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# **Solid State Physics**

by G. I. Epifanov, D.Sc.

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**Г. И. Епифанов**

**Физика твердого тела**

**Москва, «Высшая школа»**

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by **G. I. Epifanov, D.Sc.**

Moscow Institute of Electronic Engineering

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**Mark Samokhvalov, Cand. Sc.**



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## Preface

Ten years have passed since the first Russian edition of this textbook was published. In this time solid state physics has developed rapidly as the scientific background of numerous front-line branches of technology, absorbing new discoveries and theories. This has been considered in preparing the new edition.

At the same time college curricula have been changed to improve the basic preparation of versatile engineers, especially in physics and mathematics. This too had to be reflected in this book.

Also, the years that have elapsed since the first edition have seen much comment, some critical, and many proposals from Soviet and foreign readers—from college teachers and students, teachers of vocational and secondary schools, engineers and scientists. The author is grateful for all the comment and proposals.

There was a need therefore to revise the book completely.

As in the first edition, the presentation of material has followed the aim of elucidating the physical nature of the phenomena discussed. But, where possible, the qualitative relations are also presented, often though without rigorous mathematics.

The manuscript was reviewed in detail by Prof. L. L. Dashkevich, Dr. of Technical Sciences, and Prof. I. G. Nekrashevich, Honored Scientist of the Belorussian Republic. It was perused by Prof. L. A. Gribov, Dr. of Mathematical and Physical Sciences, Assistant Prof. V. B. Zernov, and Z. S. Sazonova. The author extends sincere thanks for their efforts and criticism, which he took into account when revising the manuscript.

The author is also indebted to Senior Lecturer F. Zh. Vilf, Cand. of Technical Sciences, and Assistant Prof. Yu. A. Moma, Cand. of

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The author will be most grateful for comment and proposals that might improve this book. They should be sent to the publishers.

G.I.E.

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# 1

## Bonding.

### The Internal Structure of Solids

Matter can exist in the solid state **only** because there are forces of interaction acting between the **structural** particles when the latter are brought sufficiently close **together**. For the solid to have a stable structure the forces of interaction between the particles should be of **two types**: of attraction, to prevent the particles from moving away from each other, and of repulsion, to prevent the particles from merging.

Let us discuss briefly the nature of these forces.

#### § 1 The van der Waals forces

The most general type of bond existing between any two atoms, or molecules, is due to van der Waals forces. Those forces were first introduced to explain the equation of state of real gases, the *van der Waals equation*:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (1.1)$$

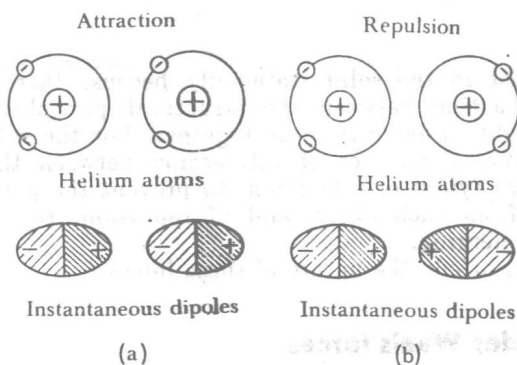
where the correction terms  $a/V^2$  and  $b$  account, respectively, for the effect of the forces of attraction and repulsion acting between the molecules of a real gas. These forces manifest themselves in an almost ideal form in the interaction between the molecules with saturated chemical bonds ( $O_2$ ,  $H_2$ ,  $N_2$ ,  $CH_4$ , etc.), as well as between the atoms of inert gases, making possible their existence in the liquid and solid states.

As a general case, the van der Waals bond is made up of the dispersion, orientational and induction interactions. Let's consider them separately.

**Dispersion interaction.** Consider the simplest example of two interacting helium atoms shown in Figure 1.1. The electron density distribution in a helium atom is spherically symmetrical and for

this reason its electric moment is zero. But this means only that the average electric moment of the atom is zero. At every moment of time the electrons occupy particular points in space, thereby creating instantaneous rapidly changing electric dipoles. When two helium atoms are brought together, the motion of their electrons

**Figure 1.1** Dispersion interaction. The interaction between helium atoms is due to the correlation in the motion of electrons resulting in the appearance of instantaneous dipoles: (a) — correlation resulting in attraction; (b) — correlation resulting in repulsion.



becomes correlated and this leads to the forces of interaction. The forces can be of two types. If the motion of the electrons is correlated, as shown in Figure 1.1(a), the instantaneous dipoles attract each other; if the correlation is as shown in Figure 1.1(b), the resulting interaction is repulsion. Since the realization of the arrangement of Figure 1.1(a) leads to a reduction in the energy of the system, this arrangement is more probable and is realized more frequently. This is in effect the cause of the constantly existing force of attraction between helium atoms.

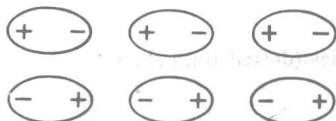
The bonds discussed above that owe their existence to a correlation in motion of the electrons in adjacent atoms are termed *dispersion* forces. They were first calculated by F. London in 1930. The calculation was based on the following model: the instantaneous electric dipole of one atom causes the other atom to be polarized and it becomes an *induced* dipole leading to the realization of the arrangement in Figure 1.1(a), which corresponds to attraction. The calculation had as its final result the following expression for the energy of the dispersion interaction of two particles:

$$U_d = -\frac{3}{4} \frac{\alpha^2 E_{exc}}{r^6} \quad (1.2)$$

where  $\alpha$  is the polarizability of the particles<sup>1</sup>,  $E_{\text{exc}}$  their energy of excitation, and  $r$  the distance between them.

**Orientalional interaction.** Should the molecules possess a constant dipole moment  $M$ , that is, should they be polar molecules, an electrostatic interaction would be established between them tending

Figure 1.2 Orientalional interaction of polar molecules.



to arrange the molecules in a strict order (Figure 1.2), since that order corresponds to the minimum energy of the system. The correct orientation of the molecules is disturbed by thermal motion. Therefore the energy of the system due to the mutual orientation of the molecules is strongly dependent on temperature. At low temperatures, when the orientation of the molecules is perfect, the interaction energy is determined from the expression

$$U_{\text{or}} = - \frac{M^2}{2\pi\epsilon_0 r^3} \quad (1.3)$$

where  $r$  is the distance between the molecules, and  $\epsilon_0$  the permittivity of free space.

In the high temperature range the energy of interaction of polar molecules, as had been demonstrated by W. H. Keesom, is of the following form:

$$U_{\text{or}} = - \frac{M^4}{24\pi^2\epsilon_0^2 k_B T r^6} \quad (1.4)$$

The type of interaction discussed above is termed *orientational interaction*.

**Induction interaction.** Lastly, in case of polar molecules of high polarizability an induced moment due to the action of the field of constant dipoles may be established (Figure 1.3; the induced dipoles are shown by dotted lines). The energy of mutual attraction due to the interaction of the rigid dipole of the first molecule and the induced dipole of the second molecule, as has been shown by Debye, is independent of temperature and is given by the expression

$$U_{\text{in}} = - \frac{\alpha M^2}{8\pi\epsilon_0^2} \frac{1}{r^6} \quad (1.5)$$

<sup>1</sup> Let us recall the physical meaning of  $\alpha$ . The charges in the molecule are displaced under the action of an external field of intensity  $\mathcal{E}$ . This leads to a dipole moment  $M$  proportional to  $\mathcal{E}$ :  $M = \alpha\mathcal{E}$ , the proportionality factor  $\alpha$  being the *polarizability* of the molecule.

where, as before,  $M$  is the constant dipole moment of the molecule, and  $\alpha$  its polarizability.

Such interaction is termed *induction*, or *deformation*, interaction.

In general, when two molecules are brought close together all three types of interaction may be established, the interaction energy being the sum of the energies of the dispersion ( $U_d$ ), orientational ( $U_{or}$ ), and induction ( $U_{in}$ ) types of interaction:

$$U = U_d + U_{or} + U_{in}$$

**Figure 1.3** Induction interaction of molecules (dotted lines show the induced dipoles).



Table 1.1 shows the relative magnitude (in percent) of each of those components of the total bonding energy for water, ammonia, hydrogen chloride and carbon monoxide. The data presented in Table 1.1 show the induction interaction for all the substances to be weak. Three quarters or a half of the bond energy in substances made up of polar molecules is due to the energy of orientational interaction; while in materials made up of nonpolar molecules almost all of the bond energy is due to the dispersion interaction.

**Table 1.1**

Substance	Type of interaction		
	Dispersion	Induction	Orientalional
Water	19	4	77
Ammonia	50	5	45
Hydrogen chloride	81	4	15
Carbon monoxide	100		

Table 1.2 shows the values of the bond energy for some molecular crystals held together by van der Waals forces.

**Table 1.2**

Substance	$U_b$ ( $10^3$ J/mole)	Substance	$U_b$ ( $10^3$ J/mole)
Neon (Ne)	1.9	Argon (Ar)	8.4
Nitrogen ( $N_2$ )	6.6	Carbon monoxide (CO)	8.4
Oxygen ( $O_2$ )	8.2	Methane ( $CH_4$ )	10.8

## § 2 The ionic bond

Atoms that occupy places in the Mendeleev periodic table next to inert gases tend to assume the electronic configuration of these gases either by giving away or accepting electrons. The valence electron of alkali metals, which immediately follow the inert gases, moves outside the closed shell and is only weakly connected with the nucleus. The halides, which immediately precede the inert

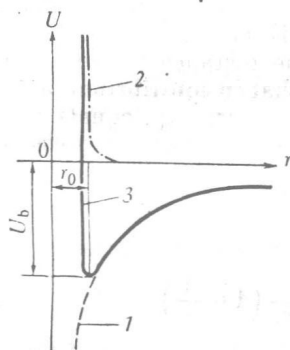


Figure 1.4 Dependence of energy of interacting ions on the distance between them: 1 — energy of attraction, 2 — energy of repulsion, 3 — total energy of interaction.

gases, lack one electron to complete a stable shell characteristic of an inert gas. Therefore they exhibit high affinity to an excess electron.

Such atoms, that is, typical metals and halides, are bonded in the following way. First a recharging of the atoms takes place. The electron from the metal moves over to the halide. This turns the metal atom into a positively charged ion and the haloid atom into a negatively charged one. These ions interact according to the Coulomb law as two opposite charges. Such a bond became known as an *ionic* bond.

The energy of attraction of two ions separated by the distance  $r$  is

$$U_{\text{att}} = -\frac{q^2}{4\pi\epsilon_0 r} \quad (1.6)$$

where  $q$  is the charge of the ions.

The curve 1 in Figure 1.4 shows the dependence of  $U_{\text{att}}$  on  $r$ . As  $r$  decreases the absolute value of the energy increases monotonically, tending to infinity as  $r \rightarrow 0$ . The force of attraction tends to bring the ions together as close as possible. This, however, is prevented by the forces of repulsion, which begin to make themselves felt at small distances and rise very rapidly with the decrease in distance. The repulsion energy  $U_{\text{rep}}$  is shown in Figure 1.4 by the



curve 2. Max Born and other scientists expressed the repulsion energy in the form

$$U_{\text{rep}} = \frac{B}{r^n} \quad (1.7)$$

where  $B$  and  $n$  are constants.

The resulting interaction energy of two ions is

$$U = \frac{B}{r^n} - \frac{q^2}{4\pi\epsilon_0 r} \quad (1.8)$$

This energy is shown in Figure 1.4 by the curve 3 which has a minimum at  $r = r_0$ ; the depth of this minimum determines the bond energy  $U_b$ , and  $r_0$  determines the distance between the ions in the molecule. Making use of the fact that in equilibrium (at  $r = r_0$ ) the force of attraction,  $F_{\text{att}} = - (dU_{\text{att}}/dr)_{r=r_0}$ , equals the force of repulsion,  $F_{\text{rep}} = - (dU_{\text{rep}}/dr)_{r=r_0}$ , we can easily express (1.8) as

$$U_b = - \frac{q^2}{4\pi\epsilon_0 r_0} \left( 1 - \frac{1}{n} \right) \quad (1.9)$$

The energy of the lattice made up of  $N$  such molecules is

$$U_{\text{lattice}} = -NA \frac{q^2}{4\pi\epsilon_0 r_0} \left( 1 - \frac{1}{n} \right) \quad (1.10)$$

where  $A$  is the *Madelung constant*, which takes account of the energy of interaction of the given molecule with all its neighbouring molecules in the crystal.

Table 1.3 shows by way of an example the experimental values of the bond energy of some ionic crystals and its values calculated with the aid of (1.10). The discrepancies do not exceed 1-2 percent, which is proof of good agreement between theory and experiment.

**Table 1.3**

Crystal	$U_b$ ( $10^3$ J/mole)	
	experiment	theory
Sodium chloride (NaCl)	752	754
Potassium iodine (KI)	650	630
Rubidium bromide (RbBr)	635	645
Caesium iodine (CsI)	595	585

### § 3 The covalent bond

The ionic and van der Waals bonds are unable to account for the existence of such compounds as  $H_2$ ,  $O_2$ ,  $N_2$ , etc., as well as for bonds in atomic crystals of the diamond type. Evidently, atoms of one kind cannot form oppositely charged ions by changing the distribu-