Recombination of Electrons and Donors in n-Type Germanium*

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A calculation is given of the recombination cross section of an electron having a spherical effective mass and a donor impurity whose bound states can be described by a hydrogenic model. The recombination takes place with an initial capture of the electron in an excited state of the donor center followed by successive transitions to lower lying states. Each of these processes takes place with emission of a phonon. The calculated cross section agrees with the experimental one within a factor of the order of unity. The agreement between the temperature dependence of the calculated and the experimental recombination cross sections is good. Also we obtain a small but significant dependence of the recombination cross section on the binding energy of the ground state of the donor.

1. INTRODUCTION

WE are concerned, in the present work, with the kinetics of the recombination of electrons in the conduction band of a germanium crystal with ionized impurity donors of the group V of the periodic table. We assume that the bound states of such donor atoms can be described by considering the electron that does not participate in the cooperative bonding in the crystal to move around the impurity ion in the same fashion as it moves around the proton in a hydrogen atom. However, the Coulomb interaction is reduced in strength by a factor K equal to the optical dielectric constant of germanium and the electron has an effective mass m^* which can be regarded as the geometrical mean of the principal effective masses in the crystal.[1] We take $K=16$ for germanium and $m^*=0.22m$, where m is the free mass of the electron. The factor 0.22 is obtained from the results of cyclotron resonance experiments.[2] We shall disregard, for the time being, all complications arising from the band structure of germanium and assume simple spherical bands with effective mass m^*.

Under these conditions the ionization energy of a donor impurity is

$$E_i = m^* e^4 / 2\hbar^2 K^2 = 0.0117 \text{ ev}, \tag{1}$$

where e is the charge on the electron and $\hbar$ is Planck's constant divided by 2π. The effective radius of the first Bohr orbit is

$$a^* = K\hbar^2 / m^* e^2 = 38.5 \text{ A}. \tag{2}$$

Because of the extension of the bound states in space, one expects a rather large recombination cross section.

In fact, at 4°K for As and Sb impurities in Ge the cross sections for recombination turn out, experimentally, to be of the order of magnitude of 10^{-11} to 10^{-12} cm². Furthermore, they vary with the temperature approximately as $T^{-2.5}$.

One can conceive of a number of recombination mechanisms. For example, a conduction electron may make a transition to the ground state of the donor center accompanied by emission of light or of a phonon of the appropriate frequency. It is also possible for the electron to recombine with an ionized donor by collision with another electron in the vicinity of the donor center; one electron is captured while the other carries away the excess kinetic energy. These mechanisms have been studied by Sclar and Burstein[3] who conclude that none of them is able to account for the large cross sections of recombination observed.

The cross section for direct recombination with emission of light is obtained by making the appropriate changes in the well-known[4] results for the radiative recombination of electrons and protons to form hydrogen. The result is

$$\sigma = 1.71 \times 10^{-18} K^{\frac{3}{2}} (m/m^*)^2 E_i(\text{ev})/T \text{ cm}^2, \tag{3}$$

where $E_i(\text{ev})$ is the ionization energy of the donors expressed in electron volts and T is the absolute temperature in degrees Kelvin. The magnitude of σ when $T=4°K$ is 4.15×10^{-19} cm². This mechanism is, therefore, too slow to account for the experimental results. Furthermore, the temperature dependence is in considerable disagreement with experiment.

If we regard direct recombination with emission of a phonon as the main process responsible for the removal of electrons from the conduction band, we find a cross section[5]

$$\sigma = 256\pi E_1^2 \hbar^5 c_s^3 / \rho a^{*6} E_i^5 kT. \tag{4}$$

[1] See, for example, W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 257.

[2] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 98, 368 (1955).

[3] N. Sclar and E. Burstein, Phys. Rev. 98, 1757 (1955).

[4] See, for example, H. A. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press, Inc., New York, 1957), p. 320ff.

[5] H. Gummel and M. Lax, Ann. Phys. 2, 28 (1957).

TABLE I. Values of β_n (sec^{-1}).

$T(^\circ K)$ \ n	2	3	4
3.0	2.46×10^4	1.17×10^8	3.23×10^9
3.5	1.17×10^5	2.37×10^8	4.88×10^9
4.0	4.56×10^5	4.53×10^8	7.29×10^9
4.5	1.38×10^6	7.71×10^8	1.00×10^{10}
5.0	3.12×10^6	1.12×10^9	1.24×10^{10}
6.0	1.03×10^7	1.97×10^9	1.77×10^{10}
7.0	2.63×10^7	3.01×10^9	2.29×10^{10}
8.0	4.95×10^7	4.15×10^9	2.78×10^{10}
9.0	8.41×10^7	5.34×10^9	3.23×10^{10}
10.0	1.29×10^8	6.54×10^9	3.66×10^{10}

In Eq. (4) E_1 is the deformation potential (to be introduced in section 2; we shall take its value to be that of bulk germanium, i.e., approximately 20 ev), c_s the longitudinal velocity of sound in Ge ($c_s = 5 \times 10^5$ cm/sec), ρ the density of Ge ($\rho = 5.35$ g/cm^3), and k the Boltzmann constant. At 4°K this cross section is $\sigma = 5.9 \times 10^{-15}$ cm^2. The same remarks regarding the applicability of the mechanism hold here as in the case of recombination with emission of light.

In the same manner impact recombination is not able to account for the observed phenomena.[3] Lax[6] has recently proposed a mechanism of recombination which consists of the capture of an electron in a highly excited state of the donor with a subsequent cascade process by means of which the electron slowly diffuses to the ground state of the impurity center. The treatment of Lax is similar to that given in the work of Thomson[7] on gaseous discharges and is entirely classical. The recombination cross section turns out to be of the correct order of magnitude but varies as the inverse fourth power of the temperature.

In the present work we suggest that the recombination takes place by capture of a conduction electron in an excited state of the donor (not necessarily a highly excited state) with a subsequent transition to lower lying states. These transitions turn out to be faster when they are accompanied by emission of phonons rather than light.

In Sec. 2 we give the results of a calculation of the cross section for capture of a conduction electron in a bound state of the donor center. In Sec. 3 we consider subsequent transitions with emission or absorption of phonons or light. Finally, in Sec. 4 we give the recombination cross sections based on the mechanism considered in this paper together with a comparison of these results with the available experimental information.

2. CAPTURE IN EXCITED STATES

The purpose of this section is to give the results of a calculation of the cross section for the capture of a conduction electron in a stationary state of an impurity donor. In order to obtain these results we make use of

[6] M. Lax, Phys. Rev. 119, 1502 (1960).
[7] J. J. Thomson, Phil. Mag. 47, 337 (1924).

the principle of detailed balance to relate the capture cross sections to the transition probabilities for thermal ionization. Let us label the stationary states of the donor by subindices j. These subindices will represent the set of quantum numbers (nlm) associated with the different bound stationary states of the donor. The number of electrons captured per unit time in the state j is

$$\nu_j = V(N_A + n) \int_{E_c}^{\infty} d\epsilon \, n(\epsilon) f(\epsilon) v \sigma_c(j,\epsilon). \quad (5)$$

Here N_A is the concentration of acceptor atoms, n the concentration of conduction electrons, $n(\epsilon)$ the density of electronic states (per unit volume) in the conduction band, v the velocity of an electron whose energy is ϵ, $\sigma_c(j,\epsilon)$ the cross section for capture of an electron with energy ϵ in the jth state of the donor center, $f(\epsilon)$ the Fermi distribution function, E_c the energy of an electron at the bottom of the conduction band, and V the volume of the crystal. Equation (5) can be rewritten in the form

$$\nu_j = V(N_A + n) n \langle v\sigma_c(j,\epsilon) \rangle \equiv V(N_A + n) n \langle v \rangle \sigma_c(j). \quad (6)$$

The symbol $\langle A \rangle$ indicates the average of the quantity A over the thermal distribution,

$$n \langle A \rangle = \int_{E_c}^{\infty} d\epsilon \, n(\epsilon) f(\epsilon) A. \quad (7)$$

The second equality in Eq. (6) is simply the definition of the mean capture cross section $\sigma_c(j)$. Now, the number of electrons in states j which are excited per unit time into the conduction band is

$$\nu_j' = V N_D{}^{(j)} \beta_j, \quad (8)$$

where β_j is the probability per unit time for thermal ionization of an electron in state j. The quantity $N_D{}^{(j)}$ is the number per unit volume of un-ionized donors in the state j. In thermal equilibrium we must have

$$\nu_j = \nu_j', \quad (9)$$

so that

$$\sigma_c(j) = N_D f_j \beta_j / n_\infty (N_A + n_\infty) \langle v \rangle, \quad (10)$$

where

$$f_j = g_j \exp\left(\frac{\zeta - E_j}{kT}\right) \left[1 + \sum_j g_j \exp\left(\frac{\zeta - E_j}{kT}\right) \right]^{-1} \quad (11)$$

TABLE II. Values of $\sigma_c(n)$ (cm^2).

$T(^\circ K)$ \ n	2	3	4
3.0	6.65×10^{-13}	5.91×10^{-12}	1.82×10^{-11}
3.5	4.62×10^{-13}	4.30×10^{-12}	1.35×10^{-11}
4.0	4.11×10^{-13}	3.68×10^{-12}	1.14×10^{-11}
4.5	3.84×10^{-13}	3.25×10^{-12}	9.78×10^{-12}
5.0	3.30×10^{-13}	2.74×10^{-12}	8.11×10^{-12}
6.0	2.43×10^{-13}	2.02×10^{-12}	6.03×10^{-12}
7.0	2.03×10^{-13}	1.58×10^{-12}	4.69×10^{-12}
8.0	1.61×10^{-13}	1.27×10^{-12}	3.75×10^{-12}
9.0	1.35×10^{-13}	1.05×10^{-12}	3.06×10^{-12}
10.0	1.15×10^{-13}	8.87×10^{-13}	2.56×10^{-12}

is the probability of having the jth state occupied at temperature T, and g_j is the degeneracy of the level j (2 for an s state, 6 for a p state, etc.). The quantity ζ is the Fermi energy, E_j is the energy associated with the state j, and n_∞ is the equilibrium concentration of electrons

$$n_\infty = N_c \exp\left(\frac{\zeta - E_c}{kT}\right); \qquad (12)$$

N_c is a quantity that depends on the temperature and the density of energy levels $n(\epsilon)$ in the conduction band. For spherical bands with an effective mass m^* it is given by

$$N_c = 2(m^* kT / 2\pi\hbar^2)^{\frac{3}{2}}. \qquad (13)$$

After some transformations we get

$$\sigma_c(j) = \frac{g_j \pi^2 \hbar^2 \beta_j}{2m^*(kT)^2} \exp(I_j/kT), \qquad (14)$$

where

$$I_j = E_c - E_j \qquad (15)$$

is the ionization energy of the jth state.

We turn now to the task of evaluating the transition probabilities β_j for thermal ionization. This can easily be done for the lower lying states with quantum numbers n from 1 to 4. It turns out that these are the only ones that we shall need. The fastest mechanism for ionization is that which is associated with the absorption of a phonon. We shall assume a simple model of the electron-phonon interaction, namely one for which the change in energy of an electron in the deformed lattice is given by

$$H' = E_1 \operatorname{div}\mathbf{s}(\mathbf{r}), \qquad (16)$$

where E_1 is the bulk deformation potential of germanium and $\mathbf{s}(\mathbf{r})$ is the displacement of an atom in the lattice occupying a position of equilibrium given by $\mathbf{r}$. We now expand $\mathbf{s}(\mathbf{r})$ in terms of operators that represent the creation and destruction of phonon modes as follows:

$$\mathbf{s}(\mathbf{r}) = (\hbar/\rho V)^{\frac{1}{2}} \sum_{q\mu} \mathbf{e}_{q\mu}(\omega_{q\mu})^{-\frac{1}{2}} a_{q\mu}^\dagger \exp(i\mathbf{q}\cdot\mathbf{r}) + \text{H.c.} \qquad (17)$$

The quantities $\mathbf{e}_{q\mu}$, $\omega_{q\mu}$, and $a_{q\mu}^\dagger$ ($a_{q\mu}$) are, respectively, a unit polarization vector, the angular frequency, and a creation (destruction) operator associated with a phonon characterized by the wave vector $\mathbf{q}$. There are three possible polarizations μ ($\mu = 1, 2, 3$). We shall make the assumption (which is only valid for an isotropic elastic continuum) that for each value of $\mathbf{q}$ there are two possible polarizations at right angles with $\mathbf{q}$ and a third

TABLE III. Values of β_n/β_n' at $T = 4°$K.

n	β_n/β_n'
1	164
2	89
3	46
4	19

TABLE IV. Sticking probability S_n.

$T(°\text{K})$	Upper value for As, lower value for Sb		
	2	3	4
3.0	1	0.26	0.36×10^{-2}
	1	0.59	1.48×10^{-2}
3.5	1	0.15	0.24×10^{-2}
	1	0.42	0.99×10^{-2}
4.0	0.9988	0.083	0.16×10^{-2}
	0.9997	0.27	0.66×10^{-2}
4.5	0.9966	0.050	1.15×10^{-3}
	0.9992	0.18	4.82×10^{-3}
5.0	0.9900	0.036	0.93×10^{-3}
	0.9982	0.13	3.90×10^{-3}
6.0	0.9762	0.020	0.66×10^{-3}
	0.994	0.080	2.75×10^{-3}
7.0	0.932	0.013	0.51×10^{-3}
	0.983	0.054	2.12×10^{-3}
8.0	0.891	0.98×10^{-2}	0.42×10^{-3}
	0.972	0.040	1.75×10^{-3}
9.0	0.837	0.76×10^{-2}	0.36×10^{-3}
	0.955	0.021	1.50×10^{-3}
10.0	0.804	0.62×10^{-2}	0.32×10^{-3}
	0.929	0.017	1.33×10^{-3}

parallel to $\mathbf{q}$. The latter lattice modes are called longitudinal phonons and, in view of our assumption (16), are the only ones that effectively interact with the electrons. All these assumptions clearly limit the validity of our detailed quantitative result. However, we are only interested in finding order of magnitude estimates for the recombination cross sections so that our model is sufficient for the present purpose.

Some of the details of the calculation of the capture cross sections are given in Appendix A. Here, it is enough to mention that capture in s states (i.e., in states with angular momentum $l=0$) is much more likely than capture in states of higher angular momentum. The results have been obtained for $n \leqslant 4$ using Coulomb wave functions for the states in the continuum and are exhibited in Tables I and II. The difference one obtains when one uses plane waves instead of Coulomb wave functions is discussed in Appendix B and summarized in Table III.

Once the electron has been captured in a bound state it may either remain attached to the impurity center or it may be re-ionized by absorption of a phonon. The probability that the electron will not be ionized is called the sticking probability. Its evaluation constitutes the object of the next section.

3. STICKING PROBABILITY

Let S_j be the probability that an electron in the bound state characterized by j will not be ionized into the conduction band. If $p_j^{(\nu)}$ is the probability for ionization

after ν transitions of the electron between the state j and other states $j' \neq j$, we have

$$S_j + \sum_{\nu=1}^{\infty} p_j^{(\nu)} = 1. \qquad (18)$$

But

$$p_j^{(\nu)} = \sum_{j' \neq j} p_{j'j} p_{j'}^{(\nu-1)}, \qquad (19)$$

where $p_{j'j}$ stands for the probability for the transition from the bound state j to j';

$$p_{j'j} = w_{j'j} \Big[\sum_{j' \neq j} w_{j'j} + \beta_j \Big]^{-1}, \qquad (20)$$

and

$$p_j^{(1)} = \beta_j \Big[\sum_{j' \neq j} w_{j'j} + \beta_j \Big]^{-1}. \qquad (21)$$

The quantity $w_{j'j}$ is the probability per unit time that an electron in state j will make a transition to state j'. It is sufficient to compute $w_{j'j}$ in order to obtain the sticking probabilities S_j with any desired accuracy.

The transition probabilities are obtained from (16) and (17) using the Born approximation. There are several cases of interest depending on the magnitude of the parameter

$$\lambda_{nn'} = qa^* = \frac{E_i a^*}{\hbar c_s}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \qquad (22)$$

In equation (22) n is the principal quantum number of a level j described by the numbers n, l, m in the hydrogenic model, and q is the wave vector of the phonon that accompanies the transition. When $\lambda_{nn'} \gg 1$ the largest transition rates are those between two s-like states. Transitions between states nl and $n'l'$ are smaller by factors $(\lambda_{nn'})^{2(l+l')}$ so that they need not concern us here. Also, transition probabilities between states for which $\lambda_{nn'}$ is not large as compared to unity are negligible compared to the previous ones. We obtain for $\lambda_{nn'} \gg 1$ and $n' < n$

$$w_{n'n} = \frac{64E_1^2 \hbar^4 c_s^3}{\pi \rho a^{*8} E_i^5} \frac{(n'n)^5}{(n-n')^5(n+n')^3}$$

$$\times [1 - \exp(-\hbar\omega_{nn'}/kT)]^{-1}. \qquad (23)$$

The frequency $\omega_{nn'}$ is given by the Bohr relation,

$$\hbar\omega_{nn'} = E_i\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \qquad (24)$$

Application of the principle of detailed balance yields $(n' > n)$

$$w_{n'n} = w_{nn'} \exp(-\hbar\omega_{n'n}/kT), \qquad (25)$$

from which we readily establish that $\sum_{n'>n} w_{n'n}$ is negligible as compared to β_n for $n \leqslant 4$.

Table IV gives the sticking probabilities as a function of the temperature T and n. In Eq. (23) we use the

TABLE V. σ (cm^2) for As and Sb.

T(°K)	σ(As)	σ(Sb)
3.0	2.27×10^{-12}	4.47×10^{-12}
3.5	1.13×10^{-12}	2.42×10^{-12}
4.0	7.36×10^{-13}	1.51×10^{-12}
4.5	5.61×10^{-13}	1.04×10^{-12}
5.0	4.38×10^{-13}	7.37×10^{-13}
6.0	2.84×10^{-13}	4.30×10^{-13}
7.0	2.14×10^{-13}	3.04×10^{-13}
8.0	1.60×10^{-13}	2.22×10^{-13}
9.0	1.24×10^{-13}	1.63×10^{-13}
10.0	1.00×10^{-13}	1.32×10^{-13}

value given in equation (1) for E_i except for the case $n' = 1$, for which we substitute the experimental values ($E_i = 0.0127$ ev for As and $E_i = 0.0096$ ev for Sb). In fact, it is known that the energy levels of the excited states of a donor center are given approximately by $E_n = -E_i/n^2$ with E_i obtained from (1). But the ground-state energy differs from the simple hydrogenic value and depends on the nature of the impurity atom. The justification of the above procedure is that the factor E_i^5 in the denominator of (23) arises entirely from the energy of the phonon associated with the transition so that it is different for different donor impurities. The term a^{*8} originates from the choice of a hydrogen-like wave function for the ground state and so we assume it to be given by (2). Naturally, it would be more rigorous to use the precise wave function for the ground state, but this should not appreciably alter the dependence of the transition probability w_{1n} on the binding energy of the ground state.

Once an electron has been captured in an excited state, it can make an optical transition to a lower lying state. Here, however, the usual spectroscopic selection rules must be satisfied because the extension of the orbits is much smaller than the wavelength of the light associated with the transition between two bound states of the donor center. In other words, the dipole approximation is adequate. The rate for an optical transition from j to j' turns out to be 2.15×10^{-4} times the corresponding transition probability for the hydrogen atom. The latter are given in the literature.[8] The transition probability to go, for example, from a $3s$ state to a $2p$ state is 1.36×10^3 sec^{-1}. Optical transition rates are thus extremely small as compared to those occurring with emission of a phonon. The rate for the transition $3s \rightarrow 2s$ with phonon emission is of the order of 10^{10} sec^{-1} so that roughly 1 in 10^7 recombinations will occur with emission of light.

4. RECOMBINATION CROSS SECTIONS AND COMPARISON WITH EXPERIMENT

The cross sections for recombination are obtained simply by substituting in the equation

$$\sigma = \sum_j \sigma_c(j) S_j, \qquad (26)$$

[8] See reference 4, p. 266.

the values given in Tables II and IV. It is immediately observed from Tables II and IV that the most important contributions to the recombination cross sections arise from capture in the $2s$ and $3s$ levels with subsequent transitions to the ground state with emission of a phonon.

The recombination cross sections for As and Sb donor impurities are given in Table V.

In recent years there have been several measurements of the parameters necessary to describe the kinetics of the recombination of electrons and donors in germanium[9-14] followed more recently by some data on similar processes in silicon.[15]

The first measurements of the recombination of electrons and donors in germanium made by Koenig[9] were followed by those of Ascarelli and Brown.[10] The cross sections measured by these authors differ by nearly a factor 20 at 4°K; this difference can be attributed in large part to Joule heating of the sample during the previous breakdown process. The reader is referred to reference 10 for a discussion of this question. If this source of error is taken into account the resulting cross sections differ by a factor 3.5 and have a similar temperature dependence: approximately $T^{-2.5}$ between 9 and 3°K. Similar results were recently obtained by Michel and Rosenblum.[11] The absolute values of the cross sections measured by Ascarelli and Brown are affected by very large unknown systematic errors connected with the evaluation of the compensation of the samples. The experimental data of references 9 and 10 are shown in Fig. 1.

The cross sections given in Table V are those corresponding to a nondegenerate spherical effective mass. If the fourfold degeneracy of the conduction band edge of germanium is taken into account there will be an increase of a factor 4 in the capture cross section. Underlying this statement is the assumption that the capture probability of an electron from one valley of the conduction band into the excited state of the donor 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. Details of such an extension to the case of the multivalleyed semiconductor are given in Appendix C.

Further attempts to refine the calculation could be envisaged: an attempt to take into account the nonsphericity of the effective masses and the differences at

[9] S. H. Koenig, Phys. Rev. **110**, 988 (1958).
[10] G. Ascarelli and S. C. Brown, Phys. Rev. **120**, 1615 (1960).
[11] R. E. Michel and B. Rosenblum, Bull. Am. Phys. Soc. **6**, 115 (1961).
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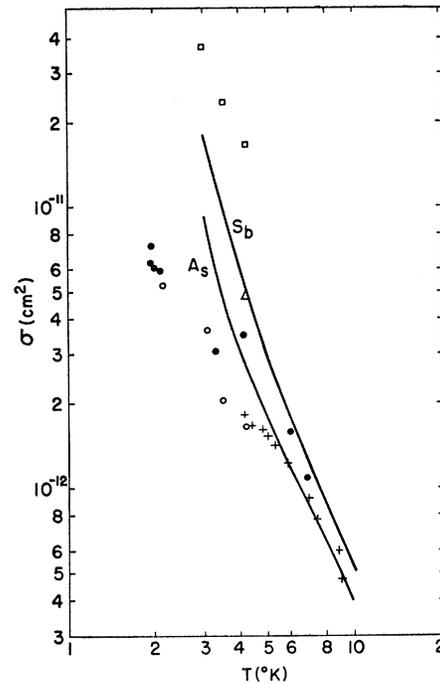
FIG. 1. Experimental and calculated values of the cross section for recombination. The solid lines represent the results of the theory developed in the present paper. The experimental points are taken from the following sources:

	Reference	Sample	Impurity
□	10	BTL1	Sb
○	10	LL2	As
△	10	n WLB 28-6	Sb
+	9	n WLB 28-6	Sb
●	6	n WLB 28-6	Sb

the donor site between the wave functions of electrons bound to different types of donors.[1] This last effect should further enhance the difference of sticking probability between As and Sb in view of the more rapid decrease of the modulating part of the Bloch function of the ground state of an electron bound to As rather than Sb.

In Fig. 1 we have also plotted the results of Table V multiplied by 4 in order to take into account the increase in σ_c due to the degeneracy of the electron states. The agreement between this simplified theoretical calculation and the available experimental data is reasonably good.

With less success we can compare other experimental data with the results of our calculation. Ascarelli and Brown[12] and Koenig and Brown[13] detected far infrared radiation emitted during low-temperature breakdown of a sample of n-type germanium. Koenig and Brown found that if they used a sample of broken-down n-type germanium doped with Sb as infrared source and a sample of As-doped germanium as detector, the efficiency was 50 times larger than in the case in which the roles of source and detector were inverted. This is astonishing in view of the fact that the binding energy

of the ground state of As donors is larger than that of Sb donors. This difference cannot be explained even if one takes into account the valley-orbit splitting and assumes that the populations of the singlet and triplet state in which the ground state splits are in the ratio $\exp(-\Delta/kT)$ (where Δ is the valley-orbit splitting). Koenig and Brown evaluate that the cross section for radiative transitions is 10^9 times smaller than that for the nonradiative ones. Our theoretical estimate would indicate that this ratio should be only 10^7.

To terminate the comparison of the experimental results with our theoretical calculation we make a few qualitative comments on the comparison with the case when the electron distribution is not Maxwellian, as is the case with "hot electrons."

We can expect in this case that the principal change brought about by an applied electric field will be to decrease the sticking probability. Thus, electrons that have not had the time to make a transition from the excited state to the ground state will be easily re-excited into the conduction band. The excited states of group V impurity donors do not depend on the impurity atom itself, thus the decrease in the sticking probability with the externally applied field will be of the same form for each of the different donors. This has been shown experimentally in the case of acceptors.[16] There is no apparent reason to expect a substantial difference in the case of donors.

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APPENDIX A

The probability per unit time for an electron in the bound state j to be thermally excited to a state in the continuum is

$$\beta_j = \frac{E_1^2 m^*}{(2\pi)^5 \rho \hbar^6 c_s^5} \int_{I_j}^{\infty} d(\hbar\omega)\ (\hbar\omega)^3 \bar{n}(\hbar\omega)\kappa$$
$$\times \int d\Omega(\mathbf{q}/|\mathbf{q}|) \int d\Omega(\mathbf{\kappa}/|\mathbf{\kappa}|)|M(\mathbf{\kappa},j)|^2. \quad (A1)$$

This result is readily obtained from equations (16) and (17) using the expression for the transition probability between two quantum states within the Born approximation. In Eq. (A1), $\bar{n}(\hbar\omega)$ is the number of phonons in a mode of energy $\hbar\omega$ at temperature T.

$$\bar{n}(\hbar\omega) = [\exp(\hbar\omega/kT)-1]^{-1}; \quad (A2)$$

[16] S. H. Koenig and J. J. Hall, Phys. Rev. Letters 5, 550 (1960).

the wave vector $\mathbf{\kappa}$ characterizes one of the electron states in the continuum. Conservation of energy requires that

$$\kappa = |\mathbf{\kappa}| = (2m^*/\hbar^2)^{\frac{1}{2}}(\hbar\omega - I_j)^{\frac{1}{2}}. \quad (A3)$$

The differentials $d\Omega(\mathbf{q}/|\mathbf{q}|)$ and $d\Omega(\mathbf{\kappa}/|\mathbf{\kappa}|)$ are elements of solid angle along the directions of the unit vectors $\mathbf{q}/|\mathbf{q}|$ and $\mathbf{\kappa}/|\mathbf{\kappa}|$, respectively. The matrix element $M(\mathbf{\kappa},j)$ is given by the expression

$$M^*(\mathbf{\kappa},j) = V^{\frac{1}{2}} \int \varphi_\kappa \exp(-i\mathbf{q}\cdot\mathbf{r})\varphi_j^* d\mathbf{r}. \quad (A4)$$

The wave function φ_κ is the Coulomb wave function corresponding to the wave vector $\mathbf{\kappa}$:

$$\varphi_\kappa = V^{-\frac{1}{2}}(2\pi\gamma)^{\frac{1}{2}}[1-\exp(2\pi\gamma)]^{-\frac{1}{2}}$$
$$\times \exp(i\mathbf{\kappa}\cdot\mathbf{r})F[i\gamma,1,i(\kappa r - \mathbf{\kappa}\cdot\mathbf{r})], \quad (A5)$$

where

$$\gamma = 1/\kappa a^*. \quad (A6)$$

φ_j is the hydrogen-like wave function which describes the jth bound state of the donor (see reference 1).

The function $F(a,b,z)$ is the confluent hypergeometric function for which it is convenient to use the following integral representation:

$$F(i\gamma,1,z) = \frac{1}{2\pi i} \oint d\zeta\ \zeta^{i\gamma-1}(\zeta-1)^{-i\gamma}\exp(z\zeta). \quad (A7)$$

The contour of integration contains the points $\zeta=0$ and $\zeta=1$ in the complex ζ plane. We need only concern ourselves with s states as these are most easily ionized. The wave function for the n-s state is

$$\varphi_n(r) = (\pi n^3 a^{*3})^{-\frac{1}{2}}$$
$$\times \exp(-r/na^*)F(-n+1, 2, 2r/na^*). \quad (A8)$$

We obtain $M(\mathbf{\kappa},n)$ as a linear combination of derivatives of the expression

$$J_n(\lambda) = \int d\mathbf{r}\ r^{-1} \exp\left[i(\mathbf{\kappa}-\mathbf{q})\cdot\mathbf{r} - \frac{\lambda r}{na^*}\right]$$
$$\times F[i\gamma,1,i(\kappa r - \mathbf{\kappa}\cdot\mathbf{r})], \quad (A9)$$

evaluated at $\lambda=1$.

After some rather simple manipulations we find[5]

$$J_n(\lambda) = 4\pi n^2 a^{*2}[\lambda^2 + (\mathbf{K}_n - \mathbf{Q}_n)^2]^{i\gamma-1}$$
$$\times [Q_n^2 + (\lambda - iK_n)^2]^{-i\gamma}, \quad (A10)$$

with

$$\mathbf{K}_n = na^*\mathbf{\kappa}, \quad (A11)$$
$$\mathbf{Q}_n = na^*\mathbf{q}. \quad (A12)$$

From these relations we obtain

$$M^*(\kappa,n) = -(2\pi^2\gamma n a^*)^{-\frac{1}{2}}[1 - \exp(-2\pi\gamma)]^{-\frac{1}{2}}$$

$$\times \sum_{\nu=0}^{n-1} \frac{2^\nu}{(\nu+1)!}\binom{n-1}{\nu} J_n{}^{(\nu+1)}. \quad \text{(A13)}$$

The quantity $J_n{}^{(\nu)}$ is the νth derivative of $J_n(\lambda)$ with respect to λ evaluated at the point $\lambda = 1$.

For temperatures of the order of $T = 4°K$ and for $n \leqslant 4$ we can make the approximation

$$\bar{n}(\hbar\omega) = \exp(-\hbar\omega/kT). \quad \text{(A14)}$$

Furthermore, the dominant contribution to β_n arises from values of $\hbar\omega$ very near to $I_n = E_i/n^2$ or, for values of $\gamma \gg 1$. For $n \leqslant 4$ we can neglect unity as compared with $Q_n{}^2$. In fact,

$$Q_n{}^2 \geqslant \left(\frac{e^2}{2\hbar c_s K}\right)^2 \frac{1}{n^2} = \frac{188}{n^2}. \quad \text{(A15)}$$

With these approximations,

$$|M(\kappa,n)|^2 = \frac{8^3\pi^2}{n^3\kappa q^8 a^{*6}} \exp\left(-\frac{4}{nq^2 a^{*2}}\right), \quad \text{(A16)}$$

so that the transition probabilities for thermal ionization turn out to be

$$\beta_n = \frac{256 E_1{}^2 m^* \hbar^2 c_s{}^3}{\pi \rho a^{*6} n^3 (kT)^4} I(n,h,g), \quad \text{(A17)}$$

where

$$h = E_i/kT, \quad \text{(A18)}$$

and

$$g = 2\hbar c_s/a^* kT. \quad \text{(A19)}$$

The symbol $I(n,h,g)$ stands for the integral

$$I(n,h,g) = \int_0^{n^2/h} dt\, t^3 \exp(-t^{-1} - g^2 t^2/n). \quad \text{(A20)}$$

These integrations have been performed numerically on an IBM 704 digital computer. In Table I we give the results obtained for β_n as a function of n and T. In Table II we show the corresponding results for the capture cross sections $\sigma_c(n)$. We need not be concerned with bound states with angular momentum higher than zero because the corresponding transition rates turn out to be of the order of those for $l = 0$ multiplied by $Q_n{}^{-2l}$. In no case do they contribute appreciably to the total cross section.

APPENDIX B

The object of this appendix is to give a calculation of the ionization rates β_n, when instead of taking for φ_κ the Coulomb wave function (A5) we simply take the plane wave

$$\varphi_\kappa = V^{-\frac{1}{2}} \exp(i\kappa \cdot \mathbf{r}). \quad \text{(B1)}$$

The calculation of the matrix element $M(\kappa,n)$ is carried out exactly as before except that whenever the function $J_n(\lambda)$ or its derivatives appear we substitute for them the function

$$K_n(\lambda) = \int d\mathbf{r}\, r^{-1} \exp\left[i(\kappa - \mathbf{q}) \cdot \mathbf{r} - \frac{\lambda r}{na^*}\right], \quad \text{(B2)}$$

and its derivatives, respectively. Equation (B2) can be rewritten in the form

$$K_n(\lambda) = 4\pi n^2 a^{*2}[\lambda^2 + (\mathbf{K}_n - \mathbf{Q}_n)^2]^{-1}. \quad \text{(B3)}$$

After some transformations we find the expression

$$\beta_n' = \frac{8 E_1{}^2 \hbar c_s{}^3 n^7}{\rho a^{*5} E_i{}^5}\left(\frac{2m^* kT}{\pi}\right)^{\frac{3}{2}} \exp(-E_i/n^2 kT), \quad \text{(B4)}$$

for the rate of thermal ionization of an n-s state assuming plane waves for the continuum states. In Table III we give a tabulation of β_n/β_n' as a function of n for $T = 4°K$. In particular when $n = 1$ we obtain

$$\beta_1/\beta_1' = 32\hbar/m^* a^* \langle v \rangle. \quad \text{(B5)}$$

APPENDIX C

In this appendix we attempt to extend the results of the calculation given in the main body of the paper to the case in which the conduction band has four different minima as occurs in germanium. However, we shall not take into account the nonsphericity of the surfaces of constant energy. We assume the minima of the conduction band are at positions $\mathbf{K}_\alpha$ ($\alpha = 1, 2, 3, 4$). An electron in a state

$$\psi_{\alpha k} = V^{-\frac{1}{2}} e^{i(\mathbf{K}_\alpha + \mathbf{k}) \cdot \mathbf{r}} u_{\alpha k}(\mathbf{r}), \quad \text{(C1)}$$

will be supposed to have energy

$$\epsilon_{\alpha k} = E_c + \hbar^2 k^2/2m^*, \quad \text{(C2)}$$

where $|\mathbf{k}| \ll |\mathbf{K}_\alpha|$. Here $u_{\alpha k}$ is a function having the periodicity of the lattice.

Let $g(\epsilon) d\epsilon$ be the number of electrons having energy in the range $d\epsilon$ at ϵ associated with one of the minima of the conduction band and having a definite spin state. Because there are four equivalent minima of the conduction band and two possible orientations of the spin we have

$$n(\epsilon) = 8g(\epsilon). \quad \text{(C3)}$$

The wave functions characterizing the stationary states of the impurity center are

$$\varphi_j \psi_\alpha, \quad \text{(C4)}$$