

Inelastic Scattering of Electrons in Germanium*

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In doped, compensated samples of germanium at low temperatures, a scattering center analogous to the hydrogen molecule ion may be formed in which an electron (or hole) is shared between two donors (or acceptors). Mobile carriers can lose energy through excitation of this molecule. This mechanism of energy loss is probably important in the explanation of the negative resistance observed in lightly doped, compensated germanium at liquid helium temperatures. In this paper, a rough calculation of the average rate of energy loss is reported, which serves to confirm previous conjectures of the importance of this process.

IN 1959, McWhorter and Rediker reported observation of a substantial apparent negative resistance occurring at the onset of breakdown of lightly doped, compensated germanium.¹ The phenomenon occurs in both *n*- and *p*-type material providing there is a substantial degree of compensation. The breakdown itself is attributed to a rapid increase in the number of free carriers caused by impact ionization of carriers loosely bound to impurity atoms.² The voltage-current characteristics of uncompensated material do not show appreciable negative resistance, but rather a rapid increase in current of several orders of magnitude at breakdown while the voltage remains essentially constant.

The electric field required to produce breakdown in the compensated material may be more than an order of magnitude greater than in the uncompensated samples. McWhorter has proposed to explain this increase in breakdown field and the negative resistance as due to the operation of an electron energy loss mechanism not present in the uncompensated material and which disappears after breakdown.³ The process is as follows: In the compensated material, which we suppose to be *n*-type, there will be both ionized and un-ionized donors. The un-ionized donors will tend to share electrons with the ionized ones, thus forming a center analogous to the hydrogen molecule ion. This ion has two states whose separation in energy is small compared to the energy required to ionize a donor for realistic values of the distance between donors. A mobile carrier may lose energy by exciting the molecule.

Throughout the rest of the paper we consider only *n*-type material. An electron in the conduction band gains energy from an external electric field at a rate μE^2 (μ is the mobility and E the field strength). This

energy may be lost in two ways (providing the electron energy is not sufficient to excite a donor): to the phonons and in the molecular excitation process. We wish to compare the relative importance of the two loss mechanisms. This can be done by computing the energy loss per unit time to molecular excitation, integrated over all molecules, and averaged over all electrons in the conduction band. A similar average energy loss can be obtained for phonon emission. In our view, the electrons which begin to produce the donor ionization at breakdown are those few which have been thermally excited into the conduction band, rather than the carriers weakly bound to donors, whose motion is conventionally described as a "hopping" process.⁴ One must also note that in thermal equilibrium in the absence of an external electric field, energy losses to molecular excitation will be balanced by corresponding energy gains from molecular de-excitation. Only when the distribution is "off balance" on the high-energy side will the losses outweigh the gains.

The calculation proceeds as follows. We determine the probability of a transition from the symmetric to the antisymmetric state of the hydrogen molecule ion, caused by a collision with an itinerant electron whose wave vector changes by $\mathbf{k} = \mathbf{k}_i - \mathbf{k}_f$ (\mathbf{k}_i is the initial wave vector and \mathbf{k}_f the final). The transition probability must be averaged over all angles between \mathbf{k} and the axis of the molecule, and between \mathbf{k}_i and \mathbf{k}_f . We then multiply by the energy of excitation, which depends strongly on the separation distance R , the probability distribution of electrons in energy, and the distribution of intramolecular separations. Since the energy difference between molecular states may be small compared to kT , even at liquid helium temperatures, it is necessary to include a Boltzmann factor to take account of the differences in population of the molecular states. We must then integrate over electron energy and intramolecular distance. Throughout this calculation, the crystal band structure has been assumed to be parabolic, characterized by an effective-mass parameter m^* . The anisotropy of the actual band structure of germanium would be very difficult to include and has been neglected. We have determined the average energy loss for temperatures in the range 1°–8°K;

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¹ A. N. McWhorter and R. H. Rediker, *Proc. Inst. Radio Engrs.* **47**, 1207 (1959).

² N. Sclar and E. Burstein, *J. Phys. Chem. Solids* **2**, 1 (1957). S. H. Koenig and G. R. Gunther-Mohr, *J. Phys. Chem. Solids* **2**, 268 (1957). S. H. Koenig, *Phys. Rev.* **110**, 986 (1958).

³ A. L. McWhorter and R. H. Rediker, *Proceedings of the International Conference on Semiconductor Physics* (Czechoslovak Academy of Sciences, Prague, 1961), p. 134.

⁴ A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).

and for donor concentrations ranging from 10^{14} to $2 \times 10^{16}/\text{cm}^3$.

We approximate the wave functions of the symmetric and antisymmetric states of the effective hydrogen molecule ion as

$$\begin{aligned}\psi_S &= [2(1+\Delta)]^{-\frac{1}{2}}(u_A + u_B), \\ \psi_{AS} &= [2(1-\Delta)]^{-\frac{1}{2}}(u_A - u_B),\end{aligned}\quad (1)$$

in which u_A and u_B are hydrogenic wave functions centered on atoms A and B of the molecule and Δ is the overlap integral. One should, of course, use properly symmetrized linear combinations of impurity wave functions, as discussed by Kohn.⁵ We have instead chosen hydrogenic wave functions,

$$u(r) = (\pi a^3)^{-\frac{1}{2}} e^{-r/a}, \quad (2)$$

in order to simplify the calculation. In (2), a is the effective Bohr radius in the material.

$$a = \kappa \hbar^2 / m^* e^2, \quad (3)$$

with κ the dielectric constant and m^* the effective mass. In order to test the sensitivity of the results to the assumed wave function, we have considered two effective masses: (1) $m^* = 0.119$, the usual average of transverse and longitudinal masses, and (2) $m^* = 0.185$, a value which gives a donor ionization energy in reasonable agreement with experiment.⁶ If the separation of the atoms forming the molecule is R , the energy difference between the antisymmetric and symmetric states, which we will call the excitation energy and denote by E_x , is, according to Margenau and Murphy⁷:

$$E_x = \frac{-2(K-J)}{1-\Delta^2} = \frac{2e^2}{\kappa R} \left[\frac{2}{3} \left(\frac{R}{a} \right)^2 - 1 \right], \quad (4)$$

in which K and J are the usual exchange and Coulomb integrals, respectively, and in the second step we have neglected terms of the order of $e^{-2R/a}$, compared with unity (this approximation will be valid for most of the molecules for reasonable concentrations).

No attempt has been made to include the effects of local electric fields due to other ions. As pointed out by McWhorter and Rediker,⁸ such fields inhibit formation of molecules when the partner donors are far apart. The contribution from such molecules is already suppressed by the Boltzmann factor previously mentioned, so that the neglect of this localizing effect should not be serious.

The transition probability for excitation of the molecular ion has been calculated by Kerner⁸ and by Ivash⁹

⁵ W. Kohn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 258.

⁶ P. Csavinsky, Phys. Rev. **119**, 1605 (1960).

⁷ H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, New York, 1955), p. 385. The expression for the excitation energy given in reference 6 is incorrect.

⁸ E. H. Kerner, Phys. Rev. **92**, 1441 (1953).

⁹ E. V. Ivash, Phys. Rev. **112**, 155 (1958).

in connection with studies of the dissociation of the molecular ion by electron impact. In the solid-state problem dissociation is impossible since the donors are bound in the lattice. It is necessary to make several approximations in the calculation, chief of which is the use of the lowest Born approximation. In addition, exchange scattering is neglected. As a result of these approximations, only an order-of-magnitude estimate of the probability can be attained. We must evaluate the matrix element

$$H_x = \int e^{i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}_1} \frac{e^2}{r_{12}} \psi_{AS}^*(\mathbf{r}_2) \psi_S(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (5)$$

We find this to be given by

$$H_x = \frac{-64\pi i e^2}{\kappa(1-\Delta^2)^{\frac{1}{2}}} \frac{e^{i\mathbf{k} \cdot \mathbf{R}/2} \text{sinc} \cdot \mathbf{R}/2}{k^2 a^4 (k^2 + 4/a^2)^2}, \quad (6)$$

in agreement with Kerner⁸ and Ivash.⁹ In the above, $\mathbf{k} = \mathbf{k}_i - \mathbf{k}_f$, where \mathbf{k}_i and \mathbf{k}_f are the initial and final wave vectors of the electron. It is now necessary to calculate the transition probability P per unit time, energy interval, and solid angle. According to the usual rule,

$$P = \frac{2\pi}{\hbar} |H_x|^2 \rho(E_f),$$

in which $\rho(E_f)$ is the density of final states. We also average over all directions of \mathbf{R} . We find (neglecting Δ^2 compared to unity)

$$P = \frac{2m^* e^4}{\hbar^3 \kappa^2} \left[1 - \frac{\text{sinc} kR}{kR} \right] \frac{k_f}{k^4 (1 + k^2 a^2/4)^4}. \quad (7)$$

An integration over the orientations of \mathbf{k} is required. It does not appear possible to express the result in closed form. The rapid increase in the denominator of (7) with increasing k suggests that only small k need be considered. Hence we neglect $(ka/2)^2$ compared to unity, and expand the term in brackets, retaining only the two leading terms:

$$1 - \frac{\text{sinc} kR}{kR} = \frac{(kR)^2}{6} \left[1 - \frac{(kR)^2}{20} + \dots \right]. \quad (8)$$

Then the sum over final directions is accomplished simply through use of the relation,

$$\int \frac{1}{k^2} d\Omega = \frac{2\pi}{k_f k_i} \ln \frac{k_f + k_i}{k_i - k_f}. \quad (9)$$

To compute an average energy loss, we multiply by the energy loss E_x and the probability of finding an incident electron of energy $E(k_i)$, which is, at temperature T :

$$\frac{2^{\frac{1}{2}} \hbar}{(m^* \pi)^{\frac{1}{2}} (KT)^{\frac{1}{2}}} k_i e^{-E/KT}. \quad (10)$$

This quantity is normalized to unity over the conduction band. There are two additional factors to be included:

(1) Since E_x can be small compared to KT , even at 4°K, the upper state will be appreciably populated. The relative excess in the lower state is given simply by $\tanh(E_x/2KT)$.

(2) The distribution of intra-molecular distances is determined as follows. Suppose there are N_D donors and N_A acceptors per unit volume. All the acceptors may be assumed to have captured an electron from a donor, leaving $(N_D - N_A)$ electrons bound to donors. The distribution of distances between donors, $\mathcal{O}(R)$ is given by a Poisson formula,⁴

$$\mathcal{O}(R) = (3R^2/R_S^3) \exp[-(R/R_S)^3], \quad (11)$$

in which R_S is determined by

$$4\pi R_S^3/3 = N_D^{-1}. \quad (12)$$

The number of molecules whose interatomic distance is R is then

$$\frac{N_A(N_D - N_A)}{N_D} \mathcal{O}(R). \quad (13)$$

The factor multiplying the Poisson formula may be seen to be correct since the number of un-ionized donors is $N_D - N_A$, and the probability that the nearest neighbor of a particular donor is ionized is just N_A/N_D .

Next, we combine the factors mentioned and perform the integration over electron energies. The integrals involved are

$$\int_{E_x}^{\infty} e^{-E/KT} \ln \left[\frac{E^{\frac{1}{2}} + (E - E_x)^{\frac{1}{2}}}{E^{\frac{1}{2}} - (E - E_x)^{\frac{1}{2}}} \right] dE \\ \approx KT e^{-E_x/KT} [\ln 2 - e^{E_x/2KT} \text{Ei}(-E_x/2KT)]. \quad (14)$$

In order to obtain (14), use has been made of the approximation

$$\ln \left(\frac{x + (x^2 - 1)^{\frac{1}{2}}}{x - (x^2 - 1)^{\frac{1}{2}}} \right) \approx \ln 2 + \ln(2x^2 - 1)$$

(with $x^2 = E/E_x$), which is valid when $x^2 \gg 1$. Ei is the usual exponential integral function. Another integral arises from the $(kR)^4/120$ term in (8). This is

$$\int_{E_x}^{\infty} e^{-E/KT} [E(E - E_x)]^{\frac{1}{2}} dE \\ = \frac{E_x KT}{2} e^{-E_x/2KT} K_1(E_x/2KT), \quad (15)$$

in which K_1 is a modified Bessel function of the second kind.¹⁰

The energy loss per electron per unit time, which we

¹⁰ E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, New York, 1952), p. 373.

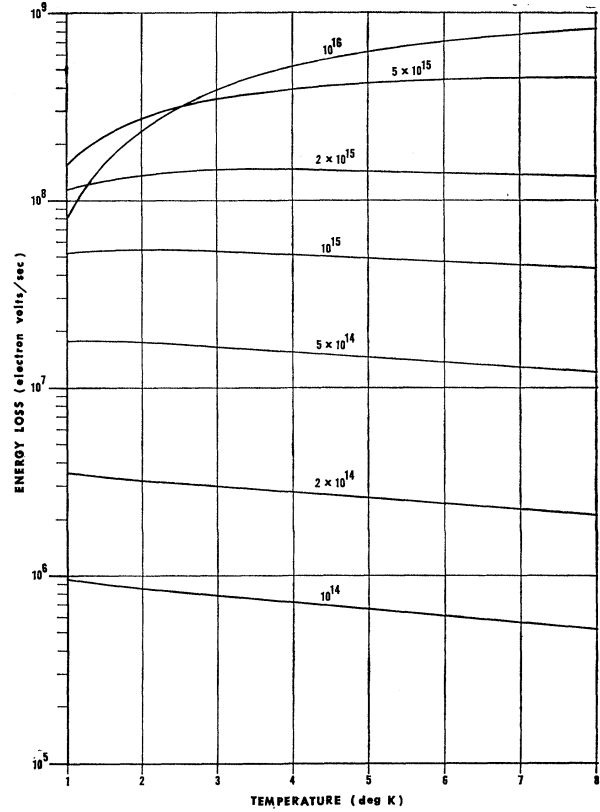


FIG. 1. The quantity A , defined by Eq. (17), is shown as a function of temperature in the range 1–8°K for seven donor concentrations in the range 10^{14} – 10^{16} cm⁻³. The curves were computed for an assumed effective mass $m^* = 0.119$.

denote as $\langle W_x/\tau \rangle$, can now be represented as a single integral over the intramolecular distance R . We find

$$\langle W_x/\tau \rangle = \frac{N_A(N_D - N_A)}{\pi N_D \hbar} \left(\frac{2\pi \hbar^2}{m^* KT} \right)^{\frac{3}{2}} (KT) \int_0^{\infty} \frac{R^2}{a^2} e^{-E_x/KT} \\ \times \left[\ln 2 - e^{E_x/2KT} \text{Ei}(-E_x/2KT) - \frac{1}{20} \right. \\ \times \left(\frac{2m^* R_S^2 E_x}{\hbar^2} \right) e^{E_x/2KT} \\ \times K_1(E_x/2KT) \left. \right] E_x \tanh(E_x/2KT) \\ \times \frac{R^2}{R_S^3} \exp[-(R/R_S)^3] dR. \quad (16)$$

The dependence of E_x on R is given by Eq. (4).

The average energy loss as given by Eq. (16) has been computed numerically on an IBM 709 computer as a function of concentration and temperature. The results are shown graphically in Fig. 1.

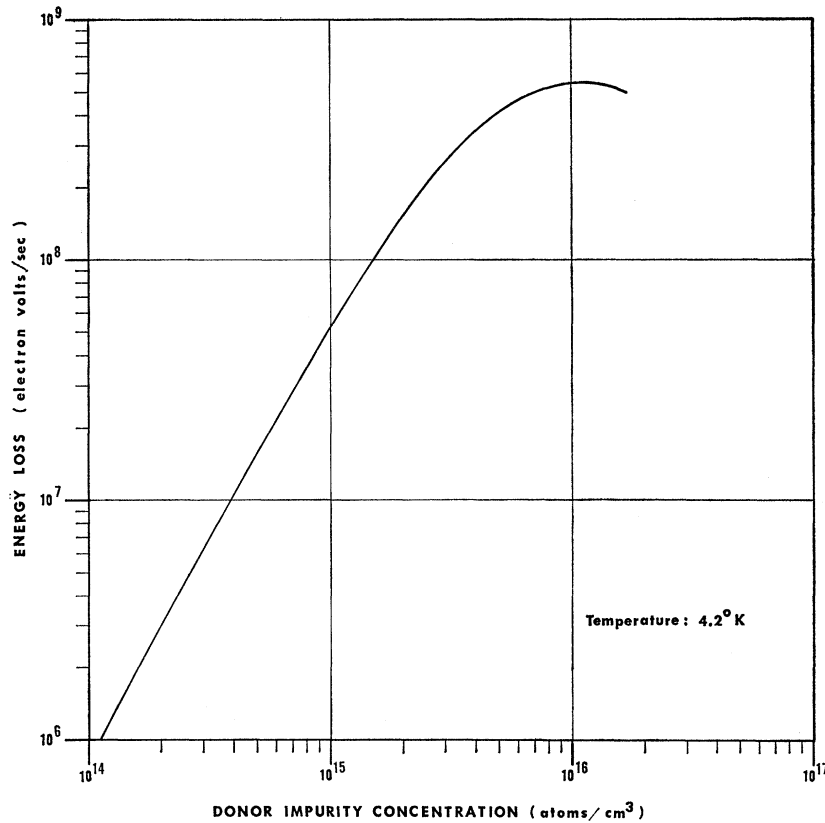


FIG. 2. The dependence of A on donor concentration at 4°K is shown. The maximum appears to occur for $N_D = 10^{16} \text{ cm}^{-3}$.

The integrand of (16) is actually a rather sharply peaked function of (R/R_s) with the maximum occurring (for 4°K, $N_D = 10^{15} \text{ cm}^{-3}$) for $R/R_s = 0.65$ (about 400 Å). Consequently only those "molecules" whose separation is of the order of $\frac{2}{3}$ of the average contribute appreciably to the energy loss. Further, the contribution from the second term of (8) is only 14% of the first term for the concentration and temperature mentioned. This confirms the validity of the small- k approximation.

The average energy loss is a function of donor and acceptor concentrations and temperature. Let us write

$$\langle W/\tau \rangle = AC(1-C), \quad (17)$$

in which $C = N_A/N_D$ is the concentration of compensating acceptors relative to donors. The quantity A , which is a function of N_D and T only, is exhibited in Fig. 1. For donor concentrations of $2 \times 10^{15} \text{ cm}^{-3}$ and smaller, A is reasonably independent of temperature throughout the range calculated (it must, however, vanish at 0°K). The dependence of A on donor concentration for a fixed temperature (4°K) is exhibited in Fig. 2. For small N_D , A is proportional to N_D^2 and rises to a maximum for $N_D = 10^{16} \text{ cm}^{-3}$ at 4°K. This behavior may be explained qualitatively as follows: When N_D is small, an increase in N_D decreases the separation between donors. This increases the excitation energy E_x , and the average energy loss rises correspondingly. As N_D and E_x continue to increase, the probability that an

electron in the conduction band has enough energy to cause a transition decreases exponentially, and this factor causes the average energy loss to decrease for large N_D .

The results presented in Figs. 1 and 2 were obtained for an assumed effective mass ratio 0.119. Unfortunately, the calculated energy loss is a fairly sensitive function of the assumed effective mass. The general temperature and concentration dependences noted in the present instance were found, however, to continue in a duplicate calculation performed for an assumed mass ratio of 0.185, while the average energy loss was, in general, lower by a factor of about 4. For this, and other reasons previously mentioned, the present calculation can be considered reliable only in respect to the order of magnitude of the effect considered.

The average energy loss which we have calculated does not itself determine the breakdown field strength. To compute this, we would have to calculate the probability of energy gain as well as that of loss in molecular transitions, as a function of electron energy (integrated over intramolecular separations R). Such a calculation would be considerably more difficult than the present one, since the integration over R must be done numerically. We can, however, compare the average rate of energy loss by molecular excitation [from (17)] with a corresponding quantity for collisions with phonons. The average rate of energy loss for an electron

of velocity v has been estimated by Shockley¹¹ as

$$(m^*S^2/\tau_L)(m^*v^2/KT),$$

in which S is the velocity of sound and τ_L is the relaxation time for lattice scattering. When we average over the electrons in the band, we find an average energy loss for collisions with phonons, $\langle W_{ph}/\tau \rangle$

$$\langle W_{ph}/\tau \rangle = 3m^*S^2/\tau_L. \quad (18)$$

At 4°K, this loss rate is about 10^5 ev/sec. Evidently the molecular excitation process can be more important.

Since only electrons of relatively high energy are involved in the ionization process, and for these electrons the probability of energy loss by molecular excitation must be much greater than the probability of energy

gain by de-excitation, one would expect that, apart from factors of the order of unity, the cautionary statement in the previous paragraph could be discarded so that the ratio of the electric field strength at breakdown in the compensated material to that in the uncompensated samples will be about

$$[\langle W_x/\tau \rangle / \langle W_{ph}/\tau \rangle]^{1/2}.$$

It is seen, in agreement with the qualitative discussion of McWhorter and Rediker,³ that the molecular excitation mechanism considered here is capable of providing the factor of 10 to 30 increase in the breakdown field required by their experimental results.

ACKNOWLEDGMENT

We acknowledge valuable discussions with L. M. Lambert.

¹¹ W. Shockley, Bell System Tech. J. **30**, 990 (1951).

Velocity Shift of the Mössbauer Resonance

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The mean square velocity of an impurity atom in a crystal lattice has been evaluated in both the low and high temperature limits. The result for the high temperature limit includes the effect of force constant differences between solute and solvent atoms as well as the effect of mass difference. The effect of a mass difference alone is quite small in both the low temperature and high temperature regions. A determination of the Mössbauer peak position as a function of temperature in the high temperature range can be used to obtain a value of isomeric shift fully correct for the second order Doppler shift associated with the vibration of the atoms. In addition, if the experimental data are sufficiently precise, the effective stiffness with which the atoms are bound in the lattice may be determined. The calculation is illustrated with experimental data for Fe⁵⁷ dissolved in beryllium and in stainless steel.

INTRODUCTION

THE energies of the various gamma rays associated with the Mössbauer transitions in nuclei vary with the environment of the active atoms as a result of several types of interactions. These interactions fall into two classes: those which remove the m degeneracy of the nuclear levels, and those that change the mean separation between the excited and ground states. In the first class are those due to magnetic fields, which interact with the nuclear magnetic dipole moment, and to electric field gradients, which interact with the nuclear electric quadrupole moment. These effects have been treated at length elsewhere and will not be discussed here.^{1,2} In the second class are the isomeric shift and the second order Doppler shift. The isomeric shift arises from the electrostatic interaction between the nuclear charge distribution and the electronic charge density at

the nucleus. Since the nucleus charge distribution is different in the ground and excited states, this interaction changes the separation of the levels by an amount proportional to the effective electronic charge at the nucleus, which varies with the environment of the atom. The second order Doppler shift is a relativistic effect associated with the mass difference between ground and excited states, and the corresponding difference in kinetic energy. This paper is largely concerned with this latter shift, and the separation of it from the isomeric shift.

ISOMERIC SHIFT

The isomeric shift of the energy levels in either source or absorber nuclei is given approximately by³

$$\Delta E = \frac{2}{5}\pi ze^2\Delta\bar{R}^2|\psi(0)|^2,$$

where z is the atomic number, $\Delta\bar{R}^2$ is the change in

¹ S. S. Hanna, J. Heberle, C. Littlejohn, C. J. Perlow, R. S. Preston, and P. H. Vincent, Phys. Rev. Letters **4**, 177 (1960).

² O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

³ L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).