Effect of Impurity Conduction on Electron Recombination in Germanium and Silicon at Low Temperatures

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There is given a prediction concerning the effect of impurity conduction on the electron-donor recombination cross section in *n*-type Ge and Si at liquid-helium temperatures. The theory suggests that the capture probability of a conduction electron and an ionized donor becomes independent of temperature below a certain critical temperature T_c, where T_c is primarily a function of the donor concentration. This proposed effect has been observed only in a single instance; in others, the experiments either were performed at insufficiently low temperatures or had inherent defects which tended to make a comparison of the theory with experiment somewhat difficult. In the latter cases, suggestions are offered to offset these difficulties. The various theories of electron recombination are contrasted; in particular, the classical theory of Hamann and McWhorter is shown to contain a number of serious deficiencies.

1. INTRODUCTION

THE original theory of electron-donor recombination in *n*-type semiconductors at low temperatures is due to Lax[1] and was later revised by Hamann and McWhorter[2] (HM), both theories being purely classical in nature. The recombination mechanism considered by HM consists in the capture of an electron in a highly excited donor state with a subsequent cascade process by means of which the electron diffuses, by phonon emission, to the ground state of the donor impurity. For the purposes of the present work, however, the theory of HM is discounted for a variety of reasons; as will be discussed below, this particular theory is shown to contain a number of serious faults, both conceptually and with regard to a comparison with experiment.

With regard to the quantum-mechanical formulation, a model for the electron-donor recombination process has been developed by Ascarelli and Rodriguez[3] (AR), and later modified by the author.[4] In this theory, there is calculated the recombination cross section of a conduction electron and an ionized donor in *n*-type Ge and Si at low temperatures. The electron is assumed to have a spherical effective mass m^* and the bound donor states are taken to be hydrogen-like. Recombination occurs with the initial capture of the conduction electron in an excited (but not necessarily a highly excited) donor state followed by successive transitions to lower-lying states, each such transition occurring with the emission of a single acoustic phonon. The band structure of Ge and Si has been taken into account[4] and, in the present paper, the effect of impurity conduction is considered. It may be mentioned that HM have raised objections to the theory of AR; the nature of their objections and the reasons why they are thought not to apply will be considered in detail in a later section.

[1] M. Lax, Phys. Rev. **119**, 1502 (1960).
[2] D. R. Hamann and A. L. McWhorter, Phys. Rev. **134**, A250 (1964).
[3] G. Ascarelli and S. Rodriguez, Phys. Rev. **124**, 1321 (1961).
[4] Ronald A. Brown, Ph.D. dissertation, Purdue University, 1964 (unpublished). Available from University Microfilms, Ann Arbor, Michigan.

There have been a number of experiments on electron recombination in Ge [5–8] and Si.[9] Some of these apparently suffer from one or more of a variety of defects which can make a comparison of theory with experiment somewhat difficult; the nature of these defects and suggestions for offsetting them will be discussed below.

In Sec. 2 the theory concerning the effect of impurity conduction on the recombination process is developed. Section 3 involves a comparsion of the theory with experiment and a discussion of the experimental difficulties. A detailed criticism of the theory of HM is given in Sec. 4.

2. THEORY

Ascarelli and Rodriguez do not consider the effect of impurity conduction which, under the appropriate conditions, is thought to be significant.[10] This is due to the fact that for sufficiently low temperatures and donor concentrations, transport effects in semiconductors are not due to free carriers but occur as a result of charge transport between impurity states. At higher donor concentrations an impurity band is formed, in which conduction can occur. However, the donor concentrations of the samples used in the above-mentioned experiments[5–9] are low enough that impurity banding should not occur. We shall accordingly consider first this so-called "low-concentration" range, namely the case where the theory of Miller and Abrahams[11] is valid. In Sec. 3.B an extension to the intermediate concentration range is made. The reader is referred to a recent article by Davis and Compton[12] on low-temper-

[5] S. H. Koenig, Phys. Rev. **110**, 988 (1958).
[6] G. Ascarelli and S. C. Brown, Phys. Rev. **120**, 1615 (1960).
[7] R. E. Michel and B. Rosenbulm, Bull. Am. Phys. Soc. **6**, 115 (1961).
[8] S. H. Koenig, R. D. Brown, and W. Schillinger, Phys. Rev. **128**, 1668 (1962).
[9] R. S. Levitt and A. Honig, J. Phys. Chem. Solids **22**, 269 (1961); M. Loewenstein and A. Honig, Phys. Rev. **144**, 781 (1966).
[10] R. A. Brown, Bull. Am. Phys. Soc. **11**, 35 (1966).
[11] A. Miller and E. Abrahams, Phys. Rev. **20**, 745 (1960).
[12] E. A. Davis and W. Dale Compton, Phys. Rev. **140**, A2183 (1965).

ature conduction in n-type Ge, which contains numerous references to past work in this area.

In the range of donor concentration and of temperature where the theory of Miller and Abrahams is valid, electron transport in excited donor states occurs by the "hopping" of electrons from occupied to unoccupied donor sites. An activation energy ϵ_3 enters into the hopping process because of the Coulomb barrier arising from the presence of compensating impurities (acceptors). The limiting donor concentrations below which the theory of Miller and Abrahams is valid are about 6×10^{15} and 10^{17} cm^{-3} for Ge and Si, respectively. We consider the impurity concentration and the temperature as criteria for determining whether or not hopping conduction is the dominant mechansim for conduction in the excited donor states. With regard to the impurity concentration, let T_3 be the temperature which is equivalent to the activation energy ϵ_3, or $\epsilon_3=kT_3$, k being the familiar Boltzmann constant. The procedure for calculating ϵ_3 as a function of the acceptor and donor concentrations is described in Ref. 11. Secondly, with regard to temperature, let T^* be that temperature below which one observes a "knee" or bend in the graph of resistivity versus reciprocal temperature, for specimens in the low-concentration range. For temperatures less than T^*, electron hopping dominates the conduction process.[12,13] T^* is known to decrease with decreasing donor concentration, and the behavior of T_3 is similar in this respect.

Of interest in the recombination process is the quantity σ_c, which is the cross section for capture of a conduction electron by an ionized donor. According to theory,[3] $\sigma_c=\alpha/\langle v\rangle$, where α is the probability per unit time for the capture of a conduction electron by an ionized donor and $\langle v\rangle$ is the average thermal electron velocity, $\langle v\rangle\propto T^{1/2}$ (T being the absolute temperature). Let T_c be the smaller of T^* and T_3 and consider the case where $T<T_c$, in the limit as $T\rightarrow 0$°K. In this limit, the hopping process will be the dominant mechanism for charge transport; conduction in the excited donor states will tend rapidly to zero, with a conductivity $\sigma\propto\exp(-\epsilon_3/kT)=\exp(-T_3/T)$. For sufficiently low temperature, whereby conduction in excited donor states becomes negligibly small, the probability for capture of a conduction electron by an ionized donor will become independent of temperature. That is, for T sufficiently less than T_c, recombining electrons are considered to be completely trapped in a nonconducting state, and a further lowering of the temperature will not noticeably alter the degree of this trapping. Accordingly, in this limit, one expects that the temperature dependence of σ_c will be given by $\sigma_c\propto T^{-1/2}$.

The hypothesis developed above is subject to certain restrictions. The theory assumes that, initially, the donor electrons are excited into the conduction band by a transient external field, either an electric field or

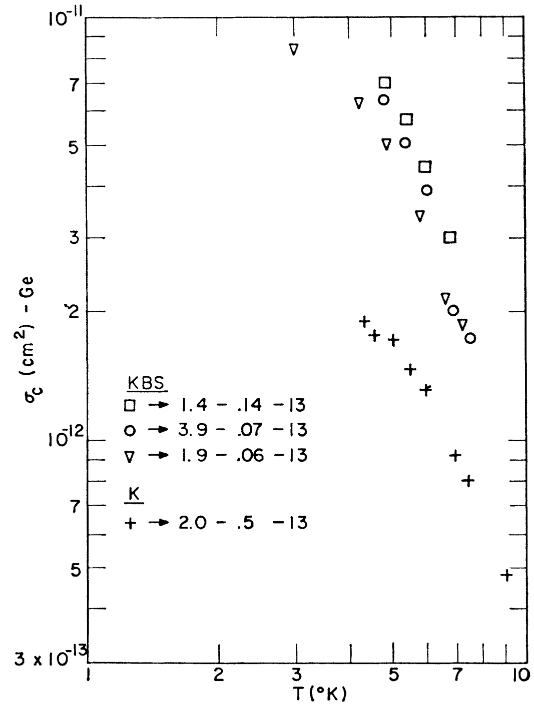

FIG. 1. The experimental values of the electron recombination cross section in n-type Ge.

extrinsic radiation. Once the exciting field has been removed, the electrons eventually come into thermal equilibrium with the lattice by means of collisions and then recombine with the ionized donors. Thus, the time-constant of the exciting field should be much less than the electron recombination lifetime, the latter time being of the order of 10^{-7} sec for Ge.[8] Also, Auger recombination of electrons[14] has been neglected; this approximation is valid at low temperatures, using weak exciting fields and for samples having low donor concentrations. The question as to whether the experiments on electron recombination conform to these restrictions, so as to make a comparison of the theory with experiment meaningful, is discussed in the next section.

3. COMPARISON OF THEORY WITH EXPERIMENT

In Figs. 1 and 2 are shown the experimental values of σ_c for Ge and Si, respectively. The values for Ge are taken from the work of Koenig[5] (K), and of Koenig, Brown, and Schillinger[8] (KBS), while the results for Si are from the work of Levitt and Honig[9] (LH). The sample designation is as follows: sample 4.5–0.15–16 in Fig. 2, for example, has a donor concentration of 4.5×10^{16} cm^{-3} and an acceptor concentration of 0.15×10^{16} cm^{-3}. The work of Ascarelli and Brown[6] (AB) has not been represented in Fig. 1. These last-

[13] H. Fritzsche, J. Phys. Chem. Solids 6, 69 (1958).

[14] G. Ascarelli and S. Rodriguez, Phys. Rev. 127, 167 (1962).

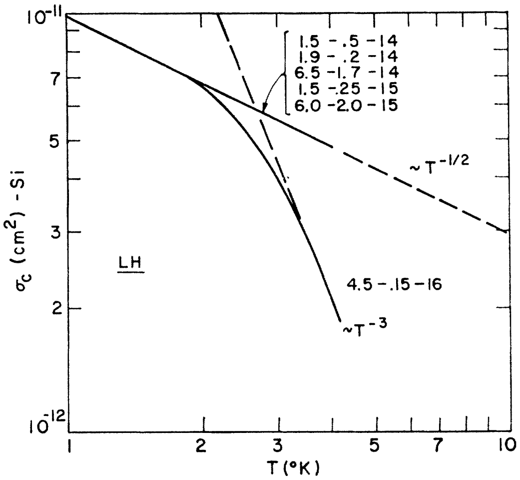

FIG. 2. The experimental values of the electron recombination cross section in *n*-type Si.

mentioned authors experienced difficulties due to Joule heating of the samples during the breakdown process and, in addition, the absolute values of the cross sections were affected by large systematic errors associated with the evaluation of the compensation of the samples.[6,8] The work of AB is felt to be insufficiently quantitative with regard to a detailed comparison with the theory, although the order of magnitude agreement is generally reasonable.

A. Germanium

The fact that the two curves in Fig. 1 differ in magnitude is not serious, since the work of K was affected by errors associated with the compensation of the sample,[8] as was the case with AB. Barring this rather minor difference, which affects the magnitude of σ_c, it is seen that the temperature dependence of σ_c is practically the same in both cases. From Fig. 1, the capture cross sections are seen to level off in the direction of decreasing temperature, below about 5°K. For the samples listed T_3 is in the range from 1.5 to 4.5°K and T^* is of the order of 3°K, so that $T_c \sim$ several °K. In order to observe the predicted $T^{-1/2}$ dependence of σ_c one must use temperatures which are sufficiently less than T_c; since the temperatures only went down to 3°K at the lowest, one would not expect to have observed the predicted effect. Michel and Rosenblum[7] have apparently observed a temperature-independent recombination lifetime[15] in a highly purified Ge sample; however, a detailed account of their investigation has not yet been made available.

Koenig, Brown, and Schillinger have found that Auger processes are not significant in their work. Although the experiments of KBS and of K were performed under steady-state conditions (i.e., in dynamic equilibrium in the presence of a constant weak electric field), the effect of hot electrons has apparently been adequately taken into consideration. This was accomplished in the following manner[5]: The sample was biased well into the breakdown region at some fixed point A, and a steeply falling voltage step was applied to reduce the electric field to a value E_B. The voltage step corresponds to a fall time $\sim 10^{-9}$ sec, which is less than the electron recombination lifetime τ_L by at least one order of magnitude. The distribution equilibrates to that appropriate to the point B in a time $\sim 10^{-10}$ sec, which is proportional to the reciprocal of the plasma frequency. The conduction-electron density subsequently decays, by means of lattice collisions, to its steady-state value at point B in a time less than τ_L. Finally, after the initial sharp drop in current due to the application of the voltage step, one observed a slower decay which is indicative of the recombining electrons. In the above manner, one can minimize the effect of hot electrons, which otherwise could ionize the neutral donors by impact (or Auger) ionization sufficiently to be a non-negligible effect. By using small electric fields of the order of several volts cm^{-1} or less, joule heating of the sample can be kept to a low value.

In spite of the precautions taken, it is still not certain whether the above experiments, even if performed at sufficiently low temperatures, would be able to establish the temperature independence of α postulated in the present work. The presence of hot electrons in a significant degree would act to hinder the onset of impurity conduction. Note that for $T=T^*$, the conductivities of the two competing processes—conduction band transport and impurity conduction—are of equal magnitude; the effect of the applied electric field would be to increase conduction band transport at the expense of impurity conduction, in effect decreasing T_c. More exactly, the principal change brought about by the applied electric field would be to decrease the sticking probabilities P_n, where P_n is the probability that an electron in the nth bound donor state will not be ionized into the conduction band. Accordingly, electrons that have not had the time to make a transition from an excited state to the ground state will be more easily re-excited back into the conduction band than if the electric field were absent. In this way, electrons in excited donor states will act more like free carriers, i.e., capable of being relatively easily excited into the conduction band where the conductivity is given by $\sigma \propto \exp(-\epsilon_1/kT)$, ϵ_1 being the familiar donor ionization energy. However, under ideal conditions, as discussed in Sec. 2, hopping (or impurity) conduction will represent the dominant mechanism for charge transport in the excited states, the conductivity in this case being given by $\sigma \propto \exp(-\epsilon_3/kT)$. It is only when hopping conduction dominates the transport of charge in excited states that one would expect a temperature-independent capture probability. Therefore, it is seen that having

[15] If Auger processes are neglected, the electron recombination lifetime is given by $\tau_L = (\alpha N_A)^{-1}$, where N_A is the acceptor concentration and α is the capture probability as defined earlier.

too strong an applied electric field in the steady-state condition may delay or prevent the onset of impurity conduction and thus disallow a meaningful comparison of the present theory with experiment.

Even in the case where an applied electric field acts to hinder the onset of impurity conduction, one can still attempt to predict the temperature dependence of σ_c under steady-state (as contrasted to the equilibrium state in the absence of an exciting field) conditions. Since AR do not consider the effect of impurity conduction, the extension of their results to extremely low temperatures implies that the electrons are still treated as free carriers, rather than in the sense as given by Miller and Abrahams. Thus, in the limit of low temperature, the theory of AR should yield the same temperature dependence of σ_c as in the case where the effect of the electric field is to increase conduction band transport at the expense of impurity conduction. At sufficiently low temperatures ($T\lesssim 5°K$), AR predict a T^{-1} dependence of the capture cross section.[4] This is because, at these temperatures, the excited donor states will effectively act as ground states for the recombining electrons, since kT will be much less than the binding energies of the excited donor states. It is known[16] that, for the capture of a conduction electron into the ground state of a donor impurity, $\sigma_c \propto T^{-1}$. It may be recalled that in the theory of AR only the first six or seven excited donor states are used, contrary to the classical theory where the highly excited states are considered to be most important; however, in Sec. 4, the validity of the classical theory is questioned in detail. Finally, if the projected experiment yields the result $\sigma_c \propto T^{-1}$ at low temperatures, this would appear to indicate that the experimental controls on the hot electrons are inadequate. On the other hand, if such an experiment were to show a $T^{-1/2}$ dependence of σ_c, as was observed by Michel and Rosenblum, this would seem to imply that the experiment had been sufficiently well controlled to allow a meaningful comparison of the present theory with experiment.

For $T>T_c$ the agreement of the theory of AR with the experimental results shown in Fig. 1 is reasonably good with regard to the temperature dependence of σ_c and agrees within a factor of 2 regarding absolute magnitude.[4] This disagreement in magnitude is not considered to be serious, because of the necessary approximations involved in the theoretical calculations.

B. Silicon

The validity of the interpretation of the results of LH on electron recombination in n-type Si is, apparently, open to question.[17] In their work, donor electrons were photoexcited into the conduction band, thus eliminating the joule heating associated with the breakdown process. The capture cross section σ_c was measured in the steady-state condition using a spin resonance technique. However, the cross section (Fig. 2) was measured using an exciting wavelength of 2 μ, corresponding to a photon energy equal to about half the energy gap in Si, although the donor ionization energy was only 0.044 eV. This restriction violates the fundamental restriction that the exciting field be weak; LH thought that donor electrons were being excited to another band or minimum above the conduction band. At any rate, the exciting field was apparently sufficiently strong that, under steady-state conditions, it is questionable as to whether the excited electrons were able to come to thermal equilibrium with the lattice within a time sufficiently less than the electron recombination lifetime. One requires, actually, an exciting wavelength $\lambda\sim 28\ \mu$, corresponding to the donor ionization energy. Since this requirement had not been fulfilled, it is thought that the investigations of LH are open to question; this is because the recombining electrons were probably "hot," or at a temperature considerably above that of the lattice. As a criterion to establish whether or not the work of LH is useful, it is suggested that their experiments be performed using exciting wavelengths in the range $2\ \mu<\lambda<28\ \mu$; if, by changing λ, the results of Fig. 2 ($\lambda=2\ \mu$) cannot be reproduced, then the experiments should be reformulated.

In anticipation of further investigations by LH, there is offered a prediction concerning the results of such a future experiment, using the same samples as in Fig. 2. For five of these samples (excluding sample 4.5–0.15–16 for the moment), T^* is in the rough range from 11 to 17°K while T_3 for these specimens lies in the range from 7 to 13°K. It would be useful to have curves of resistivity versus T^{-1} for these samples, also, so as to yield accurate values of T^* for each case. For T sufficiently less than about 7°K, one expects a temperature-independent capture probability for all the samples. In general, $T_c(\mathrm{Si})>T_c(\mathrm{Ge})$ because of the larger binding energy of donors in Si as compared with Ge; all else being equal, one should not have to go to as low temperatures with Si as with Ge in order to observe the predicted effect. For $T>7°K$, each sample would have to be considered individually; in the separate cases, for $T>T_c$, σ_c should deviate more and more rapidly from the $T^{-1/2}$ dependence with increasing temperature. Sample 4.5–0.15–16, for which $T_3\sim 50°K$ and $T^*\sim 23°K$, requires special treatment. In all of the other Si samples (and also for the Ge samples in Fig. 1), the donor concentrations were well within the low-concentration range where impurity banding should not occur to any noticeable degree.[12] Sample 4.5–0.15–16 has a donor concentration which is only a factor of 2 less than the critical concentration of 10^{17} cm^{-3} at which banding starts to occur. Also, the extrinsic photoexcitation causes a certain concentration of electrons to exist in the excited donor states in addition to that concentration which is already present in the absence of the excita-

[16] H. Gummel and M. Lax, Ann. Phys. (N. Y.) 2, 28 (1957).
[17] Dr. A. Zylbersztejn (private communication).

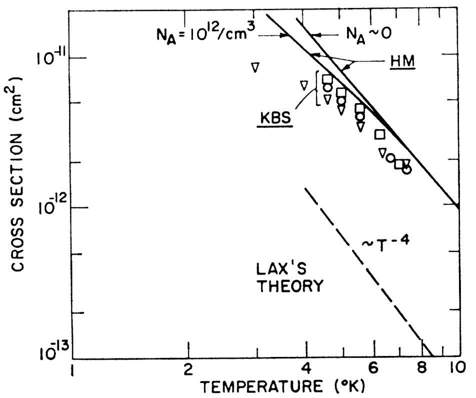

FIG. 3. Comparison of the electron capture cross section as computed by Hamann and McWhorter (see Ref. 2) with the experimental results of Koenig, Brown, and Schillinger (see Ref. 8) and the theoretical results of Lax (see Ref. 1).

tion.[18] If these two contributions are comparable in magnitude, then the effect of the excitation is equivalent to an increase in donor concentration so that banding could occur, which would not be the case if the excitation were absent. If banding should occur, then recombining conduction electrons falling into the impurity band would be more easily reactivated back into the conduction band than in the case where only hopping conduction is present. If, then, banding cannot be neglected, this situation would correspond to conduction in the intermediate concentration range. In this case, only when one goes sufficiently below some new critical temperature T_c' would thermal reactivation from the impurity band to the conduction band become negligible; T_c' should be less than the temperature T_c required in the case where only hopping conduction is present, since the impurity band may lie relatively close to the conduction band. For $T<T_c'$, in the limit as $T\rightarrow 0$°K, hopping conduction will ultimately dominate the conduction process and we are back to a $T^{-1/2}$ dependence of σ_c as before. For $T>T_c$, as T increases, electrons can be more and more easily reactivated from the impurity band back into the conduction band; thus, the effectiveness of the trapping in excited donor states will become correspondingly less and the capture cross section will decrease more rapidly with increasing temperature. Finally, the remarks at the end of Sec. 3.A concerning at T^{-1} dependence of σ_c are appropriate here, also, providing that the experimental circumstances which could give rise to the T^{-1} dependence are actually present.

After most of this article had already been prepared, the author learned from Professor A. Honig (private communication) that the original and other[9] experiments of LH have been reinterpreted as involving a hot electron distribution, and further, are not thought to be applicable to the theoretical predictions given in the present paper. Only if the experiments of LH are reformulated to conform to the restrictions discussed at the end of Sec. 2 will there be a basis for comparison; the predictions given above concerning future experiments by LH must be understood in this light. A detailed understanding of the work of LH involves other considerations in addition to those discussed in the present work and which will not be considered here.

In general it is hoped that any future experiments, either on Ge or Si, will be performed over a wider range of temperature and of impurity (both majority and minority) concentration. In particular, the use of samples having donor concentrations in the intermediate concentration range may provide interesting results. Also, experimental values of T^* for the various samples would be helpful.

[18] Since LH measured σ_c in the steady-state condition, this shows yet another way in which the design of the experiment may influence the results.

4. FAULTS OF THE CLASSICAL THEORY

The purely classical theory of Hamann and McWhorter is thought[4] to contain numerous and varied faults, which cast a serious doubt on the validity of their work. Basically, the difficulties arise because of the application of a strictly classical theory to a situation which requires a quantum-mechanical treatment. According to HM, an electron is considered to be captured initially in an excited donor state by the emission of a phonon, after which it emits or absorbs phonons until it either reaches the ground state or is ejected into the conduction band. Only the highly excited states are considered to be important in the recombination process. Also, transitions between free and bound states are treated in identically the same way as are transitions between two bound states. Recombination is treated as a steady-state process, corresponding to a situation where there is some generation mechanism, such as light, which prevents electrons from accumulating in the ground state. Impurity conduction and energy band structure (HM did their calculations for Ge) are not considered. Criticism of the classical theory of HM falls into a number of categories, as follows:

A. Impurity Conduction

Hamann and McWhorter completely ignore any complications due to impurity conduction. For *n*-type Ge and Si it is well known that impurity conduction is the dominant mechansim for the transport of charge in excited donor states at sufficiently low donor concentrations and temperatures.[11–13] The existence of impurity conduction requires the presence of acceptors[11]; all of the samples shown in Figs. 1 and 2 have non-negligible acceptor concentrations N_A, so that impurity conduction should exist in the proper temperature range. Yet, in Fig. 3 (also Fig. 3 of HM), HM show the predicted graph of σ_c for a case where $N_A\sim 0$; this case is not physically meaningful with regard to the actual experimental samples and, further, precludes the existence of impurity conduction at all. Also in Fig. 3, another graph of σ_c has been plotted using a cutoff concentration $N_A \sim 10^{12}$ cm^{-3}, in order to take account of the overlapping of the highly excited states. For this curve, the question as to the "apparent agreement" with experiment is discussed below. In Fig. 3 the experimental points are due to KBS (see also Fig. 1), the dashed curve is from the original work of Lax,[1] and the solid curves represent the theoretical predictions of HM.

Further, HM treat transitions between free and bound states in exactly the same manner as they treat transitions between two bound states. At low temperatures and for low donor concentrations, electron-hopping transitions between two bound donor states are treated according to the theory of Miller and Abrahams, and this type of calculation is quite different from the calculation of the transition rate from a bound to a free state.[3,4]

B. Energy Band Structure

From the classical viewpoint of HM, complications due to the band structure of the semiconductor are neglected. This has been shown to be a serious failing.[4] For example, when band theory is considered it is found that the electron-lattice interaction can be separated into two parts, one part being due to transverse phonons while the other part arises from the longitudinal phonons. In Ge it is found that the transverse part dominates, while in Si only the longitudinal part exists at all. In general one considers the two parts as being independent, ultimately adding the two together to get the final result. It is clear that one must be careful to use the proper values of the speed of sound and of the deformation potential which are appropriate to the particular phonon polarization under consideration. Then too, HM use the value 4×10^5 cm/sec for the speed of sound in Ge, this value being an average of the longitudinal and transverse speeds of sound and therefore incorrect. Hamann and McWhorter state that, with regard to their calculations: "The agreement in absolute magnitude (of σ_c with experiment) must be regarded as somewhat fortuitous, however, since the average values of electron mass, speed of sound, and deformation potential were chosen somewhat arbitrarily. A derivation beginning with an accurate model of the ellipsoidal conduction band valleys and phonon spectrum branches of Ge would have to be carried out to find a systematic method of computing the necessary parameters . . . ." However, a model using the conduction band valleys of Ge has been constructed,[4] which shows that the work of HM requires serious revision with regard to the very particulars they themselves have stated.

Ascarelli and Rodriguez argue that the capture cross sections for Ge should be multiplied by a factor of 4 in order to account for the fourfold degeneracy of the conduction band edge in Ge. This conclusion is based upon the assumption that the capture probability of an electron from one valley of the conduction band into an excited donor state is independent of whether this excited state is made out of Bloch functions from the same minimum from which the electron is captured or from another one degenerate with it. Hamann and McWhorter argue, on the other hand, that this factor of 4 is incorrect, since the energy of an intervalley phonon is comparable to the binding energy of the donor ground state, so that intervalley thermal excitations would proceed at a negligible rate compared to intravalley emission. Now, this criticism by HM would be valid if there were perfect translational symmetry so that an electron, in going from one valley to an equivalent one, would change its wave vector by an amount which corresponds to the energy of the intervalley phonon being of the order of the donor binding energy. However, the donor impurities present act to destroy the perfect translational symmetry of the lattice, so that the above criticism by HM is invalid. In other words, even though intervalley lattice scattering may be negligible, intervalley impurity scattering can enter the picture. Further, there is evidence that intervalley impurity scattering in n-type Ge does exist at low temperatures and is not necessarily negligible.[19,20]

C. Cutoff in the Excited States

It is evident that not all of the excited donor states need be considered in the recombination process.[21] The reasoning behind this is that, for an excited state having a sufficiently high principal quantum number n, the radius corresponding to this state will overlap the nucleus of the closest neighboring ionized donor. In this case, an electron cannot be considered as localized on any particular donor, so that the concept of a localized bound donor state breaks down. Let $a^* = h^2/4\pi^2 m^* e^2$ be the effective Bohr radius, the radius of the nth bound state being $r_n = n^2 a^*$. Let N_D^+, N_A be the concentrations of the ionized donors and of the acceptors, respectively; at liquid-helium temperatures, $N_D^+ \sim N_A$. If a random distribution of the ionized donors is assumed then the most probable separation[22] of the donor ions is given by $r_{D^+} = (2\pi N_D^+)^{-1/3}$. We define $r_0 = r_{D^+}/2$ to be the maximum radius for which bound states can yet exist. Setting $r_0 = n_0^2 a^*$, one can solve for the maximum value n_0 of the principal quantum number n for which the concept of a bound state is still meaningful. The above considerations are not intended to provide a strictly accurate definition of r_0, but the calculation should be sufficiently reliable to yield an order of magnitude estimation of n_0. For the Ge samples listed in Fig. 1, where

[19] S. H. Koenig *et al.* Ref. 8, p. 1684.

[20] G. Weinreich, T. M. Sanders, Jr., and H. G. White, Phys. Rev. **114**, 33 (1959).

[21] For a further discussion relating to this section, the reader is referred to Ref. 9.

[22] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

$N_D{}^+\sim 10^{12}$ cm^{-3} it is found that $n_0\sim 10$. For a Si sample with $N_D{}^+\sim 10^{14}$ cm^{-3} (see Fig. 2), $n_0\sim 6$. Accordingly, it is seen that the emphasis placed by HM on the very highly excited donor states is of questionable validity. For Ge, the quantum-mechanical theory[4] assumes that $n_0=7$; the neglect of the remaining states is not serious, however, because the sticking probabilities P_n in the excited states decrease rapidly with increasing n.[23]

In their justification of the use of the very highly excited states, HM use the argument that the multiplicity of the states having higher values of n is large; in this way, the very highly excited states would be of most importance because many transitions are possible from among the various substates of the initial bound state to those of the final bound state. On the other hand, the theory of AR treats only transitions between s states. The reasoning behind this assumption of AR is as follows: consider the rate $W_{n\rightarrow n'}$ for the transition of an electron from an initial state (having principal quantum number) n to the final state n'. This transition rate involves the square of the matrix element $\langle\psi_f|\exp(-i\mathbf{q}\cdot\mathbf{r})|\psi_i\rangle$; ψ_i and ψ_f are the wave functions of the initial (n) and final (n') bound states, respectively, and $\mathbf{q}$ is the wave vector of the phonon emitted during the transition $n\rightarrow n'$. Consider, for example in Ge, the transition from the first donor excited state ($n=2$) to the ground state ($n'=1$). Using as the approximate speed of sound for transverse phonons $c_t=4\times 10^5$ cm/sec and letting $r\sim a^*=38.5$ Å, the product qr is of the order of 10 (the Debye approximation $\omega=qc_t$ is used). Thus, in the above matrix element, the exponential factor $\exp(-i\mathbf{q}\cdot\mathbf{r})$ will oscillate rapidly throughout the spatial integration. The s states, whose wave functions are different from zero at the nuclear sites ($r=0$), yield a nonvanishing value of the matrix element[4] because qr is vanishingly small in the near vicinity of the nuclear sites. On the other hand, the wave functions for states of higher angular momentum than zero vanish at the nuclear sites, and peak at relatively large distances of the order of several Bohr radii from the nuclear sites. In this way, for states having high angular momentum, the above matrix element will be quite small because of the rapid oscillation of the exponential factor. Accordingly, states of angular momentum higher than zero are expected to be far less significant that the s states, with regard to electron transitions between two bound states. The claim, by HM, that the multiplicity of the highly excited states is of crucial importance, is therefore open to question.

Finally, it seems to be unusual that HM require using the degeneracy of the bound states but not the degeneracy of the free states (the factor of 4 due to AR), and yet they treat transitions between free and bound states identically the same as transitions between two bound states. Since it has already been mentioned that intervalley impurity scattering is not necessarily negligible, HM's treatment of electron transitions appears to be internally inconsistent.

D. The Classical Limit

Ascarelli and Rodriguez have taken their results to the classical limit and have calculated the ratio $\sigma_c'(n)/\sigma_c(n)$, where $\sigma_c'(n)$ is the classical limit of the quantum-mechanical cross section $\sigma_c(n)$, for the capture of a conduction electron into the nth bound donor state. This ratio, for $n\leq 4$, is considerably less than unity; for example, using $n=4$ in the case of Ge, $\sigma_c'(4)/\sigma_c(4)=1/19$. In accordance with the correspondence principle, $[\sigma_c'(n)/\sigma(n)]\rightarrow 1$ as $n\rightarrow\infty$; thus, HM were forced to use the very highly excited donor states if they were to get an order of magnitude agreement with experiment.

E. The Comparison with Experiment

In Fig. 3, HM compare the results of their theoretical predictions (solid curves) with the experimental values of KBS and with the theoretical calculation of Lax (dashed curve). Since doubts have already arisen concerning the (apparent) order of magnitude agreement of HM's work with experiment, let us concentrate on the temperature dependence of the capture cross sections as predicted by these authors. As can be readily seen from Fig. 3, HM used a much-expanded (by more than a factor of 2) scale for the abscissa T; this can be easily seen from the graph of the experimental work of KBS shown in Fig. 1, where the scale is of the more conventional log-log variety. Bearing this unusual feature of Fig. 3 in mind, it is evident that HM's curve for σ_c does not deviate particularly significantly from that of the original theory of Lax. Had the graphs derived by HM been plotted in the conventional manner, the discrepancy of their results with regard to a comparison with experiment would have shown up quite dramatically; as seen from Fig. 1, the experimental curves of K and of KBS have already reached a T^{-1} dependence of σ_c, in the range from about 3 to 4°K.

Further, HM discuss electron-donor recombination as a steady-state process, in order to simplify their treatment. In this case, as was mentioned earlier, a consideration of hot electrons may be important, depending upon the particular experimental conditions involved in each experiment. Unless one is careful about the interpretation of the experimental results, a meaningful comparison of theory with experiment is precluded. Hamann and McWhorter failed to consider sufficiently carefully the previously mentioned (see Secs. 2, 3.A) experimental qualifications, or whether their assumed choice of a steady-state recombination process was meaningful, when comparing their results to specific experiments in which certain experimental difficulties may arise; these difficulties (hot electrons, etc.) may becloud an interpretation of the experimental results (see Sec. 3.B, especially). They also failed to recognize

[23] See Figs. 6 and 7 of Ref. 4.

that the theory of AR assumes thermal equilibrium in the absence of an exciting field, so that the two theories should not necessarily agree, anyway.

F. The Proper Use of the Classical Theory

On the basis of the above (and yet other) considerations, it appears that a purely classical theory is inadequate if one desires to meaningfully and accurately predict, or interpret, the results of experiments concerned with electron-donor recombination in n-type Ge and Si at liquid-helium temperatures. The theory of HM can yield no more than a rough qualitative understanding of electron capture processes at low temperatures. However, the classical theory (with suitable modifications) can and should be used under conditions where a classical treatment is justified. For example, D'Angelo[24] has given a classical discussion of the Auger (impact) recombination of electrons and ions in a plasma. D'Angelo's theory stems from the original classical derivations of Thomson[25] in his research concerning gaseous discharges. The work of Lax, upon which the theory of HM is based, is also traced back to Thomson's work. Since the results predicted by D'Angelo agree with experiment in the classical range, it is not unreasonable to expect that the theory of HM will also be valid under the proper classical conditions.

5. SUMMARY

It is predicted that the capture probability of a conduction electron and an ionized donor impurity, in n-type Ge and Si, will become independent of temperature for $T<T_c$, where T_c is primarily a function of the donor concentration. This effect has not yet been conclusively established, either because the temperature range of the experiments did not extend to a sufficiently low value or because of defects within the experiments themselves. In the latter case, suggestions are offered to offset the difficulties, and the results of future experiments are awaited. The author has recently learned that new experiments designed to test the above hypothesis are being undertaken.[26]

On the basis of a number of varied considerations, the classical theory of Hamann and McWhorter appears to give an invalid picture of the electron-donor recombination process in n-type Ge and Si at liquid-helium temperatures. On the other hand, the quantum-mechanical theory of Ascarelli and Rodriguez is free of most of the objections which have been raised against the classical theory and the work of AR is in reasonable agreement with experiment. The work of AR, however, may require suitable modification in order to take account of impurity conduction, as suggested in the present paper.

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[24] N. D'Angelo, Phys. Rev. **140**, A1488 (1965).
[25] J. J. Thomson, Phil. Mag. **47**, 337 (1924).
[26] Dr. A. Mooradian (private communication).