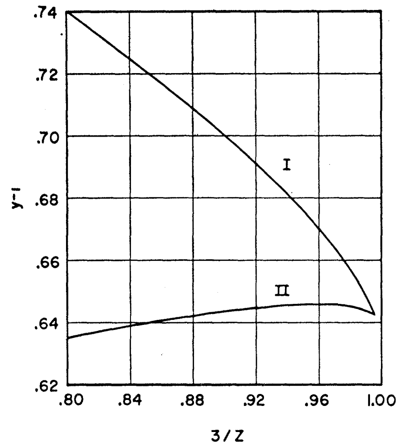

FIG. 8. The relationship between temperature and the parameter $3/Z$ for the cubic Ising lattice. The curve shows the anomalous region of Fig. 4 in greater detail.

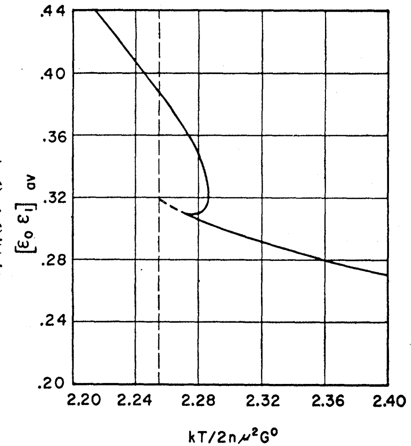

FIG. 9. The energy per dipole of the cubic Ising lattice. This curve shows the anomalous region of Fig. 6 in greater detail.

achieved at a lower temperature. It is now only necessary that the effect be most pronounced for lower values of the order parameter and the sort of reversal obtained in Figs. 5 and 6 is readily explained.

If the results for energy and magnetization as functions of temperature were taken literally, we would have a first-order phase transition. The situation is analogous to the usual treatment of a van der Waals gas, in which a multivalued function [the $V(p)$ relationship] is replaced using arguments of minimum Gibbs free energy by a $P-V$ diagram with a straight-line portion, because of the instability of the multivalued part.

However, it is well known that the most difficult task of a fundamental statistical mechanics calculation is the reproduction of the behavior of a system in the immediate vicinity of a transition. We believe, therefore, that the correct solution is a second-order phase transition and that our solution departs in only a minor way, over a very small region, from the behavior expected for a second-order transition. In particular, we believe that the correct analytic behavior near the phase transition is described by the hyperelliptic function $K(3/Z)$ near its singular point $3/Z=1$. Our approximate methods, however, have located the transition instead at $3/Z=0.995$, and hence we do not obtain the precisely correct analytic behavior near the transition temperature.

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Magnetic Properties of N-Type Silicon

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The magnetic susceptibility of n-type silicon samples with a wide range of donor concentrations (3×10^{16} to 3×10^{19} atoms/cm^3) has been measured as a function of temperature from 3°K to 300°K. By utilizing conduction-electron concentrations obtained from Hall coefficient measurements on comparison specimens over the range from 50°K to 400°K, the contributions to the susceptibility arising from the conduction electrons and electrons trapped on donor atoms have been analyzed. In the upper range of temperature the diamagnetic contribution of conduction electrons is dominant and is consistent with the model of six energy minima in the conduction band. However, comparison of the squared reciprocal mass ratio with that obtained from cyclotron-resonance experiments reveals that the former is appreciably smaller than the latter ($\sim$8 as compared to $\sim$13). As the temperature is lowered, the conduction-electron contribution becomes successively less as electrons are frozen out on donor atoms. The trapping of electrons by donors at low temperatures leads to a Curie-law paramagnetism in the specimens of higher purity, whereas in the more impure samples, deviations from Curie's law occur which are attributed to interactions between closely spaced donor centers.

I. INTRODUCTION

DETERMINATION of magnetic properties has been found to be of great value in the study of the electronic structure of semiconductors. This is in part because analysis of the magnetic susceptibility is not beset by the many difficulties inherent in interpreting electrical properties. One example is the requirement of a detailed knowledge of charge scattering.

Depending upon the design of the specific experiment

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† Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

and the choice of material, information can be obtained about a number of aspects of the band structure as well as about the configuration of various trapping levels. Most of the work to date has been concerned with band properties. Busch and Mooser,[1] who were the first to employ magnetic techniques in semiconductor investigations, obtained the width of the forbidden gap, effective masses, and some impurity ionization energies in gray tin. Similar data have been obtained for indium antimonide[2] and germanium,[3–7] the analysis having been carried further in the latter case.[3] In none of these, however, was it possible to analyze the magnetism stemming from un-ionized acceptors or donors. Silicon, with its somewhat larger impurity ionization energies, is more favorable for observing the contribution of filled donor or acceptor centers to the susceptibility.

The present experiment was designed to obtain information about the conduction band analogous to that obtained in the work cited above[3] and, in addition, to investigate the magnetic behavior of donor levels at low temperatures. It was expected that at low temperatures, interactions between donors would become apparent at higher concentractions, and that this might be of some help in understanding some of the anomalies[8–11] in the electrical properties that are usually referred to as "impurity banding."

II. BACKGROUND AND THEORY

Semiconductors, in contrast to metals, can be prepared with a large range of current carriers, both electrons and holes. Moreover, the current-carrier density is strongly temperature-dependent in a predictable and measurable way. As a result, it is possible in most cases to separate the magnetic susceptibility originating from various sources and to obtain the separate components from experimental data. For our purposes it will be sufficient to consider the total susceptibility χ to be composed of three major components, the lattice contribution χ_l, the contribution of trapped electrons χ_i, and that of free or quasi-free current carriers (i.e., electrons in the conduction band) χ_c.

The lattice term stems chiefly from the diamagnetic[12] contribution of the core electrons. However, included also is the Van Vleck paramagnetism[13] which results from virtual transitions between the equilibrium and higher states of the electronic system.[14] Both these contributions are to an extremely good approximation unaffected by small impurity additions. Comparison of impure samples with a pure one where only χ_l is present thus permits consideration of the sum $\chi_i+\chi_c$. The two terms in the sum can also be resolved. At low temperatures there are no free current carriers and χ_c vanishes. At high temperatures the number of trapped carriers is negligible so that χ_i is equal to zero.

A. Carrier Susceptibility

Pauli,[15] Landau,[16] and later Peierls,[17] Stoner,[18] and Sondheimer and Wilson[19] have treated the magnetic susceptibility of free electrons for a number of cases. Most of these calculations were designed to apply to metallic systems and required modification for use in the present work on semiconductors. It will be useful, in order to demonstrate explicitly the assumptions made, to outline a fairly simple derivation of the paramagnetic contribution.

The paramagnetic portion of the conduction-electron susceptibility results from the moment of the excess electrons lined up parallel to the magnetic field. If it is assumed that the magnetic field does not change the form of the density-of-states function, then the moment equals the difference between the product of the Fermi and density-of-states functions for spin parallel and that for spin antiparallel. For a many-valley semiconductor, the expression for the magnetic moment due to the conduction-electron spins is

$$M=\frac{2^{7/2}\beta\omega_m(m^*kT)^{\frac{3}{2}}}{h^3}\times\int_0^\infty\frac{\epsilon^{\frac{1}{2}}e^{\epsilon-\eta}\sinh(\beta H/kT)d\epsilon}{1+e^{2(\epsilon-\eta)}+2e^{\epsilon-\eta}\cosh(\beta H/kT)},\quad(1)$$

where $m^*=(m_lm_t^2)^{\frac{1}{3}}$ is the effective mass appropriate for the density of states, β is the Bohr magneton, ω_m is the number of energy minima in momentum space,

[1] G. Busch and E. Mooser, Helv. Phys. Acta **26**, 611 (1953).
[2] D. K. Stevens and J. H. Crawford, Jr., Phys. Rev. **99**, 487 (1955).
[3] Stevens, Cleland, Crawford, and Schweinler, Phys. Rev. **100**, 1084 (1955).
[4] A. Van Itterbeek and W. Duchateau, Physica **22**, 649 (1956).
[5] F. T. Hedgcock, Can. J. Phys. **34**, 43 (1956); J. Electronics **2**, 6 (1957).
[6] G. Busch and N. Helfer, Helv. Phys. Acta **27**, 201 (1954).
[7] R. Bowers, Phys. Rev. **108**, 683 (1957).
[8] H. Fritzche, Phys. Rev. **99**, 406 (1955).
[9] C. S. Hung and J. R. Gliessman, Phys. Rev. **96**, 1226 (1954).
[10] R. O. Carlson, Phys. Rev. **100**, 1075 (1955).
[11] E. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).
[12] See, for instance, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 211.
[13] An unexpected temperature variation of the susceptibility of pure germanium (reference 3) and silicon [D. K. Stevens and J. H. Crawford, Bull. Am. Phys. Soc. Ser. II, **1**, 117 (1956)], which was discovered during the early phases of this investigation, has been attributed to a temperature dependence of the Van Vleck paramagnetism [J. A. Krumhansl and H. Brooks, Bull. Am. Phys. Soc. Ser. II, **1**, 117 (1956)], the temperature changes stemming from changes in the band-to-band excitation energies.
[14] See, for instance, C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), Appendix F, p. 211.
[15] W. Pauli, Z. Physik **41**, 81 (1927).
[16] L. Landau, Z. Physik **64**, 629 (1930).
[17] R. Peierls, Z. Physik **80**, 763 (1933).
[18] E. C. Stoner, Proc. Roy. Soc. (London) **A152**, 672 (1935); **A154**, 656 (1936).
[19] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A210**, 173 (1951); A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1954), pp. 160ff.

and η and ϵ are the Fermi level and energy, respectively, both in units of kT.

The magnetic fields used in these experiments are less than 25 000 oersteds. Therefore, for the range of interest, between $3\frac{1}{2}$°K and room temperature, $\beta H \ll kT$ and the hyperbolic sine and cosine are, to an extremely close approximation, equal to unity and $\beta H/kT$, respectively. This simplifies the integral so that the paramagnetic part of the carrier susceptibility can be written in the form

$$\chi_c{}^p = \frac{n\beta^2}{\rho kT} \frac{F_{\frac{1}{2}}'(\eta)}{F_{\frac{1}{2}}(\eta)}, \tag{2}$$

where the Fermi integral $F_{\frac{1}{2}}(\eta) = \int \epsilon^{\frac{1}{2}}[1+e^{\epsilon-\eta}]^{-1}d\epsilon$ can be obtained from the density of carriers in the conduction band, n, by using the expression

$$n = 2^{7/2}\pi\omega_m h^{-3}(m^*kT)^{\frac{3}{2}}F_{\frac{1}{2}}(\eta), \tag{3}$$

and where $F'(\eta)$ is the first derivative of the Fermi integral, values for which have been tabulated.[20]

The diamagnetic contribution to the conduction-electron magnetism results from the fact that the wave functions in the plane perpendicular to H are quantized by the field. Sondheimer and Wilson's treatment for free electrons[19] is quite general and exact, lending itself readily to the modification[21] necessary for taking into consideration the details of the band structure. The only assumption necessary is that $\beta H \ll kT$. The expression that results is very similar in form to that for the paramagnetic contribution. The condition $\beta H \ll kT$ also permits writing of the total conduction-electron susceptibility as the sum of the paramagnetic and diamagnetic terms, yielding

$$\chi_c = \frac{n\beta^2}{3\rho kT}(3-\langle f^2\rangle)\frac{F_{\frac{1}{2}}'(\eta)}{F_{\frac{1}{2}}(\eta)}, \tag{4}$$

where $\langle f^2\rangle$ is the appropriately averaged effective-mass correction, which for perfectly free electrons would be equal to unity. For a many-valley model of the conduction band, $\langle f^2\rangle$ is given by

$$\langle f^2\rangle = (2M_t+M_l)/3M_t{}^2M_l,$$

where M_t and M_l are the transverse and longitudinal effective masses, respectively, both in units of the free electron mass. Use of effective-mass ratios obtained from cyclotron-resonance experiments,[22] $M_t=0.19$ and $M_l=0.98$, yields a value of 12.8 for $\langle f^2\rangle$. It should be evident from Eq. (4) that an $\langle f^2\rangle$ greater than 3 will cause the total conduction-electron susceptibility to be negative.

B. Donor Contribution

An electron localized at a donor can be described to a reasonably good approximation by a hydrogen-like wave function. As a result, there is no orbital moment; and each electron, as long as it does not interact with electrons from neighboring donors, will contribute only its spin magnetic moment and some orbital diamagnetism.

The paramagnetic spin term can be treated similarly to the free-electron spin contribution. However, it must be taken into consideration that because of electrostatic repulsion only one of the two donor spin states can be occupied. Mooser[23] has derived the expression

$$\chi_i{}^p = \frac{\beta N_d}{\rho H} \frac{\sinh(\beta H/kT)}{\frac{1}{2}\exp(\epsilon_d-\eta)+\cosh(\beta H/kT)}, \tag{5a}$$

where $\chi_i{}^p$ refers to the paramagnetic contribution to the impurity susceptibility, N_d is the number of donors, and ϵ_d is the donor ionization energy in units of kT.

The expression can be simplified for $\beta H \ll kT$, yielding

$$\chi_i{}^p = n_d\beta^2/\rho kT, \tag{5b}$$

where in the absence of compensating acceptor levels the number of filled donors, n_d, is equal to the difference between the total number of donors and the number of electrons in the conduction band.

In order to ascertain the range of validity of the simple expression, χ was calculated from Eqs. (5a) and (5b) for a number of temperatures using the maximum value for H (25 000 oersteds) that is used in the measurements. It was found that less than $\frac{1}{2}\%$ error is made at 3.3°K and that the expression (5b) is no less valid than (5a) above 3.5°K.

The orbital diamagnetism of the trapped electrons is given by the Larmor-Langevin[24] formula,

$$\chi_i{}^d = -\frac{e^2 n_d}{6\rho m_i{}^* c^2}\langle r^2\rangle, \tag{6a}$$

where $m_i{}^*$ is an effective mass for an electron in an impurity state, c is the velocity of light, and $\langle r^2\rangle$ is the mean square radius of this state. The constants $m_i{}^*$ and $\langle r^2\rangle$ are difficult to evaluate directly. However, the similarity between a donor state and a hydrogen atom can be used to evaluate $\chi_i{}^d$ in terms of the ionization energies of the donor and hydrogenic states, and the dielectric constant, K, of silicon.[25] This is most easily done by using the classical theory of the hydrogen atoms,[26] from which it can be shown that the ionization

[20] J. McDoughall and E. C. Stoner, Trans. Roy. Soc. (London) **A237**, 67 (1936).

[21] The general method is indicated by H. Fröhlich, in *Elektronentheorie der Metalle* (Verlag Julius Springer, Berlin, 1936), p. 152. The detailed calculation for ellipsoidal energy surfaces has been performed by Schweinler. [H. C. Schweinler (unpublished); see also reference 3.]

[22] Dexter, Lax, Kip, and Dresselhaus, Phys. Rev. **96**, 222 (1954).

[23] E. Mooser, Phys. Rev. **100**, 1589 (1955).

[24] J. H. Van Vleck, reference 12, pp. 206 ff.

[25] H. C. Schweinler (private communication).

[26] See for instance G. Hertzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944), pp. 15 ff.

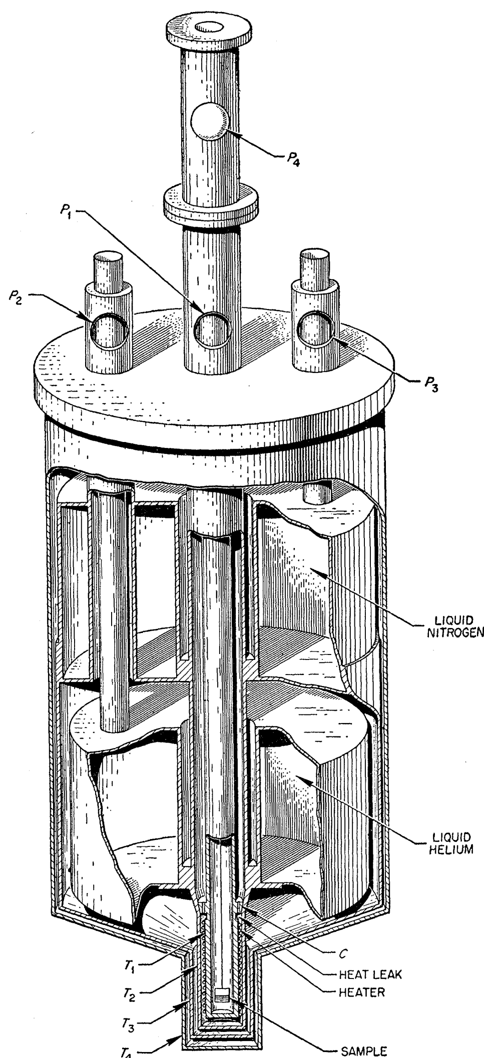

FIG. 1. Diagram of cryostat used for susceptibility measurements at low temperatures. T_2–T_4 indicate the three radiation shields that are near liquid helium, liquid nitrogen, and room temperature, respectively. C is a thermal contact which permits adjusting of T_1, the temperature of the innermost shell. P_1–P_4 indicate the points where vacuum pumps are connected.

energy of such a state is proportional to (m_i^*/K^2) and that the radius is proportional to K/m_i^*. These proportionalities are then used to eliminate $\langle r^2 \rangle$ and m_i^* by substituting for them the respective values for hydrogen and the ratios of the dielectric constants and the ionization energies. The resulting expression takes the form

$$\chi_i^d = \frac{n_d \chi(\mathrm{H})}{N_0 \rho}\left(\frac{13.5 \text{ ev}}{E_i}\right)^3\left(\frac{1}{K}\right)^4 = -1.7\times10^{-27} n_d, \quad (6b)$$

where N_0 is Avogadro's number; the molar susceptibility of atomic hydrogen, $\chi(\mathrm{H})$, is -2.4×10^{-6}; the ionization energy of the donor state, E_i, is 0.05 ev; and the density of silicon, ρ, is 2.33 and $K=11.9$.

Evidently, since the paramagnetic susceptibility of the donors is given by

$$\chi_i^p = n_d \beta^2/\rho k T = 2.67\times10^{-25} T^{-1} n_d,$$

the diamagnetic term will be a six percent correction at 10°K.

III. EXPERIMENTAL

The technique used to measure the magnetic susceptibility has been described in the past.[3,27] The method yields the absolute value of the susceptibility of a sample and the ratios of the susceptibility at various temperatures to that at room temperature. The accuracies after correcting for a small ($\sim <1\%$) contribution of the suspension are 0.5% and 0.1%, respectively. The cryostat shown in Fig. 1 permits making susceptibility determinations over the temperature range 3–350°K. For obtaining temperatures up to 38°K the lower reservoir is filled with liquid helium; for temperatures between 51 and 350°K liquid nitrogen is used. Readings between 38 and 51°K can be taken while the cryostat slowly warms. Two copper-constantan thermocouples mounted on the wall of the

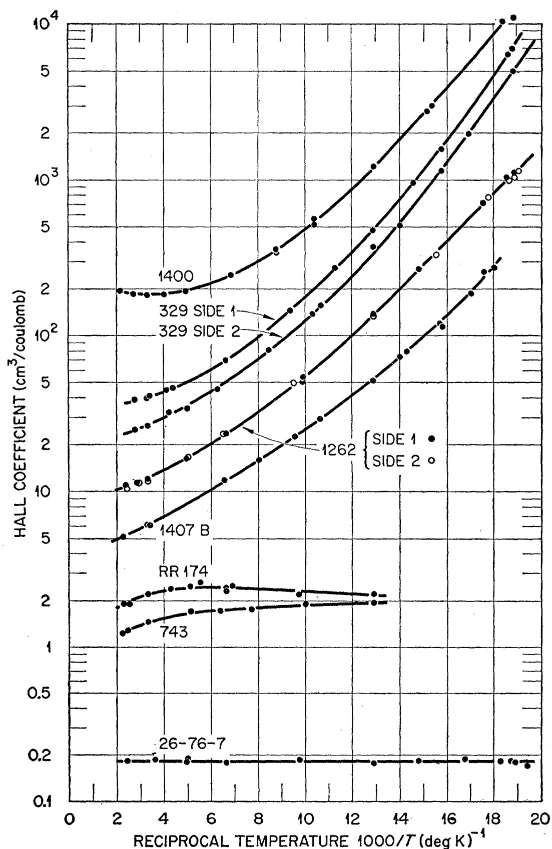

FIG. 2. The Hall coefficient of n-type silicon as a function of reciprocal temperature.

[27] D. K. Stevens, Oak Ridge National Laboratory Report ORNL-1599 (unpublished).

specimen thimble were calibrated with a standardized platinum resistance thermometer and were used to measure temperatures above 10°K. For temperatures below ten degrees, a number of 1-mm germanium cubes were used as resistance thermometers. Unfortunately, the reproducibility of these was poor, making it necessary to calibrate the germanium elements immediately after each run. This was done by condensing helium in the specimen thimble and measuring the vapor pressure. The temperatures obtained are judged to be accurate to a few tenths of a degree.

Resistivity and Hall coefficients were measured on plates cut from susceptibility specimens or from portions of the various ingots adjacent to the susceptibility samples. In the case of two ingots where a concentration gradient was expected (1262 and 329), two Hall plates, one from the high and the other from the low concentration side of the susceptibility specimen, were measured.

IV. RESULTS

The results of the Hall coefficient measurements are shown as a function of reciprocal temperature in Fig. 2. The density of conduction electrons, n, was calculated from these data using the expression

$$n=\gamma/Rec, \tag{7}$$

where R is the Hall coefficient and γ is a numerical constant of the order of unity which depends upon the degeneracy of the sample and the details of the electron scattering processes in the crystal. It has been usual in the past to use $3\pi/8$ for γ. However, more careful analyses of transport properties using a many-valley model yield values for γ that are perhaps more accurate.[28,29] In the analysis of the present results $\gamma=0.865$ was used for degenerate samples. For nondegenerate silicon the constants used were 1.08 when scattering was due to thermal vibrations and 1.67 when it was due to charged impurity centers.

In silicon, essentially all of the donors are ionized above 400°K. Consequently, the high-temperature Hall coefficient gives a good estimate of the net number of donors in a given sample. Table I lists the samples together with their room-temperature resistivity, and the donor density.

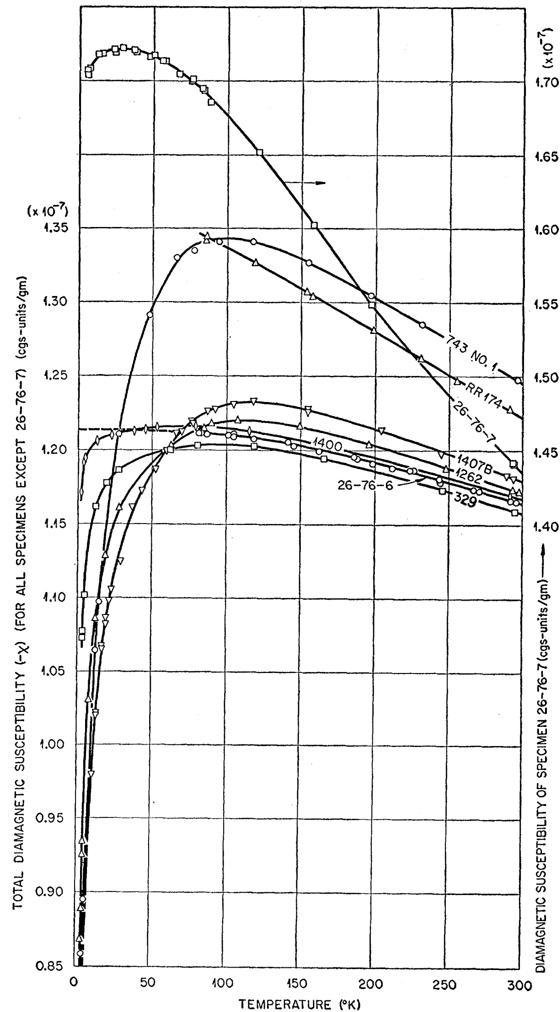

FIG. 3. The magnetic susceptibility of arsenic-doped silicon as a function of temperature.

TABLE I. Composition of samples.

Sample	Doping agent	Room-temperature resistivity (ohm cm)	Net donor density (obtained from 400°K Hall data) (cm^{-3})
26-76-7	Arsenic	0.002	2.9×10^{19}
743	Arsenic	0.008	$5\ \times10^{18}$
RR174	Phosphorous	0.013	$4\ \times10^{18}$
1407B	Arsenic	0.017	1.2×10^{18}
1262	Arsenic	0.026	5.7×10^{17}
329	Arsenic	0.046	2.5×10^{17}
		0.059	1.6×10^{17}
1400	Arsenic	0.17	3.5×10^{16}
26-76-6	Boron	(35)	(-3×10^{14})

The results of measurements of the magnetic susceptibility of silicon doped with from 3×10^{16} to 3×10^{19} donor atoms/cc are shown in Fig. 3. Also shown plotted is the measured susceptibility of a "pure" sample. Since the presence of less than 10^{15} carriers cannot be detected by this method, any sample containing fewer magnetic centers than this is considered "pure." In this instance, sample 26-76-6 was a p-type sample containing 3×10^{14} boron atoms/cc. It should be pointed out that the curve (shown dashed) below 70°K is an extrapolation based on theoretical grounds and on the expected similarity between pure silicon and germanium, the latter having been measured by Bowers[11] and Van Itterbeck and Duchateau.[8]

Figure 3 exhibits the following aspects of the mag-

[28] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).
[29] C. Herring, Bell System Tech. J. **34**, 237 (1955).

TABLE II. Values of the square of the freedom number calculated from results of Hall and susceptibility measurements on silicon.[a]

Sample	Donor density cm^{-3}	Temperature T (°K)	Fermi level $(\zeta - E_c)$ (ev)	Square of freedom number f^2: For thermal scattering $n=1.02/Rec$	For impurity scattering $n=1.67/Rec$	For degenerate statistics $n=0.865/Rec$
26-76-7	2.9×10^{19}	300	0.009	6.2	5.0	*6.8*
		200	0.021	6.9	5.4	*7.6*
		100	0.029	7.2	5.6	*7.9*
		50	0.030	7.3	5.6	*8.0*
		20	0.031	7.2	5.6	*8.0*
743	5.0×10^{18}	300	−0.047	10.6	7.7	12.0
		200	−0.021	9.8	7.1	11.0
		150	−0.010	9.3	6.8	10.4
RR174	4.0×10^{18}	300	−0.060	10.8	7.8	12.2
		200	−0.030	11.3	8.1	12.7
		150	−0.016	10.7	7.7	12.0
		100	−0.005	9.5	7.0	10.7
1407B	1.2×10^{18}	300	−0.085	*8.0*	6.0	8.9
		200	−0.052	10.1	7.3	11.4
		140	−0.035	10.1	*7.3*	11.4
1262	5.0×10^{17}	300	−0.103	*5±5*		
		200	−0.063	*10±3*		

[a] Values of f^2 calculated for conditions for which the constant in the Hall effect is fairly certain are shown in italics.

netic behavior. Except for specimen 329, all of these n-type samples[30] are more diamagnetic than pure silicon at room temperature, the difference increasing with donor concentration. (In view of the experimental error inherent in the determination of the absolute value of the susceptibility [$\frac{1}{2}$%], the position of the curve for sample 329 is probably not a departure from the trend shown by the other samples.) As the temperature drops below room temperature, the specimens become increasingly diamagnetic relative to the pure material. In the liquid nitrogen range and below, a marked difference appears between degenerate and nondegenerate silicon. Specimen 26-76-7 which, as shown by its temperature-independent Hall coefficient, is highly degenerate, remains diamagnetic down to 3.5°K. Specimens 1400, 329, 1262, and 1407B become strongly paramagnetic relative to pure silicon at temperatures below 50°K. In these specimens, as their Hall data in Fig. 2 show, there is a rapid decrease in carrier density with temperature. Hence the two contributions, i.e., diamagnetism of conduction electrons and the paramagnetism of un-ionized donors, are clearly evident.

Departures from a simple relationship between the Hall effect and the magnetic properties are exhibited by specimens whose donor density puts them into the transition range between degenerate and nondegenerate material. Specimen 743, which contains 5×10^{18} net donors, exhibits a reversal in sign of the net electron magnetism, but has an almost temperature-independent Hall coefficient. This would seem to indicate that even though the electrons carry current, at least some of them exhibit characteristics of localized magnetic centers. Specimen RR174, which contains phosphorous donors rather than arsenic, does not exhibit evidence of the reversal of sign of the donor magnetism down to 75°K. This might be explained by the fact that a phosphorous trap is more shallow than an arsenic trap (0.39 ev *vs* 0.49 ev according to the *American Institute of Physics Handbook*) and that, therefore, overlap between the conduction band and the donor levels might set in at lower concentrations in the case of phosphorous. In any case, these data make it appear that the magnetic properties of silicon with donor impurities in the range near 5×10^{18} cm^{-3} may be complicated by the nature of the donor centers and effects associated with impurity banding and impurity level-conduction band overlap.

[30] It should be emphasized that this behavior of the magnetic susceptibility is for n-type silicon. Some preliminary measurements on p-type material [Stevens, Sturm, Sonder, Cleland, and Crawford, Bull. Am. Phys. Soc. Ser. II, 2, 134 (1957)] shows that in these materials the carrier contribution to the susceptibility is paramagnetic throughout the temperature range 75°K–300°K.

V. DISCUSSION AND COMPARISON WITH THEORY

In this section, two components of the magnetic susceptibility will be analyzed in more detail. First, by use of the results of measurements made in the vicinity of room temperature, the free-carrier contribution will be compared with Eq. (4). Second, it will be of interest to compare the low-temperature data with Eq. (5) and to look for a source of the large deviations from it that occur for the specimens with larger donor concentrations.

In the vicinity of room temperature most of the donors in silicon are ionized. This is particularly true in the case of heavily doped samples, in which the impurity energy gap has been narrowed by broadening of the impurity levels. When, as is the case under the above conditions, there are no bound donor electrons, the difference between the susceptibility of a given doped sample and that of pure silicon should be in good agreement with Eq. (4); as a consequence, $\langle f^2\rangle$ may be

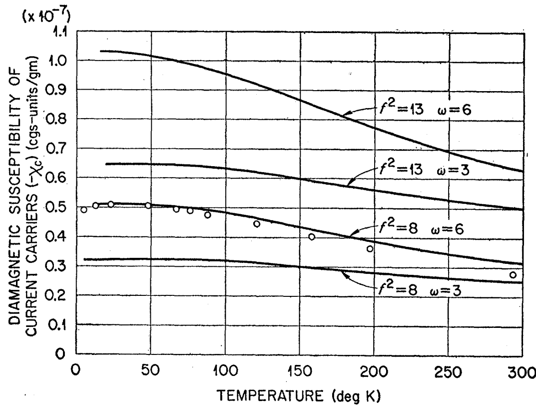

FIG. 4. Comparison of the carrier susceptibility of specimen 26-76-7 with curves derived for various assumptions about the freedom number, f, and the number of energy minima, ω_m.

calculated by using Hall data to determine the carrier concentration.

It should be pointed out that although the value for $\chi_c=\chi(\text{doped})-\chi(\text{pure})$ is accurate to about $\frac{1}{2}\%$ in the case of the most highly doped sample, 26-76-7, the accuracy is less for the purer samples, where the susceptibility approaches that of pure silicon. χ_c for sample 1262 is probably accurate only within a factor of two. Values for $\langle f^2\rangle$ calculated from Eq. (4) are shown in Table II. Since there may be some question as to the choice of constant in the Hall-effect expression [Eq. (7)], values of $\langle f^2\rangle$ are listed for the three possible choices. The results calculated for conditions for which the constant in the Hall expression is fairly certain are shown in italics. It is evident from the results that $\langle f^2\rangle$ is much closer to 8 than to the 13 expected from the cyclotron-resonance values of the effective masses.

The ratio $[F_{\frac{1}{2}}'(\eta)/F_{\frac{1}{2}}(\eta)]$ is obtained from the Hall data by use of Eqs. (3) and (7) and published tables.[20] The ratio is not appreciably affected by the choice of γ. However, the constant ω_m in Eq. (3) which refers to the number of energy minima in k space could, if incorrect, have a large effect on the ratio. Cyclotron-resonance measurements have shown that the minima are along the [100] axes. Also, it is generally agreed now that the minima do not lie at the Brillion zone boundaries. This would make ω_m equal to 6, which is the number that has been used in the calculations yielding $\langle f^2\rangle$ in Table II. However, it was felt worthwhile to check the validity of this assumption for at least one sample. Sample 26-76-7, for which there is the smallest uncertainty in $\chi-\chi(\text{pure})$ and for which there is little question about the choice of constant γ, seemed to be the best choice. The susceptibility for that sample was calculated from Eqs. (3), (4), and (7) for a number of temperatures and for two choices of each of the constants ω_m and $\langle f^2\rangle$. Figure 4 shows the results compared with the experimental data. Evidently agreement is best when one assumes six minima in k space and a value near 8 for $\langle f^2\rangle$.

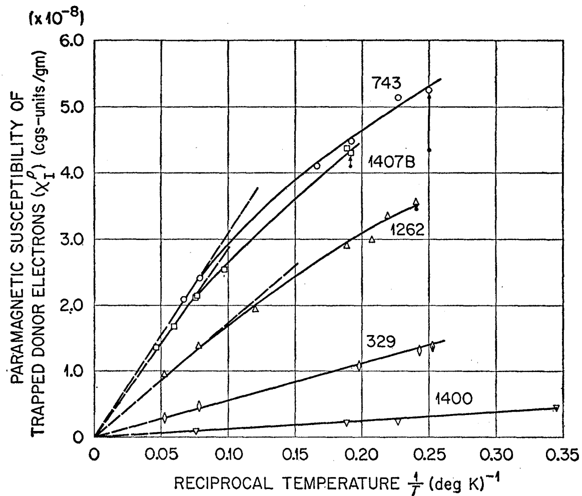

FIG. 5. The paramagnetic component of the trapped-donor susceptibility as a function of reciprocal temperature.

For nondegenerate arsenic-doped silicon below 20°K, it is safe to assume that all donors have been trapped at donor sites. This is borne out by the Hall data which show that even as high as 50°K less than 2% of the extrinsic electrons remain in the conduction band. As a result, the conduction-electron contribution to the total susceptibility vanishes, leaving only the trapped-donor contribution. This is given by Eq. (5) and Eq. (6) and will be equal to the difference between the susceptibility of the experimental samples and that of pure silicon, i.e., $\chi-\chi(\text{pure})$. In the range of interest (that is, below 20°K) the trapped-donor diamagnetism [Eq. (6)] is appreciably smaller than the paramagnetism and can therefore be estimated and treated as a correction term. The experimental results with the correction made are shown in Fig. 5 where the paramagnetic component of the trapped-donor susceptibility, χ_i^p, is plotted *versus* reciprocal temperature. The arrows pointing to the lowest temperature point of each curve indicate the magnitude of the diamagnetic correction made. It can be seen that except for sample 743 the corrections are minor. For all the samples, including 743, the corrections are not the source of the deviations to be discussed below but only increase them by a small amount.

It is readily observable that the plots of the data for specimens 1400 and 329 are straight lines, as one would expect from Eq. (5b). However, the curves for the other three samples bend over, having lower slopes as the temperature decreases. It would seem that for samples having more than 5×10^{17} donors/cm^3 the number of magnetic centers relative to the number of donors, n_d/N_d, decreases with temperature below 10°K. Moreover, in the case of highly doped specimen 743 (5×10^{18} donors), the difference between the number of magnetic centers and the number of donors is apparent even above 20°K. This can be seen from Table III where

TABLE III. Comparison of the number of donors with the number of magnetic centers at low temperatures.

Specimen	Donor density N_d (cm^{-3})	Number of magnetic centers obtained from $\chi(1/T)$ plot n_d (cm^{-3})
743	5×10^{18}	1.2×10^{18}
1407B	1.2×10^{18}	1.1×10^{18}
1262	5.7×10^{17}	6.6×10^{17}
329	2.5×10^{17}	
	1.6×10^{17}	2.1×10^{17}
1400	3.5×10^{16}	$(5\pm1)\times10^{16}$

values of n_d obtained from the high-temperature limiting slopes of the curves shown in Fig. 5 are compared with the number of donors. These results indicate that Eq. (5b) is applicable down to liquid helium temperatures for samples having less than 2×10^{17} donors per cubic centimeter, but that deviations appear below ten degrees for samples having donor densities between that figure and 2×10^{18}. For even higher donor concentrations, where degeneracy and impurity banding start to occur, deviations appear even above 20°K.

It is not difficult to account for the apparent decrease in number of magnetic centers in highly doped silicon at low temperatures. It must only be recalled that the wave function of a hydrogenic state will extend much further in material of high dielectric constant than in an isolated atom and that therefore even at a moderate concentration of filled donor states there will be enough overlap of pairs of electrons to form "hydrogen-like molecules," i.e., systems in which the spins are paired in opposite directions, causing them to be magnetically inactive. This pairing will, as the concentration of donors increases, cause more and more of them to be nonmagnetic until there remains but a small temperature-independent Pauli paramagnetism in the limit of a completely degenerate impurity band. Moreover, as the temperature is lowered the fraction of paired to unpaired centers will increase as kT approaches the energies of interaction between closely situated donors.

The more usual approach to interacting donors in solids is in terms of band theory. However, it is by no means clear that the usual assumptions made for periodic structures can be carried over to a situation where the location of the "lattice" sites is random. It is for that reason that we feel that, for nondegenerate silicon, approaching the problem from the point of view of interactions of systems of two, three, or four electrons is more realistic. This is borne out by some spin-resonance experiments[31] which have demonstrated interactions between 2- and 3-electron groups in silicon containing 10^{17} phorphorus donors.

Mooser[23] has attempted to derive expressions that would apply to a "donor band." Agreement between his expression for the susceptibility of weakly banded donors and our data is poor. However, this may be due to the fact that electrostatic forces which repel a second electron from a singly filled donor site are neglected in the derivation, rather than any lack of applicability of band theory.

VI. SUMMARY

1. Analysis of the carrier contribution to the magnetic susceptibility of n-type silicon yields a value of 8 for the square of the freedom number rather than the 13 one would expect from the effective mass ratios. Aside from that, the data agree well with theory and with the assumption that there are six energy minima in k space for n-type silicon.

2. For donor concentrations of less than 3×10^{17} cm^{-3} the behavior of the trapped-donor magnetism can be accounted for by assuming that the trapped electrons are independent centers, each with a magnetic moment equal to the Bohr magneton.

3. The trapped-donor susceptibility of silicon doped with more than 5×10^{17} arsenic atoms/cc does not follow a simple Curie law. The deviations can be explained qualitatively by interactions of closely neighboring donor centers.

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[31] Feher, Fletcher, and Gere, Phys. Rev. **100**, 1784 (1955).