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Semiconductors
Made Simple

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Chapter 1

The Band Theory of Solids

When researchers first come across semiconductors, there was a clear-cut division of all solids into two large groups, viz. conductors (including all metals) and insulators (or dielectrics) and these differed in principle in their properties. These new semiconductor materials could not be included in either of these groups. On the one hand, they conducted electric current, although to a much lesser extent than metallic conductors, and on the other, they did not always conduct. Nevertheless, they did conduct electricity and so were named semiconductors (or half conductors).

Later, it was discovered that semiconductors differ from metals both in the way they conduct and in the way external factors influence their conduction. For example, the effect of temperature on conductivity of metallic conductors and semiconductors is quite opposite. In metals, an increase in temperature causes a gradual decrease in conductivity, while the heating of semiconductors results in a sharp increase in conductivity. The introduction of impurities also has different effects on conductivity of metallic conductors and semiconductors. In metals, as a rule, impurities worsen conductivity, while in semiconductors the introduction of a negligibly small amount of certain impurities can raise the conductivity by tens or even hundreds of thousands of times.

Finally, if we send a beam of light of a flux of some particles onto a conductor, it will have practically no effect on its conductivity. On the other hand, irradiation or bombardment of a semiconductor causes a drastic increase in its conductivity.

It is interesting to note that these properties of semiconductors are, to a considerable extent, typical of dielectrics, hence it would be much more correct to call semiconductors semi-insulators or semidielectrics.

In order to explain the behaviour of semiconductors in various conditions, to account for their properties and to predict new effects, we must consider their structural peculiarities. That is why we shall start with the discussion of the atomic structure of matter.

Sec. 1. Structure of Atoms. Hydrogen Atom

From the course of physics you should know that an atom consists of a nucleus and electrons rotating around it. This model of an atom was proposed by the English physicist Rutherford. In 1913, the Danish physicist Niels Bohr, one of the founders of quantum mechanics, used the model for the first correct calculations of hydrogen atom that agreed well with experimental data. His theory of the hydrogen atom has played an extremely important role in the development of quantum mechanics, though it underwent considerable changes later.

Hydrogen Atom. Bohr's Postulates. According to the Rutherford-Bohr model, hydrogen

atom consists of a singly charged positive nucleus and one electron rotating around it. To a first approximation, it can be assumed that the electron moves along the trajectory which is a circle with the fixed nucleus at its centre. According to the laws of classical electrodynamics, any accelerated motion of a charged body (including the electron) must be accompanied by the emission of electromagnetic waves. In the model under consideration, the electron moves with a tremendous centripetal acceleration, and therefore it should continuously emit light. Should it do so, its energy would gradually decrease and the electron would come closer and closer to the nucleus. Finally, the electron would unite with the nucleus ("fall" on it). Nothing of this kind occurs in reality, and atoms do not emit light in their unexcited state. In order to explain this fact, Bohr formulated two postulates.

According to Bohr's first postulate, an electron can only be in an orbit for which its angular momentum (i.e. the product of the electron momentum mv by the radius r of the orbit) is a multiple of $h/2\pi$ (where h is Planck's constant)*. While the electron is in one of these orbits, it does not emit energy. Each allowed

* Planck's constant is a universal physical constant and has the meaning of the product of energy and time, which is called *action* in mechanics. Since the quantity h is so to say an elementary action, Planck's constant is called the *quantum* (portion) of *action*. The introduction of the quantum of action laid the basis for the most important theory of the 20th century physics, viz. the quantum theory. The magnitude of the quantum of action is very small: $h = 6.62 \times 10^{-34}$ J·sec.

electron orbit corresponds to a certain energy, or certain *energy state of the atom*, which is called a *stationary state*. Atoms do not emit light in a stationary state. The analytic expression of Bohr's first postulate is

$$mvr = n \frac{h}{2\pi},$$

where $n = 1, 2, 3, \dots$ is an integer called the *principal quantum number*.

Bohr's second postulate states that absorption or emission of light by an atom occurs during transitions of the atom from one stationary state to another. The energy is absorbed or emitted upon transition in certain amounts, called quanta, whose value $h\nu$ is determined by the difference in energies corresponding to the initial and final stationary states of the atom:

$$h\nu = W_m - W_n,$$

where W_m is the energy of the initial state of the atom, W_n the energy of its final state, and ν the frequency of light emitted or absorbed by the atom. If $W_m > W_n$, the atom emits energy, and if $W_m < W_n$, the energy is absorbed. Quanta of light are called *photons*.

Thus, according to Bohr's theory, the electron in an atom cannot change its trajectory gradually (continuously) but can only "jump" from one stationary orbit to another. Light is emitted just when the electron goes from a more distant stationary orbit to a nearer stationary orbit.

Atomic Radii of Orbits and Energy Levels. The radii of allowed electron orbits can be found by using Coulomb's law, the relations of classi-

cal mechanics, and Bohr's first postulate. They are given by the following expression:

$$r = n^2 \frac{h^2}{4\pi^2 m e^2}.$$

The nearest to the nucleus allowed orbit is characterized by $n = 1$. Using the experimentally

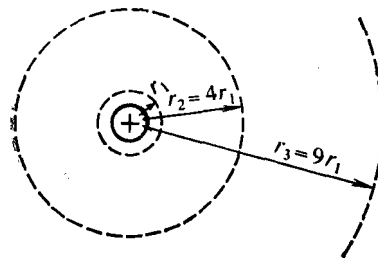


Fig. 1

obtained values of m , e and h , we find for the radius of this orbit

$$r_1 = 0.53 \times 10^{-8} \text{ cm.}$$

This value is taken for the radius of the hydrogen atom. Any other orbit with a quantum number n has the radius

$$r_n = n^2 r_1.$$

Hence, the radii of successive electron orbits increase as n^2 (Fig. 1).

The total energy of an atom with an electron in the n th orbit is given by the formula

$$W_n = -\frac{2\pi^2 m e^4}{n^2 h^2}.$$

These energy values are called atomic *energy levels*. If we plot the possible values of energy of an atom along the vertical axis, we shall obtain the *energy spectrum* of the allowed states of an atom (Fig. 2).

It can be seen that with increasing n , the separation between successive energy levels rapidly

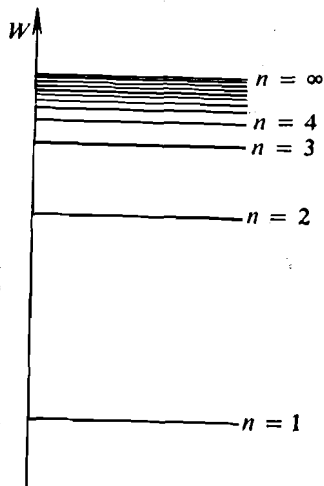


Fig. 2

decreases. This can be easily explained: an increase in the energy of an atom (due to the energy absorbed by the atom from outside) is accompanied by a transition of the electron to more remote orbits where the interaction between the nucleus and the electron becomes weaker. For this reason, a transition between neighbouring far orbits is associated with a very small

change in energy. The energy levels corresponding to remote orbits are so close that the spectrum becomes practically continuous. In the upper part the continuous spectrum is bounded by the ionization level of the atom ($n = \infty$) which corresponds to the complete separation of the electron from the nucleus (the electron becomes free).

The minus sign in the expression for the total energy of an atom indicates that atomic energy is the lower the closer is the electron to the nucleus. In order to remove the electron from the nucleus, we must expend a certain amount of energy, i.e. supply a definite amount of energy to the atom from outside. For $n = \infty$, i.e. when the atom is ionized, the energy of an atom is taken equal to zero. This is why negative values of energy correspond to $n \neq \infty$. The level with $n = 1$ is characterized by the minimum energy of the atom and the minimum radius of the allowed electron orbit. This level is called the *ground*, or *unexcited level*. Levels with $n = 2, 3, 4, \dots$ are called *excitation levels*.

Quantum Numbers. According to Bohr's theory electrons move in circular orbits. This theory provided good results only for the simplest atom, viz. the hydrogen atom. But it could not provide quantitatively correct results even for the helium atom. The next step was the planetary model of an atom. It was assumed that electrons, like the planets of the solar system, move in elliptical orbits with the nucleus at one of the foci. However, this model was also soon exhausted since it failed to answer many questions.

This is connected with the fact that it is im-

possible in principle to determine the nature of the motion of an electron in an atom. There are no analogues of this motion in the macroworld accessible for observation. We are not only unable to trace the motion of an electron but we cannot even determine exactly its location at a particular instant of time. The very concept of an orbit or the trajectory of the motion of an electron in an atom has no physical meaning. It is impossible to establish any regularity in the appearance of an electron at different points of space. The electron is "smeared" in a certain region usually called the *electron cloud*. For an unexcited atom, for example, this cloud has a spherical shape, but its density is not uniform. The probability of detecting the electron is highest near the spherical surface of radius r_1 corresponding to the radius of the first Bohr orbit. Henceforth, we shall assume that the electron orbit is a locus of points which are characterized by the highest probability of detecting the electron or, in other words, the region of space with the highest electron cloud density.

The electron cloud will be spherical only for the unexcited state of the hydrogen atom for which the principal quantum number is $n = 1$ (Fig. 3a). When $n = 2$, the electron, in addition to a spherical cloud whose size is now four times greater, may also form a dumb-bell-shaped cloud (Fig. 3b). The nonsphericity of the region of predominant electron localization (electron cloud) is taken into account by introducing a second quantum number l , called the *orbital quantum number*. Each value of the principal quantum

number n has corresponding positive integral values of the quantum number l from zero to $(n - 1)$:

$$l = 0, 1, 2, \dots, (n - 1).$$

For example, when $n = 1$, l has a single value equal to zero. If $n = 3$, l may assume the values

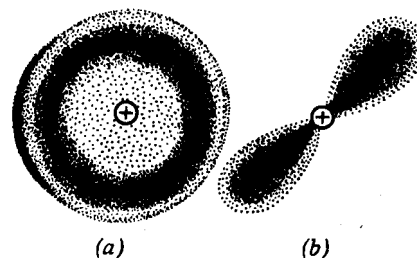


Fig. 3

0, 1, and 2. For $n = 1$ the only orbit is spherical, therefore $l = 0$. When $n = 2$, both the spherical and the dumb-bell-shaped orbits are possible, hence l may be equal either to zero or unity. For $n = 3$, $l = 0, 1, 2$. The electron cloud corresponding to the value $l = 2$ has quite a complicated shape. However, we are not interested in the shape of the electron cloud but in the energy of the atom corresponding to it.

The energy of the hydrogen atom is only determined by the value of the principal quantum number n and does not depend on the value of the orbital number l . In other words, if $n = 3$, the atom will have the energy W_3 , regardless of the shape of the electron orbit corresponding to

the given value of n and various possible values of l . This means that upon a transition from the excitation level to the ground level, the atom will emit photons whose energies are independent of the value of l .

While considering the spatial model of an atom, we must bear in mind that electron clouds have definite orientations in it. The position of an electron cloud in space relative to a certain selected direction is defined by the *magnetic quantum number* m , which may assume integral values from $-l$ to $+l$, including 0. For a given shape (a given value of l), the electron cloud may have several different spatial orientations. For $l = 1$, there will be three, corresponding to the -1 , 0, and $+1$ values of the magnetic quantum number m . When $l = 2$, there will be five different orientations of the electron cloud corresponding to $m = -2, -1, 0, +1, \text{ and } +2$. Since the shape of the electron cloud in a free hydrogen atom does not influence the energy of the atom, the more so it applies to the spatial orientation.

Finally, a more detailed analysis of experimental results revealed that electrons in the orbits may themselves be in two different states determined by the direction of the *electron spin*. But what is the electron spin?

In 1925, English physicists G. Uhlenbeck and S. Goudsmit put forward a hypothesis to explain the fine structure of the optical spectra of some elements. They suggested that each electron rotates about its axis like a top or a spin. In this rotation the electron acquires an angular momentum called the *spin*. Since the rotation

can be either clockwise or anticlockwise, the spin (in other words, the angular momentum vector) may have two directions. In $h/2\pi$ units, the spin is equal to $1/2$ and has either “+” or “-” sign depending on the direction. Thus, the electron orientation in the orbit is determined by the *spin quantum number* σ equal to $\pm 1/2$. It should be noted that the spin orientation, like the orientation of the electron orbit, does not affect the energy of hydrogen atom in a free state.

Subsequent investigations and calculations have shown that it is impossible to explain the electron spin simply by its rotation about the axis. When the angular velocity of the electron was calculated, it was found that the linear velocity of points on the electron equator (if we assume that the electron has the spherical shape) would be higher than the velocity of light, which is impossible. The spin is an inseparable characteristic of the electron like its mass or charge.

Quantum Numbers as the Electron Address in an Atom. Thus, we have learned that in order to describe the motion of the electron in an atom or, as physicists say, to define the state of an electron in an atom, we must define a set of four quantum numbers: n , l , m , and σ .

Roughly speaking, the principal quantum number n defines the size of the electron orbit. The larger n , the greater region of space is embraced by the corresponding electron cloud. By setting the value of n , we define the number of the electron shell of the atom. The number n itself can acquire any integral value from 1

to ∞ :

$$n = 1, 2, 3, \dots$$

The orbital quantum number l defines the shape of the electron cloud. From the entire set of orbits corresponding to the same value of n , the orbital number l selects those having the same shape. To each value of l there corresponds its own subshell. The number of subshells is equal to n , since l may acquire the values from 0 to $(n - 1)$:

$$l = 0, 1, 2, \dots, (n - 1).$$

The magnetic quantum number m defines the spatial orientation of the orbit in the group of orbits with the same shape, i.e. belonging to the same subshell. In each subshell, there are $(2l + 1)$ orbits with different orientations, since m may assume the values from 0 to $\pm l$:

$$m = -l, -(l - 1), \dots, -1, 0, +1, \dots, + (l - 1), +l.$$

Finally, the spin quantum number σ defines the orientation of the electron spin in the given orbit. Spin has only two values:

$$\sigma = \pm 1/2.$$

While considering the hydrogen atom and using the concepts of "shell", "subshell" and "orbit", we spoke about the opportunities available to the single electron in this atom rather than about the atomic structure. The electron in the hydrogen atom may go from one shell to another and from orbit to orbit within the same shell.

The pattern of electron distribution in many-electron atoms and their possible transitions are much more complicated.

Sec. 2. Many-Electron Atoms

Pauli's Exclusion Principle. In discussing the structure of many-electron atoms, we must consider a very important principle formulated in 1925 by the Swiss physicist W. Pauli. This principle states that there cannot be two electrons in an atom in the same quantum state described by the set of four quantum numbers (n , l , m , and σ). In other words, only one or two electrons may be simultaneously in any stationary orbit in an atom. In the latter case, the spins of the electrons must have opposite directions, i.e. for one electron $\sigma = +1/2$, while for the other $\sigma = -1/2$.

Taking into account the Pauli exclusion principle and knowing the number of stationary orbits characterized by different quantum numbers, we can determine the possible number of electrons in every atomic shell and subshell (see Table 1).

Distribution of Electrons over the Shells. The first shell, whose principal quantum number is $n = 1$, does not split into subshells, since it has only one quantum number l associated with it and this is equal to zero. In this case $m = 0$ as well, so we may conclude that the first shell consists of only one orbit which can be occupied, according to Pauli's exclusion principle, by only two electrons.

Table 1

Quantum numbers		Quantum numbers		Notation for a subshell level	Number of orbits in a subshell	Number of electrons in a level	Total number of electrons in a shell
		l	m				
1	0	0	$\pm 1/2$	1s	1	2	2
	0	0	$\pm 1/2$	2s	1	2	
2	1	0, ± 1	$\pm 1/2$	2p	3		6
	0	0	$\pm 1/2$			3s	
3	1	-1, 0, +1	$\pm 1/2$	3p	3	6	18
	2	-2, -1, 0, +1, +2	$\pm 1/2$				

The second shell ($n = 2$) consists of two subshells since l can be either 0 or 1. In atomic physics, letter symbols instead of the numerical values of l are used for describing subshells. For example, regardless of the value of the principal quantum number n , all subshells with $l = 0$ are denoted by s , subshells with $l = 1$ are denoted by p , for $l = 2$ the symbol d is used, and so on. In this connection, it is said that the second shell consists of the s - and p -subshells. The s -subshell ($l = 0$) consists of one circular orbit and may contain only two electrons, while the p -subshell consists of three orbits (m may be equal to $-1, 0$, and $+1$) and may contain six electrons. The total number of electrons in the second shell is equal to eight.

Similarly, we can calculate the possible number of electrons in any shell and subshell. For example, there can be 10 electrons in the $3d$ -subshell ($n = 3, l = 2$), viz. two electrons in each of the five orbits characterized by different values of the quantum number m . The maximum number of electrons in any subshell is equal to $2(2l + 1)$. In spectroscopy, letter symbols (terms) are ascribed to different shells: the first shell is denoted by K , the second by L , the third by M , and so on.

The single electron in a hydrogen atom is in a centrally symmetric field of the atomic nucleus; its energy is determined solely by the value of the principal quantum number n and does not depend on the values of the other quantum numbers. On the other hand, in many-electron atoms each electron is in the field created both by the nucleus and by the other electrons.

Consequently, the energy of an electron in many-electron atoms turns out to depend both on the principal quantum number n and on the orbital number l , though remaining independent of the values of m and σ .

This feature of many-electron atoms leads to considerable differences between their energy

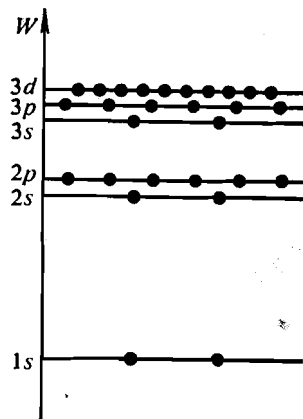


Fig. 4

spectrum and the spectrum of hydrogen atom. Figure 4 shows a part of the spectrum for many-electron atom (the energy levels of the first three atomic shells). Dark circles on the levels indicate the maximum number of electrons which can occupy the corresponding subshell.

It is well known that a system not subjected to external effect tends to go into the state with the lowest energy. Atom is not an exception

in this respect. As the atomic shells are filled, the electrons tend to occupy the lowest levels and would all occupy the first level if there were no limitations imposed by Pauli's exclusion principle. The only electron in the hydrogen atom occupies the lowest orbit belonging to the $1s$ -level. In the helium atom, the same orbit contains also the second electron, and the first atomic shell is filled. It should be noted that helium is an inert gas, and its great stability is due to the complete outer shell.

In the lithium atom, there are only three electrons. Two of them occupy the first shell, and the third is in the second shell with $n = 2$ (it cannot occupy the first shell due to Pauli's exclusion principle). Lithium is an alkali metal whose valency equals unity. This means that the electron in the second shell is weakly bound to the atomic core and can be easily detached from it. This can be judged from the ionization potential which for lithium is only equal to 5.37 V, while for helium it is equal to 24.45 V.

As the number of electrons in an atom increases, the outer subshells and shells are filled. For example, starting with boron, which has 5 electrons, the $2p$ -subshell is filled. This process is completed in inert gas neon which has a fully filled second shell and is thus characterized by the great stability. The eleventh electron in the sodium atom starts populating the third shell ($3s$ -subshell), and so on.

Sec. 3. Degeneracy of Energy Levels in Free Atoms. Removal of Degeneracy by External Effects

Degenerate States. We have already noted that in many-electron atoms the energy of electrons is only determined by the values of the quantum numbers n and l and does not depend on the values of m and σ . This can be illustrated by the energy spectrum shown in Fig. 4. Indeed, all six electrons in the $3p$ -subshell, for example, have the same energy, although they have different values of m and σ . States described by different sets of quantum numbers but having the same energy are called *degenerate*. Similarly, the energy levels corresponding to these states are also called degenerate. The levels are degenerate while the atoms are in the free state. If, however, the atoms are placed in a strong magnetic or electric field, the degeneracy is partially or completely removed. Let us illustrate this removal of degeneracy with respect to the quantum number m .

Degeneracy, Removed by an External Field. Different values of the quantum number m correspond to different spatial orientations of similar electron orbits. In the absence of an external field, different orientations of the orbits do not affect the energy of the electrons. If, however, we place an atom in an external field, the field will act differently on the electrons in orbits oriented in different ways with respect to the direction of this field. As a result, changes in energies of electrons in similarly shaped but differently oriented orbits will be different both

in magnitude and in sign: energies of some electrons will increase while those of others will decrease. The energy levels for different electrons in the spectrum will also change their arrangement. Moreover, instead of one energy level corresponding to all electrons in similar

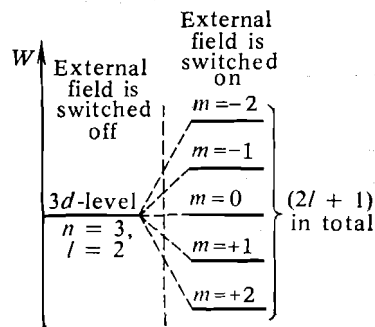


Fig. 5

orbits several sublevels appear in the spectrum, the number of sublevel being equal to the number of differently oriented similar orbits, i.e. to the number of possible values of the quantum number m . Figure 5 shows the result of an external electric field acting on the $3d$ -level, for which $n = 3$ and $l = 2$. It can be seen that splitting of the level into sublevels and the displacement of sublevels occur simultaneously.

The process in which previously indistinguishable (from the point of view of energy) degenerate levels become distinguishable is called the *removal of degeneracy*. Let us illustrate degeneracy removal with another example.

We consider an electron having a certain energy W_0 in a one-dimensional space characterized by the coordinate x (Fig. 6). In the absence of an external field, the state of this electron is described by one energy level W_0 irrespective of the direction of its motion. In other words, in the absence of an external field the energy level

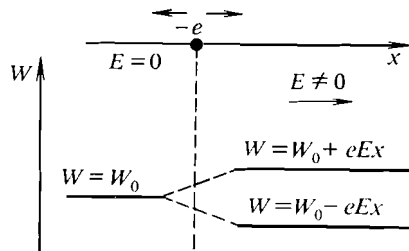


Fig. 6

W_0 is doubly degenerate. If we apply an external electric field, say, along the x -axis, the energy of the electron becomes dependent on the direction of its motion. If the electron moves along the x -axis, it will be decelerated by the external field, its energy becoming $W_0 - eEx$ (where x is the distance covered by the electron).

If the electron moves in the opposite direction, its energy becomes $W_0 + eEx$. Correspondingly, the appearance of two different states is manifested in the energy spectrum by the splitting of the degenerate level W_0 into two nondegenerate levels $W_0 - eEx$ and $W_0 + eEx$. In other words, the degeneracy is removed under the effect of the external field.

Sec. 4. Formation of Energy Bands in Crystals

Splitting of Energy Levels in a Crystal. Let us do the following mental experiment. Take N atoms of a substance and arrange them at a sufficiently large distance from each other but in such a way that this arrangement reproduces the crystalline structure of the material. Since the separation between the atoms is large, we can ignore their interaction and consider them free. In each of these atoms, there are degenerate levels with degeneracies equal to the number of differently oriented similar orbits in corresponding subshells. Let us now start bringing the atoms closer, retaining their mutual arrangement. As the atoms converge, come closer, they begin to experience the influence of their approaching neighbours, which is similar to the influence of an external electric field. The smaller the separation between the atoms, the stronger is the interaction between them. Owing to this interaction, degeneracy of the energy levels characterizing the free atoms is removed: each degenerate level splits into $(2l + 1)$ nondegenerate levels. All the atoms in a crystal generally exist under the same conditions (except for those which form the external boundary of the crystal). It could seem therefore that each atom should contribute the same set of nondegenerate sublevels into the energy spectrum that characterized the crystal as a whole viz. one $1s$ -sublevel, three $2p$ -sublevels, five $3d$ -sublevels, and so on. Each sublevel may contain two electrons with opposite spins. Although this splitting

actually occurs, the corresponding sublevels obtained from similar atomic levels differ from each other in energy, some of them are higher in the energy spectrum of the crystal than the initial levels of the individual atoms, while others lie somewhat lower. This difference can be explained by Pauli's exclusion principle generalized for the entire crystal as a single entity. According to this principle, no two nondegenerate sublevels in a crystal may have the same energy. Therefore, when the crystal is formed, each energy level spreads into an energy band consisting of $N(2l + 1)$ nondegenerate sublevels differing in energy. For example, the $1s$ -level spreads into $1s$ -band consisting of N sublevels which may contain $2N$ electrons, the $2p$ -level spreads into $2p$ -band consisting of $3N$ sublevels which may contain $6N$ electrons, and so on.

The formation of energy band in a crystal from discrete energy levels of individual atoms is shown schematically in Fig. 7. The shorter the distance r , the stronger the effect of the neighbouring atoms and the more the levels are "smeared". The energy spectrum of a crystal is determined by the smearing of the levels corresponding to the interatomic distance a_0 typical of a given crystal.

The degree of smearing of levels depends on their depth in an atom. The inner electrons are strongly coupled to their nuclei and are screened from external effects by the outer electron shells. Therefore the corresponding energy levels are weakly smeared. Naturally, the electrons in the outer shells are most strongly affected by the field of the crystal lattice, and the energy levels

corresponding to them are smeared the most. It should be noted that smearing of levels into energy bands does not depend on whether there are electrons on these levels or whether they are empty. In the latter case, the smearing of levels

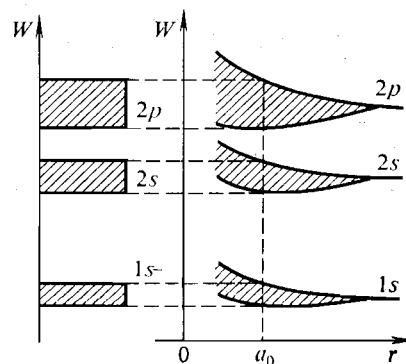


Fig. 7

indicates the broadening of the range of possible energies which the electron may acquire in the crystal.

Allowed and Forbidden Bands. From what has been said above, it follows that there is an entire band of allowed energy values corresponding to each allowed energy level in a crystal, i.e. there is an *allowed band*. Allowed bands alternate with the bands of forbidden energy, or *forbidden bands*. Electrons in a pure crystal cannot have an energy lying in the forbidden bands. The higher the allowed atomic level on the energy scale, the more the corresponding band

is smeared. As the energy increases, the forbidden bands become narrower.

The separation of sublevels in an allowed band is very small. In real crystals ranging from 1 to 100 cm^3 in size, the sublevels are separated by 10^{-22} - 10^{-24} eV. This difference in energy is so small that the bands are considered to be continuous. Nevertheless, the fact that sublevels in the bands are discrete and the number of sublevels in the band is always finite plays a decisive role in crystal physics, since depending on the filling of the bands by electrons, all solids can be divided into conductors, semiconductors, and dielectrics.

Sec. 5. Filling of Energy Bands by Electrons

Filled Levels Create Filled Bands While Empty Levels Form Empty Bands. Since the energy bands in solids are formed from the levels of individual atoms, it is quite obvious that their filling by electrons will be determined above all by the occupancy of the corresponding atomic levels by electrons.

Let us consider by way of an example the lithium crystal. In the free state, the lithium atom has three electrons. Two of these are in the $1s$ -shell, which is thus completed. The third electron belongs to the $2s$ -subshell, which is half-filled. Consequently, when a crystal is formed, the $1s$ -band turns out to be filled completely, the $2s$ -band is half-filled, while the $2p$ -, $3s$ -, $3p$ -, etc. bands in an unexcited lithium crystal are empty,

since the levels from which they are formed are unoccupied.

The same is true for all alkali metals. For example, when a sodium crystal is formed, the $1s$ -, $2s$ -, and $2p$ -bands are completely filled, since the corresponding levels in sodium atoms are completely packed by electrons (two electrons in the $1s$ -level, two electrons in the $2s$ -level, and six electrons in the $2p$ -level). The eleventh electron in the sodium atom only half-fills the $3s$ -level, hence the $3s$ -band too is half-filled with electrons.

When crystals are formed by atoms with completely filled levels, the created bands in general are also filled completely. For example, if we constructed a crystal from neon atoms, the $1s$ -, $2s$ -, and $2p$ -bands in the energy spectrum of such a crystal would be completely filled (each neon atom has 10 electrons which fill the corresponding energy levels). The remaining upper-lying bands ($3s$, $3p$, etc.) would turn out to be empty.

Overlapping of Energy Bands in a Crystal.

In some cases the problem of filling the energy bands by electrons is more complicated. This refers to crystals of rare-earth elements and those with a diamond-type lattice, among which the most interesting for us are the crystals of typical semiconductors, viz. germanium and silicon.

At a first glance, the crystals of rare-earth elements must only have completely filled and empty bands in their energy spectrum. Indeed, the beryllium atoms, for example, which have four electrons each, are characterized by two completely filled levels, $1s$ and $2s$ levels. In mag-

nesium atom, which has 12 electrons, the levels $1s$, $2s$, $2p$ and $3s$ are also completed. However, the upper energy bands in crystals of the rare-earth elements, which are created by completely filled atomic levels, are in fact only partially filled. This can be explained by the fact that the

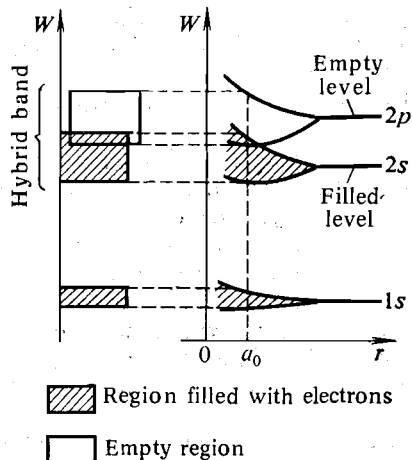


Fig. 8

energy bands corresponding to the upper levels are smeared so much in the process of crystal formation that the bands overlap. As a result of this overlapping, *hybrid bands* are formed, which incorporate both filled and empty levels. For example, a hybrid band in a beryllium crystal is formed by the completed $2s$ -levels and the empty $2p$ -levels (Fig. 8), while in the magnesium crystal, by the filled $3s$ -levels and empty

$3p$ -levels. It is due to the overlapping that the upper energy bands in rare-earth crystals are filled only partially.

In semiconductor crystals with diamond-type lattices band overlapping leads to quite the opposite result. In silicon atoms, for example, the $3p$ -level ($3p$ -subshell) contains only two

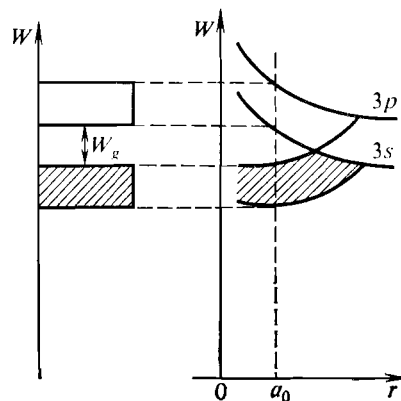


Fig. 9

electrons, though this level may be occupied by six electrons. It is natural to expect that during the formation of a silicon crystal, the upper energy band (the $3p$ -band) will only be filled partially, while the preceding band (the $3s$ -band) will be filled completely (since it is formed by the completely filled $3s$ -level). Actually the overlapping during the formation of a silicon crystal not only leads to the appearance of a hybrid bands composed of the $3s$ - and $3p$ -sublevels, but also to a further splitting of the hybrid band

