range order" in a crystal and the "short-range order" in a liquid, let us consider potassium in the solid and liquid states. Potassium, like the other alkali metals has the body-centered cubic structure (Fig. 1-4b), the cube edge being 5.344 Å at 20°C. Taking the nucleus of a given K atom in the crystal as origin, suppose we were to plot the number of nuclei of other K atoms as function of the radial distance r from the central atom. We would then obtain a number of vertical lines as in Fig. 1-2a at

specific distances from the origin. For example, there are eight atoms at a distance $\frac{1}{2}a\sqrt{3}$, six atoms at a distance a, etc. In the liquid state the situation is rather different. Suppose the origin of the coordinate system is attached to a given K atom and moves with this atom. At a given instant there will be a certain configuration of the other atoms, but the configuration changes continually with time. Taking the time average of these different configurations, one could then plot the average number of nuclei as function of the distance from the central atom. Such information may actually be obtained from X-ray diffraction experiments. Thus, in Fig. 1-2b the fully drawn curve $f(r)$ represents the density of K atoms per Å^3 at 70°C as function of the radial distance from an arbitrary K atom in the liquid;[3] the dashed line corresponds to 395°C. Note that the set of discrete lines of Fig. 1-2a has been transformed into a continuous curve. Also, only the first few "shells" of other atoms are distinguishable in the 70°C curve, whereas in the 395°C curve only the first two are somewhat pronounced. For distances larger than $\sim 10\,\text{Å}$ the curves show little or no structure and the density becomes independent of r; for the crystal, however, the discrete lines extend over the whole piece of material, at least when it is a single crystal. It is of interest to remark that the integral of $4\pi r^2 f(r)$ over the first peak determines the average number of nearest neighbors of the central atom; for the alkali metals we find that this is approximately equivalent to 8 nearest neighbors, as it is in the solid (only there, it is exactly 8).

1-2. Unit cells and Bravais lattices

We shall now discuss somewhat further the periodicity of structure, which is the fundamental feature of a crystal. Consider part of a two-dimensional crystal, the atoms of which are arranged in a pattern as illustrated in Fig. 1-3. Each cluster of atoms (in this case a dot and two open circles) will be referred to as a pattern-unit. It is observed that when a parallelogram such as $ABCD$ is repeatedly translated by the vectors a and b, corresponding respectively to AB and AD, the whole pattern may be obtained; thus $ABCD$ is called a "unit cell." The choice of a unit

Fig. 1-3. Two-dimensional crystal and various unit cells.

cell is by no means unique; for example, $EFGH$ or $KLMN$ would serve the purpose just as well and so would many others. All three unit cells

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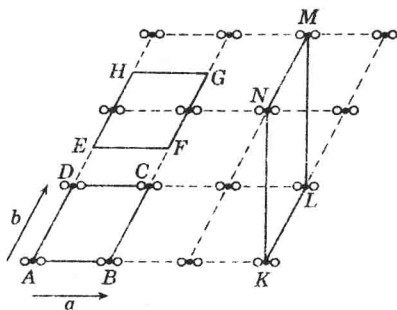[3] D. E. Thomas and N. S. Gingrich, *Phys. Rev.*, **56**, 415 (1938); for a review of this topic, see N. S. Gingrich, *Revs. Mod. Phys.*, **15**, 90 (1943).

mentioned contain one pattern-unit, since each of these units located at a corner belongs to four neighboring parallelograms and each pattern unit located at an edge belongs to two parallelograms. The areas of all unit cells containing one pattern-unit are equal. It is usually convenient to choose as a unit cell a parallelogram with the shortest possible sides.

In three dimensions, a similar procedure may be followed by stacking parallelepipeds in a regular manner; a convenient unit cell then contains again pattern-units only at the corners. In some cases, however, there
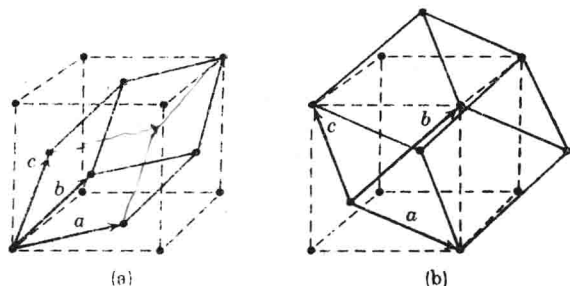

Fig. 1-4. The true (fully drawn) and compound (dashed) unit cells of the f.c.c. (a) and b.c.c. (b) lattices.

are reasons, to be given below, for choosing a "compound unit cell" which contains more than one pattern-unit. Consider, for example, the arrangement of atoms in a crystal of nickel, illustrated in Fig. 1-4a. The true unit cell corresponds to the parallelepiped based on the translation vectors *a*, *b*, *c*; it contains Ni atoms only at the corners, i.e., there is one atom per unit cell. On the other hand, the lattice may also be divided into a system of cubes with atoms at the corners and at the centers of the cube faces. It is convenient to consider a cube of this kind as a new "unit cell," even though it contains four atoms and has a volume four times as large as the "true" unit cell. One refers to the face-centered cube loosely as the "unit cell," although strictly speaking this is not correct since it is a combination of four unit cells. The most important reason for choosing the face-centered cube as a new unit cell is that the symmetry properties of the atomic arrangement in nickel are the same as in crystals which have a cube as the true unit cell. In fact, the essential symmetry elements of a simple cube (atoms only at the corners) are four threefold axes running diagonally through the cube; whenever the cube is rotated about any of these axes over 120°, it is brought into a position indistinguishable from the original position. The same symmetry is seen to be possessed by the face-centered cube. Another reason for choosing the compound unit cell is the fact that cubic axes provide a more convenient reference system than those corresponding to a rhombohedron.

In a similar way, the structure of the alkali metals represented in Fig.