

From this the following conclusions may be drawn:

(1) By calculating the zero-point energies and motions of these modes as in reference 3, the next higher-order corrections to the B.C.S. theory could be obtained. We justify this theory in that we show that these reasonably large corrections do not change the excitation spectrum in essentials.

(2) Collective and plasma effects indeed reinforce the B.C.S. theory in the way predicted in reference 1, even though the exact matrix elements in B.C.S. are incorrect because of the neglect of collective effects.

I am indebted to H. Suhl for help with some of the calculations and for many conversations. A more complete description of the method will be published later.

¹ P. W. Anderson, Phys. Rev. **110**, 985 (1958), this issue.

² Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957). This is called B.C.S. hereafter.

³ K. Sawada, Phys. Rev. **106**, 372 (1957); Sawada, Brueckner, Fukuda, and Brout, Phys. Rev. **108**, 507 (1957); R. Brout, Phys. Rev. **108**, 515 (1957).

⁴ This is related to a method used by D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953), Appendix II.

⁵ M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

⁶ N. N. Bogoliubov, J. Exptl. Theoret. Phys. U.S.S.R. (to be published). Similar relations were also derived by J. G. Valatin (private communication via J. Bardeen).

⁷ By Feynman's argument [see reference 1; also Phys. Rev. **94**, 262 (1954)], this implies that zero-point motions greatly reduce the long-range correlation in the Bardeen theory.

Sign of the Cubic Field Splitting for Mn^{++} in ZnS

G. D. WATKINS

General Electric Research Laboratory, Schenectady, New York

(Received April 1, 1958)

THE electron spin resonance of Mn^{++} in cubic ZnS has been studied by Matarrese and Kikuchi.¹ They report that in the spin Hamiltonian

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + \frac{1}{6}a(S_x^4 + S_y^4 + S_z^4) + A\mathbf{I} \cdot \mathbf{S},$$

one has $a = -8.35 \pm 0.06$ gauss and $A = +68.4 \pm 0.1$ gauss. Actually, since the measurements were made at room temperature, a change of sign for both the cubic field splitting constant a and the hyperfine interaction constant A would also produce the same spectrum. In order to distinguish between the two possibilities, it is necessary to measure the relative intensities of the transitions at low temperature.² We have made such a measurement³ at 4°K and at a frequency of 20 kMc/sec, and find that the signs reported were in error. They should be $a = +8.35 \pm 0.06$ gauss, $A = -68.4 \pm 0.1$ gauss.

This is of interest because of a recent theoretical treatment of Mn^{++} in cubic fields by Watanabe.⁴ He concludes that a should be positive regardless of the sign of D in the cubic potential $-eV = D(x^4 + y^4 + z^4 - \frac{2}{3}r^4)$.

Most measurements for manganese have been in solids where the ion is surrounded by six negative ions in approximate octahedral symmetry. In these solids D is positive, and the sign of a has been found to be positive also.⁵ In ZnS, the ion is presumed to be surrounded by a tetrahedron of four negative sulfur ions and the sign of D would therefore be negative. As a result, this system provides an important test for the theory, and the positive sign for a appears to confirm Watanabe's result. Similar agreement has been found for manganese in germanium, where the sign of a has also been determined to be positive.⁶

However, the crystalline model does not predict the correct sign of the g shift in these substantially covalent solids. Watanabe's result states that the g value should always be less than the free electron value (2.0023). The measured values are 2.0025 ± 0.0002 in ZnS¹ and 2.0061 ± 0.0002 in germanium.⁶ Positive g shifts are also indicated in powders of CdS, ZnSe, and CdTe.⁷ As a result, the agreement in the sign of a does not necessarily indicate that the crystalline field model can be successfully applied to such highly covalent solids.

¹ L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids **1**, 117 (1956).

² See, for instance, W. Low, Phys. Rev. **105**, 793 (1957).

³ The crystal used for this measurement was kindly supplied by Professor Kikuchi.

⁴ H. Watanabe, Progr. Theoret. Phys. Japan **18**, 405 (1957).

⁵ K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 342.

⁶ G. D. Watkins, Bull. Am. Phys. Soc. Ser. II, **2**, 345 (1957).

⁷ J. S. VanWieringen, *Discussians Faraday Soc.* **19**, 118 (1955).

Rate Processes and Low-Temperature Electrical Conduction in n -Type Germanium

SEYMOUR H. KOENIG

International Business Machines Watson Laboratory at
Columbia University, New York, New York

(Received March 17, 1958)

THE low-temperature electrical conduction of n -type germanium as a function of applied electric field is characterized by an ohmic region for fields less than ~ 0.2 v/cm, a region of steadily increasing conductivity, and finally a critical "breakdown" field at which the current rises "vertically" with the applied electrical field.¹ The large variation of conductivity is due mainly to an increase in carrier density as, with increasing electric field, the mean carrier energy increases from its equilibrium value. The breakdown is associated, in a general way, with ionization of neutral donors by the impact of "hot" electrons.¹ In Fig. 1, data obtained by pulse techniques are presented to illustrate the behavior at high current densities.² The essential feature to be noted is that after a significant "vertical" rise the j - E curve becomes concave downwards.

In addition to the above data, the time constant τ for response to a small change in applied voltage has been measured at various points along the j - E curve for a range of lattice temperatures. The data are shown in Fig. 2.

An understanding of the details of the data in Figs. 1 and 2 may be had by considering the balance of the kinetic processes that determine the carrier density, n ,

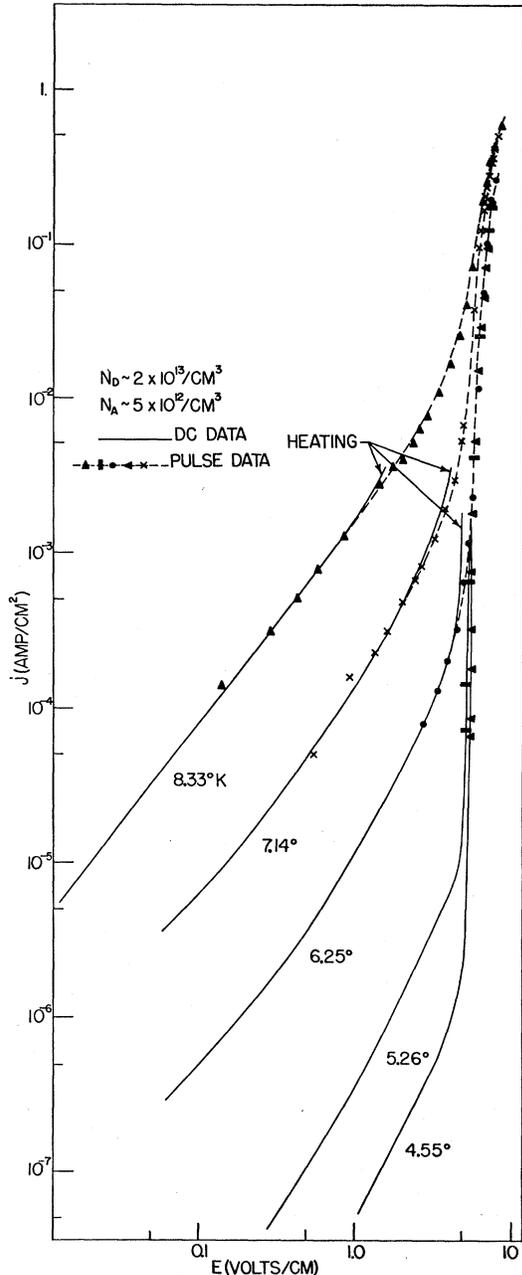


FIG. 1. Variation of current density with applied electric field for various temperatures. The points represent data obtained by using short pulses to avoid heating, whereas the solid lines indicate data obtained by dc methods.

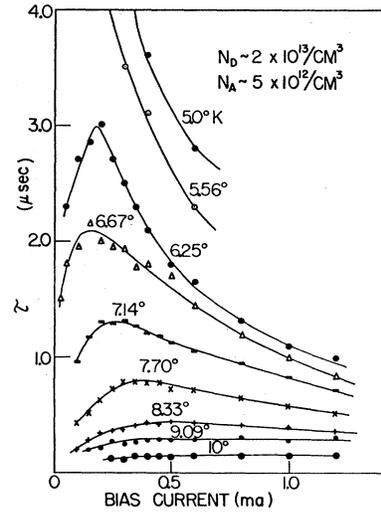


FIG. 2. Variation of τ , the time constant for response to a small step voltage, vs the dc bias current, shown for various temperatures.

at a particular electric field and lattice temperature. Thus

$$A_T(T)(N_D - N_A - n) + n\{A_I(f)(N_D - N_A - n) - B_T(f, T)(N_A + n)\} - n^2 B_I(f, T)(N_A + n) = dn/dt. \quad (1)$$

Here N_D is the donor density, N_A the acceptor density. The terms in A_T and A_I represent the rates of carrier production by thermal generation and impact ionization, respectively, and those in B_T and B_I the respective inverse processes, single-electron capture and Auger recombination. The dependence of the coefficients on the lattice temperature T and the electron distribution function f is indicated. For the steady state, n is given by the solution of Eq. (1) with the right-hand side equated to zero. In practice we have $n \ll N_A$, $N_D - N_A$. If in addition the last term on the left of Eq. (1) may be neglected, the result simplifies to

$$n = A_T(N_D - N_A) / \{B_T N_A - A_I(N_D - N_A)\}. \quad (2)$$

Until an appreciable number of electrons have energies sufficient to ionize neutral donors by impact, A_I should be small, so that at low electric fields n will vary inversely as B_T . It is known that B_T decreases with increasing electron energy,³ and therefore we conclude that n will increase with electron temperature. For larger electric fields, A_I will increase and the denominator in Eq. (2) will approach zero.⁴ In this region, even a fairly slow dependence of f , and therefore of B_T and A_I , on electric field will cause n to rise "vertically" as a function of the applied field; hence, the "breakdown." The rapid increase of n will continue until terms in n^2 in Eq. (1) become important, at which point behavior as shown in the upper part of Fig. 1 would be expected.

An expression for τ may be obtained from Eq. (1). On the assumptions stated below, the result is

$$\tau^{-1} = n(B_T + B_I N_A) + A_T(N_D - N_A)/n. \quad (3)$$

Here the term $n^3 B_I$ in Eq. (1) has been neglected, and A_I has been eliminated by using Eq. (1). Implicit in the derivation of Eq. (3) is the assumption that the distribution function follows any change in applied voltage with a time lag small compared to τ . This is expected to be a valid assumption since the distribution should change in a time on the order of several collision times, or $\sim 10^{-10}$ sec, while τ from Fig. 2 is much greater. The first term on the right-hand side of Eq. (3) arises from the coefficient of n^2 in (1). Unfortunately, from the measurements made so far, one cannot determine B_T and $B_I N_A$ separately, and thus it is not known as yet whether the term in n^2 is determined by Auger recombination or simply a bimolecular recombination process. If the coefficients in Eq. (3) vary slowly along the steep part of the current-voltage characteristic, τ reaches a maximum when

$$n^2(B_T + B_I N_A) = A_T(N_D - N_A).$$

For this condition

$$\tau_{\max} = [A_T(B_T + B_I N_A)(N_D - N_A)]^{-\frac{1}{2}}. \quad (4)$$

The only term on the right-hand side of Eq. (4) that varies rapidly with lattice temperature, and hence would explain the large temperature variation of τ_{\max} shown in Fig. 2, is the term A_T , which should vary approximately as $\exp(-\epsilon/kT)$, where ϵ is the activation energy for donors. In Fig. 3 the temperature dependence of τ_{\max} is plotted. The agreement with the slope expected from the value of ϵ for Sb donors in Ge, 0.0097 ev, is quite good. The agreement can be improved (the dashed line in Fig. 3) by taking into account, roughly, the dependence of the coefficients in Eq. (4) on low powers of the lattice temperature. On incorporating a correction for this in Fig. 3, one finds the value of ϵ

obtained from these data to be in excellent agreement with the value 0.0097 ev.

The significance of these results is that they demonstrate that the phenomenological interpretation of the low-temperature static and dynamic electrical characteristics of n -type germanium, as given essentially by Eq. (1), is correct. Breakdown must be considered in the light of the earlier discussion pertaining to Eq. (2) rather than⁵ as occurring at the electrical field for which the mean electron energy becomes equal to ϵ . For example, from Eq. (2) the breakdown field should decrease upon adding more donor impurities at constant N_A , as long as the donor density is low enough ($\lesssim 5 \times 10^{14}/\text{cm}^3$ in a typical case) so that neutral impurity scattering is not significant in determining the mobility.

I should like to acknowledge the able assistance of Mr. Walter Schillinger in designing equipment and obtaining the experimental data. In addition, I wish to thank P. J. Price for many helpful discussions and stimulating arguments.

¹ S. H. Koenig and G. R. Gunther-Mohr, J. Phys. Chem. Solids **2**, 268, (1957).

² See also Ryder, Ross, and Kleinman, Phys. Rev. **95**, 1342 (1954).

³ Reference 1, p. 280; also S. H. Koenig, Phys. Rev. **110**, 988 (1958), following Letter.

⁴ The denominator does not become zero until the value of current appropriate to τ_{\max} (to be discussed) is reached, as may be seen by combining Eqs. (1) and (4). This corresponds roughly to the end of the vertical part of the current-voltage characteristic, when terms in n^2 are important and the approximations of Eq. (2) are no longer valid.

⁵ Burstein, Picus, and Sclar, in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954* (John Wiley and Sons, New York, 1956), p. 393; E. Burstein and P. Egli, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 43.

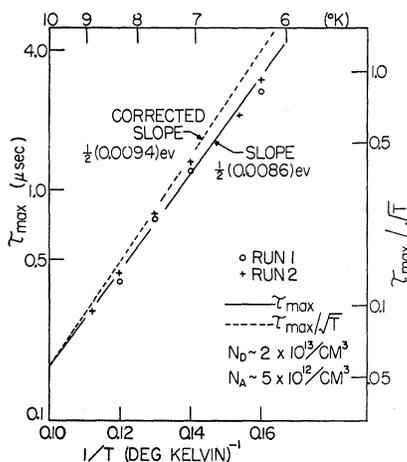


FIG. 3. The variation of τ_{\max} (solid curve and experimental points) and τ_{\max}/\sqrt{T} (dashed curve) with temperature. The considerations pertaining to Eq. (4) show that the slope of the dashed curve should correspond to an energy equal to $\frac{1}{2}$ the activation energy for Sb donors in Ge.

Recombination of Thermal Electrons in n -Type Germanium below 10°K

SEYMOUR H. KOENIG

*International Business Machines Watson Laboratory at
Columbia University, New York, New York*

(Received March 17, 1958)

THE magnitude of the thermal recombination coefficient¹ B_T has been determined for thermal electrons in n -type germanium as a function of lattice temperature in the range 4–10°K. Preliminary results are shown in Fig. 1. Also shown are the smoothed data expressed in terms of a cross section obtained by dividing B_T by a velocity $v = (3m^*kT)^{\frac{1}{2}}$, with m^* , the effective mass, taken as $\frac{1}{4}$ of the free electron mass. The magnitude, $\sim 10^{-12}$ cm² at 4.2°K, of the effective cross section so obtained is several times the geometrical cross section for a donor ground state in germanium.

The experimental details are discussed below to indicate the manner in which measurements of B_T for