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**THE LIFETIMES OF FREE ELECTRONS
AND HOLES IN SOLIDS**



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This bulletin describes a method of analysis for appraising free carrier life times and shows how to apply it to photoconductors, phosphors, and semiconductors. The concept of a *demarcation level* is shown to be a useful tool for estimating the occupancy of discrete states in the forbidden zone and their contribution to life time. The demarcation level separates states into those whose occupancy is determined by being in thermal equilibrium with one of the band edges and those whose occupancy is determined by the kinetics of recombination. The displacement of this level as a function of temperature, excitation, and chemical doping can be used to describe a great variety of observed behaviour in phosphors, photoconductors, and semiconductors. In particular, one is led to the concept of *electronic doping*. The demarcation level allows an easy visualization of the dependence of minority carrier life time in transistors on the position of the Fermi level. It also helps to describe the complex transition between semiconductors and insulators.

Introduction

The life times of free electrons and holes in solids are of central importance in the several broad fields of luminescence, photoconductivity and semi-conductor control devices. At the same time, the analysis of the factors that control life times quickly leads to a complex array of algebraic relations or of physical concepts or both. Most of the complexity is inescapable. The still unplumbed variety of behaviour, particularly of luminescent materials and photoconductors bears direct witness to a maze of inner parameters in these materials. Some of the complexity may, however, at least be relieved by a happy choice of approximations or concepts. This is one of the aims of the present bulletin. It must be stated as an aim since the judgement of whether or not a particular concept is simple is largely a matter of taste.

There exists in the literature numerous analyses of the life time or recombination properties of special models. The models have been chosen to fit the behaviour of semiconductors^{1,2} of phosphors³, of photoconductors⁴, and of phosphors and photoconductors combined⁵. On the one hand, these models have brought with them separate systems of concepts, terminology and operating conditions; on the other hand, the physical processes governing life times are the same in all three fields. In fact it is becoming increasingly common to examine new materials for all three properties: electrical control of conductivity, luminescence and photoconductivity.

It is worth trying to develop a method of analysis that is not peculiar to any one of the fields and a method that allows one to change the operating conditions smoothly between wide limits. This is the second aim of the present work.

The writer has no illusions that one can set up a tidy, universal model ready to illuminate all problems. Quite the contrary. Most real problems involve the simultaneous influence of several different types of recombination centers. The shifting competition between these centers as the temperature of the rate of generation of free pairs is changed is not always easy to describe nor to comprehend. At the same time, a useful insight into or *feel* for the problem can be attempted by emphasizing the physical concepts.

Some Background Information

To compute the life time of a free carrier one must know the distribution of electrons and holes among the discrete states lying in the forbidden zone. For a solid in thermal equilibrium, the distribution is characterized by a single parameter, the Fermi level. If, now, additional free carriers of *one sign only* are introduced, the new distribution can, to a good approximation, be described by a new value for the Fermi level, called the steady-

state or quasi Fermi level. Such an analysis was carried out for carriers optically excited out of deep lying discrete states⁶ and for carriers injected at one electrode giving rise to space-charge-limited current flow⁷.

Another type of problem that can be treated readily is that of an insulator in which additional free carriers of both signs are generated – the new free carrier densities being large compared with the thermal equilibrium concentrations. Here the use of two steady-state Fermi levels, one for free electrons and one for free holes, reproduces most of the observed behaviour^{5,8}. But even here the treatment remains simple only for one type or class of discrete states in the forbidden zone. A class is defined by its capture crosssections for free electrons and holes; the states may still be distributed over a range of energies. When more than one class of states is introduced, a pair of steady-state Fermi levels must be computed for each class taking into account possible re-distributions of electrons and holes between the classes. Much of the behaviour of phosphors and photoconductors is traceable to the presence of several classes of states^{3,4,5,9}.

In contrast with the many analyses of life times for phosphors and photoconductors, there are only a few discussions especially centered on semi-conductors. The three papers^{1,2,10} all treat the problem of life time in the presence of a single level of discrete states. The solutions are involved algebraic expressions that do not lend themselves either to visualizing the physical processes or to including states distributed in energy. The extensive and careful analysis of Haynes and Hornbeck¹¹ illustrates the complexity of the problem when more than one class of discrete states is present.

What is missing is a frame work within which the shifting distribution of electrons and holes in the various levels of discrete states can be visualized. Especially is this lack evident in the transition from semi-conductors in which the thermal concentrations of carriers play a large role to insulators in which the optically (or electronically) excited carriers dominate the distribution.

Quick reference is made here to an earlier paper⁴ in which the following items were discussed: the enormous range of life times encountered in solids, extending from at least some seconds to 10^{-13} seconds; the large range of capture crosssections extending from about 10^{-13} cm², a value derivable from capture by an attractive coulomb field to values less than 10^{-22} cm² that are probably associated with capture in the face of a repulsive coulomb field (capture of an electron by an already negatively charged center); the existence generally of two independent life times, one for electrons and one for holes; and the logical collapse of these two life times into a single common life time when the added carrier densities are greater than the densities of discrete states.

A final introductory remark should be made even though it may appear gratuitous. In a field as broad as the study of carrier life times in solids, understanding is enhanced by a variety of approaches. The present analysis is not intended to be competitive but rather supplementary to other analyses already published. Its distinguishing feature is its emphasis on the physics rather than the mathematics of recombination.

Survey of Method of Analysis

Consider a free electron wandering around in the conduction band. In an energy level diagram, the electron looks down and sees a number of energy levels (empty states from the point of view of an electron) into which it can jump. These include the very shallow lying states, called shallow traps or ionized donors; the deeper lying states called variously by the names traps, recombination centers, activators, killers, and ground states; and finally the free holes in the valence band. From the point of view of the electron about to jump, the only significant information is the number of these states and their capture crosssections for free electrons. It is necessary then, as a first step to know the distribution of empty places into which the electron can jump. This implies knowing the distribution of both electrons and holes in all the states of the energy level diagram.

After the electron has jumped into one of the empty states, it has two possible paths. It may jump back up into the conduction band by thermal excitation or it may be captured by a free hole. It is significant to know which of these events will take place first.

If the electron jumps back into the conduction band, one calls the state into which it had jumped a trap. That is, the life of the free electron has been interrupted or suspended but not terminated. Furthermore, if the jumping back and forth between the conduction band and the "trap" is more frequent than the capture of the trapped electron by a free hole, the fractional occupation of these states by electrons is determined by the density of electrons in the conduction band. The electrons in these states are said to be in thermal equilibrium with the conduction band. In particular, one can draw a Fermi function pinned down at the one point by the fractional occupation in the conduction band. The Fermi function extending below the conduction band describes the occupation of those states that are in thermal equilibrium with the conduction band.

If the electron is captured by a free hole before it is thermally re-excited into the conduction band, the life of the free electron has in fact been terminated. A

new optical excitation, electronic excitation or injection is required to replace the lost electron. Furthermore, the states in which capture by a free hole is much more probable than thermal excitation into the conduction band are not in thermal equilibrium with the conduction band. The occupancy of these states is determined either by the kinetic processes of first capturing a free electron and then a free hole or by thermal exchange with the filled band. For those states in which the kinetic processes are dominant, one can easily verify that the ratio of the time a state is occupied by an electron to the time it is occupied by a hole is ns_n/ps_p . n and p are the free electron and hole densities; s_n and s_p are the capture cross-sections of the state for free electrons and holes respectively. Finally, the occupancy of these states is not dependent on their position in the energy scale.

The second step is then to separate the states in the forbidden zone into those whose occupancy is determined by thermal exchange with one of the band edges, and those whose occupancy is determined by the kinetics of recombination. It is significant to make this separation only if the transition between the two types of occupancy is sharp. For most materials and most temperatures of interest, the transition can be considered sufficiently sharp. For example, at room temperature the rate of thermal excitation varies by a factor of almost 100 for a tenth of a volt shift in energy. Since the kinetic processes are not a function of energy, this means that the ratio of thermal to kinetic processes also varies at the rate of a factor 100 per tenth of a volt. Thus, if one locates the energy at which thermal and kinetic processes are equal, one can be confident that, in moving a tenth of a volt towards the nearest band edge, thermal processes are dominant and similarly that a movement of a tenth of a volt in the opposite direction will insure the dominance of kinetic processes. At lower temperatures, the transition is, of course, still sharper.

The argument can be summarized at this point by reference to Fig. 1. Here, it is assumed that the added densities of carriers are large compared with their thermal equilibrium values, not because the added densities are large but because the thermal densities are negligibly small. The states in the forbidden zone have been separated into those for which thermal exchange with free carriers is dominant and those for which the kinetics of capture are dominant. This separation is done once for electrons and once for holes. The demarcations between thermal and kinetic processes are labeled D_n and D_p for electrons and holes respectively. The occupancy of states between D_n and the conduction band is determined by thermal exchange of electrons with the conduction band and is measured by the Fermi function adjusted to fit the known occupancy of the conduction band. Similarly, the occupancy of states between D_p and the filled band is determined by thermal exchange of holes with the filled

band and is measured by the Fermi function adjusted to fit the known occupancy of the filled band by holes. The occupancy of states between D_n and D_p is uniform or independent of energy and is measured as already mentioned by the ratio ns_n/ps_p .

The life time of a free electron can be visualised easily. It is approximately the time required for an electron to be captured by any one of the empty states lying below D_n . The actual life time is somewhat shorter since a small fraction of the electrons falling into the states lying above D_n are captured by holes. The correction can readily be introduced by computing the "kinetic" traffic of holes into these states. Similarly, the life time of a hole is approximately the time required for a hole to be captured by any one of the electron-occupied states above D_p .

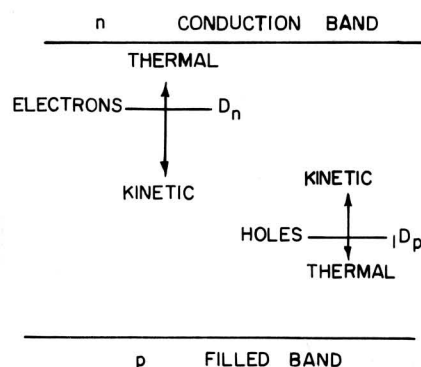


Fig. 1 - Demarcation levels for excited carrier densities large compared with thermal densities.

Determination of the Demarcation Levels D_n , D_p

We seek here the energy level D_n at which a trapped electron has an equal chance of being thermally excited into the conduction band and of being captured by a free hole. Quantitatively this is expressed by:

$$\nu^* e^{-E/kT} = p v s_p \quad (1)$$

where the left hand side gives the rate of thermal excitation and the right hand side the rate of capture by free holes. ν^* is the attempt-to-escape frequency multiplied by a transition probability. E is the energy difference between the trapping state and the conduction band; p is the free hole density, v the thermal velocity and s_p the capture cross-section of the trapping state for a free hole. In an earlier paper⁴, Eq. (1) was solved for E with the result that the level in question, D_n , to a first approximation was located at the steady-state Fermi level for electrons. Similarly, the level D_p for holes was located approximately at the steady-state Fermi level for

free holes. Both levels D_n and D_p are actually shifted a small amount, $kT \ln n_g/p_g$, from their respective steady-state Fermi levels, n_g refers to the density of states occupied by electrons and lying between D_n and d_p , and p_g refers to the density of such states occupied by holes.*

The same results, obtained above mathematically, can be deduced by inspection of Fig. 2. Fig. 2 shows the distribution function for electrons and holes in the states in the forbidden zone and in the free states. Starting with known values for the free electron and hole densities, n and p , the corresponding steady-state Fermi levels, E_{fn} and E_{fp} , are located. Next the Fermi functions are sketched in at these two levels. It is to be noted that the Fermi function shows a very sharp transition, at the Fermi level, between almost complete and almost zero occupation values.

A determination is now made of the fraction of states lying between E_{fn} and E_{fp} that are occupied by electrons. The fraction occupied by holes is, of course, one minus the fraction occupied by electrons. The fractional occupancy is drawn in, as in Fig. 2, as a line of constant occupancy since the occupancy of these states is controlled by kinetic processes and is independent of energy. Finally the intersections of the line of constant occupancy with the two Fermi functions defines the two demarcation levels D_n and D_p . The complete occupancy curve is shown in Fig. 2 as a solid line extending from the conduction band to the filled band and including two parts of a Fermi function at its ends and a straight line portion in the middle. From the point of view of the free electron and hole densities, the forbidden gap has been narrowed by an amount equal to the straight line portion of the curve. This is a result of the excitation that generated the free carrier densities in excess of their thermal equilibrium values.

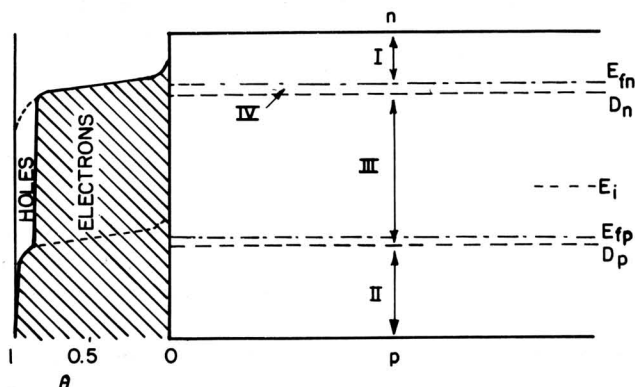


Fig. 2 - Distribution of electrons and holes for excited carrier densities large compared with thermal densities.

*In reference 8, the states $N_g = n_g + p_g$ were called ground states because the life times of free electrons and holes were terminated by capture into these states.

The use of the states lying between E_{fn} and E_{fp} in order to determine the demarcation levels, D_n and D_p , is an approximation but an approximation that becomes increasingly good as D_n and D_p approach E_{fn} and E_{fp} respectively. Since the Fermi function rises so steeply near the Fermi level, the intersections with the straight line portion of the curve are not likely to depart far from the Fermi levels. The facts that D_n and D_p are shifted by the same amounts from E_{fn} and E_{fp} and that the shift is a logarithmic function of the ratio n_g/p_g is clear from Fig. 2 and the Fermi function.

Life Times - Excited Densities Predominant

When the densities of electrons and holes, excited by light or other means, are large compared with their densities at thermal equilibrium, the two steady-state Fermi levels are well separated as shown in Fig. 2. This is the situation common in phosphors and in many photoconducting insulators. There is a large region (marked III in Fig. 2) of states whose occupancy is determined by kinetic processes. These states tend to dominate the life times of electrons and holes since most of the recombination traffic passes through them.

Consider, for example, a free electron looking down into the various empty states into which it might be captured. Capture into any of the states below D_n essentially terminates the life of the electron. There are many of these states lying between D_n and D_p . Below D_p , however, the fraction of empty states into which an electron can be captured falls off exponentially. For that reason, the states in region II of Fig. 2 can usually be neglected. Only if the density of these states becomes large enough to offset the exponentially decreasing Fermi function or if their capture crosssections for electrons is unusually large, need they be considered.

In region I (states lying above E_{fn}), there are many states into which an electron can jump since substantially all of these states are empty. An electron jumping into these states, however, will be thermally re-excited into the conduction band long before it can capture a free hole. A measure of the contribution of these states to life time can better be obtained by looking at the traffic of free holes into them. Whatever free holes are caught in these states (see Fig. 1) will remain there until neutralized by a free electron. That is, the rate of permanent capture of free electrons into the states of region I must equal the rate of capture of holes into the same states. But the rate of capture of holes in region I is small compared with that in region III, since the fraction of electron occupied states into which a hole can be captured falls off exponentially above E_{fn} . This is the

same argument used for neglecting the contribution of the states in region II to life time.

$$\tau_n = 1/vs_n p_g \quad (2)$$

The states in region IV present a more complex problem. Even though electrons captured into these states are likely to be thermally re-excited before capturing a hole, the fraction of electrons *permanently* captured is significant. Again, one uses the traffic of free holes into these states as a guide. The states in region IV, because they lie below the Fermi level, are more than half occupied by electrons and therefore have substantially the same occupancy as the states in region III. The rate of capturing holes by states in region IV will accordingly be approximately the same as if the states were in region III. Since the recombination electron traffic into these states must equal the hole traffic, the states in region IV can be as effective in determining life times as those in region III. On the other hand, the width of region IV is likely to be small compared with region III in insulators in which the excited densities of carriers are large compared with their thermal densities. For the purposes of many discussions, region IV may be lumped with region III.

$$\tau_p = 1/vs_p n_g \quad (3)$$

In summary, the states in regions III and IV, that is, those lying between E_{fn} and D_p are the most important for determining the life times of electrons and holes. It remains to determine the fractional occupancy of these states by electrons and holes.

These life times are independent and, in general, widely different since the capture crosssections s_n and s_p are, in general, widely different. By way of example, it is known¹² that the electron life time in sensitized crystals of CdS is about 10^{-3} seconds. The life time of a free hole in these crystals may be estimated from the poor efficiency of the photo voltaic effect to be less than 10^{-9} seconds. It is only in some relatively pure and insensitive crystals of CdS that the electron and hole life times have been observed by Smith¹³ and by Sommers¹⁴ to approach equality at about 10^{-7} seconds.

Excited Carrier Densities Less Than the Densities of Recombination Centers

Let the densities of electrons in the conduction band plus those in region I be small compared with the density of holes (p_g) in regions III and IV. Similarly, let the densities of holes in the filled band plus those in region II be small compared with the density of electrons (n_g) in regions III and IV. This is a common situation for photoconducting insulators and for optically excited phosphors. The above conditions insure that the densities of holes and electrons in regions III and IV remain substantially the same after excitation as they were before excitation. (By the condition of charge neutrality the difference between the excited electron and hole densities outside III and IV must be reflected by the opposite change inside III and IV.) The density of holes (p_g) in III and IV is then equal to the density of states lying between E_f , the thermal equilibrium value of the Fermi level, and E_{fn} ; the density of electrons (n_g) in III and IV is equal to the density of states lying between E_f and D_p . These are the electron and hole densities existing in regions III and IV before excitation.

The electron and hole life times can now be written in the usual form:

One can readily see in terms of Fig. 2 that, as the excitation is increased, the levels E_{fn} and D_p , embracing the states through which recombination takes place, pull apart to include more states. If the states are all of one kind, the effect is to shorten the life times of carriers by increasing n_g and p_g . This is a comparatively slow effect and readily accounts for the frequent observations that photocurrents increase as the 0.7 or 0.8 power of the light intensity^{12,15,16}. Such odd powers over large ranges of light intensity are difficult to account for without a distribution of states in energy.

The increased separation of E_{fn} and D_p at higher excitations means also that higher energy jumps are possible from the conduction band into one of the p_g states or between the valence band and one of the n_g states. One sees here, in simple fashion, a mechanism that can account for the frequent observation that the luminescence of phosphors shifts toward the blue at higher excitations¹⁷.

An increase in temperature, on the other hand, tends to bring the levels E_{fn} and D_p closer together. The distance of E_{fn} from the conduction band is defined by:

$$E_{fn} = kT \ln N_c / n \quad (4)$$

where N_c is the density of states in the bottom of the conduction band. Again, if there is only one class of states and if the temperature does not affect the capture crosssections, an increase in temperature has the opposite effect from an increase in intensity of excitation. There are many instances in photoconductivity and luminescence where the opposing actions of temperature and excitation are evident. Experimentally this means that an effect that occurs at a given temperature will occur at a higher temperature if the excitation is increased. Good quantitative evidence for this correlation has been reported by

Bube¹⁸ in measurements of superlinearity in photoconductors. Other evidence is found in the known facts that the color changes of luminescence occur at higher excitations for higher temperatures and that the temperature "break point" for phosphors increases with increasing excitation. The temperature changes slowly with carrier density by the relation (obtained from Eq. 4):

$$\Delta T/T = kT/E_{fn} \ln n_2/n_1 \quad (5)$$

ΔT is the temperature change needed to compensate for an increase of carrier density from n_1 to n_2 . In this way the Fermi level E_{fn} is maintained constant. The relative shifts of the temperature break points for excitation densities in the ratios 1:3:40 found by Nail, Pearlman and Urbach and shown in Fig. 106 of H.W. Leverenz¹⁷ LUMINESCENCE OF SOLIDS appear to fit Eq. (4).

More Than One Class of States

The behaviour of a single class of states, even though distributed in energy, in the forbidden zone is comparatively simple. One need only bear in mind that more of these states are embraced by E_{fn} and D_p and thus shorten the life times of electrons and holes at higher intensities of excitation. Most real solids, however, have two or more significant classes of states in the forbidden zone. These states arise variously from chemical impurities, non-stoichiometry, and departures from perfect crystallinity. The arguments outlined above for locating the demarcation levels D_n and D_p for one class of states must be repeated for each class of states. But for each class of states, the recombination traffic of electrons into those states must be identically equal to the recombination traffic of holes. This is the condition for steady-state. When only one class of states was considered, the equality of traffics was easily satisfied by adjusting the densities of free electrons and holes to fit the already given capture cross sections and occupancies of the ground states n_g/N_g and p_g/N_g (see Eqs. 2 and 3). These occupancies were the same after excitation as before excitation. When, now, a second class of ground states is introduced, it would be highly fortuitous that its capture cross sections and occupancies would fit the densities of electrons and holes already determined by the first class of states. It is almost certain that there will be an imbalance of electron and hole recombination traffic into the second class of states. This imbalance will continue until the occupancies of the second class are sufficiently altered to cancel the imbalance*. But if the numbers of electrons and holes in the second class of

states is appreciably altered there must be some place for these electrons and holes to go. They cannot go into the free states or into regions I and II, since the densities of electrons and holes in these states have been assumed to be small in comparison with the ground state densities. The only remaining possibility is that the excess electrons or holes from the second class of states be transferred to the first class of states. In brief, the introduction of a second class of states compels a redistribution of electrons and holes between it and the first or already existing class of states.

It is this redistribution of electrons and holes between different classes of states that lies at the bottom of some of the most complex, varied and dimly decipherable behaviour of phosphors and photoconductors^{16,17}. The redistribution, by changing the values of n_g and p_g (see Eqs. 2 and 3) may obviously either increase or decrease the life times of the free carriers. Further, the recombination traffic may be shifted from one class of states to another. Some of these effects have been described in earlier papers^{4,18}. One can readily imagine how a second class of states can sensitize or desensitize a photoconductor, activate or poison a phosphor. These are some of the manifold results that come from deliberately incorporating impurities in a solid by physical or chemical means.

Electronic Doping

There is a completely parallel set of results that comes about by electronically incorporating impurities. The meaning of this statement is easily seen from Fig. 2. Suppose that in region III there is one class of states while in regions I or II there is a second class of states. The life times of the free carriers will be determined substantially only by the states in region III, that is, by the first class of states. But the demarcations D_n and D_p , setting the boundaries of region III, are electronically adjustable. At high excitations, these levels pull apart so that states that were originally in regions I or II are now included in region III. The same adjustments can be made by variations in the temperature of the solid. Since the states in region III play the dominant role for the life times of free carriers, *it is the introduction of a second class of states into region III rather than just into the solid, that is significant*. From this point of view, it is all the same whether new states are introduced into region III by physical diffusion or by electronic envelopment by the levels D_n and D_p . One might describe the last process as "electronic doping".

What is conceptually significant is that the long catalogue of effects that are known to arise from the physical and chemical addition of impurities should also be producible electronically by varying the excitation intensity or temperature. The electronic doping is, of

*In the steady-state, the ratio $s_p n_g / s_n p_g$ must be the same for each class of states.

course, reversible. The superlinear curves found in photoconductors¹⁸ and phosphors¹⁷ are the electronic equivalent of sensitization and activation. The sub-linear curves are the electronic equivalent of desensitization and deactivation. Infra red quenching is the electronic equivalent of poisoning. And the color shifts found in luminescence, as the excitation intensity is varied, are the electronic equivalent of multiple activation.

Interlaced Densities

In the foregoing discussion, the densities of free and shallow trapped electrons and holes were taken to be small enough to have little effect on the occupancy of the states in region III. Most photoconducting insulators and phosphors fit these conditions for moderate intensities of optical excitation. Also, it is generally true that the density of one sign of carrier is much larger than the density of the other sign of carrier. This means that the difference between the densities of carriers is substantially equal to the larger density. This difference must appear (with opposite sign) in the states of region III. As the intensity of excitation is increased, it will happen, for example, that the free plus shallow trapped electrons exceed the number of holes normally present in region III. Holes will then be forced to appear in region III equal in number to the free plus shallow trapped electrons. Since the shallow trapped electrons are in thermal equilibrium with the free electrons their numbers will be proportional to the numbers of free electrons. Consequently, the number of holes in region III will also be proportional to the number of free electrons. The result is immediately recognizable as bi-molecular recombination.

In this intermediate range of excitations, the density of majority carriers (electrons) increases only as the one half power of the excitation. The life time of the majority carrier is becoming shorter. Meantime, the minority carrier density (holes), is increasing linearly, or slightly faster than linearly, with excitation. This pattern continues until the numbers of free electrons and holes, and therefore, their life times, approach equality. The densities of free carriers will at that point be greater than the densities of states in region III or greater than about $10^{15}/\text{cm}^3$. It is difficult to optically excite photoconductors or phosphors into this range. The excitation density needed is likely to be greater than $10^{22}/\text{sec}/\text{cm}^3$. Excitation by electron beams, however, can achieve this or even higher rates.

Excited Carrier Densities Larger Than Recombination Center Densities

If one can excite an insulator to such sufficiently high levels that the free carrier densities are greater

than the densities of states in region III, then the free carrier densities and their life times must be substantially equal. This follows logically since there are not sufficient available states into which the electrons or holes, resulting from any appreciable difference in free carrier densities, can be located. It is likely that one needs the high excitation densities of electron beams to achieve this condition.

It was emphasized earlier that at low excitations, the various classes of states in region III had to exchange electrons and holes in order to satisfy the boundary conditions – that is, equal rates of electron and hole flow into each class. When the free carrier density is larger than the density of states in region III, this exchange of electrons and holes between classes of states no longer takes place. Rather the occupancy of each class of states is adjusted, independently, by exchange of electrons or holes with the free carriers. A large adjustment of occupancy in a class of states can be made without altering the substantial equality of free carrier densities. The result is then quite simple. Owing to the equality in free carrier densities, the occupancy of each class of states is given by (see Eqs. 2 and 3 with equal life times):

$$n_g/p_g = s_n/s_p \quad (6)$$

One finds now that the introduction of any type of additional states into region III can only have the effect of reducing the life time of both signs of carriers. (It is to be understood that the number of additional states is still less than the number of free carriers). By way of contrast, at low excitations, the introduction of states into region III could increase or decrease the life time of one sign of carrier while having the opposite effect on the other sign of carrier. The sensitivity of photoconductors like *CdS*, for example, may, by the addition of states in region III, be made 10^5 times more sensitive at low excitations¹⁹. The electron life time has been increased by a factor 10^5 . In the present high excitation range, the sensitivity (electron life time) must recede at least to where it was before the introduction of the additional states. For this reason some very sensitive photoconductors appear to saturate toward high light intensities.

Finally, one must, at these high densities of carriers, begin to be concerned with direct recombination between free electrons and free holes. The capture cross section of a free hole for a free electron is quite small^{4,20}, in the neighborhood of 10^{-20} cm^2 . The small cross section and low density of free holes normally allows one to neglect their contribution to life time. When however, the density of free holes approaches $10^{18}/\text{cm}^3$, the life time of an electron looking down at the free holes

alone would be $(v_s n_p)^{-1} = 10^{-5}$ secs. If competing recombination processes are no faster than this, direct recombination of free electrons and holes will predominate. As pointed out by Redfield²¹ this is more likely to occur in materials with a small forbidden gap (≤ 0.3 volts) where there is less room for states in the forbidden zone to contribute to recombination.

Life Times – Thermal Carrier Densities Predominant

Up to this point, the major properties of phosphors and photoconductors could be discussed by reference to Fig. 2. Materials with forbidden gaps greater than one electron volt can be described by this figure since in these materials the thermal density of carriers can be negligibly small. At lower temperatures, proportionally smaller gap widths would be included. The major feature of Fig. 2 is the division of the states in the forbidden zone into a group near the middle of the zone, through which most of the recombination takes place and whose occupancy is determined by kinetic processes, and two groups near the band edges that are in thermal equilibrium with the free carrier densities and do not contribute significantly to recombination.

If we now postulate that the thermal equilibrium densities of carriers are large compared with the optically excited densities, a new division of states is called for. By postulate, thermal processes predominate throughout the forbidden zone. Consequently, region III in which kinetic processes had been predominant disappears. The boundaries D_n and D_p of region III collapse into a single level $D (= D_n, D_p)$ Fig. 3. Also, the two steady-state Fermi levels collapse into the single thermal equilibrium Fermi level E_f of Fig. 3. The location of D relative to E_f is determined by the same argument given in Eq. (1). To a first approximation the level D is the same distance from the filled band as the Fermi level is from the conduction band. The correction term is $kT \ln \frac{S_n}{S_p}$. (See Appendix I).

The level D is such a level that an electron is equally likely to be thermally excited into the conduction band and to be captured by a free hole. Similarly, a hole at the level D is equally likely to be thermally excited into the valence band and to be captured by a free electron. One can still use the level D to make the kind of separations already made in Fig. 1. That is, states above D are dominated by thermal exchanges with the conduction band. Electrons falling into these states are more likely to be thermally re-excited into the conduction band. Electrons falling into states below D are more likely to be captured by a free hole. Similarly, from the point of view of free holes, the states below D are

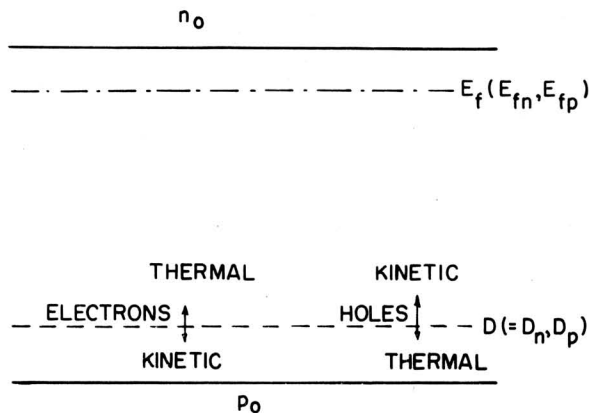


Fig. 3 – Demarcation level for thermal densities of carriers large compared with excited densities.

dominated by thermal exchange with the filled band. Holes, captured into these states, are more likely to be thermally re-excited into the filled band. Holes captured into states above D are more likely to capture a free electron.

In Fig. 4 is shown three groups of states in the forbidden zone using the same designations as in Fig. 2. Region III which was predominant in Fig. 2 has collapsed into a line at the level D . Region IV which was of secondary importance in Fig. 2 is now of major importance in Fig. 4. Regions I and II remain and retain their same significance as in Fig. 2.

One uses the same procedure as before to examine the life time of an electron and a hole. A free electron looks down into the various empty states into which it might be captured. The states in region I are substantially empty so that, other factors being equal, an electron has an equal chance of falling into any of the states. If the electron falls into a state lying near the conduction band, it is more quickly thermally excited into the conduction band and has less chance of capturing a free hole than if it falls into a state near the Fermi level. Since the rate of thermal excitation increases exponentially above the Fermi level, one can neglect the contribution to life time by states more than kT higher than the Fermi level relative to states at the Fermi level.

The number of empty states in region IV decreases exponentially as one departs downward from the Fermi level. At the same time, the residence time of an electron in these states before being thermally re-excited increases exponentially. The combination of these two opposing factors makes the states at various energy levels equally effective for recombination traffic. The same result will be even more evident when one considers the recombination traffic of free holes. A strong caution needs to be inserted here. The arguments leading to equal effectiveness of states in region IV for recombination do not necessarily mean that they make an

equal contribution to electron life time. In transistor materials, where the electron and hole life times are equal, equal contribution to recombination means equal contribution to electron life time. In many sensitive, high dark current photoconductors, where the electron life time is longer than the hole life time, the states in region IV contribute equally to electron recombination but not necessarily, as will be discussed below, to electron life time.

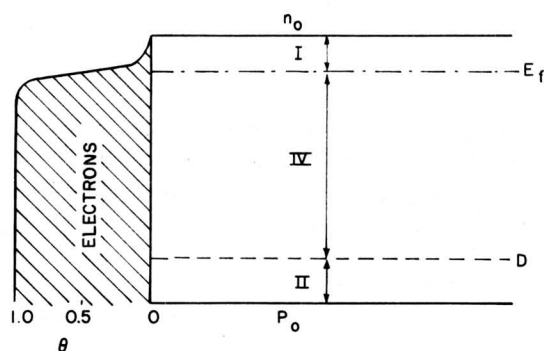


Fig. 4 - Distribution of electrons and holes for thermal densities of carriers large compared with excited densities.

Returning to the examination of the empty states in region IV, the effectiveness of these states for electron recombination was found to be constant because the probability of capture by a free hole increased as fast as the density of empty states decreased. At the level D , the probability of capture by a hole is already near unity. This has two consequences. It means that the contribution of all the empty states in region IV to recombination would be the same if the density of empty states in region IV were everywhere equal to the density of empty states at D and if an electron captured in these states were certain to be captured by a free hole. In brief, region IV could be replaced by a region III in which the density of holes at each energy level was that at the level D .

The second consequence is that the effectiveness of the states below D for electron recombination decreases exponentially. Already an electron captured near D is almost certain to be captured by a hole. This factor cannot increase below D . The number of empty states below D , however, does decrease exponentially so that their contribution to recombination also decreases exponentially.

In summary, the various levels in region IV were found to be equally effective for electron recombination while the levels outside region IV make an exponentially decreasing contribution to recombination. Region IV, then, plays the same role as did region III in the discussion of insulators. The arguments leading to this conclusion have been more involved than they need be. In

treating electron recombination, one is trying to separate out a small capture process from a large thermal exchange process. The same conclusions follow more quickly in treating the recombination of the minority carrier.

Consider a hole looking up into the various electron occupied states. The states in region II may be neglected by arguments already given, that a hole captured in these states is more likely to be thermally re-excited into the filled band. The states in region IV are substantially filled with electrons and since these states lie above D , a hole captured in them is almost certain to recombine with a free electron from the conduction band. Thus, the recombination traffic of holes is uniformly distributed throughout the states in region IV, a result already obtained for the recombination traffic of electrons. The number of electron occupied states into which a hole may jump above E_f decreases exponentially and so, therefore, does their contribution to recombination. Again, the conclusion is that the states in region IV carry the major recombination traffic.

MINORITY CARRIER LIFE TIME - Single Level - Small Perturbation

Once having established the importance of region IV for recombination, the analysis of the minority carrier life time goes quickly. In particular, we review, as is done by Shockley and Read¹, the behaviour of a single level of recombination states as the Fermi level is swept through the forbidden zone. The review is carried out for state densities large compared with thermal carrier densities. The slight modification needed to fit the opposite case of small state densities is then indicated.

The review of minority carrier life time is at the same time the review of majority carrier life time for transistor materials. The simplifying feature of transistor materials is that electron and hole life times are equal and one need only examine the life time of one sign of carrier - the more convenient one - in this case the minority carrier. Equality of life times is insured for logical reasons by having the added carrier densities larger than the density of states in region IV. While this was difficult to achieve in photoconducting insulators and phosphors because the state densities were likely to be greater than $10^{15}/\text{cm}^3$, it is comparatively easy to achieve in transistor materials where, by careful preparation, the state densities can be brought below $10^{12}/\text{cm}^3$. The higher densities of the usual donor and acceptor levels are neglected here because they lie close to the band edges in regions I and II. At sufficiently high densities, they can, of course, contribute significantly to recombination.

Fig. 5 shows six successive stages in the movement of the Fermi level (E_f) across the forbidden zone from

strongly n-type to strongly p-type material. The geometric center of the forbidden zone is denoted by E_i . The demarcation level (D), except for a small correction term $kT \ln \frac{s_n}{s_p}$, is the mirror image of the Fermi level reflected at E_i . The single level of recombination states (N_T) is located above the middle of the forbidden zone.

The argument followed below can be briefly summarized. As the Fermi level E_f sweeps through the forbidden zone from conduction band to filled band, the demarcation level D sweeps through the forbidden zone at the same rate but in the opposite direction. States embraced by these two levels are counted in full, states outside the two levels make an exponentially decreasing contribution to recombination.

In Fig. 5a the Fermi level is near the conduction band; the demarcation level is near the filled band. The states N_T are embraced by the levels E_f and D and these states are almost fully occupied by electrons. The life time of a hole, the minority carrier, is therefore given by:

$$\tau_{p0} = 1/\nu s_p N_t \quad (7)$$

The same result would be obtained for any other location of the N_t states between E_f and D . This means that as E_f moves away from the conduction band toward N_t the life time remains constant and equal to τ_{p0} .

In Fig. 5b, the material is still n-type but the Fermi level now lies below the N_t states but above E_i . By previous arguments, the efficacy for recombination of states lying outside the range E_f - D , decreases as $e^{-\Delta E/kT}$ where ΔE is the distance to E_f or D whichever is nearer.

In this instance, it is clear why the contribution of N_t to recombination decreases. The thermal equilibrium occupancy of N_t by electrons decreases as $e^{-\Delta E/kT}$. Thus a free hole sees fewer electron occupied states into which it can be captured. As the Fermi level moves from N_t to E_i the life time increases exponentially and is given by:

$$\tau_{p0} e^{+\Delta E/kT}$$

In Fig. 5c the Fermi level coincides with E_i and the material is intrinsic. Note that E_f and D do not coincide. The energy interval E_f - D is the small correction term $kT \ln \frac{s_n}{s_p}$. The maximum life time for n-type material is achieved here but not the maximum life time for p-type. As the Fermi level moves through and below E_i the material becomes p-type. The minority carrier is now a free electron. There is a discontinuity in minority carrier life time since the capture cross section s_n is larger than s_p . The life time of a free electron increases as the Fermi level continues to move from E_i to a distance $\frac{1}{2} kT \ln \frac{s_n}{s_p}$ below E_i . This is a result of the increasing distance between the N_t states and the Fermi level.

In Fig. 5d, the Fermi level and the demarcation level coincide at the energy level $\frac{1}{2} kT \ln \frac{s_n}{s_p}$ below E_i . The maximum life time of a free electron is achieved here because this represents the maximum departure of N_t from E_f and D .

In Fig. 5e, E_f and D have moved past each other, E_f moving toward the filled band and D toward the con-

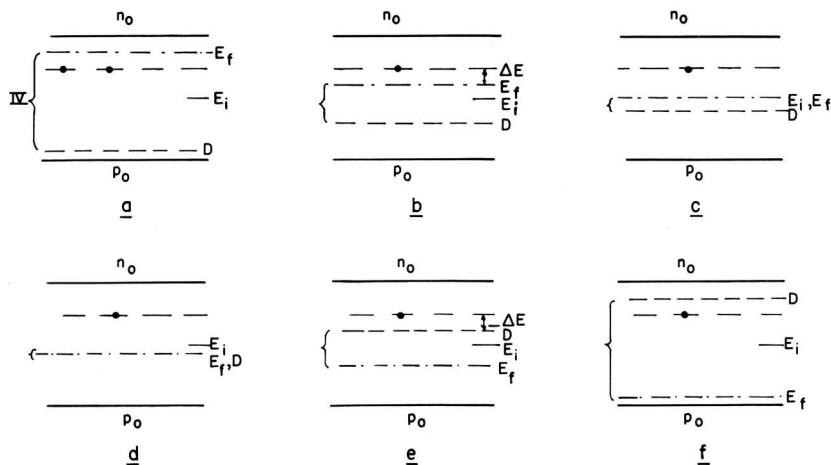


Fig. 5 - Schematic analysis of minority carrier life time as a function of position of the Fermi level. The brackets on the left show the extent of region IV through which the major recombination traffic normally takes place.

duction band. The N_t states still lie outside the interval $E_f - D$. The efficacy of the N_t states for recombination is reduced by the factor $e^{-\Delta E/kT}$ compared with their efficacy when embraced by the levels E_f and D . As E_f approaches the filled band, its approximate mirror image D approaches the N_t states. The interval ΔE becomes smaller and the life time decreases at the rate

$$\tau_{no} e^{+\Delta E/kT}$$

τ_{no} is used here in anticipation of Fig. 5f.

In Fig. 5f, the Fermi level has moved close enough to the filled band that its mirror image D now lies above N_t . Since N_t is again embraced by the levels $E_f - D$, these states have attained their maximum contribution to recombination. The N_t states are substantially empty and the time required for them to capture a free electron is

$$\tau_{no} = 1/vs_n N_t \quad (8)$$

This life time remains constant as long as N_t is embraced by E_f and D .

The variation of minority carrier life time with Fermi level is summarized in Fig. 6. This is the same type of curve shown by Shockley and Read for large state densities. The various parts of the curve are identified with the series of Figs. 5a – 5f by the letters a-f.

The treatment for low state densities – sufficiently low to insure the equality of electron and hole life times – parallels that for large state densities except near the intrinsic range. Here, there can be no discontinuity since electron and hole life times are equal. The approximate behaviour is shown by the dotted line.

Fig. 5 shows visually a number of the conclusions reported by Shockley and Read. When $\tau_{no} = \tau_{po}$, the capture cross-sections s_n and s_p are equal according to Eqs. (7) and (8), and the correction term $kT \ln s_n/s_p$ vanishes. Under these conditions, complete symmetry is obtained in Figs. 5 and 6. The states N_t have the same effect on life time on either side of the intrinsic level E_i . Asymmetry is introduced when the two capture cross-sections are not equal. The ratio of capture cross-sections is likely to be two or three powers of ten, reflecting the difference between capture by a neutral state and capture by a charged state. The correction term is then only about a tenth of a volt.

Single Level – Large Perturbation

Fig. 5 also aids one in visualizing what happens to the life time when the added carrier densities become

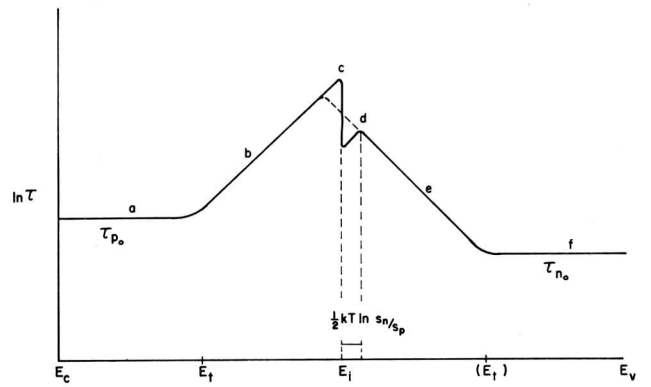


Fig. 6 – Minority carrier life time plotted as a function of position of the Fermi level. The single level of recombination states is located at E_T . The level (E_T) is the mirror image of E_T reflected at E_i . The solid line shows the behaviour for recombination state densities large compared with thermal carrier densities. The dotted line is the estimated correction for the case of small densities of recombination states – that is, equal life times of electrons and holes.

large, that is larger than the thermal densities. If one starts with the states N_t embraced by the levels E_f and D , then these states are either substantially filled by electrons or substantially empty of electrons depending upon whether the material is n-type or p-type. These occupancies are controlled by thermal equilibrium processes. The corresponding life times τ_{no} and τ_{po} are given by Eqs. (7) and (8). At sufficiently high densities of added carriers the states N_t are embraced by the two levels D_n and D_p . This means, as discussed earlier, that the occupancy of the N_t states is determined by kinetic processes. In particular the ratio of electron occupied states, n_t , to hole occupied states, p_t is:

$$n_t/p_t = s_n/s_p \quad (9)$$

The life time is $\tau_{\infty} = 1/vn_t s_p = 1/vp_t s_n$

$$= \left(v \frac{s_n}{s_n + s_p} N_t s_p \right)^{-1} \quad (10)$$

If the capture cross-sections are nearly equal, then $\tau_{\infty} \cong 2\tau_{no}$. Other types of behaviour are easily deduced from Eqs. 7, 8 and 10.

If one started at low excitations with the N_t states well outside the interval $E_f - D$, the life time would be quite large because these states are only partially effective. At high excitations, the N_t states would be embraced

by the levels D_n , D_p and would be completely effective. Under these conditions τ_∞ would be smaller than the starting life time.

Multiple Levels

What is perhaps more significant is that Fig. 5 allows a quick estimate to be made of the effect on life time of adding other levels of states either of the same type or different types. Suppose, for example, that in Fig. 5a the N_t states, instead of being only at one energy level, were distributed uniformly between E_f and D . Qualitatively, the same pattern of behaviour of life time with position of Fermi level would be observed as already obtained for a single level. That is, the life time would increase, as the Fermi level approached the middle of the forbidden zone starting from either n or p type material. The quantitative difference is that the rise of life time toward intrinsic material, instead of being exponential, would be a slow rise varying approximately as the reciprocal of the interval $E_f - D$. This is a significant result for the rate of generation of free pairs in not too well purified materials. The rate of thermal generation is given by the minority carrier density divided by the minority (= free pair) life time. As the Fermi level approaches the middle of the forbidden zone the minority carrier density must increase exponentially. If, at the same time, the life time increases only slowly as it would for a distribution of recombination states, the thermal generation of pairs would increase almost exponentially. This behaviour can readily account for the frequent observations that the reverse currents in p-n junctions are generated predominantly in the intrinsic section rather than at the n and p terminals.

It is not necessary that the E_f states be distributed continuously in energy in order to void the exponential pattern of Fig. 6. States scattered at a few levels throughout the interval $E_f - D$ in Fig. 5a is sufficient. The new levels may have the same or different cross sections from the N_t states. The effect will always be to attenuate the exponential dependence of life time on position of the Fermi level. It must be noted here that the addition of other classes of states in the interval $E_f - D$ (region IV) is quite different from their addition in the interval $D_p - D_n$ (region III). In the latter case, as already discussed, there was an exchange of electrons or holes between the added and the previously existing states which resulted in a great variety of possible behaviour. The new states added in region IV, on the other hand, do not interact with the existing states. Their occupancy is determined by thermal exchange with the conduction band.

The Shockley-Read, as well as the Hall analysis of a single level of states has pointed out that the location of the level could be established in transistors by

observing the temperature dependence of life time. This is true for a level lying, for example, above the Fermi level. Then, for a fixed Fermi level, the present analysis, also, shows that the efficacy of these states for recombination will increase exponentially with increasing temperature at a rate given by the energy interval ΔE between these states and the Fermi level. If there is more than one level of states present, the simple exponential dependence is voided and a slower more complex dependence on temperature will occur. If the capture cross section varies with temperature, the life time may either increase or decrease with increasing temperature.

High Dark-Current Photoconductors

There are many materials in which, like transistors, the thermally generated carrier densities are high and in which significant photocurrents are observable. These include conducting samples of CdS , $CdSe$, ZnS , ZnO , grey selenium, PbS , TlS , intermetallic compounds and silicon and germanium even when the latter two materials are not of transistor quality. Unlike transistors, these materials, in general, do not have a sufficiently low density of states in the forbidden zone to insure the equality of electron and hole life times. It has been stated already that when the added carrier densities exceed the density of states in the forbidden zone, particularly in regions III and IV, the equality of life times is insured for logical reasons. When the added carrier densities are less than the state density, the electron and hole life times may or may not be equal and, in general, are not.

In the case of transistors, since the two life times were equal, one could choose to analyze the more convenient life time, that of the minority carrier. Even when the state density is large and the two life times are not equal, one can still analyze the minority carrier life time using Figs. 4 and 5 as was carried out in the preceding section. The life time of the majority carrier, however, must be separately analyzed. The analysis does not lend itself to easy visualization. For that reason an algebraic analysis quite similar to that of Shockley and Read is used (see appendix II) to obtain the ratio of electron to hole life times for a single level of states. The following result applies to an n-type semi-conductor in which the level of recombination states lies above the middle of the forbidden zone. In this way, terms involving the minority carrier density can be neglected. The ratio is

$$\tau_n/\tau_p = \frac{(n_o + n_1) s_n + n_g s_p}{(n_o + n_1) s_n + p_g s_n} \quad (11)$$

Here, n_o is the thermal equilibrium density of free electrons, n_1 the density of free electrons (as in Shockley-Read) if the Fermi level were at the level of recombination states; n_g and p_g the number of recombination states occupied in thermal equilibrium by electrons and holes, respectively, and s_n and s_p the capture cross sections of these states for electrons and holes. All three terms in the denominator are multiplied by s_n ; the separation into two groups has been made for reasons of visual symmetry.

Shockley and Read make the statement that the two life times will be equal if either n_o or n_1 is large compared with the density of recombination states $n_g + p_g$. The statement is valid if the two capture cross sections are equal or nearly so. But the very nature of a sensitized photoconductor, that is, one made sensitive by the addition of recombination states, is that these states have a very small cross section ($\approx 10^{-20}$ cm²) for one sign of carrier^{4, 5, 12, 16, 22, 23}. Further, in so far as this small cross section is achieved by having doubly charged states, the capture cross section for the other sign of carrier is likely to be large ($\approx 10^{-13}$ cm²). The ratio of capture cross sections can then be as high as 10^7 . In Eq. (11), if $s_p \approx 10^7 s_n$, the free electron density, n_o , could be many powers of ten greater than the density of recombination states and still allow the ratio τ_n/τ_p to be greater than unity. The more exact criterion for equality of life times is that $n_o s_n$ or $n_1 s_n$ be large compared with $n_g s_p$.

The equality of life times is attained by large n_o and by large n_1 in opposite ways. Large n_1 means that the level of recombination states approaches close to the conduction band. For $n_1 = n_o$, the states are at the Fermi level and for $n_1 > n_o$ the states lie above the Fermi level in region I. As the states depart from the Fermi level in the direction of the conduction band their contribution to recombination decreases exponentially. The minority carrier life time *increases* until it equals the majority carrier life time. It is as if the effective number of recombination states decreased until they were less than the added carrier densities. Under these conditions, the two life times must be equal. Large n_1 , then, brings about equality by increasing the minority carrier life time.

Large n_o , on the other hand, has little effect on the minority carrier life time, but a first order effect on the majority carrier life time. The latter decreases as n_o^{-1} until it becomes equal to the minority carrier life time.

If either n_o or n_1 is large enough to insure equality of life times the problem becomes that already treated in the preceding section. When n_o and n_1 are small, so that $n_g s_p$ and $p_g s_n$ are the dominant terms, the ratio of life times is:

$$\tau_n/\tau_p = n_g s_p / p_g s_n \quad (12)$$

Here one sees immediately that the life time of the free electron is given by the time to be captured by one of the empty recombination states, and the life time of the hole by the time to be captured by one of the electron occupied recombination states. The occupation ratio n_g/p_g is the thermal equilibrium value. The ratio τ_n/τ_p can be either greater or less than unity.

The intermediate case is that $n_g s_p$ is the dominant term in the numerator and either $n_o s_n$ or $n_1 s_n$ is the dominant term in the denominator. The term $n_1 s_n$ is of less interest. Its contribution to recombination when $n_1 > n_o$ is likely to be small compared with states lying below the Fermi level. To a good approximation one can then write:

$$\tau_n/\tau_p = n_g s_p / n_o s_n \quad (13)$$

Since $n_g s_p$ was taken to be the largest term in the numerator and accordingly larger than $n_o s_n$, the electron life time is larger than the hole life time. Also the added electrons will exceed the added holes. The difference will appear as holes in the recombination states and will be substantially equal to the number of added electrons. In a sense then, the life time of a free electron is the life time of an added hole in the recombination states. It is the time taken for one of the free electrons to recombine with this hole. That time is, as in Eq. (13), $(v s_n n_o)^{-1}$.

One has here a clue to account for an optimum in photosensitivity as a photoconductor is made more n-type. The photoconductor can be made more sensitive by making it more conducting if, by so doing, doubly negatively charged states are introduced into region IV. Once these states are introduced, further increases in conductivity will decrease the electron life time by the relation $(v s_n n_o)^{-1}$.

Multiple Levels

A curious and complex problem arises now if the recombination states are distributed in energy. Consider, for example, one level of states near the Fermi level such that $p_{g1} > n_o$. The level by itself would give an electron life time from Eq. (12) of $(v s_n p_{g1})^{-1}$. Let a second level of states, equal in number to the first level, be located well below the Fermi level so that $p_{g2} < n_o$. Then, by Eq. (13), this level by itself would give an electron life time of $(v s_n n_o)^{-1}$. The life time for the second level alone is larger than that for the first level alone. The problem is how to combine their contributions to life time when both levels are present.

Ordinarily, one expects that the shorter of two life

time mechanisms predominates. Actually, the reverse is true here. The flow of holes into both levels is substantially equal. The *extra* holes appearing in each level give rise to *extra* free electrons numerically equal to the *extra* holes. The problem then is to compute the steady-state increase in density of holes at each level. This requires a knowledge of the life time of the hole at each level. In the states near the Fermi level the life time of a hole is $(\nu s_n p_g)^{-1}$ and is shorter than the life time $(\nu s_n n_o)^{-1}$ of a hole in the states located well below the Fermi level. Accordingly, there will be a larger density of *extra* holes in the second group of states and these will make the larger contribution to the density of *extra* free electrons.

One has here two life times that remain operationally separate. That means that when the exciting radiation is cut off, the *extra* free electrons decay in two steps. A small fraction decays rapidly into the states near the Fermi level; the rest decay slowly into the lower level of states.

Another feature worth noting is that even though the same recombination traffic passes through both levels of states and even though they make equal contributions to the life time of free holes, they do not make equal contributions to the life time of free electrons.

Finally, one must recognize that only half the exciting radiation, the half that contributes holes to the lower group of states, is supporting the bulk of the *extra* free electrons. As discussed elsewhere⁴, this increases the noisiness of the photo current.

Transition From Semi-Conductors to Insulators

The life times of electrons and holes have been discussed thus far for two broad classes of materials: relative insulators in which the added carrier densities were large compared with the thermal densities and in which the major recombination traffic is carried by states (region III, Fig. 2) whose occupancy is determined by kinetic processes; and relative semi-conductors in which the added carrier densities were small compared with the thermal densities and in which the major recombination traffic is carried by states (region IV, Fig. 4) whose occupancy is substantially that of thermal equilibrium. What is missing is the transition from semi-conductors to insulators. It is useful to outline the transition in terms of the shift from thermal to kinetic control of the occupancy of states. This is done below in Fig. 7 using the concepts of the demarcation levels already developed.

The life time of the minority carrier (e.g., holes) can always be estimated with good accuracy as the time

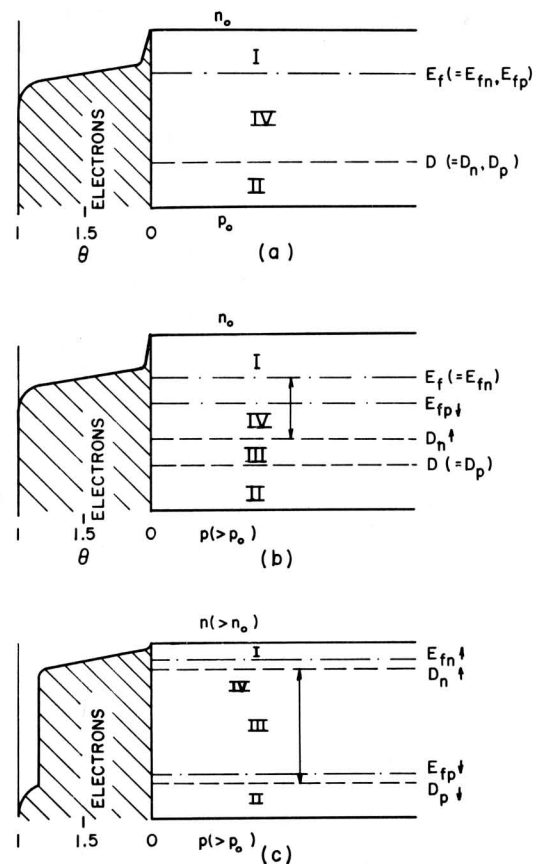


Fig. 7 - Transition of distribution function for electrons and holes from semi-conductors to insulators.

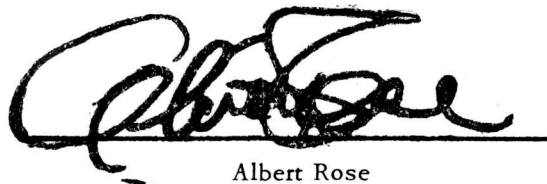
it takes a free hole to be captured by any of the electron occupied states in region III and IV. If the state density is small compared with the added carrier density, the minority carrier life time is also the majority carrier life time. In general, this will not be true and one must separately compute the life time of the majority carrier.

If the life times are not equal and if, at the same time, the thermal density of electrons, n_o , is large compared with the density of states in regions III and IV then, by arguments given in the previous section, the electron life time is $(\nu s_n n_o)^{-1}$. If the thermal density is not large, compared with the density of states, then there will be some level below the Fermi level for electrons at which the thermal density, n_o , is large compared with the density of empty states, p_g . The electron life time is still $(\nu s_n n_o)^{-1}$ but is referred to the states in regions III and IV below this level. The significance, as discussed in the previous section, is that only part of the exciting radiation, the part that contributes holes to these lower states, supports the bulk of the added free electron density.

As the added carrier densities increase in Fig. 7, region III, the region of kinetic processes, increases.

The first significant increase comes when the minority carrier density exceeds its thermal value (Fig. 7b). It is not possible to show on the left side of Fig. 7b that the occupancy of region III is constant and controlled by kinetic processes as opposed to thermal exchange pro-

cesses. At still higher excitations the majority carrier density also exceeds its thermal value. By this time region III plays the dominant role in recombination and life time (Fig. 7c). The problem becomes that discussed at the beginning of this bulletin.

A handwritten signature in black ink, appearing to read 'Albert Rose', written over a horizontal line.

Albert Rose



The condition for equality of kinetic and thermal processes for a hole-occupied level in n-type material is (like Eq. (1)):

$$\nu_p^* e^{-\Delta E/kT} = n_o \nu s_n \quad (\text{A-1})$$

Where ΔE is the energy distance from the filled band. From Eq. (A-1):

$$\begin{aligned} \Delta E &= kT \ln \frac{\nu_p^*}{n_o \nu s_n} \\ &= kT \ln \frac{\nu_p^*}{n_o \nu s_p} \frac{s_p}{s_n} \end{aligned} \quad (\text{A-2})$$

From detailed balance, $\frac{\nu_p^*}{\nu s_p} = N_\nu = N_c$

Eq. (A-2) then becomes

$$\begin{aligned} \Delta E &= kT \ln \frac{N_c}{n_o} + kT \ln \frac{s_p}{s_n} \\ &= (E_f)_n + kT \ln \frac{s_p}{s_n} \end{aligned} \quad (\text{A-3})$$

Eq. (A-3) says that the demarcation level D is the same distance from the filled band as the Fermi level E_f is from the conduction band plus the correction term $kT \ln \frac{s_p}{s_n}$.

If the same argument is carried out for an electron occupied level the result is

$$\Delta E = (E_f)_p - kT \ln \frac{s_p}{s_n} \quad (\text{A-4})$$

where ΔE is measured from the conduction band and $(E_f)_p$ from the filled band. In a material in thermal equilibrium $(E_f)_n$ and $(E_f)_p$ are the same level measured from the conduction and filled band respectively. Eq. (A-4), then defines the same level D as does Eq. (A-3).



In thermal equilibrium one can write:

$$\nu_p^*/\nu_{sp} = N_v$$

$$n_o p_g \nu_{sn} - n_g \nu_n^* e^{-E_{tn}/kT} = 0 \quad (\text{A-5})$$

by definition:

$$n_1 = N_c e^{-E_{tn}/kT}$$

$$p_1 = N_v e^{-E_{tp}/kT}$$

and

$$p_o n_g \nu_{sp} - p_g \nu_p^* e^{-E_{tp}/kT} = 0 \quad (\text{A-6})$$

where the first term in each expression describes the capture of electrons or holes into the recombination states and the second term describes the thermal generation of electrons or holes from these states. E_{tn} and E_{tp} are the energy separations of the recombination states from the conduction and filled bands respectively. If thermal equilibrium is now disturbed by optical excitation, n_o , p_o , n_g and p_g become $n_o + \delta n$, $p_o + \delta p$, $n_g + \delta n_g$, $p_o + \delta p_g$. These values are inserted in (A-5) and (A-6) and the two equations are set equal to satisfy the condition of steady state. Further side conditions are:

by charge neutrality:

$$\delta n - \delta p = \delta p_g$$

$$- \delta p_g = \delta n_g$$

by detailed balance:

$$\nu_n^*/\nu_{sn} = N_c$$

$$\tau_n/\tau_p = \delta n/\delta p$$

The result is:

$$\tau_n/\tau_p = \frac{(n_o + n_1) s_n + (n_g + p_o + p_1) s_p}{(n_o + n_1 + p_g) s_n + (p_o + p_1) s_p} \quad (\text{A-7})$$

For n-type material and for the recombination states located above the middle of the forbidden zone, one may frequently neglect the terms in p_o and p_1 compared with terms in n_o and n_1 .

The approximate result is then:

$$\tau_n/\tau_p = \frac{(n_o + n_1) s_n + n_g s_p}{(n_o + n_1) s_n + p_g s_n} \quad (\text{A-8})$$



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