text. However, these authors did not refer to the very low-density case where the Wigner transition takes place.

H. BROOKS (Harvard University): The real point is that you were dealing experimentally with very highly compensated samples so that the screening was minimized. I should point out one effect which would alter the screening although I don't think it will alter your explanation. That is that some years ago I showed that if you take into account in highly compensated samples the presence of both the donors and the acceptors and the fact that some of them can be populated and so on, there is an additional contribution to the screening due to the statistical population of the donors around another donor, so to speak, but this can double the screening but it can't change it in order of magnitude.

L. J. NEURINGER (Massachusetts Institute of Technology): Magnetic freeze-out *has* been studied in the high-field region to 200 kG. In a recent paper [Phys. Rev. Letters **18**, 773 (1967)] by Hanamura, Beckman, and myself, we found that both the magnitude and magnetic-field dependence ($\epsilon_i \sim H^{1/3}$) of the ionization energy, determined from Hall-coefficient measurements on uncompensated, heavily doped specimens ($n \sim 10^{16}$ cm^{-3}), obeyed the Yafet, Keyes, and Adams theory. It would appear that our results have serious consequences for your theory with regard to the importance of screening and with respect to the magnetic-field dependence of the ionization energy which your theory would predict at high magnetic fields. It also appears that in deducing the ionization energy from the Hall coefficient data you have neglected the fact that there is present two-band conduction. With regard to the threshold magnetic field for freeze-out H_0, we found good agreement with experiment by simply equating the volume occupied by the electronic wave function in this high magnetic field to the volume occupied by a single impurity, as a result $H_0 \sim N_{\mathrm{imp}}^{6/7}$. I would venture to say that magnetic freeze-out can best be studied at high magnetic fields using heavily doped, uncompensated samples because (a) one is free of the complications introduced by two-band conduction, and (b) the fluctuation in the electric field at the various donor sites in the crystal, produced by the compensating acceptors, does not play a role as it does in the compensated samples.

N. H. MARCH: Well, I regret of course that I did not know about those results. They seem to agree satisfactorily with our prediction that the Yafet–Keyes–Adams ionization energy should be almost regained in very high fields.

REVIEWS OF MODERN PHYSICS VOLUME 40, NUMBER 4 OCTOBER 1968

Semiconductor-to-Metal Transition in *n*-Type Group IV Semiconductors*

MICHAEL N. ALEXANDER†
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York and *Materials Research Laboratory, Army Materials and Mechanics Research Center, Watertown, Massachusetts*
DONALD F. HOLCOMB
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

A synthesis is given of the most significant experimental features of the semiconductor-to-metal transition in group IV semiconductors. Two characteristic concentrations are discussed, the first being for a delocalization of electrons (the "Mott" transition), and the second being associated with the entry of the Fermi level into the conduction band of the host material. Experimental values are given for the two concentrations in several materials. Experimental data covering measurements of Hall coefficient, electrical resistivity and carrier mobility, NMR properties, magnetoresistance, magnetic susceptibility, and ESR properties are employed in arriving at values for the two characteristic concentrations. Si:P is taken as the model system because of the completeness of experimental measurements. Si:As is also briefly considered. Existing data for *n*-Ge are examined, as well as the more restricted evidence concerning *n*-SiC.

I. INTRODUCTION

Transitions from insulating to metallic behavior occur in a number of types of solid systems as some parameter of the system or some external variable is changed. It was recognized some time ago that increasing the concentration of shallow donors or acceptors in semiconductors could produce such a change,[1] and certain aspects of the theory were developed rather completely at an early stage.[2] A qualitatively new feature was injected into the picture by Mott,[3] who pointed out that this change might not be a continuous one, as implicitly assumed by the early workers. Mott proposed that the transition would be an abrupt one, smeared out only insofar as random positioning of impurity atoms leads to a distribution of local concentrations around a given average concentration. Mott also gives references to earlier work in those articles.

Mott showed, for a monovalent system such as that of donor or acceptor impurities in semiconductors, that as the interdonor atom spacing is reduced, free carriers will not appear until a critical concentration is reached, at which screening by the electrons of nearby atoms prevents binding by electron–hole pairs. That is, the activation energy for carrier production falls to zero,

---

* This work partially supported by the U. S. Army Research Office (Durham), under Contract No. DA-31-124-ARO-D-407, Tech. Rept. No. 8.

† Present address: Materials Research Laboratory, Army Materials and Mechanics Research Center, Watertown, Mass.

[1] G. Busch and H. Labhart, Helv. Phys. Acta **19**, 463 (1946); C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950); C. S. Hung, Phys. Rev. **79**, 727 (1950).

[2] W. Baltensperger, Phil. Mag. **44**, 1355 (1953); E. M. Conwell, Phys. Rev. **103**, 51 (1956).

[3] N. F. Mott. Proc. Phys. Soc. (London) **62**, 416 (1949); Phil. Mag. **6**, 287 (1961); Advan. Phys. **16**, 49 (1967).

and we have a "metallic" system. Mott developed an approximate theory of the effect[4] and derived the following expression for the critical concentration n_c:

$$n_c \cong (0.25/a_H)^3, \qquad (1)$$

where a_H is the atomic radius of the particular impurity atom in question. Although more sophisticated theories than Mott's have been developed,[5] none, to our knowledge, permits numerical calculation of the critical concentration for a given doped semiconductor system.[6] Consequently, after describing the available experimental data, we compare that data with the Mott relation. Mott himself made this comparison in 1956.[4] Our aim in considering this question is to sharpen the comparison by examination of the much more extensive data now available.

In this paper, we draw together a variety of experimental data for a number of n-type group IV semiconductor systems in an attempt to describe as completely as possible the known features of the electron systems. The following types of measurements are included: (a) electrical conductivity, (b) Hall coefficient, (c) Hall mobility, (d) magnetoresistance, (e) magnetic susceptibility, (f) NMR properties, and (g) ESR properties.

We restrict our considerations to n-type systems because experimental information is generally more complete than for p-type materials. We expect the general features we catalog to be present in the p-type materials also, with the hole system replacing the electron system of our discussion. Within the n-type systems, we take Si:P as our prototype, because the kinds of measurements on that system are the most comprehensive (Ge:Sb runs a close second). However, nothing which we say appears to be limited in application to Si:P and we also include shorter discussions of heavily doped Si:As, of Ge:Sb, Ge:As, and Ge:P, and of SiC:N. Although the nature of the host material is the primary governing factor in the characteristics of the transition, there is a weaker dependence upon the particular nature of the donor. We bring out this feature at appropriate points.

We wish to make clear that we consider only high donor concentration samples in which compensation does not play a major role. Conduction by various hopping mechanisms has been exhaustively treated by a number of workers. The paper by Mott and Twose[7] gives a detailed discussion, along with a number of references.

Because of the desire to deal with observations which are uncluttered by the presence of thermally excited carriers, we concentrate on measurements near 0°K. The low-temperature range has the added advantage of insuring degenerate behavior of the electron system, thus promoting simplicity. (The Fermi temperature T_F for a system of free conduction electrons with mass $m^* = m_0$ is 38°K at electron density $n = 10^{18}$ cm^{-3} and 176°K at $n = 10^{19}$ cm^{-3}. These concentrations are the approximate span of our range of primary interest.)

The discussion to follow is organized around a model which includes three main features:

(a) Above some characteristic donor concentration n_c, electrons are delocalized. For donor concentrations n_d below n_c, they are bound to single donors or small clusters of donors. Thus, n_c designates the Mott-transition concentration [cf. Eq. (1)].

(b) Above a second characteristic concentration n_{cb}, the Fermi level of the electron system passes into the conduction band of the host crystal, and electrons at the Fermi level acquire properties appropriate to that band. This feature is not inherent in the metallic transition itself. It results from the practical matter that we must imbed our impurity system in a matrix in order to hold it together.

(c) For $n_{cb} > n_d > n_c$, the electrons exist in a poorly understood "impurity band." (We note, as other authors have done, that one must use the term "band" with care, since it tends to evoke images generated by working with periodic structures. In these systems it simply implies a continuum of energy states.) We discuss the rather fragmentary information concerning the nature of the band. We warn the reader that the properties of electrons in this band are incompletely known.

In the following three sections, we first discuss completely the case of Si:P, bringing out all that is known about these three features in that system. We then add information about Si:As, Ge:Sb, Ge:As, and SiC:N to the framework set up for Si:P.

Finally, in Secs. V and VI, we discuss topics about which final returns are not in. The most prominent of these are the question of the proper interpretation of the magnetoresistance data and the question of the existence of localized magnetic moments in these systems. We also examine a number of unresolved questions about the electron-spin susceptibility and some unexplained features of the ESR data in Si:P.

II. SILICON

Delocalization of Electrons

We first discuss Si:P completely, then add fragmentary comments concerning Si:As. The delocaliza-

---

[4] N. F. Mott, Can. J. Phys. **34**, 1356 (1956).

[5] J. Hubbard, Proc. Roy. Soc. (London) **A281**, 401 (1964); W. Kohn, Phys. Rev. **133**, A171 (1964); G. Kemeny, Ann. Phys. (N.Y.) **32**, 69, 404 (1965); W. Kohn, Phys. Rev. Letters **19**, 789 (1967).

[6] It should be noted that recent work to be presented at the International Conference on the Metal-Nonmetal Transition, 14–16 March 1968, may modify the theoretical situation. In particular, N. F. Mott and E. A. Davis have examined more completely the question of the manner in which the activation energy vanishes at the transition. We are grateful to Professor Mott for sending a preprint of the paper by Mott and Davis in advance of the conference.

[7] N. F. Mott and W. D. Twose, Advan. Phys. **10**, 107 (1961).

tion concentration n_c is most clearly seen in the low-temperature transport-property measurements, Hall coefficient, and electrical conductivity.[8,9] Figure 1 shows the Hall data of Yamanouchi *et al.*[9] The number of Hall carriers n at 4.2°K rises extremely sharply as a function of donor concentration n_d for values of n_d somewhat greater than 10^{18} cm^{-3}. For n_d greater than 4×10^{18} cm^{-3}, n is equal to n_d.

Figure 2 shows the resistivity data of Yamanouchi *et al.*[9] plotted as a function of n_d. This form of presentation of the data, used by Fritzsche for Ge:Sb,[10] is particularly useful. These data support the Hall data, since the precipitous drop in ρ is centered at 3×10^{18} cm^{-3}. At low temperatures, the resistivity is independent of temperature for samples with n_d greater than 3×10^{18} cm^{-3}.

The spin-lattice relaxation rate for the ^{29}Si nuclear-spin system, $1/T_1$, when plotted as a function of n_d, shows a sharp decrease between samples at $n_d=2.5\times10^{18}$ cm^{-3} and at $n_d=6\times10^{18}$ cm^{-3}.[11] This behavior is also consistent with delocalization. It arises from the fact that an itinerant electron is, in general, a less effective nuclear-relaxation agent than a localized electron. Moreover, the product T_1T is constant at 4°K and below for the sample with $n_d=6\times10^{18}$ cm^{-3} but not for the sample with $n_d=2.5\times10^{18}$ cm^{-3}. Constancy of the product T_1T is characteristic of relaxation by a degenerate system of free electrons.

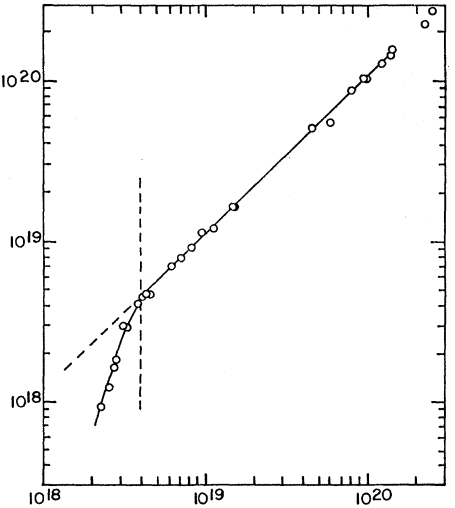

FIG. 1. The density of Hall carriers, $1/R_{He}$, is plotted as a function of donor concentration n_d in Si:P. Measurements were made at 4.2°K. (This is Fig. 3 from Ref. 9, reproduced with permission of the authors.)

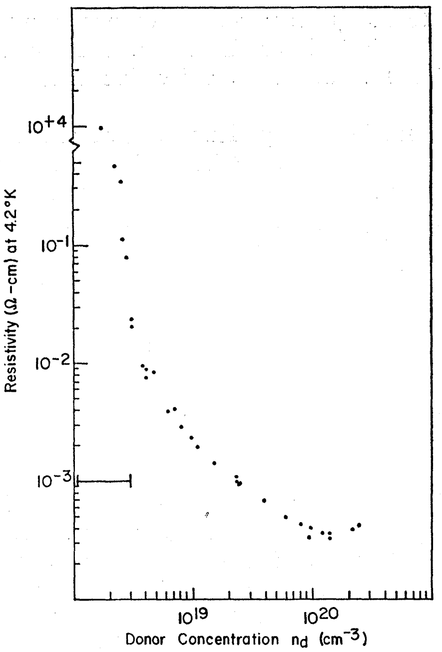

FIG. 2. The resistivity data of Yamanouchi *et al.* (Ref. 9) for Si:P at 4.2°K is plotted as a function of donor concentration, n_d. The data are taken from Table I of Ref. 9.

Some aspects of the ESR data are also understandable in terms of such a value for n_c. There is only a single ESR line visible for $n_d>7\times10^{17}$ cm^{-3}.[12,13] This observation is naturally interpreted as implying that, in this regime, donor electrons move over clusters of donor sites rather than each being bound on an individual donor site. The linewidth at 4.2°K decreases throughout the range $7\times10^{17}<n_d<3\times10^{18}$, from 4 to 0.45 G. Presumably the exchange narrowing is becoming more and more effective as electrons typically move over larger and larger clusters of donors. The ESR linewidth has a minimum, as a function of n_d, at $n_d\cong3\times10^{18}$ cm^{-3}. The existence of this minimum is consistent with the notion that a metallic transition occurs at that concentration. The transition short circuits any further narrowing. The line broadening for $n_d>3\times10^{18}$ is, presumably, lifetime broadening.

We have shown that effects of delocalization are seen in a variety of types of experimental data, all in the range of n_d from about 2.5×10^{18} to 4.0×10^{18} cm^{-3}. Two questions remain. (1) Is the transition really sharp, as in the transition metal oxides,[14] if we properly unravel the effects of a distribution in local concentration in the semiconductor system? (2) What value is to be

---

[8] P. W. Chapman, O. N. Tufte, J. D. Zook, and D. Long, J. Appl. Phys. **34,** 3291 (1963).

[9] C. Yamanouchi, K. Mizuguchi, and W. Sasaki, J. Phys. Soc. Japan **22,** 859 (1967). There are, of course, transport-property measurements dating back many years. While realizing the important contributions of these early investigators, we shall draw most heavily upon the recent work of Yamonouchi, Mizuguchi, and Sasaki, because of the completeness of their data taken in a set of samples with a very fine concentration grid. Moreover, ESR[13] and susceptibility[19,20] data obtained for the same samples are available.

[10] H. Fritzsche, J. Phys. Chem. Solids **6,** 69 (1958).

[11] R. K. Sundfors and D. F. Holcomb, Phys. Rev. **136,** A810 (1964).

[12] G. Feher, Phys. Rev. **114,** 1219 (1959).

[13] S. Maekawa and N. Kinoshita, J. Phys. Soc. Japan **20,** 1447 (1965).

[14] F. J. Morin, Phys. Rev. Letters **3,** 34 (1959).

assigned to the quantity n_c? We cannot answer these questions with high precision, but some comments about simple models for density fluctuations are in order.

For a sample at any donor concentration n_d we would expect a roughly Poisson distribution of local densities if we establish our sampling volume as $1/n_d$. With this sampling volume, the mean number for the Poisson distribution, $\bar{m}$, is 1. Then the quantity mP_m, where m is the number in the sampling volume and P_m is the Poisson probability distribution

$$P_m = \bar{m}^m \exp(-\bar{m})/m!, \tag{2}$$

gives us the number of atoms at that value of m in the distribution. Examining the characteristics of the graph for mP_m leads to the construction of the bar in Fig. 2. We assume that n_c has the value 3×10^{18} cm^{-3}. The left end is at a value of n_d such that about 25% of atoms are already in local densities of n_c or greater. The right end marks the value of n_d at which about 75% are in local densities n_c or greater. The bar suggests that the width of the transition could be accounted for entirely by statistical variations in local density, and that the transition could be discontinuous. However, a more precise examination of this question requires the development of a genuine "percolation" model for the transport properties in the real Si lattice structure. That is, the direct transport current requires a connected conduction path through the sample. Thus, clusters of impurities with local concentration above n_c will only contribute to the direct current if they are connected. The necessary percolation model is not presently available. It is possible that its addition could contribute a significant narrowing to the transition width suggested by the Poisson model.[15]

The Poisson model is really more applicable to spin-resonance experiments, which sample microscopic properties. It is invoked again in Sec. VI in a more complete discussion of the ESR experiments.

Figure 3 summarizes the observations outlined in the preceding paragraphs, as well as the conclusions of some of the following sections of this paper. The conclusions we draw from the material presented thus far are that $n_c = 3\times10^{18}$ cm^{-3} for Si:P, and that the existence of a well-defined delocalization transition supports the Mott picture. The Mott theory leaves open the fundamental question of the exact form of the function which describes the vanishing of the carrier activation energy.[6] Until a full account of the effects of local density variations is available, it will be difficult to establish that form experimentally.

Fermi Level into Conduction Band

The second characteristic concentration n_{cb} is evidenced most clearly by the striking change in the character of the NMR data for ^{29}Si which occurs at $n_d \cong 2\times10^{19}$ cm^{-3}. The most important signals are changes in the absolute magnitude of the Knight shift K, its concentration dependence, and the behavior of the so-called "Korringa product" K^2T_1T.

If the nuclei are coupled to a mobile system of independent electrons by an isotropic exchange interaction of the form $A\mathbf{I}\cdot\mathbf{S}$, where $\mathbf{I}$ is the nuclear spin and $\mathbf{S}$ the electronic spin, the Knight shift can be written in the form

$$K = (8\pi/3)\chi_s\langle|\psi(0)|_k^2\rangle, \tag{3}$$

where $\langle|\psi(0)|_k^2\rangle$ is the amplitude of the electron wave function at the nuclear site, averaged over the electrons on the Fermi surface, and χ_s is the electronic-spin susceptibility. For a degenerate system of free electrons, $\chi_s \propto n^{1/3}$, where n is the electron density.

If K is given by Eq. (3), and if, in addition, the nuclear-relaxation mechanism proceeds via the same $A\mathbf{I}\cdot\mathbf{S}$ interaction with the system of degenerate electrons, Korringa[16] showed that the value of K and of T_1 are related by a simple expression:

$$K\left[\frac{T_1T}{(h/4\pi k)(\gamma_e/\gamma_n)^2}\right]^{1/2} = 1, \tag{4}$$

where T is the Kelvin temperature, and the denominator contains only physical constants. Thus, values of the product on the left side of Eq. (4) become a sensitive test of the nature of the electron–nucleus interactions, and of certain properties of the electron system.

Figure 4 shows the data for K in Si:P as a function of concentration, taken from Table II of the paper by Sundfors and Holcomb.[11] (In plotting their data,

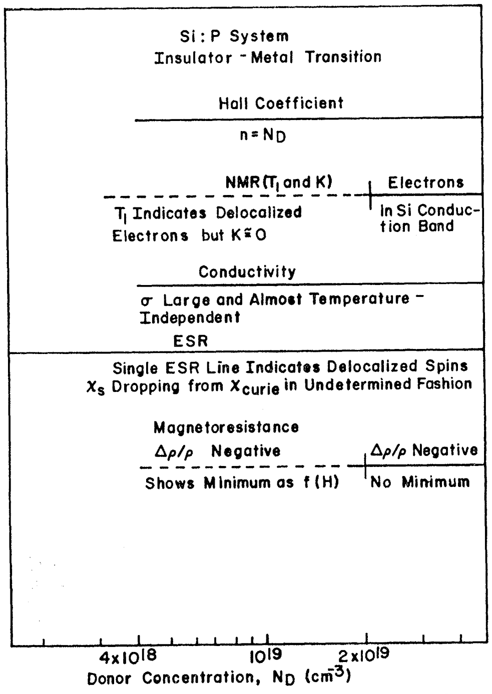

FIG. 3. Information bearing on the insulator–metal transition in Si:P, gathered from various kinds of experiments, is schematically summarized. The different experimental results are discussed more completely at various points in the text.

---

[15] M. E. Fisher and J. W. Essam, J. Math. Phys. **2**, 609 (1961).

[16] J. Korringa, Physica **16**, 601 (1950).

Sundfors and Holcomb placed several points incorrectly. They are correctly plotted here.) For samples with $n_d > 2\times10^{19}$ cm^{-3}, K is proportional to $n_d^{1/3}$, while values of K drop sharply away for $n_d < 2\times10^{19}$ cm^{-3}.

Table I gives values of the left-hand side of Eq. (4) for Si:P taken from Ref. 11.

Table I shows that, for $n_d > 2\times10^{19}$ cm^{-3}, the electron–nuclear interaction in Si:P agrees with the Korringa model very well—in fact, better than in any simple metals. This agreement probably occurs because Si:P is a low electron-density metal, and, hence, the effects of electron–electron interactions are relatively small.

One can now proceed to make a direct test of the nature of the electron wave functions in these high-concentration samples. If we assume the electron-spin susceptibility in Eq. (3) to be the Pauli susceptibility, χ_p, and if one uses the effective mass appropriate to the conduction band of Si in computing χ_p, one can use the value of K to calculate the mean electron-wave-function density at the ^{29}Si nuclei.[17] It is found to be, within about 30%, the same as that measured for electrons which are thermally excited into the conduction band at room temperature.[11,18]

We conclude that, for $n_d > 2\times10^{19}$ cm^{-3}, the electrons on the Fermi surface have the properties of those in the conduction band of pure Si, and, thus, that the Fermi level is in the conduction band of the host Si lattice. For $n_d < 2\times10^{19}$ cm^{-3}, the Knight shift decreases sharply, and does not have the value that would be expected for electrons in the Si conduction band. The Korringa relation is, moreover, not obeyed for $n_d < 2\times10^{19}$ cm^{-3} (see Table I). Thus, we take n_{cb} to have the value 2×10^{19}/cc for Si:P.

(In the discussion above, we have not attempted to employ experimental values of χ_s. There are a number of these in the literature.[19,20] None, however, appears to be entirely reliable. We discuss the susceptibility data in Sec. VI. The important thing to note here is that *none* of the experimental values shows χ_s to be *less than* χ_p in the range $n_d < 2\times10^{19}$. Thus, our conclusion that the drop in values of K in Fig. 5 is to be ascribed to changes in electron wave function as the Fermi level drops below the conduction band appears to be supported.)

TABLE I. Experimental relationship between Knight shift K and T_1T for Si:P samples (data are from Ref. 11). The material in this table is to be compared to the Korringa relation, Eq. (4).

n_d	$K[T_1T/(h/4\pi k)(\gamma_e/\gamma_n)^2]^{1/2}$
6.0×10^{18}	0.17
1.1×10^{19}	0.26
1.8×10^{19}	0.40
4.5×10^{19}	0.98
9.0×10^{19}	0.92
1.4×10^{20}	1.00

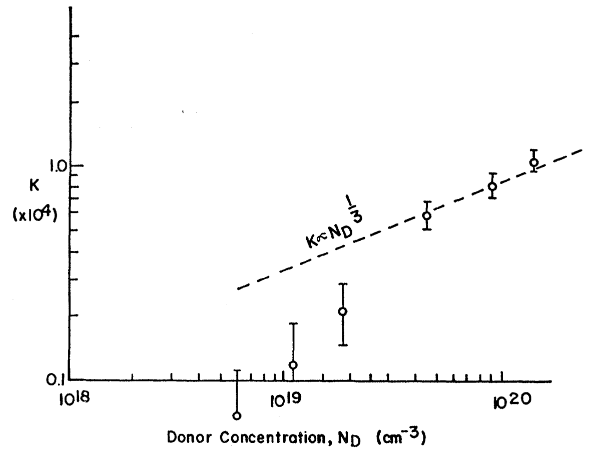

FIG. 4. The Knight shift of the ^{29}Si NMR signal, measured in Si:P at 1.6°K, is shown. This figure is a plot of data from Table II in Ref. 11.

Considering further evidence bearing on the question of the value of n_{cb}, we turn to the transport property data. Figure 5 gives our extraction of Hall-mobility μ_H values from the data of Yamanouchi *et al.*[9] The mobility, after rising rapidly at values of n_d just below and at n_c, rises more slowly for $n_d > n_c$, reaches a maximum at $n_d = 1.5\times10^{19}$ cm^{-3}, then drops onto what appears to be a $\mu_H \propto n^{-1}$ dependence. A similar decrease in Hall mobility observed for $n_d > 1\times10^{19}$ by Gränacher and Czaja[21] at 77°K is interpreted by them as arising from the merging of the impurity band and the conduction band; their interpretation supports our identification of the value of n_{cb}, although we consider the proper description to be not in terms of merging of bands, but rather in terms of the position of the Fermi level.

Figure 6 shows a synthesis of magnetoresistance data from Ref. 9. The magnetoresistance is negative, a property that seems to be common to heavily doped semiconductors in the metallic range. We discuss the negative magnetoresistance in more detail in Sec. V. At this point, we wish to note that the shape of the magnetoresistivity vs magnetic field curve is qualitatively different for samples having $n_d > 2\times10^{19}$ cm^{-3} than for samples with $n_d < 2\times10^{19}$ cm^{-3}. Moreover, the temperature dependence, suggesting thermal activation, vanishes for samples with $n_d > 2\times10^{19}$ cm^{-3}. We have no detailed interpretation of this behavior to offer, but simply note that these changes coincide with our value of n_{cb}.

---

[17] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), p. 201ff.

[18] R. G. Schulman and B. J. Wyluda, Phys. Rev. **103**, 1127 (1956).

[19] A. M. Portis, A. F. Kip, C. Kittel, and W. H. Brattain, Phys. Rev. **90**, 988 (1953); D. Jerome, Ch. Ryter, and J. Winter, Physics **2**, 81 (1966); S. Maekawa, J. Phys. Soc. Japan (Suppl.) **21**, 574 (1966); S. Maekawa and H. Ue, J. Phys. Soc. Japan **22**, 401 (1967).

[20] W. Sasaki, S. Maekawa, and N. Kinoshita, J. Phys. Soc. Japan **22**, 928 (1967).

[21] I. Gränacher and W. Czaja, J. Phys. Chem. Solids **28**, 231 (1967).

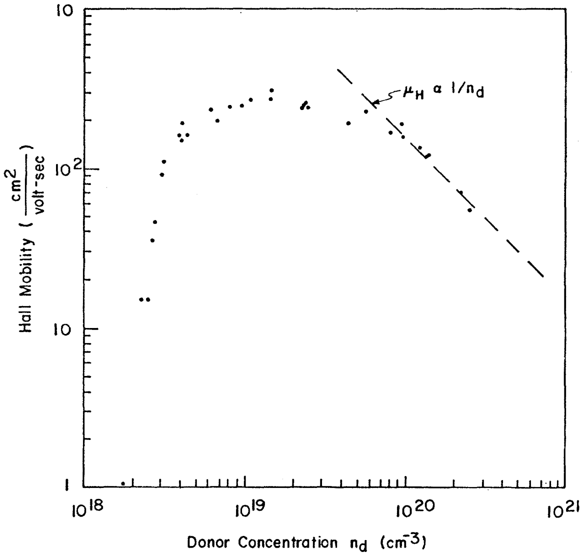

FIG. 5. The Hall mobility of Si:P, μ_H, is plotted as a function of donor concentration n_d. The Hall mobility has been calculated from the data of Ref. 9 for resistivity ρ and Hall constant R from the relation $\mu_H = R_H/\rho$.

The paper by Conwell[2] predicted that n_{cb} would occur at a concentration somewhat greater than 2×10^{19} in n-type Si. More recent work by Matsubara and Toyozawa[22] relates the Bohr radius of the donor electron in the hydrogenic model to the donor concentration at which the Fermi level should pass into the conduction band of the host lattice. They employ a parameter p, which is defined by the equation

$$p = 32\pi N a_H^3, \tag{5}$$

where N is the donor density and a_H is the Bohr radius for a hydrogenic model. The quantity a_H is defined by the relation

$$a_H = e^2/2\epsilon E_0, \tag{6}$$

where E_0 is the experimental ionization energy, and ϵ the dielectric constant. Their theoretical calculations predict that the Fermi level will pass into the conduction band at a value of $p \cong 8$. With this criterion, one would calculate

$$n_{cb} = (1/4\pi) a_H^{-3}. \tag{7}$$

E_0 has the value 0.045 eV for Si:P, giving the value of n_{cb} to be 3.1×10^{19} cm^{-3}.

It is useful to note that the Matsubara and Toyozawa criterion for n_{cb} can be related to the Mott criterion for n_c, Eq. (1), thus giving the relation

$$(n_{cb})_{\mathrm{MT}} = 16/\pi (n_c)_{\mathrm{Mott}} = 5.1 (n_c)_{\mathrm{Mott}}. \tag{8}$$

Intermediate Range

We now discuss the available evidence concerning the nature of the electron system in the intermediate-concentration range $3 \times 10^{18} < n_d < 2 \times 10^{19}$ cm^{-3}. This range of impurity concentration can be characterized by assuming the existence of a conducting "impurity band." Implications concerning the detailed nature of the electron system on the basis of the various types of experimental data available in this range are somewhat clouded. Consequently we only briefly survey the situation.

We have noted previously the fact that the small values of the NMR Knight shift for ^{29}Si in the impurity-band range of concentration, indicate a different electron–nucleus coupling for the electrons than that which is present when the electrons are in the Si conduction band. There appears to be little else in the way of sharp distinction of the electron properties in this range. The Hall mobility, Fig. 5, shows a small increase with increasing concentration in this range. The resistivity, Fig. 2, drops monotonically throughout the concentration range above n_c, with no clear break at n_{cb}.

The most interesting properties may well be the spin susceptibility and the magnetoresistivity. Unfortunately, interpretation of the experimental data for those two properties is sufficiently confused at this time that one does not feel confident in attempting to explain existing data. The susceptibility data are discussed in Sec. VI. The magnetoresistivity, Fig. 6, shows the minimum as a function of field through the intermediate range. It has previously been noted that this minimum is no longer visible in Si:P when $n_d > n_{cb}$. Interpretation of these data is not yet on firm ground. The possibility that the data imply the presence of localized magnetic moments is discussed in some detail in Sec. V.

Data for Si:As are much less extensive than those for

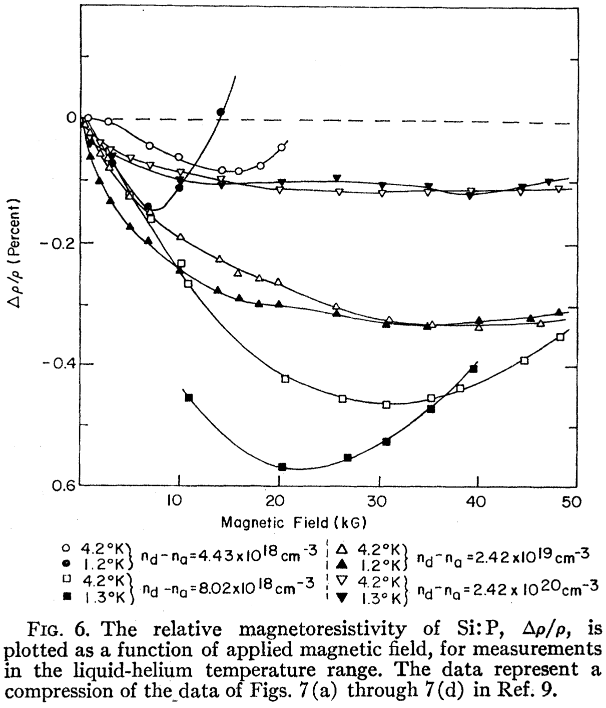

FIG. 6. The relative magnetoresistivity of Si:P, $\Delta\rho/\rho$, is plotted as a function of applied magnetic field, for measurements in the liquid-helium temperature range. The data represent a compression of the data of Figs. 7(a) through 7(d) in Ref. 9.

---

[22] T. Matsubara and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **26**, 739 (1961).

Si:P. The only significant difference expected is that the characteristic concentrations n_c and n_{cb} may be shifted up slightly because of the somewhat higher ionization energy—0.049 eV, compared to 0.045 eV for Si:P. We first consider experimental data bearing on the value of n_c. Hall-coefficient data of Morin and Maita[23] places n_c above 2.2×10^{18} cm^{-3} and below 2.7×10^{19} cm^{-3}. Swartz[24] has extensive transport-property data up to $n_d=3.0\times10^{18}$ cm^{-3}. No transition is evident at that concentration. Moreover, the Hall coefficient and resistivity are markedly temperature dependent. By qualitative comparison to the Hall-coefficient data of Yamanouchi *et al.*[9] for Si:P, these Swartz data suggest a value of n_c higher than the value of 3×10^{18} cm^{-3} for Si:P, in agreement with one's expectations. The bulk-susceptibility data of Sonder and Stevens[25] for Si:As, by comparison to that of Sasaki, Maekawa, and Kinoshita[20] for Si:P, also suggests a displacement of corresponding effects to higher concentration (see Fig. 10 and discussion in Sec. VI). In general, however, experimental data are insufficient to pin down the value for n_c as closely as has been done for Si:P. To our knowledge, there is no sharp evidence bearing on the value of n_{cb} in Si:As.

III. GERMANIUM

The metallic transition in n-type germanium occurs at a donor concentration which is one order of magnitude smaller than the transition concentration in silicon. This shift is not surprising, on the basis of the Mott formula, Eq. (1), since the "Bohr radius" of the donor electron in Ge is approximately twice the size of the "Bohr radius" of the donor electron in Si.

There is not, of course, one single metallic transition concentration for Ge, but rather a different transition concentration corresponding to each donor species. The dependence on donor species is more pronounced in Ge than in Si, because of the larger percentage spread in ionization energies for donor centers in Ge.

Delocalization of Electrons

Measurements by Fritzsche of the Hall coefficient and resistivity of Ge:Sb[10,26] show complete carrier delocalization at $n_d=1\times10^{17}$ cm^{-3}. Resistivity measurements[26] show $n_c\cong2.5\times10^{17}$ for Ge:P and $n_c\cong3\times10^{17}$ for Ge:As.

Fritzsche, in his paper on Ge:Sb,[10] proposed that the transition from nonmetallic to metallic conduction can be identified precisely by observing the effect of compensation on samples. When $n_d>n_c$, compensation increases the resistivity by decreasing the number of mobile carriers and increasing the number of scattering centers, whereas when $n_d<n_c$ compensation decreases the resistivity by increasing the number of empty centers between which carriers can tunnel. (This tunneling is the mechanism for nonmetallic impurity conduction.[7]) Thus, the metallic transition should occur at an impurity concentration such that compensation neither increases nor decreases the resistivity. We have not emphasized Fritzsche's method for identifying n_c because the method has rarely been employed in practice. The only work known to us in which the method was employed consists of Fritzsche's own study of Ge:Sb[10] and a later study of Ge:Sb by Yamanouchi.[27] The resistivity and Hall measurements by Yamanouchi yield the same value for n_c as had been obtained by Fritzsche.

Fermi Level into Conduction Band

Evidence bearing on the value of n_{cb} is not as clear for n-Ge as for Si:P. A determination of n_{cb} through NMR, similar to that done for Si:P,[11] would be more difficult in n-Ge than in n-Si, although it would not be impossible. Wyluda measured[28] T_1 for samples of n-Ge (dopant unspecified). Since his primary interest was in nuclear quadrupolar relaxation processes in pure Ge, only one of his samples had $n_d>n_c$. His data for that sample cannot be used to test the constancy of T_1T, because the temperatures at which he measured T_1 are comparable to or greater than the Fermi temperature for the electron system of the sample.

Although there are, therefore, no NMR measurements for n-Ge comparable to those on Si:P, there are other measurements which bear on n_{cb}. Mott and Twose[7] have pointed out that, for samples having n_d somewhat above n_c, the bump at $T=20°$–$250°$K in the graph of the Hall coefficient vs $1/T$ suggests the existence of an impurity band which has not merged with the conduction band of the host Ge (hence, the Fermi level is not in the conduction band of the host Ge). The data in Ge:Sb[10] show this bump vanishing at a value for n_d of about 1×10^{18} cm^{-3}.

The low-temperature bulk-susceptibility data are consistent with this picture. The values of $|\chi|$ for Ge:Sb and Ge:As[29] rise sharply as a function of n_d, the rise beginning for n_d somewhat less than n_c.[30] As shown in Fig. 7, $|\chi|$ continues to increase sharply as a function of n_d throughout the region $n_c<n_d<1\times10^{18}$ cm^{-3}. For Ge:As, $|\chi|\propto n_d^{1/3}$ for $n_d>1\times10^{18}$. This change in concentration dependence suggests that $n_{cb}\approx1\times10^{18}$ for Ge:As. As can be seen from Fig. 7, the donor-concentration dependence of $|\chi|$ in Ge:Sb is quite different from that for Ge:As. It appears from the data in Fig. 7 that for Ge:Sb, an interpretation similar to that for Ge:As places n_{cb} somewhere between 5×10^{17} and 1×10^{18} cm^{-3}.

The mobility for n-Ge[31–33] as a function of donor concentration resembles that for Si:P shown in Fig. 5.

---

[23] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1955).

[24] G. A. Swartz, J. Phys. Chem. Solids **12**, 245 (1960).

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

[26] H. Fritzsche, Phys. Rev. **125**, 1552 (1962).

[27] C. Yamanouchi, J. Phys. Soc. Japan **18**, 1775 (1963).

[28] B. J. Wyluda, J. Phys. Chem. Solids **23**, 63 (1962).

[29] The bulk susceptibility in n-Ge is dominated by the diamagnetic component because the effective mass is small.

[30] D. H. Damon and A. N. Gerritsen, Phys. Rev. **127**, 405 (1962).

[31] Y. Furukawa, J. Phys. Soc. Japan **17**, 630 (1962).

[32] M. Cuevas and H. Fritzsche, Phys. Rev. **137**, A1847 (1965).

[33] M. Cuevas and H. Fritzsche, Phys. Rev. **139**, A1628 (1965).

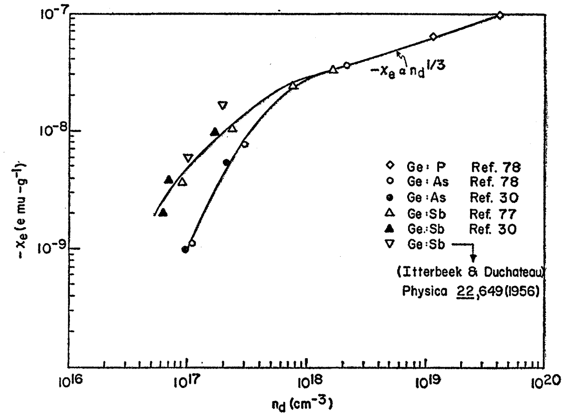

FIG. 7. The magnetic susceptibility of the carrier system in heavily doped Ge is given as a function of donor concentration n_d. The susceptibility of pure Ge has been subtracted from experimental data to yield these values. (This figure is a slight modification of Fig. 6 from Ref. 30 and is reproduced with permission of the authors.)

The mobility, which is an increasing function of n_d for $n_d < n_c$, continues to increase when $n_d > n_c$, reaching a maximum at $n_d \sim 10^{18}$ cm^{-3}. The mobility then decreases somewhat at higher values of n_d. One surprising feature for n-Ge is the fact that the maximum in the mobility occurs for Ge:As at a smaller donor concentration than for Ge:Sb.[33]

The magnetoresistance measurements on heavily doped n-Ge show many of the properties discussed above for n-Si samples (cf. Fig. 6). At low temperatures a negative magnetoresistance is observed.[34–40] The magnetoresistance becomes increasingly negative as temperature decreases below 4.2°K, the temperature dependence weakening as n_d increases (see Refs. 35–38). The magnetoresistance becomes positive at temperatures in the range between 4.2° and 77°K. The particular temperature at which the magnetoresistance becomes positive depends on the particular sample.[36–38] For Ge:Sb, $|\Delta\rho/\rho|_{\max}$ increases with n_d up to $n_d = 5\text{–}7 \times 10^{17}$,[41] and decreases thereafter.[36] Unlike the case of Si:P shown in Fig. 6, each of the curves for $\Delta\rho/\rho$ vs H for n-Ge—even at the highest donor concentrations—passes through a definitely identifiable minimum,[35,36,38] instead of apparently saturating. For example, the curve for a Ge:As sample at 4.2°K, having $n_d = 1.2 \times 10^{19}$ cm^{-3}, shows the usual negative (transverse) magnetoresistance at low magnetic field, but with the magnetoresistance increasing at higher fields and finally becoming positive at 20 kG.[38]

As mentioned in Sec. II, Matsubara and Toyozawa[22] have developed a theory which gives the value of n_{cb}. Substituting the appropriate numbers into their formula [Eq. (7)] we obtain

$$n_{cb} = 7.2 \times 10^{17} \text{ cm}^{-3} \text{ for Ge:Sb},$$

$$n_{cb} = 1.7 \times 10^{18} \text{ cm}^{-3} \text{ for Ge:As}$$

(n_{cb} for Ge:P should be essentially the same as for Ge:As.)

These results are considerably larger than the $n_{cb} = 2.9 \times 10^{17}$ Matsubara and Toyozawa themselves calculated for Ge:Sb.[22] In obtaining their result, Matsubara and Toyozawa used a Bohr radius of 65 Å. As noted earlier, we have calculated the Bohr radius from the impurity ionization energy (in keeping with the way Matsubara and Toyozawa defined the Bohr radius in their equations). This procedure leads to "Bohr radii" for Ge:As and Ge:Sb that are substantially smaller than 65 Å, and, hence, to larger values of n_{cb} than those obtained by Matsubara and Toyozawa. Recently, Majlis[42] used a Monte Carlo technique to calculate the density of states and the Fermi energy in heavily doped Ge. He also assumed a "Bohr radius" of 65 Å (using the same definitions as Matsubara and Toyozawa), and found $n_{cb} = 6 \times 10^{17}$ cm^{-3}.

ESR Measurements

ESR in n-Ge has been experimentally more difficult than in n-Si. However, several experiments have been performed, and some of the results are of interest here. The ESR spectrum in Ge:As has been found to consist of a single line for n_d as small as 6×10^{16} cm^{-3}, the linewidth being highly anisotropic.[43] An ESR spectrum for Ge:P, consisting of a single line, has been observed at a donor concentration reported to be 10^{17} cm^{-3}.[44] The linewidth for Ge:P is also anisotropic. The linewidth is believed[44] to arise from a spread in electron g values induced by strains in the crystals and which is incompletely averaged out by motional narrowing. Wilson[43] has plotted the line width of the motionally narrowed ESR line as a function of n_d, for Ge:P and Ge:As. The linewidth decreases with increasing n_d, in a fashion similar to the decrease of the ESR linewidth in Si:P for samples with $n_d < n_c$.[45] Wilson's measurements on Ge:As and Ge:P extend in donor concentration only up to $n_d \approx 10^{17}$, so a more complete comparison cannot be made with the ESR data in Si:P.

Wilson also measured g values of the motionally

---

[34] W. Sasaki and R. de Bruyn Ouboter, Physica **27**, 877 (1961).

[35] W. Sasaki, J. Phys. Soc. Japan **20**, 825 (1965).

[36] M. Mirzabaev, B. M. Tuchkevich, and Yu. V. Shmartsev, Fiz. Tverd. Tela **5**, 1625 (1963) [Sov. Phys.—Solid State **5**, 1179 (1963)].

[37] G. Sadasiv, Phys. Rev. **128**, 1131 (1962).

[38] H. Roth, W. D. Straub, W. Bernard, and J. E. Mulhern, Jr., Phys. Rev. Letters **11**, 328 (1963).

[39] Y. Furukawa, J. Phys. Soc. Japan **17**, 630 (1962).

[40] Y. Furukawa, J. Phys. Soc. Japan **18**, 1374 (1963).

[41] Mirzabaev *et al.* (Ref. 36) have found that the Hall coefficient for their Ge:Sb sample with $n_d = 1.71 \times 10^{18}$ cm^{-3} shows a definite dependence on magnetic field (above 10 kG), whereas there exists no such H dependence for their sample having 1.71×10^{18} Sb/cm^3 (measurements were made up to 20 kG). This suggests that useful information may be gained from investigating the magnetic-field dependence of the Hall coefficient for $n_d > n_c$.

[42] N. Majlis, Proc. Phys. Soc. (London) **90**, 811 (1967).

[43] D. K. Wilson, Phys. Rev. **134**, A265 (1964).

[44] G. Feher, D. K. Wilson, and E. A. Gere, Phys. Rev. Letters **3**, 25 (1959).

[45] S. Maekawa and N. Kinoshita, J. Phys. Soc. Japan **20**, 1447 (1965).

narrowed line in the Ge:P and Ge:As samples discussed above.[43] The g values are isotropic[44] and, for donor concentrations up to 10^{17} cm^{-3}, they do not shift measurably from the values appropriate to electrons localized on the donors[43] ($g=1.56$ for Ge:P and $g=1.57$ for Ge:As.[44] In a similar set of measurements on Si:P, Kodera[46] found a constant g value, $g=1.999$, for the motionally narrowed line in samples with $n_d<3\times10^{18}$ cm^{-3}. For $n_d>3\times10^{18}$ cm^{-3}, Kodera found the g value to decrease. Thus, by comparison to Si, the constant g value in the Ge samples for $n_d<10^{17}$ cm^{-3} is consistent with the assumption that the transition to the delocalized state has not taken place at these concentrations. (It should be mentioned that Kodera's measurements on Si:P were made at 77°K, a temperature not too different from the Fermi temperature for a free electron gas having 3×10^{18} carriers/cm^3. Therefore, it would be useful to have the same measurements made at liquid helium temperature to ensure that the electronic properties measured are appropriate to the fully degenerate electron system.)

Thus, although there are special features in Ge because of the large g shift and large strain dependence of g, the ESR measurements in n-Ge reproduce both the general features and the ambiguities of the ESR measurements in n-Si.

IV. SILICON CARBIDE

6*H* SiC:N

Resistivity and Hall coefficient measurements by Lely and Kröger[47] and by Violina *et al.*[48] on the 6*H* polytype[49] of SiC doped with nitrogen (SiC:N) suggest electron delocalization at $n_d\approx2\times10^{19}$ cm^{-3}. These measurements were made at temperatures $T>90$°K.

NMR measurements have been made at 1.4°, 4.2°, and 77°K.[50,51] In 6*H* SiC:N, the ^{29}Si NMR line narrows with increasing temperature, for samples having donor concentrations as large as $n_d\cong6.0\times10^{19}$ (the upper limit in n_d for the 6*H* samples studied by NMR).[52] This line narrowing strongly indicates that there remain some bound electrons at low temperatures in these samples, the electrons being thermally freed at higher temperatures. A similar, but less pronounced, effect was found for ^{13}C. Moreover, T_1T is not constant for either ^{29}Si or ^{13}C (the ^{29}Si T_1 is virtually independent of temperature between 1.4° and 4.2°K for the samples having $n_d=1.9\times10^{19}$ and $n_d=4.2\times10^{19}$ cm^{-3}). The general behavior of T_1 vs T for both ^{29}Si and ^{13}C in these samples is such as to indicate a mixture of relaxation mechanisms. As a function of donor concentration, T_1 increases in the range $n_d=1.9-6.0\times10^{19}$ (Fig. 8), showing the effects of the donor delocalization.

The electron-transport and the NMR experiments suggest different values for n_c in 6*H* SiC:N. It may be that, indeed, $n_c\approx2\times10^{19}$, as indicated by the transport measurements; if so, the transition to delocalized electrons is not complete, with perhaps 10% of the electron spins remaining localized on donor sites or donor complexes. These localized spins would then give rise to the observed "nonmetallic" NMR properties reported. This "incomplete" metallic transition is a feature that apparently is not encountered in Ge or Si (unless it turns out to be connected with the same kinds of "localized moments" which have been reported for Ge and Si, and which are treated later in this article). It would be highly desirable for electron-transport measurements to be extended downward in temperature to the liquid-helium temperature range, to complete the picture for 6*H* SiC:N.

ESR studies of 6*H* SiC:N[53–56] have been made on samples with $n_d<1\times10^{19}$ cm^{-3}—i.e., for concentrations $n_d<n_c$. As n_d increases, the hyperfine lines in the ESR spectrum begin to disappear, and a central line grows.[57–59] At $n_d\cong1\times10^{19}$ the hyperfine structure is not visible at 77°K,[53,55] but very weak hyperfine satellites are visible at 1.2°K.[55]

Determination of a value for n_{cb} for 6*H* SiC:N has not been possible. At nitrogen pressures adequate to give concentrations greater than $n_d\approx6\times10^{19}$, that is, for pressures more than 1 atm, the cubic polytype β-SiC results from the crystal growth process.[50,51,60] Thus, the NMR measurements establish a lower limit for n_{cb} of about 6×10^{19} cm^{-3}. A calculation of the value

---

[46] H. Kodera, J. Phys. Soc. Japan **21**, 1040 (1966).

[47] J. A. Lely and F. A. Kröger, in *Proceedings International Colloquium Partenkirchen*, M. Schön and H. Welker, Eds. (Interscience Publishers, Inc., New York, 1958), p. 525.

[48] G. N. Violina, Yeh Liang-hsiu, and G. F. Kholuyanov, Fiz. Tverd. Tela **5**, 3406 (1963) [Sov. Phys.—Solid State **5**, 2500 (1964)].

[49] For a discussion of polytypism and the properties of SiC polytypes, see A. R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (John Wiley & Sons, Inc., New York, 1966).

[50] M. N. Alexander, Ph. D. thesis, Cornell University, Ithaca, N.Y. 1967 (unpublished).

[51] M. N. Alexander, Phys. Rev. **172**, 331 (1968).

[52] A warning on quoted nitrogen concentrations in SiC should be made. Analysis for nitrogen in SiC is extremely difficult. In the NMR experiments (Refs. 50, 51, 64) the nitrogen donor concentration was obtained by use of a graph in Ref. 47 which relates nitrogen concentration in SiC to the pressure of nitrogen gas during the growth of the SiC. The extrapolation of this graph to higher concentrations was checked at 35 atm of N$_2$ pressure and was found (Ref. 60) to be good. Use of the graph in Ref. 47 in assigning donor concentrations for the NMR samples probably makes the donor concentrations quoted for NMR measurements reasonably consistent with those quoted for electron-transport measurements (Ref. 47). However, one feels uncomfortable without reliable chemical analysis.

[53] J. S. van Wieringen, Ref. 47, p. 367.

[54] H. H. Woodbury and G. W. Ludwig, Phys. Rev. **124**, 1083 (1961).

[55] G. E. G. Hardeman, J. Phys. Chem. Solids **24**, 1223 (1963).

[56] A. I. Veinger, Fiz. Tekh. Poluprov. **1**, 20 (1967) [Sov. Phys.—Semicond. **1**, 14 (1967)].

[57] Veinger (Ref. 56) estimated donor concentrations by comparing ESR line intensities of his SiC:N samples with the line intensity of a calibrated sample of DPPH. This gives the density of paramagnetic centers. However, the density of paramagnetic centers is less than the total density of donors when the donor concentration is large enough so that electrons from different donor sites interact with each other (Refs. 53, 58, 59). An extremely rough estimate of the true donor concentration on Veinger's samples might be made through use of the data in Ref. 53.

[58] E. Sonder and H. C. Schweinler, Phys. Rev. **117**, 1216 (1960).

[59] C. P. Slichter, Phys. Rev. **99**, 479 (1955).

[60] G. A. Slack and R. I. Scace, J. Chem. Phys. **42**, 805 (1965).

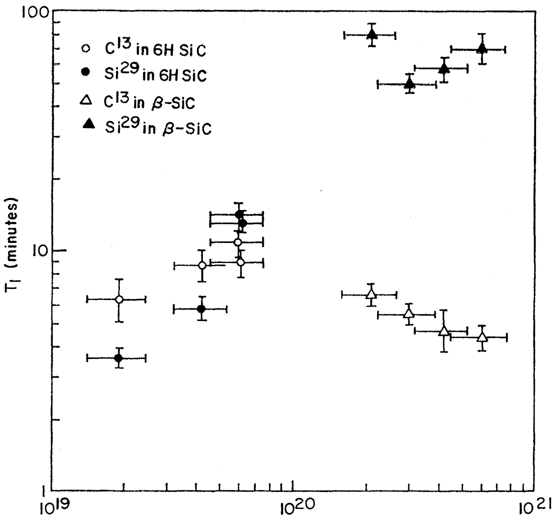

FIG. 8. The nuclear spin-lattice relaxation time, T_1, is shown for both the ^{29}Si and ^{13}C spin systems in SiC:N, as a function of nitrogen concentration. All measurements were made at 1.4°K by direct transient methods. It should be noted that for values of n_d below 10^{20} cm^{-3}, the SiC was in the *6H* polytype structure, whereas, for values of n_d above 10^{20} cm^{-3}, it was in the cubic or β structure.

of n_{cb} via the Matsubara–Toyozawa theory,[22] using 0.20 eV as a "typical" donor ionization energy,[61] yields $n_{cb}=1.7\times10^{21}$ cm^{-3}. This number must be treated with skepticism, since the effective mass theory should not apply well to *6H* SiC:N (the Bohr radius as measured by ENDOR[55] is 8 Å).

β-SiC:N

Considerably less work has been done on β-SiC than on *6H* SiC, partly because good pure single crystals of β-SiC have until recently been difficult to obtain.[62,63] The only study of the electron system at high donor concentration has been made via NMR.

The NMR data[50,51,64] for nitrogen-doped β-SiC show quite different coupling of the electron system to the silicon and carbon sublattices. Thus, as can be seen in Fig. 8, the ^{29}Si T_1's are an order of magnitude larger than the ^{13}C T_1's; the ^{13}C T_1's have a magnitude consistent with that observed for ^{29}Si and ^{13}C T_1's in the *6H* SiC:N samples. The donor concentration dependence of the ^{13}C T_1's is consistent with what should be expected for a degenerate electron system. The ^{13}C Knight shifts are observable, have a dependence on n_d similar to that shown for Si:P at high donor concentration (Fig. 4), and agree with the Knight shifts predicted via the Korringa relation[16] from the T_1's. The Knight shift for ^{29}Si is not observable. T_1T is constant, at liquid helium temperatures, for ^{13}C; although T_1T is not quite constant for ^{29}Si, the deviations from T_1T are small, and can be ascribed to nuclear relaxation to paramagnetic impurities (through spin diffusion), since the observed T_1's are so long.

The picture that thus emerges from the NMR data is that the electron system in the β-SiC:N samples for $n_d>2\times10^{20}$ cm^{-3} is degenerate, and that the electron probability density is considerably greater on the carbon sublattice than on the silicon sublattice. This latter property can be interpreted[50,51] on the basis of band-structure calculations[65,66] as indicating that the electrons in the β-SiC:N samples are in states appropriate to the conduction band of the host β-SiC, for $n_d>2\times10^{20}$.

We thus conclude $n_{cb}<2\times10^{20}$ cm^{-3} for β-SiC:N. No other data presently exist, to our knowledge, from which reliable values of n_c or n_{cb} can be inferred for β-SiC.

V. THE ORIGIN OF THE NEGATIVE MAGNETORESISTANCE

The existence of negative magnetoresistance in *n*-Si and *n*-Ge has been discussed earlier. This phenomenon has been observed in a wide range of semiconductors[67]; thus it seems reasonable, in seeking an explanation of the negative magnetoresistance, to seek a general explanation rather than an explanation which exploits properties peculiar to a given material. Toyozawa has proposed such a general explanation,[68] and because it has received some attention in the literature, we shall discuss it briefly in this section.

Toyozawa begins by noting the similarities between the negative magnetoresistance in heavily doped semiconductors and the negative magnetoresistance encountered in Cu:Mn alloys, in which the negative magnetoresistance is due to magnetic moments localized on the Mn sites. In the event that a localized magnetic moment exists, one can write the resistivity $\rho(H)$ as consisting of $\rho_1(H)\propto(1+cM)$ and $\rho_2(H)\propto(1-cM)$, depending on whether the spin of the scattered conduction electron is parallel or antiparallel with the spin of the magnetic moment. Since the resistivities here are added in parallel, one finds

$$\Delta\rho/\rho\equiv[\rho(H)-\rho(0)]/\rho(0)\propto(-M^2). \qquad (8)$$

---

[61] D. R. Hamilton, W. J. Choyke, and L. Patrick, Phys. Rev. **131,** 127 (1963).

[62] W. E. Nelson, F. A. Halden, and A. Rosengreen, J. Appl. Phys. **37,** 333 (1966).

[63] J. S. Ziomek and P. B. Pickar, Phys. Status Solidi **21,** 271 (1967).

[64] M. N. Alexander and D. F. Holcomb, Bull. Am. Phys. Soc. **12,** 469 (1967).

[65] F. Bassani and M. Yoshimine, Phys. Rev. **130,** 20 (1963).

[66] F. Herman, R. L. Kortum, and C. D. Kuglin, Intern. J. Quantum Chem. **15,** 533 (1967).

[67] We make no attempt to provide anything more than a coarse sampling of references, to give the reader some feeling for the fact that negative magnetoresistance has been observed in many heavily doped semiconductors: for InSb, see Y. Katayama and S. Tanaka, Phys. Rev. **153,** 873 (1967); for PbS, see D. M. Finlayson and A. E. Mathewson, J. Phys. Chem. Solids **28,** 1501 (1967); for GaAs, see J. F. Woods and C. Y. Chen, Phys. Rev. **135,** A1462 (1964).

[68] Y. Toyozawa, J. Phys. Soc. Japan **17,** 986 (1962); Y. Toyozawa, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 104.

A general theory of the magnetoresistance of Cu:Mn was developed starting along this line, by Yosida.[69]

Toyozawa then, in this spirit of local moment theory, defines the quantity S as

$$S=\lim_{H\to 0}\{-[\rho(H)-\rho(0)]/\rho(0)\mathrm{H}^2\}, \tag{9}$$

where $S^{1/2}$ is a quantity which would be proportional to the susceptibility of localized spins [cf. Eq. (8)]. A plot by Toyozawa[68] of $1/S^{1/2}$ vs temperature, from experimental data, is shown in Fig. 9. In Fig. 9 it would appear that (for $T>1°\mathrm{K}$) the "susceptibility" $S^{1/2}$ follows a Curie–Weiss law with antiferromagnetic coupling.

Since there is no s–d interaction for doped semiconductors, as there is in Cu:Mn, the physical origin of local moments in semiconductors must be sought elsewhere. Toyozawa asserts it is to be found in variation of the density of donors (or acceptors) in the sample.[70] If, in a given region, the local density is n, where $n<n_c$, then in that region there will be localized electrons. (We are discussing samples in which $n_d=\bar{n}>n_c$, so that the bulk of the solid is "metallic.") If n is very much smaller than n_c, the delocalized electrons will not be able to tunnel into the region. But if n is almost as great as n_c, the mobile electrons will be able to tunnel into the region containing localized electrons, and strong interactions between the two kinds of electrons may be possible. It is to this mechanism that Toyozawa ascribes the local moment—a local polarization of the mobile electrons by localized electrons. This polarization is introduced, in part, to account for the fact that simple calculations, based on the experimental data, of the size of local moment necessary to account for the magnetoresistance data, have indicated the moment must be as much as tens of Bohr magnetons.[68,71] The conditions derived by Toyozawa for formation of a local moment are similar to those derived by Anderson[72] for the formation of local moments in transition metal alloys.

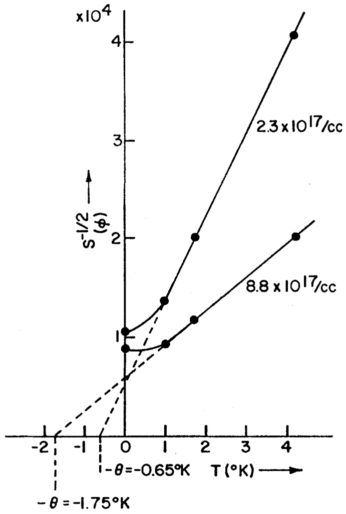

FIG. 9. The quantity $1/S^{1/2}$, where S is defined by Eq. (9), is plotted as a function of temperature. The data were obtained from magnetoresistance measurements in Ge:Sb by Sasaki and co-workers. (Figure 9 is a reproduction of Fig. 1 from Ref. 68, reproduced with permission of the author.)

This theory gives a qualitative agreement with many aspects of the magnetoresistance data. On the basis of the theory, however, one should expect the negative-magnetoresistance effect to disappear at high donor concentrations. This disappearance is not observed for n-Ge[34–40] or for n-Si,[8,9,73] although the negative-magnetoresistance effect is smaller at high concentrations.

Roth *et al.*[38] have measured magnetoresistance in heavily doped Ge and Si samples, and have fitted their results to the relation

$$\Delta\rho/\rho=aH^c+bH^2. \tag{10}$$

They found that at high-impurity concentrations and low temperatures, the value of c approaches $\frac{1}{2}$, with a less than zero. For n_d only slightly greater than n_c, c falls in the range 1.0 to 1.5.[74] This field dependence is not expected on the basis of the Yosida theory[69] employed by Toyozawa, which would predict that the negative component of $\Delta\rho/\rho$ would be proportional to H^2. This problem has not, to our knowledge, been investigated. The discrepancy might have its origin in the fact that the Yosida theory uses second-order perturbation theory. Sasaki,[35] for example, has ascribed some low-temperature resistance anomalies to the Kondo effect,[75] which results from use of a higher order

---

[69] K. Yosida, Phys. Rev. **107**, 396 (1957).

[70] This variation is merely a statistical fluctuation around the average impurity concentration; no systematic clustering of impurities is being assumed. If we place ourselves on a given impurity and ask how many other impurities are within a distance R of "our" impurity, the probability of finding N such impurities will be given by a Poisson distribution whose average is N_0.

[71] F. T. Hedgcock, Can. J. Phys. **45**, 1473 (1967).

[72] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[73] M. Balkanski and A. Geismar, Solid State Commun. **4**, 111 (1966). This paper shows the negative magnetoresistance disappearing at high donor concentration in n-Si. Curves of $\Delta\rho/\rho$ vs H are in strong disagreement with those of Refs. 8 and 9. We have accepted the data of Refs. 8 and 9 because there is detailed quantitative agreement between the data in Refs. 8 and 9 and because their results are much more detailed than the sketched graphs of Balkanski and Geismar.

[74] Roth *et al.* (Ref. 38) also found an anomalous positive magnetoresistance for p-Ge and p-Si, for which $|a|$ and c in Eq. (10) were the same as for the n-type samples. They conclude that the mechanism for the positive and negative magnetoresistances which depend upon H^c must have a similar origin. Sugiyama [K. Sugiyama, J. Phys. Soc. Japan **22**, 109 (1967)] has found that if a large uniaxial stress is applied along [100] to p-Ge, thus eliminating the degeneracy of the valence band maximum, the positive magnetoresistance disappears and is replaced by the familiar negative magnetoresistance. He concludes from this observation that band-structure effects are responsible for the sign of the magnetoresistance in p-Ge. The positive anomalous magnetoresistance of p-Ge and p-Si is, on the basis of the Toyozawa theory, an unexpected phenomenon.

[75] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

of perturbation theory than for the Yosida theory (see also Ref. 76). Moreover, if one accepts Toyozawa's explanation of the origin of the localized moment, one might ask whether a Born approximation (second-order perturbation theory) description of scattering from localized moments should be accurate: since in Toyozawa's theory the localized moment exists in regions of density $n<n_c$, the spatial dimension of the localized moment must have a typical "diameter" in excess of 100 Å (the "diameter" would be of the order $d>n_c^{-1/3}$). It is not immediately obvious that this would represent a "small" scattering potential, even though the wavelength for electrons on the Fermi surface would be large in such low electron density systems.

If local moments exist in semiconductors—especially if they have a moment of many Bohr magnetons—one would expect strong effects in magnetic resonance experiments. No effects were present for NMR in Si:P.[11] Although in 6*H* SiC:N the NMR results[50,51] could be interpreted as indicating the presence of localized electrons when $n_d>n_c$, more experiments will be needed in order to elucidate the nature of those localized electrons. Maekawa found anomalies in the ESR spin susceptibility[19] in Si:P, which he ascribed to the presence of localized moments (see Sec. VI of this article); calculations of the spin susceptibility from measurements of the bulk susceptibility[20] failed to show such anomalies.

The static susceptibility measurements of Hedgcock[77] and of Bowers[78] in Ge (see Fig. 7) have been reexamined by Hedgcock and Mathur.[79] There are no qualitative anomalies in these susceptibility data, in keeping with observations for Si:P. However, Hedgcock and Mathur did find that the measured susceptibilities do not agree with those they calculate from the Landau–Peierls theory. The difference $\Delta\chi$, where $\Delta\chi$ is defined to be $\Delta\chi=\chi_{\exp}-\chi_{\mathrm{LP}}$, is greater than zero and is such that, for "high temperature," $\Delta\chi$ is proportional to $1/(T+\Theta)$, where Θ is less than zero. Hedgcock and Mathur ascribe this discrepancy to the presence of localized moments. It should be noted, however, that both the sign of Θ and its magnitude obtained from this analysis differ from those inferred by Toyozawa[68] from the magnetoresistance data.

Hedgcock and Mathur used the Landau–Peierls formula because of Bowers's conclusion in his work[78] that the bottom of the Ge conduction band is parabolic. Bowers's measurements were, indeed, made in the donor concentration range in which $n_d>n_{cb}$. However, in their analysis, Hedgcock and Mathur also used data from Hedgcock[77] on two samples for which n_d is almost surely less than n_{cb}, as well as for two samples for which n_d is probably just slightly above n_{cb}. Hence, it is not obvious that Bowers's conclusion is applicable to all these samples. Moreover, calculations of the susceptibility from the simple form of the Landau–Peierls theory do not always lead to realistic results. Zawadski[80] has shown, for example, that deviations from parabolicity of the conduction band can have large effects on the magnitude of the susceptibility without, in certain cases, destroying the $n_d^{1/3}$ dependence which appears to imply the existence of a parabolic band. Interband effects can also be important[81] (see also Sec. VI).

In summary, we do not find analysis of the susceptibility data to provide convincing evidence for the existence of localized moments in Ge.

We note, finally, that Hedgcock and Mathur[82] have found an anomaly in the low-temperature thermoelectric power of *n*-Ge. The anomaly occurs at approximately the Curie–Weiss temperature inferred from magnetoresistance data, and the authors interpret the anomalous thermoelectric power as arising from localized magnetic moments.

To summarize Section V, our judgment is that the existence of localized moments in the heavily doped semiconductors is still questionable. Hence, the origin of the negative magnetoresistance remains in a similarly questionable state. No other mechanism has been quantitatively analyzed as a possible candidate.

VI. MAGNETIC PROPERTIES

Spin Susceptibility

In Sec. II, we noted that experimental values of the spin susceptibility χ_s seem to have a particularly important place in interpretation of the intermediate, impurity-band concentration range. However, existing experimental data appear to be inadequate. Figure 10 gives a synthesis of available experimental measurements performed at or very near 4.2°K. The static susceptibility measurements of Sasaki *et al.*[20] in Si:P and of Sonder and Stevens[25] in Si:As are the most complete. One should hasten to point out that the Sonder and Stevens data result from correcting the raw experimental values only for core diamagnetism of the silicon background. Sasaki *et al.*, on the other hand, state that their values also contain a correction for the diamagnetism of the conduction-electron system calculated using the Landau–Peierls formula. Thus, the apparent joining of the two sets of data is not meaningful. Comparison of the two sets of data is complicated by the shift of n_c to an unquestionably higher but not precisely measured value in Si:As.

---

[76] W. Sasaki and M. Nakamura, J. Phys. Soc. Japan **20**, 1092 (1965); W. Sasaki, J. Phys. Soc. Japan **20**, 2293 (1965).

[77] F. T. Hedgcock, J. Electron **2**, 513 (1957).

[78] R. Bowers, Phys. Rev. **108**, 683 (1957).

[79] F. T. Hedgcock and D. P. Mathur, Can. J. Phys. **41**, 1226 (1963).

[80] W. Zawadski, Phys. Status Solidi **3**, 1421 (1963).

[81] E. N. Adams, Phys. Rev. **89**, 633 (1953).

[82] F. T. Hedgcock and D. P. Mathur, Can. J. Phys. **43**, 2008 (1965).

Corrections to measured susceptibility, using the Landau–Peierls formula, in an attempt to obtain χ_s for metals have not been particularly successful. Hence, one must take the absolute magnitude of the Sasaki *et al.* data to be somewhat uncertain. However, the shape of the curve seems to bear out the assumption that nothing exceptional is happening to the susceptibility in the concentration range with n_d above 6×10^{18} cm^{-3} for Si:P. In particular, one certainly sees no sign of local-moment effects in the impurity-band region. Data at 77°K differ from the 4.2° data at the low-concentration end in the Si:P system, which is entirely consistent with the expected appearance of the first temperature-dependent correction term to the Pauli susceptibility. It should also be noted that the analysis of the Knight-shift data in Sec. II in terms of a change in electron wave function for $n_d<3\times10^{19}$ cm^{-3} seems to be supported, since no precipitous drop in χ_s is observed.

In principle, integration of the ESR absorption line gives χ_s unambiguously. However, good measurements are, in practice, very difficult to obtain. There are two problems: (1) Calibration of apparatus sensitivity must be done by comparison to a sample with known values of χ_s. Proper location of samples in and knowledge of the microwave field distribution is critical. (2) Broad wings in the ESR absorption line may be difficult to pick up experimentally.

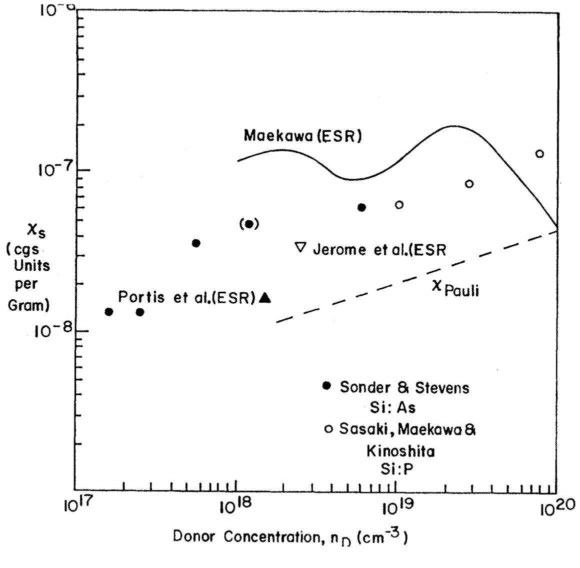

FIG. 10. Values of the electron-spin susceptibility, χ_s, measured by various workers at or near 4.2°K, is plotted as a function of donor concentration n_d. All data were measured on Si:P except that of Sonder and Stevens, which was measured on Si:As. The measurements by Maekawa (Ref. 19), Jerome, Ryter, and Winter (Ref. 19), and Portis, Kip, Kittel, and Brattain (Ref. 19) were made by integration of the ESR line. The latter two values on the graph were not given directly by the authors, but were calculated by us on the basis of statements in the papers describing calibration to $CuSO_4\cdot5H_2O$. Those of Sonder and Stevens (Ref. 25) and Sasaki, Maekawa, and Kinoshita (Ref. 20) are static measurements, corrected for core diamagnetism in both cases, and also for a Landau–Peierls diamagnetic term in the case of the Sasaki *et al.* data.

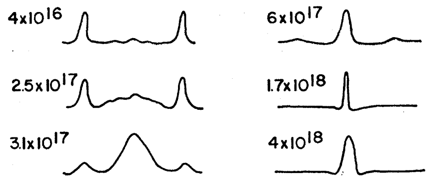

FIG. 11. Sketches are given of the shapes of ESR signals observed by Maekawa and Kinoshita (Ref. 13) in Si:P at 4.2°K at various donor concentrations.

Without casting aspersions on any particular measurement, we simply observe that there are substantial discrepancies among the measurements shown in Fig. 10. The static data are probably the most useful for the time being. The provocative peak in the Maekawa[19] data at $n_d=2\times10^{19}$ cm^{-3} has been interpreted to give evidence for the existence of localized moments, following up the Toyozawa hypothesis.[68] In the data of Sasaki, Maekawa, and Kinoshita,[20] obtained in an effort to check this feature, the peak does not appear. It should also be noted that the Maekawa ESR data show an unusual temperature dependence at liquid helium temperatures.

ESR Data

The most complete set of ESR measurements in heavily doped Si:P appear to be those of Maekawa and Kinoshita.[13] In Fig. 11 we have sketched the salient features of the ESR line shapes observed by them at various concentrations. (There appears to be a small discrepancy between these data and the earlier data of Feher[12] in the matter of the phosphorus concentration, above which only a single electron line is observed. Such a small discrepancy could arise from differences in compensation levels of the samples.) At first sight, the existence of a single ESR line above $n_d=7\times10^{17}$ cm^{-3}, rather than the hyperfine-split ESR line characteristic of electrons bound on donor sites, might seem to argue the presence of mobile electrons. Since this line appears at a donor concentration considerably lower than the metallic-transition concentration identified by Hall-effect data, the ESR data might appear to be inconsistent with the Hall data. On the next level of sophistication, however, one realizes that this single ESR line implies *only* that all electrons move over large, but not necessarily connected, clusters of donors. That is, the ESR results are sensitive to partial delocalization, whereas the dc transport results are not. A temperature independent resistivity and Hall coefficient indicates the "percolation" of electrons through the "lattice" of impurities.

Detailed comparison of the ESR data to determine its consistency with the model which places n_c at 3×10^{18} cm^{-3} is complicated by several factors, a number of

TABLE II. Insulator–metal transition in Group IV semiconductors.

Material	$(n_c)_{\text{exp}}$ (in cm^{-3})	Empirical value of x	$(n_{cb})_{\text{exp}}$ (in cm^{-3})	$(n_{cb})_{\text{M-T}}$ (in cm^{-3})
Si:P	3×10^{18}	0.20	2×10^{19}	3.2×10^{19}
Si:As	$\sim5\times10^{18}$			4.0×10^{19}
Ge:Sb	0.95×10^{17}	0.21	1×10^{18}	7.2×10^{17}
Ge:As	3.5×10^{17}	0.25		1.7×10^{18}
Ge:P	2.5×10^{17}	0.23		
β-SiC:N			$<2\times10^{20}$	
6H-SiC:N	$\sim2\times10^{19}$		$>6\times10^{19}$	$(\sim2\times10^{21})$
	$n_c=(x/a_H)^3$	$x_{\text{Mott}}=0.25$		

which have not been completely analyzed. Hence, we simply list these factors, without a final conclusion. Most of them are discussed rather more completely in the paper of Maekawa and Kinoshita.[13]

(1) The most important point may be the fact that the delocalization seen in ESR effects might be expected to occur at lower concentrations than that involved in the transport-property measurements. Delocalization which only involves extending the wave function over several centers, with no electron excitation, does not require that one create the electron–hole pair which appears naturally in the Mott theory of the transition. In other words, the exchange energy need only be of the order of magnitude of the magnetic hyperfine energy rather than comparable to the electron–hole binding energy.[83]

(2) The Poisson-distribution model, discussed in Sec. II, suggests that only when n_d reaches a value of about 1×10^{18} cm^{-3} should one see a significant contribution from electrons in large clusters with local density higher than n_c, which is 3×10^{18} cm^{-3}.

(3) It is not entirely certain that one is sampling all of the donor electrons in the ESR patterns which have been observed. For example, Maekawa and Kinoshita observe a "background line" whose origin is unknown.[13]

(4) Compensation may play a major role in promoting excursion of electrons over several donor centers.

Full interpretation of ESR data must await a more complete clustering model as well as careful consideration of the overlap requirements for formation of ESR clusters as opposed to the requirements for the completely delocalized electron system.

VII. SUMMARY

Table II summarizes our evaluation of presently established values of the two characteristic impurity concentrations, n_c and n_{cb}, in the group IV semiconductors.

ACKNOWLEDGMENTS

The authors wish to acknowledge useful discussions with Dr. J. A. Kaeck, Professor N. W. Ashcroft, Professor B. W. Maxfield, and Professor J. W. Wilkins of Cornell University, with Dr. R. J. Harrison and Dr. K. J. Tauer of the Army Materials and Mechanics Research Center, and Professor M. W. Klein of Brandeis University. Technical assistance through the Central Facilities of the Cornell Materials Science Center is gratefully acknowledged.

Discussion of Alexander and Holcomb's Paper

W. KOHN (University of California, San Diego): Is there any experimental data available on the frequency-dependent conductivity for the regime that you have discussed?

D. F. HOLCOMB: I know of none. Such measurements would certainly be interesting.

W. KOHN: It seems to me, particularly in virtue of the interplay that we have here between the classic type of Mott transition and the Anderson transition, that perhaps such frequency-dependent measurements might help to clarify the role which is played by these two effects. If I may make a very tentative comment that occurred to me while I was listening to you. It has to do with a point of principle in referring to disordered systems. We use the word "transition" here, and I think quite appropriately, but I think at the same time it might be useful to try and distinguish clearly between what appears to me to be two quite different uses of the word "transition." For example, if I can go back to what Professor Mott has called the Anderson model, that is, a model that was discussed by Anderson in terms of a one-electron Hamiltonian. You have a set of disordered centers and you ask whether because of the disorder an electron can in fact get away from a particular site to infinity or whether it remains confined to a given neighborhood. Now the kind of situation which Anderson suggests on an energy-level scheme would look something like this. There would be a range and I don't have to discuss that in any detail, let's say up to an energy E_0 so that below this energy level we have only nonconducting states and above this energy level we have some conducting states. Now in this kind of situation with a one-particle Hamiltonian you cannot have a transition in the thermodynamic sense at all. For a given arrangement of centers, as a function of temperature, you have a completely smooth dependence of the thermodynamic properties, or at a given finite temperature, as a function of concentration of the centers, you will necessarily have a smooth dependence. With a one-particle Hamiltonian it is a trivial matter to verify that has to be so. So the Anderson kind of transition, at least when it is discussed in terms of a one-particle Hamiltonian, is not a thermodynamic transition. Once you include interactions between the electrons it is possible that a thermodynamic transition may also be involved. I suggest however, that in this case it would have to be a first-order transition. I cannot visualize a second-order transition since I don't see any appearance of an order parameter. So summarizing what I have said just now, my feeling is that in such disordered systems there are two possibilities as far as thermodynamics is concerned, either no sharp transition in the thermodynamic sense at any finite temperature, or a first-order transition. On the other hand, I think that one can still make a quite sharp, precise distinction between metallic and insulating behavior

---

[83] R. H. Silsbee has emphasized the possible importance of this effect (private communication).

even in such disordered systems. But it is not a thermodynamic distinction. One can make a distinction in terms of conducting or insulating properties of a given *eigenstate* of the whole system. Again go back to the Anderson model for the noninteracting situation. It is clear that if I have Fermi statistics and I look at the ground state, and if my Fermi level falls below E_0, then I will have an insulator at zero temperature. But if the Fermi level falls above E_0, then I'll have a conductor. So given states, and the most relevant state is the ground state, even a disordered system can be clearly separated into one of the two categories, either conducting or insulating, even though thermodynamically there might be no sharp transition. I am not at all confident that I have explained what is in my mind but I think that is perhaps the best I can do. I'll perhaps make one more reference in case anyone wishes to pursue that a little further. I have discussed this kind of question in a paper about four years ago on the theory of the insulating state, and by *state* I mean state in the sense of quantum mechanics rather than quantum statistics. In that paper I tried to show that there is a quite sharp distinction between given eigenstates of a system (ordered or disordered) which, depending on a certain characterization, would have to be classified as conducting or insulating. That sharp distinction can exist both in ordered and disordered systems, but a thermodynamically sharp transition may not exist in disordered systems.

N. F. MOTT (Cambridge University): I entirely agree with Professor Kohn who has put more clearly than I the idea of an "Anderson transition" which I mentioned in my lecture. If one takes an Anderson band, that is, a band of atoms well separated, so that the tight binding approximation is valid, but with a random potential energy on each atom, then near each extremity of the band there will be a critical energy E_c to one side of which $\langle\sigma(0)\rangle$ vanishes and on the other side of which it does not. One ought not to deduce from percolation theory that there are "channels" along which at $T=0$ conduction can occur; such channels, when averaged over all configurations, will make a contribution to the conductivity which tends to zero as the size of the specimen is increased. This is discussed in a paper of mine to appear shortly (Ref. 25 of my introductory paper to this conference). But there is no phase change at E_c; by this I mean, as I believe Kohn does, that only at $T=0$ is there a discontinuity in any physical quantity at $E=E_c$. My guess at what happens at E_c is as follows: (a) There is a discontinuity in $\langle\sigma(0)\rangle$; (b) there is no discontinuity in the activation energy for conduction, which tends to zero as in Fig. 2 (a) and Fig. 6 of my paper; (3) the activation energy for conduction ought to tend to zero as $T\rightarrow 0$ because the electron will "hop" over large distances to find a site with nearly the same energy. This does not come out of the work of Miller and Abrahams, and a proper application of percolation theory to impurity-band hopping at finite T would be desirable.

R. W. KEYES (IBM): There is one other piece of experimental information that one might bring to bear on this question of whether the Fermi level is in the conduction band or not. It is relatively easy to take the band model for germanium and calculate the effect of the electrons in the band on the shear elastic constants [R. W. Keyes, IBM J. Res. Develop. 5, 266 (1961)]. The electrons in the conduction band can lower the energy of a strained crystal via the deformation potential effect and change the elastic constant C_{44}; a calculation of this effect is straightforward. The experiment is a little more difficult to do because one requires a fairly large sample of homogeneously doped material, but in germanium doped with Sb the experiment has been done at 1.5×10^{18} donors cm^{-3} [W. P. Mason and T. B. Bateman, Phys. Rev. **134**, A1387 (1964)]. The experiment is in good agreement with the theory [R. W. Keyes, Solid State Phys., **20**, 37 (1967)] showing that in Sb-doped Ge the Fermi level is in the conduction band at that concentration. I'd like to ask a question about the intermediate range. What about the effect of compensation? If all the electrons were in a band, one would expect that a little bit of compensation would increase the resistivity, but if one were still thinking of an impurity band with hopping playing a role, compensation might increase the conductivity.

D. F. HOLCOMB: Well, I think the only comment I can make is that it is not my expectation that hopping plays a role in this intermediate regime. The mobility is of the order of 10^2 to 10^3 in this intermediate regime. Looking both at temperature dependence and absolute magnitudes of quantities, I see no evidence for hopping in that impurity-band regime. I don't know whether there are any good compensation experiments in that regime or not.

H. FRITZSCHE (University of Chicago): I think that this question about the intermediate concentration range will be discussed by Dr. Mikoshiba and he will clarify many of these points. I noticed that you also emphasized the existence of a region between n_c and n_{cb}: the concentration of zero activation energy and the higher concentration at which the metallic behavior is more normal and the Fermi level is really in the conduction band. This intermediate metallic range has much in common with the intermediate concentration range on the nonmetallic side as is indicated by the anomalous magnetoresistance effect.

R. J. SLADEK (Purdue University): Just an experimental question. I noticed on your data for silicon carbide there seems to be a large error bar on the concentration. Since you had concentrations on the order of 10^{20}, why is there such a large error in the concentration? One would think that mass spec or some other type of analysis could determine the concentration more accurately.

M. N. ALEXANDER: Since I did those experiments, maybe I had better answer. Nitrogen analysis in silicon carbide is a very very dirty business. Specifically as regards mass spectroscopy, the ^{14}N and the ^{28}Si would interfere, so mass spectroscopy is out. Just about everything else that has been tried, to my knowledge, is out. My expert on this was the supplier, who is at the research division of Carborundum Company. What we did do to get the nitrogen concentrations was the following: Some workers at Philips Research Labs had prepared a graph based upon a kind of chemical analysis and also on Hall data; they plotted nitrogen concentrations for various samples as a function of the pressure of nitrogen gas in which the material was grown. There is a fair amount of scatter in the data—a look at it indicated that there would be a 20%–25% error in the concentration to be gotten off that graph. The nitrogen concentrations obtained constitute something better than a best guess. Some chemist, I hope, will really be able to crack this problem of analyzing for nitrogen in SiC. SiC is a very very recalcitrant material, and very few things can presently be done with it from a chemical standpoint. Just to give one example: Nitrogen analysis is something that is ordinarily routine chemistry; you usually dissolve some material in an acid, form some nitrogen bearing compound, and weigh it. I used to clean my samples by boiling them in aqua regia.