

## X

# SEMI-CONDUCTORS AND LUMINESCENCE

### 10.1. Semi-conductors

IN Chapter IV we divided solids into two classes, those in which, in the state of lowest energy, the highest occupied state was the top end of a band, and those in which the last occupied level was somewhere inside a band. This is the distinction between insulators and metals. Since the definition refers to the state of lowest energy, it is appropriate to the absolute zero of temperature, and is then a sharp division. However, if the energy gap between the last full and the next empty band is small, a few electrons will be moved up by thermal agitation, so that there are a few conduction electrons, and a few holes in the lower band.

In such substances the number of carriers should increase very rapidly with temperature. They are characterized by a low electric conductivity which increases with temperature, and are called semi-conductors. The type I have described, in which temperature causes a transition between the bands of a perfect crystal, is known as an intrinsic semi-conductor.

This type is fairly rare, since it requires a rather small value of the energy gap to give a reasonable conductivity at, say, room temperature. In principle, any non-conducting crystal should be a semi-conductor at sufficiently high temperature, but usually the effect is quite negligible.

The substance may also contain impurities in which there exists an occupied electron state, or a vacant level, in the gap between the highest filled and the lowest empty state of the crystal. If the occupied level lies near the upper edge of the gap, a small addition of energy is sufficient to raise an electron into the conduction band; if an empty level lies near the lower edge of the gap, a small addition of energy will raise an electron from the occupied band to the impurity level, and leave a hole in the band. These two cases are referred to as 'donor' and 'acceptor' levels respectively.

Such impurities need not consist of foreign atoms; they may simply consist of an excess or deficiency of the atoms making up the normal lattice. For example, a missing Cl ion in a rock salt crystal causes an excess positive charge in the neighbourhood, and this neighbourhood must therefore contain electron levels which are lower than the unoccupied levels of the main crystal.

Similarly one finds in oxides, particularly those which exist chemically in different stages of oxidation, that the oxygen content of the crystal may differ from that of the perfect crystal, and any vacant lattice sites or additional ('interstitial') atoms count as impurities for the present purpose.

At first sight it seems surprising that also in impurity semi-conductors the conductivity should always disappear at low temperatures, since there ought to be cases in which a donor level in the impurity atom lies higher than the bottom edge of the empty band, or an acceptor level below the upper edge of the filled band. In such a case one would expect the number of carriers to be equal to that of suitable impurity atoms and independent of temperature.

The answer to this apparent difficulty lies again in the fact that we must not for this purpose neglect the electron interaction. If, in a neutral lattice, an extra atom is inserted which loses an electron to an empty band of the lattice, the atom will be left ionized, and therefore attract the electron. The state of lowest energy, and therefore the only one realized at zero temperature, is therefore an orbit of the electron bound to the positively charged centre. An electron in such a bound orbit is, of course, not free to take part in the conduction process, and hence a finite energy is required to release it for this purpose.

The same states in all probability exist also in intrinsic semi-conductors, so that the production of electrons and holes which are bound together requires somewhat less energy than the state in which they are separated. Only the particles in the latter state act as carriers of electricity, and its energy determines the temperature dependence of the number of carriers in the semi-conductor.

## 10.2. Number of carriers

To calculate the number of carriers in an intrinsic semi-conductor, we assume that  $E_r$  is the top of the occupied band,  $E_2$  the bottom of the empty band.  $Z_1(E_1 - E)$  is the number of states in the lower band above energy  $E$ , and  $Z_2(E - E_2)$  the number of states in the upper band below  $E$ .

Then, using Fermi's distribution, and allowing for spin, we have

$$n_1 = 2 \int \left| \frac{dZ_1}{dE} \right| \frac{dE}{1 + e^{-\beta(E - \eta)}}; \quad n_2 = 2 \int \frac{dZ_2}{dE} \frac{dE}{e^{\beta(E - \eta)} + 1}, \quad (10.1)$$

where  $n_1$  and  $n_2$  are the numbers of holes in the lower, and of electrons in the upper band, respectively. These two quantities must be equal if the crystal is to be neutral, and at moderate temperatures both will be

small. To make both expressions small, both denominators must be large, and therefore the 1 can be neglected. We then have

$$\left. \begin{aligned} n_1 &= 2e^{-\beta(\eta-E_1)} \int_0^\infty \frac{dZ_1(\epsilon)}{d\epsilon} e^{-\beta\epsilon} d\epsilon = e^{-\beta(\eta-E_1)} K_1 \\ n_2 &= 2e^{-\beta(E_2-\eta)} \int_0^\infty \frac{dZ_2(\epsilon)}{d\epsilon} e^{-\beta\epsilon} d\epsilon = e^{-\beta(E_2-\eta)} K_2 \end{aligned} \right\}, \quad (10.2)$$

where we have used in the first integral  $E_1 - E$ , and in the second  $E - E_2$  as variable of integration.

If we may assume the energy to be a quadratic function of the wave number near the maximum or minimum energy in either band, we may characterize the states in each by an effective mass (this has to be a suitable average over directions if the energy is anisotropic near the maximum or minimum), so that, per unit volume,

$$K_1 = \frac{1}{4} \left( \frac{2m_1 kT}{\pi \hbar^2} \right)^{\frac{3}{2}}, \quad K_2 = \frac{1}{4} \left( \frac{2m_2 kT}{\pi \hbar^2} \right)^{\frac{3}{2}}, \quad (10.3)$$

$m_1$  and  $m_2$  being the effective masses. This shows that, to make  $n_1$  and  $n_2$  equal,

$$\eta = \frac{1}{2}(E_2 + E_1) + \frac{3}{2}kT \log \frac{m_1}{m_2}. \quad (10.4)$$

Our approximation assumes that the gap  $E_2 - E_1$  is much larger than  $kT$ , and, unless the masses are very different indeed, the second term is negligible. The Fermi energy  $\eta$  then lies just in the middle of the gap, and it is now easy to verify that the neglect of the 1 in both denominators of (10.1) is justified. Inserting in (10.2),

$$n_1 = n_2 = \frac{1}{4} \left( \frac{2m^* kT}{\pi \hbar^2} \right)^{\frac{3}{2}} e^{-(E_2 - E_1)/2kT}, \quad (10.5)$$

where

$$m^* = \sqrt{(m_1 m_2)}. \quad (10.6)$$

Equation (10.5) shows the characteristic exponential variation of the number of carriers with temperature. The occurrence of one-half the required energy in the exponent is typical of dissociation reactions.

The electric conductivity depends on the number of carriers and their collision time, but the latter will be a slowly varying function of temperature compared to the exponential in (10.5), and therefore in general the law (10.5) also gives the variation of the conductivity with temperature.

In an impurity semi-conductor, which has  $n_d$  donor atoms per unit

volume, each containing one electron in an energy level  $E_d$ , the second equation (10.2) is still valid, but the first has to be replaced by

$$n_1 = n_d e^{-\beta(\eta - E_d)}, \quad (10.7)$$

where  $n_1$  is now the number of vacant donor levels, which must again equal  $n_2$ .

$$\text{Then} \quad \eta = \frac{1}{2}(E_d + E_a) + \frac{1}{2}kT \log(n_d/K_a). \quad (10.8)$$

$$\text{Hence} \quad n_2 = \frac{1}{2} \sqrt{n_d} \left( \frac{2m_2 kT}{\pi \hbar^2} \right)^{\frac{3}{2}} e^{-(E_1 - E_d)/2kT}. \quad (10.9)$$

The important features of this formula are again the exponential variation with temperature, and the proportionality to the square root of the concentration of donor atoms.

An analogous formula holds, of course, for an acceptor level.

If there are at the same time donor and acceptor atoms and the donor levels are higher than the acceptor levels, electrons leave the donor atoms and go to the acceptors, until either type is exhausted. Then (10.9) must be modified. If the acceptor level lies above the donor level, the Fermi energy lies between them, and hence either the number of electrons in the upper band or the number of holes in the lower is less than it would be in the absence of either kind of foreign atom.

However, in the same substance, different kinds of foreign atoms may in varying conditions produce either predominantly excess electrons, or predominantly vacant places.

### 10.3. Electrical properties

Once the number of carriers is given, we can discuss the properties of the substance in the same way as was done in Chapter VI for a metal. One important difference is that the electron density is generally small, so that the electrons or holes do not form a degenerate Fermi gas, and the equations of Boltzmann statistics apply instead. The small number means also that some of the properties of the electrons, such as their contribution to thermal conductivity, or to the specific heat, are swamped by the contributions from the lattice vibrations, and are of no great practical interest.

As regards the conductivity, the considerations of Chapter VI apply in general. If we are dealing with a cubic crystal, and if the energy surface of the empty band has only one minimum (or that of the full band only one maximum) the energy function  $E(\mathbf{k})$  is isotropic. Collisions with impurities will, on the average, also be isotropic, since the electron waves

are long, and the crystallographic anisotropy of the scattering centres is therefore unimportant. One may therefore apply the collision time concept with reasonable confidence.

Collisions with phonons are also approximately isotropic, though the anisotropy of the elastic constants makes the sound velocity depend on the direction of travel of the phonon relative to the crystal axes. It is also still possible to regard the collisions as elastic, even though the kinetic energy of the electrons is now only of the order of  $kT$ . This is because the most energetic phonon which a given electron can absorb is one which will just reverse the direction of motion of the electron. Conservation of wave vector and of energy then require that

$$f = 2k + \frac{2m^*c}{\hbar}, \quad (10.10)$$

where  $m^*$  is the effective mass and  $c$  the sound velocity. The phonon energy is then small compared to the initial energy of the electron, provided

$$4m^*c \ll \hbar k, \quad (10.11)$$

in other words, provided the electron velocity is large compared to the velocity of sound. The mean thermal velocity at room temperature, assuming  $m^* \sim m$ , is about  $10^7$  cm./sec. This is large compared to  $c$ , and therefore the energy transfer in a collision is negligible.

Hence we may apply the collision-time concept. The collision time of an electron may be obtained from (6.49), neglecting  $n(\mathbf{k}, l)$  and  $n(\mathbf{k}', l')$  compared to unity, and assuming  $n(\mathbf{k}, l)$  to contain a term proportional to the cosine of the angle between  $\mathbf{k}$  and a fixed direction. Subject to the condition (10.10), we may then neglect the phonon frequency. For fixed  $\mathbf{k}$  the temperature enters only through the phonon numbers, and if the temperature is not too low, so that the quantum properties of phonons of wave number less than  $2k$  are still not important,  $N$  and  $N+1$  are proportional to the temperature. The collision frequency for a given electron state is thus still proportional to  $T$ .

As regards the dependence on  $\mathbf{k}$ , we note that the summation over  $\mathbf{k}'$  may be replaced by an integration, the volume element in  $k$  space being  $k'^2 dk' d\Omega'$ , where  $d\Omega'$  is the element of solid angle. Since the differential of the energy is  $dE' = \frac{\hbar^2}{m^*} k' dk'$ , we are left with a factor  $k$  after removing

the  $\delta$ -function by integrating over energy. The square of the matrix element  $|\langle \mathbf{k}', l' | A | \mathbf{k}, l \rangle|^2$  is by (6.61) proportional to the phonon frequency. On the other hand, the phonon number  $N$  is, by (2.4), inversely proportional to the phonon frequency in the classical limit. It therefore

follows that the collision frequency is proportional to the wave vector, or to the velocity of the electron, and this may be expressed by saying that the mean free path is independent of the velocity.

As regards the Hall effect, the existence of a definite collision time makes the theory of § 7.4 applicable, as far as (7.58). Since, however, the electrons do not all have substantially the same velocity, (7.59) must be replaced by a more careful calculation of  $J_y$  from (7.58) and (7.57). One then sees that in (7.59)  $\tau$  is replaced by

$$\overline{\tau^2 v^2 / \tau v^2},$$

where  $v$  is again the electron velocity, and the average is to be taken with a Maxwell distribution, while in the conductivity (6.16) the appropriate mean value is

$$\overline{\tau v^2 / v^2}.$$

Hence, using the result that  $v\tau$  is independent of velocity, (7.61) must be multiplied by the ratio

$$\overline{v^2} / (\overline{v})^2,$$

which for a Maxwell distribution is  $3\pi/8$ . Hence the Hall coefficient of a semi-conductor in which only electrons or holes contribute, and in which there is isotropy, is

$$R = \frac{3\pi}{8ecN}. \quad (10.12)$$

One must, however, be certain that the conditions for the validity of this equation are satisfied before using it to estimate the number of electrons or holes. In particular in an intrinsic semi-conductor, in which the electrons and holes generally give comparable contributions, one must replace the equation by (7.65), and this usually cannot be evaluated from the observations without further assumptions about the model.

#### 10.4. Density gradients and space charge (cf. Mott, 1938)

So far we have been concerned only with cases in which the electron density is uniform in space. In semi-conductors one is also interested in the case in which the density is non-uniform, either because the density of impurity atoms which act as donors or acceptors is non-uniform, or because electrons are raised to the upper band by a light wave which either has an intensity gradient because of the absorption of the substance or, because of its direction, gives a preferential direction to the electron velocity. I shall discuss only the first of these alternatives in detail; the other is of importance in connexion with the contact layer photoelectric effect, which will not be treated.

Suppose that a region in the crystal contains a density  $n_d$  of donor

levels per unit volume, so that the equilibrium density of electrons would be given by (10.9), and suppose that the energy gap between filled and empty band is much larger than  $kT$ , so that the 'intrinsic' effect is negligible. Suppose also that in the neighbourhood there are other sources of electrons (such as a region with more donor atoms, or a contact with a substance of high electron density and low work function or the reverse) so that the electron density will differ from the equilibrium value. Within the given region, we may still use the second equation (10.2) for the electron density, and (10.7) for the number of vacant donor levels, but we may no longer require the two to be equal. There will then in general be a space-charge density, given by

$$e(n_2 - n_1), \quad (10.13)$$

and this will cause an electrostatic potential  $\phi(r)$  which has to be allowed for in discussing electronic levels. This potential will vary by a negligible amount over atomic dimensions, and we may therefore simply replace the energies  $E_2$  and  $E_d$  by  $E_2 - e\phi$  and  $E_d - e\phi$ , respectively. From Poisson's equation and (10.13), assuming  $\phi$  to depend only on one coordinate  $x$ ,

$$\frac{d^2\phi}{dx^2} = -4\pi e(n_2 - n_1). \quad (10.14)$$

For equilibrium the parameter  $\eta$  must still be a constant, independent of  $x$ . Inserting for  $n_2$  and  $n_1$  from the second equation (10.2) and (10.7),

$$\frac{d^2\phi}{dx^2} = -4\pi en_2^0(e^{e\phi/kT} - e^{-e\phi/kT}), \quad (10.15)$$

where  $n_2^0$  is the equilibrium electron density, which is given by (10.9). It might be objected that in obtaining (10.15) we have used the value (10.8) for  $\eta$ , which would seem arbitrary; however, a change in  $\eta$  is equivalent to adding a constant to the electric potential  $\phi$ , which is compatible with (10.14). Taking  $\eta$  equal to the equilibrium value amounts to the convention that  $\phi = 0$  where the electron density has its equilibrium value.

The solution of (10.15) for which  $d\phi/dx = 0$  when  $\phi = 0$  is

$$e\phi = 2kT \log \coth \left( \frac{x - x_0}{l} \right), \quad (10.16)$$

where

$$l^2 = \frac{kT}{2\pi e^2 n_2^0} \quad (10.17)$$

and  $x_0$  is arbitrary. Hence for small deviations from equilibrium, when  $\phi$  is small,

$$e\phi = 4kT e^{-2(x-x_0)/l}, \quad (10.18)$$

so that to the same accuracy

$$n_2 - n_2^0 = \text{constant} \times e^{-2x/l}. \quad (10.19)$$

On the other hand, if the source gives rise locally to a density greatly exceeding  $n_2^0$ , so that  $e\phi$  is much larger than  $kT$ , we have

$$n_2 = n_2^0 e^{e\phi/kT} = n_2^0 \frac{l^2}{(x-x_0)^2} = \frac{kT}{2\pi e^2 (x-x_0)^2}. \quad (10.20)$$

The last form shows that the result is now independent of  $n_2^0$  and the formula applies therefore also when there are no donor levels present. The result may be expressed by saying that  $1/n_2$  increases linearly with  $x$ .

We conclude therefore that small deviations from the normal electron density are evened out over a distance of the order (10.17), which for low values of the equilibrium density may be very large compared to the lattice spacing. It is also obvious why it is not worth considering the corresponding problem for a metal, since then the electron density is high and deviations are adjusted almost at once. Our formulae are, of course, not valid for metals, since the electron degeneracy has to be taken into account, so that the results contain  $\eta$  rather than  $kT$ , but the length that then replaces  $l$  is again very small indeed.

If, instead of static conditions, we assume the presence of an external potential gradient, there will be an electric current  $J$  of the form

$$J = -\sigma \frac{d\phi}{dx} - D \frac{dn}{dx}, \quad (10.21)$$

where  $\sigma$  is the conductivity, and  $D$  is a diffusion coefficient. We know from the preceding discussion that the electrons must be in equilibrium, and hence the current zero, if

$$n_2 = \text{constant} \times e^{-e\phi/kT},$$

and this shows that 
$$D = \frac{kT}{e} \frac{\sigma}{n_2} = kTu, \quad (10.22)$$

a relation due to Einstein.  $u = \sigma/n_2 e$  is independent of the electron density, and is called the mobility.

In the most general case of non-uniform electron density and an electric current, (10.21), in which for steady conditions  $J$  must be constant, i.e. independent of  $x$ , should be combined with the Poisson equation (10.14). This situation is, however, too general for a simple analysis, and we shall consider in the next section only a particular application.



### 10.5. Rectifying contacts

An important phenomenon involving semi-conductors is the rectifying contact. This is a contact between a metal and a semi-conductor which has, for zero current, a high resistance to flow across the surface, and in which the resistance diminishes rapidly with increasing voltage in one direction, the direction of easy flow, whereas for a potential difference of opposite sign the resistance increases strongly, at least over a certain range.

Several possible mechanisms are known which could give rise to a dependence of the contact resistance on the potential difference. We shall here discuss only one particular model, the theory of which is due to Mott (1939), and which is well borne out by the experiments in the case of copper-cuprous oxide contacts.

The high resistance of the contact is then due to a poorly conducting layer ('blocking layer') and it is known that in many cases this is a layer in which the impurity atoms are lacking. An important type of contact is that in which a metal surface is oxidized. On one side we then have an oxide in which excess oxygen is the activating impurity; it is reasonable that where the oxide is in contact with pure metal the excess oxygen should be lacking.

Suppose now for uniqueness that the carriers are electrons rather than holes and suppose that the work function of the metal exceeds that of the normal semi-conductor. Then there must exist a contact potential between the two layers, which is produced by the metal absorbing a few electrons from the semi-conductor. However, these electrons cannot come from the blocking layer, which contains practically no electrons, and must therefore come from the 'good' semi-conductor beyond it. In other words, the double layer which produces the contact potential has a thickness equal to that of the blocking layer. Instead of being restricted to a few atomic layers, the rise of the potential is thus spread over a layer which, in typical cases, has been found to be  $10^{-4}$  to  $10^{-3}$  cm. thick.

This state of affairs is shown in Fig. 17 (a). The Fermi level of the metal is at the same energy as that of the semi-conductor, which lies half-way between the bottom of the conducting band and the donor levels. The electrons from the donor levels penetrate somewhat into the blocking layer, but the rising potential makes their density fall rapidly.

If now a field is applied in such a direction as to pull electrons towards the semi-conductor, the situation will be as indicated in Fig. 17 (b). The main part of the additional potential difference resides in the

blocking layer, and helps to make the gradient steeper. This diminishes the number of electrons which come, by thermal energy fluctuations, from the semi-conductor, and does not appreciably assist the electrons from the metal in reaching the blocking layer. It is only when the field becomes strong enough to give the conditions for 'cold emission' (cf. § 4.7) that the resistance will again diminish.

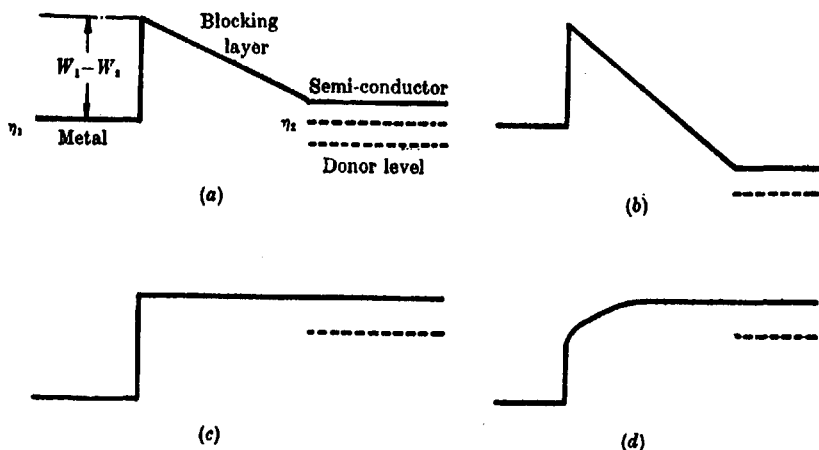


FIG. 17

On the other hand, if the sign of the applied potential difference is such as to pull electrons towards the metal, the potential distribution will approach that of Fig. 17 (c), with the potential in the blocking layer practically constant, so that the electron density will be the same as in the presence of the donor levels; the resistance of the blocking layer is then negligible.

To be precise, a high conductivity of the blocking layer means a high electron density, and therefore a space charge. We ought therefore to think of the limiting case in terms of Fig. 17 (d), in which the curvature of the potential in the blocking layer is due to the space charge.

The treatment by Mott neglects this space-charge effect, and assumes therefore that the potential gradient in the blocking layer is uniform.

Then, from (10.21),

$$J = u \left( neF - kT \frac{dn}{dx} \right), \quad (10.23)$$

where now  $u$ ,  $F$ , and  $J$  may be regarded as constant. I have omitted the suffix 2 on  $n$ . The integral of (10.23) is

$$n = \frac{J}{euF} + Ce^{-eFx/kT}. \quad (10.24)$$

The electron density is given at the metal surface, where it equals the first part of (10.2), with the value of  $\eta$  adjusted to that in the metal. It is also known for  $x = d$ , in the normal semi-conductor.

$$\text{Then} \quad J = euF \frac{e^{eFd/kT}n(0) - n(d)}{e^{eFd/kT} - 1}. \quad (10.25)$$

If the exponent is not a large positive number, the electron density will be large throughout the blocking layer, and the resistance negligible. If the exponent is large we neglect the 1 in the denominator,

$$J = euF\{n(0) - n(d)e^{-eFd/kT}\}. \quad (10.26)$$

Remembering that, in the absence of an external potential difference, as in Fig. 17 (a),

$$\frac{n(d)}{n(0)} = e^{eF_0d/kT},$$

$$\text{we have} \quad J = \frac{eun(0)}{d}(V_0 - V)(1 - e^{eV/kT}), \quad (10.27)$$

where  $V$  is the applied potential difference and

$$V_0 = F_0 d.$$

(10.27), which is valid only for  $V < V_0$ , shows the characteristic unsymmetric behaviour of a contact rectifier.

This treatment depends on the thickness of the blocking layer being large compared to the mean free path of the electrons, since otherwise higher derivatives of the density would appear in (10.23). It also neglects space charges, as I have pointed out. It can, of course, be immediately extended to hole conduction, with the appropriate changes in sign.

### 10.6. Electrons not in thermal equilibrium

In the preceding sections, we were concerned with thermal equilibrium, so that the number of electrons in the upper band, or holes in the lower band, was in each case a constant, independent of time, except for fluctuations. We are then in general not interested in the mechanism by which the electrons are raised, since the result follows from statistical mechanics, independently of the mechanism.

The situation is different when the electrons are raised into the upper band by an external agent, such as a light beam, and we are then concerned with the mechanism, and also with the subsequent fate of the electrons. To fix our ideas, let us consider a case in which an electron is raised to the upper band by absorption of light from a state in the filled band.

In this case the result is an electron in the upper and hole in the lower

band. There will be an electrostatic attraction between the two, and, if their kinetic energy is low, they may remain in a bound state, in which they revolve about each other, losing energy by various processes fairly rapidly and ending up after a short time with emission of light of a frequency slightly lower than that of the incident radiation and the return of the electron to the lower band. If the energy of the transition is high enough, the electron and hole can overcome their attraction and separate. Each then travels independently of the other, but is subject to changes of direction, due to collisions with lattice waves, as discussed in the preceding section, and imperfections of the lattice, and also a gradual loss of energy, due again mainly to the interaction with lattice waves. During this period, it is free to cover appreciable distances and, if an electric field is also present, will on the average carry a current in the field direction. If no other processes were possible, the electron and hole would ultimately end up in a state of very low velocity but would still contribute to the conductivity. In fact, since we have seen that the collision time varies as the inverse velocity, such slow carriers are particularly effective.

However, the life of these free carriers is, in fact, limited, since they are liable to other processes.

(a) *Recombination.* An electron may encounter a hole, and may then drop into the lower band, generally with the emission of radiation. It may alternatively lose, by collisions, enough energy while close to a hole to be confined to a closed orbit. The ultimate result will also be recombination.

(b) *Non-radiative recombination.* In some cases the recombination with the emission of radiation may be forbidden by the selection rules. This is important in particular if the lowest state in the upper band and the highest in the lower band do not belong to the same wave number. In this case the emission of radiation is still possible if simultaneously a phonon is produced or absorbed. This does not affect the energy balance appreciably, but may restore the balance of wave vectors. This, however, is a process of higher order and correspondingly less frequent.

Alternatively, the transition may take place without the emission of radiation, all surplus energy appearing in the form of phonons. Since the energy gap between the two bands is usually much larger than the energy of the hardest phonon, this usually means the simultaneous production of a large number of phonons. Such transitions are well known in the theory of molecular spectra, and the condition for them is that the potential energies of the two electronic states, plotted against the nuclear

coordinates, should have an intersection. Fig. 16 represents such energy curves schematically, against some symbolic variable representing the motion of the nuclei in the lattice. If the curves intersect, we may regard the system as following the upper curve to the intersection and continuing on the lower curve with a corresponding increase of vibrational kinetic energy, which will be rapidly dissipated. However, the problem is essentially a many-body problem, so that such simple diagrams can only have a very qualitative meaning. A quantitative theory of this effect would have to be much more complicated.

(c) *Trapping*. Without returning to the lower band, the electron may lose its mobility by being trapped. One kind of trapped state is the one which we discussed in § 9.4, in which the lattice has distorted itself so as to conform to the forces due to an electron in a particular position, and thereby created an attractive centre for the electron. This process is referred to as 'self-trapping', and, while it seems theoretically likely that such states may exist, this form of trapping does not seem to have been definitely identified experimentally.

Alternatively, a trap may be some irregularity in the lattice which favours the presence of an electron. An example is a fault in an ionic crystal where a negative ion is missing, so that the neighbourhood contains too much positive charge (Mott and Gurney, 1940). It is likely that grain boundaries and other irregularities also can provide energy levels in which electrons can be trapped.

The same remarks apply to holes, which may also be trapped.

Trapped holes or electrons can be released by thermal energy fluctuations, which may give them enough energy to return to the mobile state, or by the absorption of light of much lower frequency than would be required to cross the gap between the full and the empty band.

This provides the mechanism for the most common type of phosphorescence. A 'phosphor' is a transparent crystal which contains a small number of impurity centres which absorb visible or ultra-violet light. The absorption process leads to a transition of an electron from an impurity centre into the empty band. Some of the electrons return to vacant impurity levels at once, with emission of radiation; others are trapped before they have found a vacant level. If the binding energy of the trap is comparable with  $kT$  at room temperature, they may after some time return to the empty band and then have another chance of radiating. The emission of light from such a phosphor continues therefore for some time after the irradiation has ceased. This process can be accelerated by heating, since this releases the electrons more frequently

from the traps, and also releases those caught in deeper traps. The emission may also be accelerated by irradiation with infra-red light.

The frequency of the emitted light is usually less than that which excited the electrons in the first place. There are two reasons for this. Firstly, the electron may have been raised to a state above the bottom of the empty band but will in general lose energy by collision before it radiates. Secondly, when the electron is first removed from the impurity centre, the arrangement of the atoms surrounding this centre is very nearly the equilibrium arrangement corresponding to the electron being present. When it returns, the arrangement will be that most favourable for an ionized impurity atom, and when the electron has returned, the atoms will be in a configuration of higher potential energy, thus making less energy available for the transition. The remainder of the energy is, of course, then dissipated in the form of lattice waves.

Phosphorescence is of practical interest for producing luminous paints, which in the dark emit radiation as a result of the light they absorbed during daylight or when previously illuminated, and also for converting ultra-violet light into visible for greater efficiency and pleasanter appearance in fluorescent lighting.

Crystals may also be activated by fast electrons or other charged particles instead of light, and then provide a means of converting particles into light flashes, a possibility utilized in the scintillation counters of nuclear physics.

Because of these applications, as well as because of their intrinsic interest in the study of solids, the properties of luminescent substances have been studied very extensively (cf. Garlick, 1949).