

Magnetism of Interacting Donors

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The magnetic susceptibility of donor centers in semiconductors is calculated for the case of small interactions between closely adjacent donors. A hydrogenic model is assumed for the donor centers. The random distribution of the centers, as well as the variation of the energy of interaction with separation distance of pairs of donors, is taken into consideration. A twofold modification to the Curie law (which is correct for independent donors) is predicted by the resulting expression, namely, a curvature as well as a decrease of the slope of the Curie plot of the susceptibility versus inverse temperature. Both of these effects increase with the donor density, becoming appreciable in silicon with 10^{17} – 10^{18} donors/cm³ and in germanium in the range around 10^{16} donors/cm³. The theory is in good agreement with results of measurements.

I. INTRODUCTION

THE magnetic behavior of semiconductors at low temperature is very strongly dependent upon the degree of doping. In highly doped material, after merging of the conduction band and impurity levels has occurred, the magnetism of the impurity centers is completely overwhelmed by the band magnetism of the merged band. This has been observed in heavily doped germanium,¹ where for donor densities greater than 10^{18} cm⁻³ the conduction band diamagnetism sufficed to explain the data. The other extreme case, that of such low doping density that the overlap between donor centers was negligible, has also been observed, in this case in silicon² with less than 2×10^{17} cm⁻³ donor. Here the contribution of the conduction band is absent below 50°K because all of the conduction electrons are frozen out on donor centers. The magnetism of these centers is well represented by a Curie law and is proportional to the number of donors. Both of these extreme situations are reasonably simple, and agreement between theory and experiment seems to obtain. However, when the amount of doping is between these extremes, a more complicated behavior is observed. We shall be concerned here with the magnetic behavior when the doping becomes somewhat greater than in the simple isolated donor extreme case. The experimental facts which have clearly been observed in the case of silicon² are that the slope of the Curie curve of susceptibility versus inverse temperature decreases as the temperature is lowered and that, even at higher temperatures, as the donor density is increased above about 2×10^{17} cm⁻³, the slope deviates more and more from that expected for independent donor centers. In germanium there seems to be an indication of a similar behavior¹; however, it occurs in appreciably purer samples (5×10^{16} cm⁻³). Because of limitations on the sensitivity of the measurements, no systematic data on impurity contribution have been obtained for germanium.

Theoretically, there are two obvious approaches to the treatment of this intermediate situation. One is to start from ideas related to impurity banding and to apply these to the magnetic properties. Such a calculation has been made by Mooser.³ There seem to be two problems in this type of approach. The first is that a band resulting from a "random lattice" has not yet been satisfactorily treated in a theoretical sense and that, therefore, the impurity band is usually approximated by one for a direct lattice of appropriately large lattice spacing. The second is that the one-electron picture neglects the electrostatic repulsion between electrons, which becomes appreciable as the band gets narrower, becoming so great in the limit of weakly overlapping atomic orbitals as to reduce effectively the number of states in the band by a factor of two. (A completely banded donor band has states for $2N_d$ electrons, while for the separated donors there are available one-electron states for only N_d electrons.) The other approach to the treatment of weakly interacting donors, which is the one we shall use, starts from the independent donors and permits weak interactions of only two at a time. This approach was suggested independently by Hedgcock⁴ and by Sonder and Stevens² to explain the experimental results for germanium and silicon, respectively. Hedgcock has made an estimate of the effect by dividing the donors into two groups, those which are independent and therefore magnetically active and those which are paired as diatomic molecules and are consequently nonmagnetic. He has used the hydrogen molecule equilibrium distance, corrected, of course, for the dielectric constant of the semiconductor and the effective mass of the donor electrons, as the distance which determines whether a given pair of donors is to be considered a molecule or a pair of independent atoms. The correct order of magnitude for the effect was obtained from this simple model, making it seem worthwhile to calculate the consequences of interactions of donors in pairs more carefully, taking into consideration the variation of electron binding energy with

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¹ R. Bowers, Phys. Rev. **108**, 683 (1957).

² E. Sonder and D. K. Stevens, Phys. Rev. **110**, 1027 (1958).

³ E. Mooser, Phys. Rev. **100**, 1589 (1955).

⁴ F. T. Hedgcock, Can. J. Phys. **37**, 381 (1959).

distance between donors as well as the change with temperature in the ratio of bound-to-unbound pairs of electrons.

II. THE HYDROGENIC MODEL FOR THE DONOR CENTER

The problem of equilibrium energy levels of a particle in an inverse square force field (the hydrogen atom) has been solved exactly both semiclassically⁵ and quantum mechanically.⁶ Using these solutions, it is quite simple to compare the expressions for the energy levels, as well as the mean radii of the wave functions (Bohr orbits in the semiclassical treatment) for particles of unit electronic charge but different masses moving in a media with different dielectric constants. The following expressions result:

$$\frac{E_1}{E_2} = \frac{m_1/K_1^2}{m_2/K_2^2}, \quad (1-a)$$

$$\frac{\bar{r}_1}{\bar{r}_2} = \frac{K_1/m_1}{K_2/m_2}, \quad (1-b)$$

where the subscripts 1 and 2 refer to two particles, respectively, of mass m_1 and m_2 in media of dielectric constant K_1 and K_2 . \bar{r} refers to the mean radius, while E refers to the energy of a given state of the system. In the hydrogenic model of the donor center in a semiconductor, this type of comparison is made between the donor (electron mass, m^* , in a medium of dielectric constant, K) and the hydrogen atom (electron mass, m , in vacuum). The assumptions that are implicit in this derivation should be kept in mind, however. A semiconductor is not really a continuous medium; neither is the concept of a dielectric constant perfectly valid in a region containing only a few hundred atoms. If these assumptions are accepted, however, then the model can be used to treat the interactions of two centers. Solutions for the energies and separation distances of the lowest-lying eigenstates of a hydrogen molecule or molecule ion have been calculated⁷⁻¹¹ or deduced from spectroscopic data.¹² These, in conjunction with Eqs. (1), will yield the energies of the magnetic and nonmagnetic states of donor pairs as a function of their separation

⁵ See, for instance, G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944), p. 15 ff.

⁶ See, for instance, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 80 ff.

⁷ E. Teller, *Z. Physik* **61**, 458 (1930).

⁸ H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).

⁹ H. M. James, A. S. Coolidge, and R. D. Present, *J. Chem. Phys.* **4**, 187 (1936).

¹⁰ J. C. Slater, Technical Report No. 3, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, 1953 (unpublished).

¹¹ O. W. Richardson, *Proc. Roy. Soc. (London)* **152**, 503 (1935); *Molecular Hydrogen and its Spectrum* (Yale University Press, New Haven, 1934).

¹² R. Rydberg, dissertation, Stockholm, 1934 (unpublished); reproduced by G. Herzberg, *Molecular Spectra and Molecular Structure. I. Diatomic Molecules* (Prentice-Hall, Inc., Englewood Cliffs, 1939).

distance. This information will then make it possible to obtain the magnetic susceptibility as a function of donor density and temperature.

III. THE MAGNETIC SUSCEPTIBILITY OF TWO-DONOR MOLECULES

The magnetization, M (magnetic moment per unit volume), may be defined in terms of the partition sum, Z , of a system by the expression

$$M = kT(d \ln Z/dH), \quad (2)$$

where H is the magnetic field strength, k is the Boltzmann constant, and T is the absolute temperature. The system which we shall consider will consist of unit volume of the crystal containing $N_d/2$ two-donor systems, in which we shall assume that all electrons are frozen out of the conduction band. The grand partition sum in the presence of a magnetic field will then contain only terms for zero-, one-, and two-electron states of the two-donor centers, giving

$$Z = \prod_{i=1}^{N_d/2} Z^i = \prod_{i=1}^{N_d/2} [e^0 + \sum_j e^{\eta - \epsilon_j} (e^{\beta H/kT} + e^{-\beta H/kT}) + \sum_k e^{2\eta - \epsilon_k} (e^{2\beta H/kT} + 1 + e^{-2\beta H/kT}) + \sum_{k'} e^{2\eta - \epsilon_{k'}}]. \quad (3)$$

Here ϵ and η are the energy of a given eigenstate and the Fermi energy, respectively, both in units of kT , and β is the Bohr magneton. The sum over j refers to a sum over all one-electron states of a single two-donor center, while the sums over k and k' refer to sums over triplet and singlet two-electron states of one molecule, respectively. The two lowest one-electron molecule ion orbitals ($1s\sigma$ and $2p\sigma$) suffice to describe atom and bare donor, and the lowest singlet and triplet two-electron states ($^1\Sigma_g$ and $^3\Sigma_u$) suffice to describe all neutral atoms in the ground state. All other excited states are much higher in energy¹³ for the conditions which we are considering. Our two-donor grand-partition function can thus be approximated by a sum of five terms.

It should be pointed out here that the terms Z_i within the product in Eq. (3) are not all the same since the electronic energies $E = kT\epsilon$ differ for different separation distances of the molecules. However, the partial potential of the electrons (Fermi energy) $\mu = kT\eta$ is a constant throughout the whole sample and is determined by the number of electrons present, which is, of course, equal to the donor concentration N_d . The relation between this number and the Fermi energy is given by

$$N_d = kT(d \ln Z/d\mu) = (d \ln Z/d\eta). \quad (4)$$

Performing the differentiation indicated in Eqs. (2) and (4) and expanding terms of the form $\exp(\beta H/kT)$

¹³ The lowest excited singlet two-electron state, for instance, is the $^1\Sigma_u$ which in hydrogen is more than 11 eV above the ground state. (See diagram by G. Herzberg, reference 12, p. 340.) This would correspond to about 0.03 to 0.04 eV in silicon or a temperature above room temperature.

to first order in $\beta H/kT^{1/4}$ yields for N_d and M the following expressions:

$$N_d = \sum_i (N_d)_i = \sum_i \frac{2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 6e^{2\eta-\epsilon_3} + 2e^{2\eta-\epsilon_1}}{1 + 2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 3e^{2\eta-\epsilon_3} + e^{2\eta-\epsilon_1}}, \quad (5)$$

$$M = \frac{\beta^2 H}{kT} \sum_i \frac{2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 8e^{2\eta-\epsilon_3}}{1 + 2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 3e^{2\eta-\epsilon_3} + e^{2\eta-\epsilon_1}}, \quad (6)$$

where ϵ_s and ϵ_p are the energies of the one-electron states and ϵ_1 and ϵ_3 are the energies of the singlet and triplet two-electron states, respectively, all in units of kT . If it is noted that the denominators in Eqs. (5) and (6) are identical, these expressions can be combined as follows:

$$M = \frac{\beta^2 H}{kT} \sum_i \left((N_d)_i \frac{2(e^{2\eta-\epsilon_1} - e^{2\eta-\epsilon_3})}{1 + 2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 3e^{2\eta-\epsilon_3} + e^{2\eta-\epsilon_1}} \right). \quad (7)$$

Equation (7) can be simplified by defining the energy difference $\epsilon_{31} = \epsilon_3 - \epsilon_1$ and assuming that the compensation, if it exists at all, is not of very great magnitude (e.g., is less than 25%), permitting the neglect of zero- and one-electron states.¹⁵ The resultant expression for the magnetic moment is

$$M = \frac{\beta^2 H}{kT} \sum_{i=1}^{N_d/2} \left((N_d)_i \frac{2(1 - e^{-\epsilon_{31}})}{1 + 3e^{-\epsilon_{31}}} \right). \quad (8)$$

The first term in this sum is, of course, simply the total number of electrons.

IV. DISTRIBUTION OF SEPARATION DISTANCES FOR TWO-DONOR SYSTEMS

The sum in Eq. (8) may be converted to an integral, since $N_d/2$ is a very large number. However, it must be recalled that the triplet-singlet splitting energy, ϵ_{31} , may be a strong function of the donor-pair separation so that, if our integral is to be over the separation distance, r , a weighting function, or probability of finding a donor pair with a given separation distance, must be determined. This we shall now do.

If the donors are distributed at random, then we can fasten our attention on one donor and determine the probability that there is *no* nearest neighbor closer than r and also *one* neighbor in the spherical shell volume

¹⁴ The assumption $\beta H \ll kT$ is good above 3°K, since for the magnetic fields usually used in susceptibility measurements $H \lesssim 20$ koe or $\beta H/k \lesssim 0.4$.

¹⁵ In *n*-type silicon, for instance, at temperatures in the neighborhood of 10°K the Fermi level is ~ 0.025 eV below the conduction band edge, while the energies of the one- and two-electron states of a pair of donors of intermediate separation are -0.06 and -0.10 eV, respectively. The exponents $\eta - \epsilon_s$ and $2\eta - \epsilon_1$ at this temperature are accordingly 41 and 58, respectively.

element $4\pi r^2 \Delta r$ at r . This will give the probability of finding a nearest neighbor in Δr at r . We use the Poisson distribution, which gives the probability $P(N)$, of exactly N events in terms of the expectation value, $G: P(N) = (N!)^{-1} G^N \exp(-G)$. The expected number of donors in a volume V is $N_d V$, where N_d is the donor density. This gives for the probability of no neighbors closer than radius r , $P(0,0:r) = \exp[-(4\pi/3)N_d r^3]$, and for the probability of finding one neighbor in a shell of thickness Δr at r ,

$$P(1,r:r+\Delta r) = N_d 4\pi r^2 \Delta r \exp[-(N_d 4\pi r^2 \Delta r)].$$

The product of these two probabilities will yield the expression applicable for our case, which for infinitesimal Δr is given by

$$dP = 4\pi N_d r^2 dr \exp[-(4/3)\pi N_d r^3]. \quad (9)$$

The relative probability dP/dr of finding the nearest neighbor at r is graphed in Fig. 1.

The remainder of this section will be devoted to a discussion of the validity of the assumptions made concerning the above distribution function; the reader may wish to go directly to Sec. V, where an approximate expression for the magnetic moment is obtained.

Equation (9) is strictly correct only for the donors which make up the first pair. It would be correct for all pairs if already-paired donors were still available for further pairing. This is obviously not the case. However, let us point out that we are here interested in the situation where only a fairly small fraction of donors are close enough to be considered effectively paired (i.e., such that some of the magnetism is removed). The fraction of groups of three in such cases will be even smaller. Moreover, if we pick our pairs in such a way as to remove from consideration first the pairs of closest spacing, then by the time deviations between Eq. (9) and the actual distribution of distances becomes significant, we will be dealing with pairs that

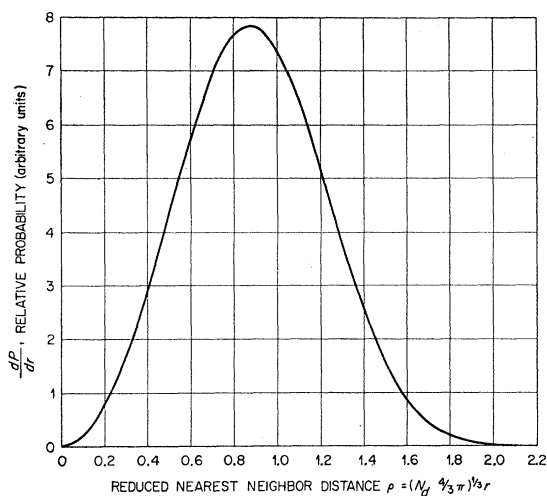


FIG. 1. Relative probability, dP/dr , of finding the nearest neighbor of a given donor at a distance r from it.

have such large separation that their contribution to the magnetic moment is exactly what it would be if the donors were unpaired and is thus independent of the separation distance.

In order to make a more quantitative estimate of the error resulting from use of Eq. (9), we can define a separation distance, beyond which pairs will act like independent donors by such criterion as $E_{31}=2kT$. Then let all the $N_d(N_d-1)/2$ inter-donor distances be listed in order of increasing magnitude, and use them in this order to fill in the low separation tail of the distribution given by Eq. (9). Eventually one of the members of the pair currently being chosen will be found to have been paired with another donor previously. An estimate of the possibility for this event is given by the probability that the neighbor at distance r is a *next* nearest neighbor, i.e., that there exists *one* atom within the sphere of radius r and, also, one in the vicinity of the surface. This probability is given by

$$dP' = (4/3)\pi N_d r^3 4\pi N_d r^2 dr \exp[-(4/3)\pi N_d r^3]. \quad (10)$$

The over-all probability for this should be doubled because either of the atoms of the pair we are currently picking might have been chosen previously; the probability that both have been selected previously is neglected. Summing over all of the pairs as we pick them, starting from the first, will give an estimate of the total number which have been discarded due to prior pairing. This total number discarded is given by

$$D = 2 \int dP' = 2 \int_0^{V'} N_d V \exp(-N_d V) N_d dV, \quad (11)$$

where $V = (4/3)\pi r^3$ is the volume. For small V , which is now the range of interest, $D \approx (N_d V)^2$. Comparing this with the total number of pairs which have already been picked,

$$\# = \int dP = \int_0^{V'} \exp(-N_d V) N_d dV \approx N_d V \quad (12)$$

we find for the ratio $D/\# = N_d V$. This shows that the relative number of discards to the number of pairs picked is, for $V < 1/N_d$, $\approx N_d V$ or $N_d(4/3)\pi r^3$. Therefore, if the criterion $E_{31} = 2kT$ is satisfied when r is approximately $\frac{1}{3}$ of the maximum of the distribution given by Eq. (9), as is the case here, then the error resulting from the use of Eq. (9) will be only a few per cent.

It might be pointed out from the foregoing discussion that, when r approaches r_{\max} too closely, the number of rejects becomes appreciable and the present calculation may overestimate the effect of pairing by a factor of two. This is also evident from a qualitative consideration of the pairing process.

The assumption of a statistically random distribution of donor centers is, strictly speaking, not exact because there is an energy of interaction between every pair of

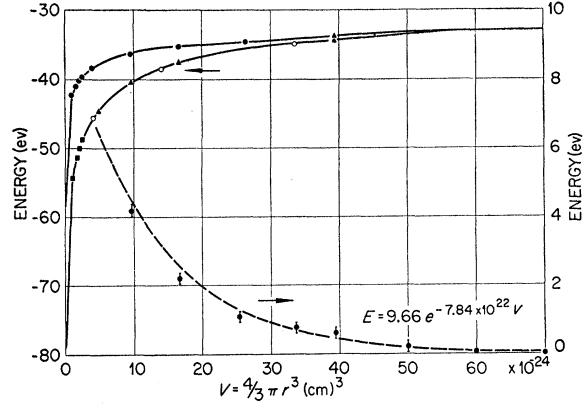


FIG. 2. Energies of the singlet and triplet ground states of the hydrogen molecule with fixed atoms and the energy difference between the two states as a function of atom separation. The points on the two upper curves were obtained from the literature as follows: ● James, Coolidge, and Present, reference 9; ■ James and Coolidge, reference 8; ▲ Slater, reference 10; ○ Herzberg, reference 12. The points on the difference curve were obtained from the difference between the singlet and triplet curves, while the dashed line is of the functional form shown.

donors. This energy rises sharply for small internuclear distances for the same reason that the hydrogen molecule and hydrogen molecule ion have high energies in the corresponding case of small internuclear distances. If the energy of electrostatic interaction e^2/Kr ¹⁶ of the two donor ions be equated to a multiple of kT_m , say $2kT_m$, and the volume corresponding to this radius be excluded from consideration, the effect on the final results is slight (less than 1%) for the conditions of validity of this theoretical analysis. Such an effect will be neglected in the following.

V. EVALUATION OF THE MAGNETIC MOMENT

From Eq. (8) we get for the magnetic moment of the crystal, using Eq. (9) and the appropriate normalization to a total of $N_d/2$ two-donor systems,

$$M = \frac{\beta^2 H}{kT} \int \frac{N_d}{2} \left(2 - \frac{2[1 - \exp(-\epsilon_{31})]}{1 + 3 \exp(-\epsilon_{31})} \right) \times \exp(-VN_d) N_d dV, \quad (13)$$

where $V = (4/3)\pi r^3$. If it is recalled that the magnetic moment for isolated donors is $\beta^2 H N_d / kT$, then it is evident that the value given by Eq. (13) is that for isolated donors multiplied by the correction factor $(1-I)$, where

$$I = \int \frac{1 - \exp(-\epsilon_{31})}{1 + 3 \exp(-\epsilon_{31})} \exp(-VN_d) N_d dV. \quad (14)$$

This latter expression, of course, has the correct

¹⁶ Actually, the ions are screened by the conduction electrons with a Debye length of $\lambda_D = (4\pi N_d e^2 / KkT)^{-1/2}$. However, near the melting point $\lambda_D \approx 100$ Å, which is much larger than the pertinent distances here (~ 5 Å).

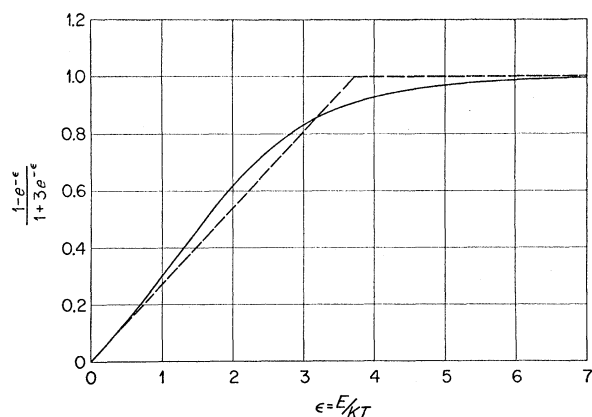


FIG. 3. The function $[1 - \exp(-\epsilon)]/[1 + 3 \exp(-\epsilon)]$ vs ϵ and the approximation to it (dashed curve) used.

asymptotic behavior, vanishing for small ϵ_{31} and causing the paramagnetism to disappear for large ϵ_{31} .

In order to evaluate the correction I , it is necessary to know how E_{31} varies with separation distance. This can be obtained from calculations on the hydrogen molecule. Figure 2 shows the variation with internuclear distance of the energies of the singlet and triplet states of a hydrogen molecule, as well as the difference $E_3 - E_1 = (E_{31})_H$. The points shown on the difference curve of Fig. 2 are obtained from the calculated values of E_3 and E_1 shown, while the dotted curve shows the approximation to be used later, $(E_{31})_H = A_H \times \exp(-B_H V)^{17}$ where $A_H = 9.66$ ev and $B_H = 7.84 \times 10^{22}$ cm $^{-3}$. The hydrogenic expression must be scaled for dielectric constant and effective mass, giving $E_{31} = (m^*/K^2)(E_{31})_H = (m^*/K^2)A_H \exp[-B_H(m^*/K)^3 V]$ where the effective mass, m^* , and dielectric constant K have been left in the equation explicitly as parameters. In Fig. 3 is shown the function $f(\epsilon) = [1 - \exp(-\epsilon)]/[1 + 3 \exp(-\epsilon)]$. As can be seen from the figure, the broken line is a reasonably good approximation ($\sim 10\%$) and will be used in the integration of Eq. (14). (The explicit form is $f(\epsilon) = \epsilon/3.7$ for $0 < \epsilon < 3.7$ and $f(\epsilon) = 1$ for $\epsilon > 3.7$.) These approximations lead finally to the following simple expression for the correction factor:

$$1 - I = \frac{(3.7kT/m^*A)^\alpha}{1 + N_d/B(m^*)^3}, \quad (15)$$

where $\alpha = N_d/B(m^*)^3$, $A = A_H/K^2 (= 0.068$ ev for silicon), and $B = B_H/K^3 (= 4.65 \times 10^{19}$ cm $^{-3}$ for silicon). These expressions give finally for the magnetic suscepti-

¹⁷ A Heitler-London calculation [See, e.g., L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 340 ff.] gives for the splitting $E_{31} = f(r) \exp(-2r)$, where $f(r)$ is a moderately complicated function. However, as Fig. 2 shows, the fit of $A \exp(-BV)$ is quite satisfactory in the range of greatest importance. The use of this latter function makes it possible to perform certain integrations which occur later.

bility per gram, $\chi = M/\rho H$.

$$\chi = C/T^{1-\alpha} \quad (16-a)$$

where

$$C = \frac{N_d \beta^2}{\rho k} (3.7k/m^*A)^\alpha \left(1 + \frac{N_d}{Bm^*3}\right)^{-1}. \quad (16-b)$$

VI. DISCUSSION AND COMPARISON WITH EXPERIMENT

A. Silicon

It is found experimentally² that the plot of χ vs $1/T$ is curved and has a smaller slope than $N_d \beta^2/\rho k$. These two effects are both predicted by Eqs. (16). The power of the inverse T dependence is diminished by the term N_d/Bm^*3 , and the constant C , which for no interactions

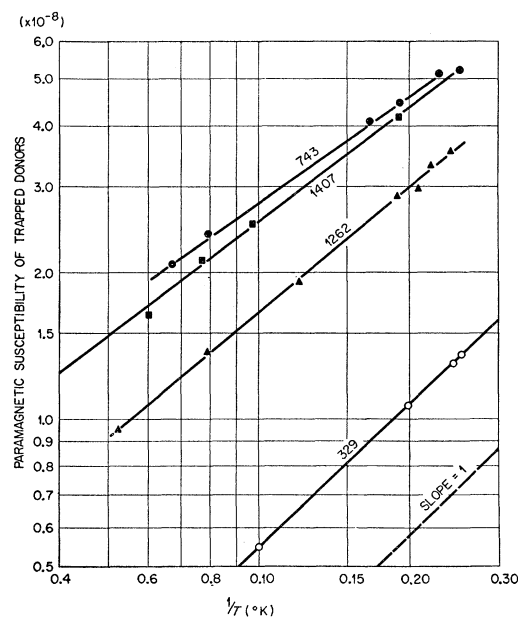


FIG. 4. The paramagnetic susceptibility of donors vs reciprocal temperature plotted on log-log paper. The data are obtained from reference 2. ● Specimen 743 (5×10^{18}); ■ Specimen 1407 ($12-20 \times 10^{17}$); ▲ Specimen 1262 ($6-10 \times 10^{17}$); ○ Specimen 329 (2.4×10^{17}).

is simply $N_d \beta^2/\rho k$, is diminished by two factors, both increasing with N_d . Figures 4 and 5 show an attempt to fit the temperature dependence of the derived expression to the experimental data reported for silicon.² The data of Fig. 5, reference 2, have been replotted in log-log form, so that the slope of the resulting curve is $1 - N_d/Bm^*3$. The factor N_d/Bm^*3 thus obtained has then been compared with N_d reported from Hall measurements. It should be pointed out that there is a rather large uncertainty in the values of N_d obtained from Hall measurements, depending upon the assumptions which are made concerning the mode of electron scattering and degree of degeneracy of the sample.¹⁸

¹⁸ To obtain the donor density, N_d , from the Hall coefficient, R , the equation $N_d = (\mu_H/\mu)/\text{Rec}$ is used. (μ_H/μ) is the ratio of Hall

In Fig. 5 the values of N_d determined on the basis of assuming phonon scattering (circles) and impurity scattering (squares) have been plotted versus the factor N_d/Bm^{*3} obtained from the slopes of the curves of Fig. 4. A straight line connecting the points should be proportional to $1/Bm^{*3}$. If the model is good, m^* should be the effective mass of an electron frozen on an arsenic donor in silicon. Lines for $m^*=0.51$, 0.53, and 0.55 have been drawn on Fig. 5. The m^* calculated from the donor activation energy¹⁹ and Eq. (1a) is 0.513. As can be seen, the agreement is fairly good for samples having less than 10^{18} cm⁻³ donor. The deviation in a sample having 5×10^{18} cm⁻³ donors is quite large, but in this range the assumptions which entered this theory are not satisfied. {It might be pointed out that in the sample with 10^{18} cm⁻³ donors the maximum of the distribution of distances [Eq. (9)] occurs for such interatomic distances that the splitting energy is

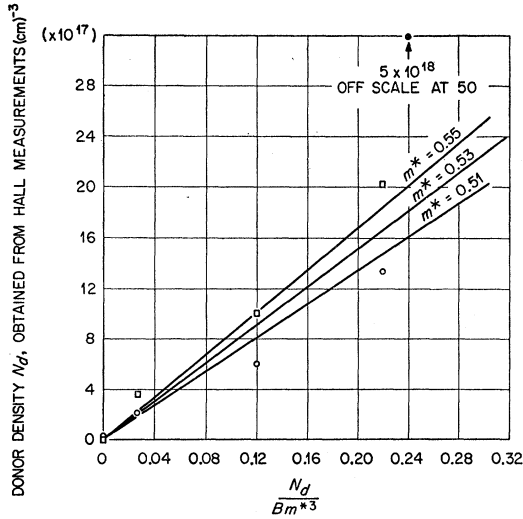


FIG. 5. The donor density, N_d plotted vs N_d/Bm^{*3} . The points are from the experimental data shown in Fig. 4, while the straight lines are predicted by the theory for different values of the effective mass of electrons in donor states.

0.0007 eV, which, together with the criterion $E=2kT$, gives a temperature of about 4°K, below which this theory would tend to break down.}

B. Germanium

In germanium the effective mass is much smaller than in silicon, and the donor levels are much closer to the conduction band. Moreover, the dielectric

to conductivity mobility, equal to $3\pi/8$ for spherical energy bands and phonon scattering. For the more complicated conduction band of silicon and for an admixture of thermal and impurity scattering, the ratio may vary between 0.8 and 1.9. See reference 2 and references 28 and 29 therein for a fuller discussion.

¹⁹ Morin, Maita, Shulman, and Hannay, Phys. Rev. **96**, 833 (1954).

TABLE I. Comparison of constants used in the expression of the magnetic susceptibility.

	H ₂	Si	Ge
Ionization energy, E (eV)	13.6	0.049	0.012
Dielectric constant	1	11.9	16
Effective mass (electron masses)	1	0.51	0.23
m^*A_H/K^2 (eV)	9.66	0.0348	0.0087
$(m^*)^3B_H/K^3$ (cm ⁻³)	7.84×10^{22}	6.17×10^{18}	2.33×10^{17}

constant is greater; and so the donors interact at larger distances. In Table I is shown a comparison of the constants m^*A_H/K^2 and $(m^*)^3B_H/K^3$ for silicon and germanium. Since it is the ratio of N_d to the second of these which determines the deviation from a linear dependence on $1/T$, it is evident that the situation in germanium corresponding to that which we have discussed in silicon arises in samples which are purer by a factor of 25. This means that the present discussion applies to germanium only when the concentration of impurities is less than about 5×10^{16} cm⁻³ donor. It is in just such a specimen (5.5×10^{16} cm⁻³) that Bowers¹ has observed a slight paramagnetism at low temperature, with a slope less than one would expect for non-interacting donors. There actually seems to be a slight curvature in the data presented by Bowers,¹ which also is in qualitative agreement with the foregoing.

SUMMARY

The magnetic susceptibility of donor centers distributed at random in a semiconductor has been calculated for the case in which interactions between pairs of donors is small but not negligible. A hydrogenic model was assumed for the donor center; the energy difference of singlet and triplet donor-molecule states was scaled from corresponding values for the hydrogen molecule. The difference, or splitting energy, was approximated by a mathematical expression which permitted the evaluation of certain integrals. Only the singlet and triplet ground states were retained in the partition sum, which included terms for a range of values of internuclear distances. Summing over the distance between donors and differentiation of the partition sum gave the final expression for the susceptibility.

Even though there are no adjustable parameters in the theory, agreement with experiment seems fairly good in the case of silicon. The theory predicts an onset of pairing in germanium at a value which is also in qualitative agreement with experiment.

One of the results of this calculation is to raise some questions about the procedure of using the temperature-limiting slope of the Curie plot to obtain the donor density of the specimen. A sizeable correction factor, of the order of 10 to 50%, seems to be required even when no large curvature is apparent in the data.