Magnetic properties of boron-doped silicon

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Measurements of the susceptibility between 1.25 and 300 K and of the magnetization from 0 to 50 kG are reported for a series of boron-doped silicon samples spanning the metal-nonmetal transition. As for Si:P, the magnetic properties change gradually in this field and temperature range as the boron concentration is varied across the transition. The susceptibility consists of (at least) two contributions: a component associated with the randomly distributed localized holes interacting via short-range antiferromagnetic exchange, and a component which maps the evolution of extended holes from a degenerate to a nondegenerate gas. The latter is a positive term which decreases in magnitude as the number of delocalized holes increases with increasing boron concentration. The impurity magnetization is not saturated at 1.25 K and 50 kG, and is small compared to the magnetization of an equivalent number of uncoupled boron impurities. Results for both the susceptibility and magnetization indicate that exchange plays a more important role in Si:B than it does in Si:P.

INTRODUCTION

Doped semiconductors undergo a transition from nonmetallic to metallic behavior as the dopant concentration is increased. The physical properties of these materials have been the subject of numerous investigations,[1] with recent interest centered on their behavior near the metal-nonmetal (M-NM) transition. Various properties, such as resistivity[2] and dielectric susceptibility,[3] are found to change rapidly with impurity concentration near the critical concentration N_c, while others, such as magnetic susceptibility and specific heat,[4] appear to change quite gradually in size and character as the concentration is varied across the M-NM transition.

The magnetic susceptibility[5–13] and magnetization[13] have been studied almost exclusively for donor systems, both on the insulating and on the metallic side of the transition. The susceptibility of insulating samples increases rapidly with decreasing temperature, due to the presence of local moments. These localized spins are associated with the randomly distributed impurity centers and interact via short-range antiferromagnetic exchange with a broad distribution of coupling strengths determined by the random interimpurity distance. Measurements[11,12] down to millikelvin temperatures show that the donor susceptibility does not follow a simple Curie or Curie-Weiss law, and can be approximately characterized by the expression $\chi \sim T^{-\alpha}$ with $0<\alpha<1$. This behavior has been ascribed to antiferromagnetic pairing of increasing numbers of neighboring moments as the temperature is reduced below the broad semicontinuous distribution of exchange energies. Good fits to the observed power-law dependence have been obtained by cluster calculations,[9–11,14] by a random-exchange model proposed by Andres *et al.*,[11] and in recent scaling studies of Bhatt and Lee.[15]

The susceptibility of "metallic" samples is Pauli-like, as expected for conduction electrons. However, in the "just-metallic" range of composition, as $N \rightarrow N_c$ from above, the temperature dependence of the susceptibility (at low temperatures) is unexpectedly strong, and there appears to be a gradual change to the behavior characteristic of insulating samples as the concentration is further decreased. This strong temperature dependence has been attributed to the persistence of local moments into the metallic range of composition and/or to the effect of strong electron correlations near the M-NM transition.[1,16–18]

Silicon has six equivalent conduction-band minima. Donors in silicon have no orbital angular momentum so that the magnetic moment is due solely to the spin. In contrast, the valence band consists of two degenerate bands (at $k=0$) with different curvatures giving rise to "heavy" and "light" holes, and a third spin-orbit-split band, so that the acceptor wave functions are relatively more complicated. The magnetic moments of the acceptors has both orbital and spin components with a ground state $J=\frac{3}{2}$. Relatively little experimental or theoretical work has been done to date on the susceptibility of acceptors in these materials.

In this paper we present and discuss the first systematic investigation of the magnetic susceptibility and magnetization of the p-type system Si:B containing boron acceptor concentrations spanning the M-NM transition.

EXPERIMENTAL PROCEDURE

Static susceptibility and magnetization measurements were obtained between 1.25 and 300 K in magnetic fields from 0 to 50 kG using a Faraday balance. The force on a sample was measured by a Cahn microbalance in the field of a superconducting magnet and the field gradient produced by a separate "reverse" Helmholtz coil. Measurements were obtained with an absolute accuracy of 3% and

a relative precision of 2×10^{-9} emu/g below and 1×10^{-9} emu/g above 4.2 K. Details of the experimental apparatus are published elsewhere.[19]

Grown by the Czochralski technique, the Si:B samples were obtained from G. A. Thomas of AT&T Bell Laboratories, except for the sample with the lowest boron concentration, which was obtained from Mulab. Samples used for the magnetic studies were cut in the form of parallelopipeds about $0.6\times0.6\times1.0$ cm^3 in size, and carefully etched and cleaned prior to measurement to eliminate surface contamination. Care was also taken to prevent condensation at low temperatures of trace amounts of oxygen on the surface of the sample. These proved to be important considerations, particularly for samples with low concentrations which have a small magnetic response. Two (or more) runs, some with intermediate etches, were performed on almost all samples to insure reproducibility.

Room-temperature resistivities were measured by the method of van der Pauw,[20] and the corresponding boron concentrations were determined from data of Thurber *et al.*[21] In the text and figures that follow, the samples are identified by the following labels:

Sample designation	Boron concentration (cm^{-3})
I1	3.6×10^{17}
I2	1.4×10^{18}
I3	3.0×10^{18}
T	3.5×10^{18}
M1	4.9×10^{18}
M2	7.7×10^{18}
M3	5.2×10^{19}

Based on determinations of the boron concentrations using the Irvin curve,[22] Staunton[23] found the critical concentration for Si:B to be 5×10^{18} cm^{-3} (in agreement with earlier work of Longo *et al.*[24]). Using the recent, more accurate data of Ref. 21, the same room-temperature resistivity implies a lower critical concentration of 3.6×10^{18} cm^{-3}. A careful determination of N_c of the type obtained by Rosenbaum *et al.*[2] for Si:P at millikelvin temperatures has yet to be carried out for Si:B. Resistivity measurements at room temperature, 77 K, and 4.2 K confirmed that three of the samples used in our experiments were metallic, three were insulating, and one was very near the M-NM transition. We have therefore labeled the insulating samples with the prefix I, metallic samples with the prefix M, and the sample near the transition is labeled T.

Homogeneity of the samples used for the measurement of susceptibility was checked by measuring the resistivities of thin slices cut from opposite ends of each parallelopiped. The boron concentration of all samples except the most concentrated was found to vary by less than 1%, which was the limit of precision determined by the measurement of resistivity. Opposite slices of the samples with the highest boron concentration differed in concentration by 3%. Measurements are also presented for one Si:P sample; its concentration was determined from the measured room-temperature resistivity using the curve of Mousty *et al.*[25] obtained from neutron-activation studies.

RESULTS AND DISCUSSION

Susceptibility

The measured magnetic susceptibilities of "pure" Si and the seven boron-doped Si samples are shown as a function of temperature in Figs. 1 and 2; a semilogarithmic scale is used for convenience and clarity, and the curves are drawn to guide the eye.

There are (at least) two distinct contributions to the susceptibility. The "knee" observed at $\sim$50 to 100 K, which is clearly evident for the metallic samples M1 and M2, persists into the insulating range of concentration and is a Pauli-like contribution associated with delocalized holes. This term maps the evolution of delocalized holes from a degenerate to a nondegenerate gas as the temperature is raised. In addition, there is a strongly-temperature-dependent component at low temperature which is associated with the presence of local moments in the insulating samples (I1, I2, and I3), which in turn appears to persist into the metallic range of composition, as evidenced by the low-temperature behavior found for sample M1.

An interesting feature of the high-temperature (delocalized hole) contribution in Si:B is that it is always positive relative to pure Si, unlike n-type Si (Ref. 26) and both n and p-type germanium (Ref. 27), for which the equivalent term is found to be negative. As the boron concentration is reduced toward the critical concentration N_c, the temperature of the "knee" associated with the degeneracy or Fermi temperature decreases, as expected. However, although one would expect the magnitude of this contribution to decrease as the number of delocalized holes decreases, it becomes, instead, unexpectedly larger as the critical concentration is approached, as seen most clearly for samples M2 and M3.

Gel'mont and McLure[28] have calculated the susceptibility of heavy and light holes in Si, Ge, and InSb and find that they yield, respectively, positive and negative terms which are large compared to their net sum. This calculation predicts a net negative susceptibility for all cases. Our measurements indicate that the heavy (rather than light) holes dominate in the case of Si:B and that the con-

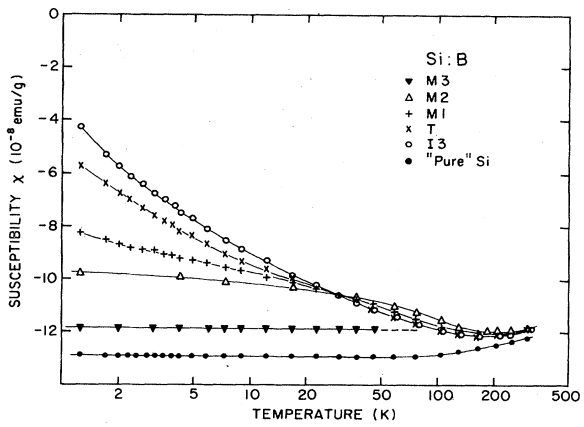

FIG. 1. Susceptibility of Si:B as a function of temperature. Note the semilogarithmic scale. The curves are drawn to guide the eye.

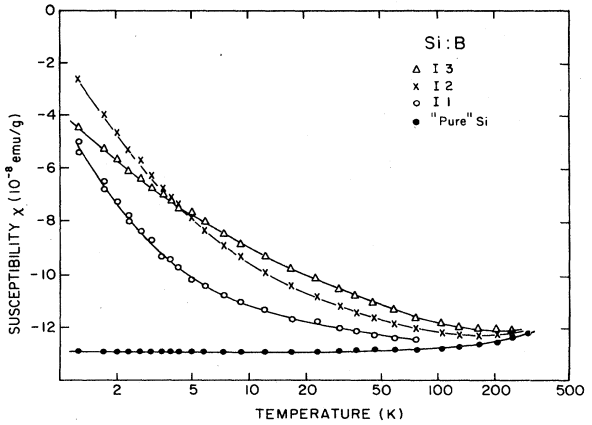

FIG. 2. Susceptibility of Si:B as a function of temperature. Note the semilogarithmic scale. The curves are drawn to guide the eye.

tribution of these heavy holes may become increasingly important as the M-NM transition is approached.[29]

The susceptibility associated with the boron was obtained by subtracting the large diamagnetic term of the Si host, and the results are presented on double-logarithmic plots in Figs. 3 and 4. Figure 3 shows four concentrations spanning the entire range from the most insulating to the clearly metallic, while Fig. 4 shows four concentrations near the transition, where T is a sample very close to the transition. The "knee," its increasing temperature with increasing boron concentration, and the expected Curie-law (T^{-1}) behavior at high temperatures are quite evident on these plots. It is also clear that the susceptibility at low temperatures does not follow a Curie law (or even Curie-Weiss behavior, as shown in Fig. 5) for any concentration. It is consistent, rather, with $T^{-\alpha}$, with $\alpha < 1$, as found for Si:P to much lower temperatures by Andres *et al.*,[11] and Murayama, Clark, and Sanny.[12]

The data for the four samples of Fig. 4 indicate that for temperatures down to 1.25 K there is a very gradual change in the behavior of the susceptibility as the M-NM transition is crossed. The persistence of the high-temperature term for insulating samples is not surprising. Based on the behavior of the electronic g value in "just-

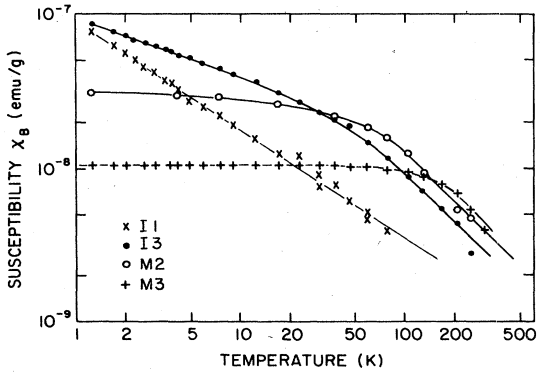

FIG. 3. Susceptibility of boron impurities in Si:B as a function of temperature. The curves are drawn to guide the eye.

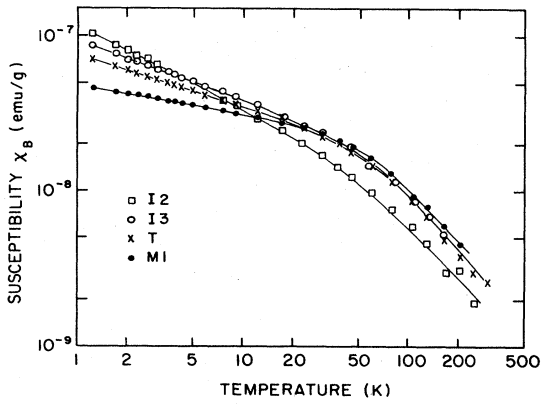

FIG. 4. Susceptibility of boron impurities in Si:B as a function of temperature. The curves are drawn to guide the eye.

insulating" Si:P at 4.2 K, Kodera[30] suggested that a substantial fraction of the electrons responsible for the susceptibility are delocalized to some extent. Furthermore, one would surely expect that localized holes become delocalized via thermally activated hopping in the temperature range encompassed by our measurements. On the other hand, the presence of a strong temperature dependence at low temperatures for metallic samples near the transition is not well understood, and may be due to the presence of localized moments and/or strong correlations between extended holes. In any event, it is clear that any abrupt or qualitative change in magnetic behavior which may be associated with the M-NM transition will require careful study at much lower temperatures, where effects of the M-NM transition manifest themselves more sharply and clearly.

As mentioned above, the data obtained in these studies down to 1.25 K are consistent with results for Si:P to lower temperatures[11,12] and show a power-law dependence $\chi \sim T^{-\alpha}$, where $\alpha < 1$ and varies with concentration N. The values of α deduced from our data (see Figs. 3 and 4)

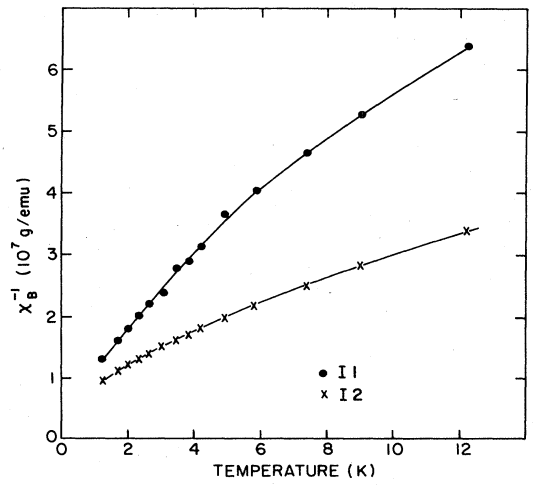

FIG. 5. Inverse susceptibility as a function of temperature for samples I1 and I2, illustrating a continuous downward curvature with decreasing temperature and consequent deviation from a simple Curie-Weiss law.

in the restricted low-temperature range covered by our measurements are plotted as a function of concentration in Fig. 6. The dashed line denotes values of α for Si:P obtained from the theoretical work of Bhatt and Lee[15] and experimental results of Andres *et al.*,[11] Murayama *et al.*,[12] and the present authors.[31] The data for Si:B show quite clearly that, for temperatures down to 1.25 K, a temperature-dependent term persists into the metallic range and does not fall abruptly to zero at the M-NM transition as one might naively expect. Furthermore, the exponent α is considerably smaller for Si:B than it is for Si:P. Thus, there is a more pronounced departure from Curie-law behavior for Si:B, indicating that exchange plays a more important role.

A simple model calculation for the susceptibility of a single pair of acceptors is presented in the Appendix. Exchange interactions in these materials vary over many decades due to the random distribution of the dopant and the short-range nature of the exchange. However, the spin-orbit interaction ($\sim$500 K) is large compared to most of the exchange energies, which have typical median values of $\sim$10 K at low impurity concentrations. We thus assume that the spin-orbit interaction is much larger than the spin-spin exchange coupling between acceptors, and use the Wigner-Eckart theorem to determine the energy-level diagram shown in Fig. 11(a).

The low-field susceptibility of an acceptor pair relative to the susceptibility of the two individual uncoupled acceptors is then given by the expression

$$\chi_p/2\chi_c = 0.8[(x+5x^3+14x^6)/(1+3x+5x^3+7x^6)] ,$$

where $x=\exp(-E_{ss}/9kT)$, E_{ss} is the spin-spin interaction between the two acceptors, T is the temperature, and $\chi_c = 5Ng^2\mu_B^2/4kT$, the susceptibility of an individual $J=\frac{3}{2}$ acceptor. The corresponding expression for a donor pair with $J=S=\frac{1}{2}$ is

$$\chi_p/2\chi_c = 4/[\exp(E_{ss}/kT)+3] ,$$

with $\chi_c = Ng^2\mu_B^2/4kT$ appropriate to $J=\frac{1}{2}$ moments.

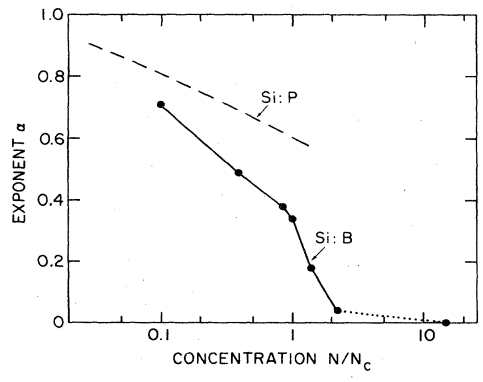

FIG. 6. Exponent α as a function of normalized concentration N/N_c where α is obtained for Si:B by fitting the low-temperature data (see Figs. 3 and 4) to the expression $\chi \sim T^{-\alpha}$. The dashed line denotes α for Si:P deduced from the work of Bhatt and Lee (Ref. 15), Andres *et al.* (Ref. 11), and Murayama *et al.* (Ref. 12). The lines are drawn to guide the eye.

The ratio $\chi_p/2\chi_c$ of the susceptibility of paired to uncoupled moments is shown as a function of kT/E_{ss} for acceptors and donors in Fig. 11(b). Deviations from 1 denote deviations from the Curie-law behavior of two uncoupled moments. Figure 11 (b) shows that acceptor pairs cause weaker deviations from Curie-law behavior than do donor pairs as the temperature is lowered to values comparable to and below the exchange energy E_{ss}. On the other hand, our experimental measurements indicate that deviations from a Curie law are more pronounced for acceptors. Our results thus imply that the exchange coupling E_{ss} is considerably stronger for acceptors than for donors.

A detailed comparison with our data will require a more complete calculation which takes into account the full distribution of exchange energies determined by the random spatial distribution of impurities and the detailed nature of their wave functions.

Magnetization

Magnetization data to 50 kG were obtained for all samples at several temperatures down to 1.25 K. We assume that the total magnetization can be written as separate terms due to the silicon host and boron, and that the silicon magnetization is linear with field:

$$M = M_{\rm Si} + M_{\rm B} = \chi_{\rm Si}H + M_{\rm LM} + M' .$$

Here, $M_{\rm LM}$ is due to local moments, and M' is a term associated with delocalized holes. Then,

$$\frac{dM}{dH} = \chi_{\rm si} + \frac{dM_{\rm LM}}{dH} + \frac{dM'}{dH} .$$

One expects the magnetization $M_{\rm LM}$ associated with localized moments to saturate in sufficiently high magnetic fields. If one assumes, in addition, that the delocalized hole magnetization is linear with field, then $M'=\chi' H$ and

$$\left.\frac{dM}{dH}\right|_{H\to\infty} = \chi_{\rm Si} + \chi' .$$

Data for dM/dH are shown in Fig. 7 for a single insulating sample at several temperatures. For insulating Si:B one expects the delocalized-hole contribution χ' to be zero, and dM/dH to approach the value $\chi_{\rm Si} = -12.9$ emu/g of pure Si at high magnetic fields. It is apparent that this is not the case in the available fields to 50 kG. The magnetization appears to consist of a Brillouin-like component which saturates at moderate fields and an additional portion which saturates much more slowly, as noted by Walstedt *et al.*[10] for CdS:In.

Figure 8 shows dM/dH at 1.25 K as a function of magnetic field for several boron concentrations. It is clear that the magnetization is far from saturation for all samples at 1.25 K and 50 kG (dM/dH has not reached a constant value). This is consistent, for insulating samples, with the broad distribution of exchange fields expected for these materials,[9–11,15] such that quite large external magnetic fields are required to uncouple the strongly bound moments which are separated by small distances in the spatially random distribution of impurities. The most in-

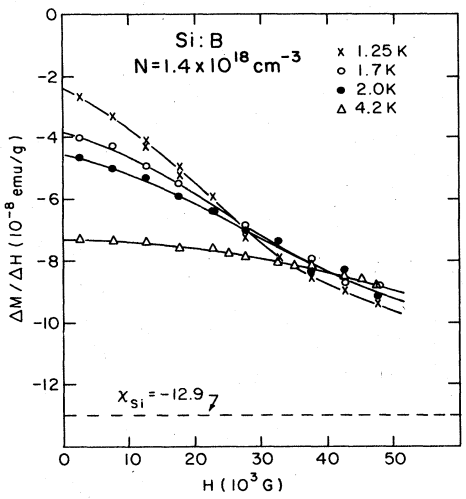

FIG. 7. $\Delta M/\Delta H$ as a function of magnetic field for Si:B sample I2 at several temperatures. The curves are drawn to guide the eye. The dashed horizontal line is the value for pure silicon.

sulating sample, I1, is reasonably close to the expected high-field value of $\chi_{Si}=-12.9$ emu/g. However, sample I2, whose boron concentration is less than half of the critical concentration N_c, is quite far from this value. This may be due to the fact that much higher fields are necessary to overcome very strong internal fields in this more concentrated sample. It is possible also that dM/dH approaches a different value $\chi_{Si}+\chi'$ at high fields, due to the presence at 1.25 K of a contribution χ' due to delocalized holes. We have undertaken measurements[32] to higher fields at lower temperatures to determine whether, how, and to what value saturation occurs in the metallic as well as in the insulating materials.

For perfectly free, noninteracting centers of magnetic moment $gJ\mu_B$, the magnetization is given by a Brillouin function:

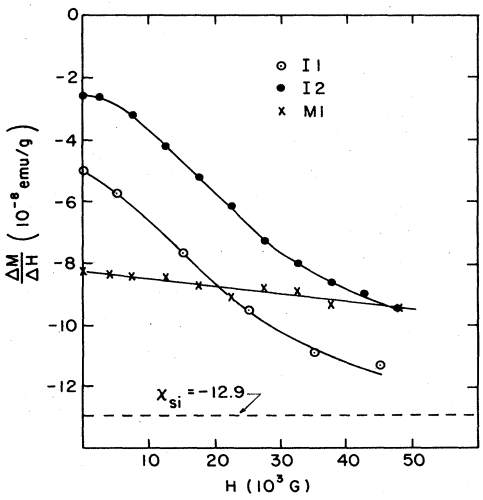

FIG. 8. $\Delta M/\Delta H$ as a function of magnetic field for several Si:B samples at 1.25 K. The curves are drawn to guide the eye. The dashed horizontal line is the value for pure silicon.

$$M_{\text{free}}(H,T)=NgJ\mu_B B_J(gJ\mu_B H/kT)\ .$$

M_{free} is the magnetization one might expect to approach at very high fields or very high temperatures, where field or thermal energies exceed all internal interaction energies. The ratio $M_B(H,T)/M_{\text{free}}(H,T)$, where M_B is obtained by subtracting $M_{Si}=\chi_{Si}H$ from the total measured magnetization M, represents the actual magnetization of N boron atoms relative to that of a set of N uncoupled moments. The departure of M_B/M_{free} from unity reflects the fact that moments interact with their neighbors, thus inhibiting their response to an externally applied magnetic field. M_B/M_{free} was calculated using $J=\frac{3}{2}$ and $g=1.2$ for boron in silicon,[33] the measured magnetization M, and the boron concentrations N deduced from resistivity measurements. Figure 9 shows M_B/M_{free} plotted as a function of magnetic field at several temperatures for the three insulating Si:B samples. Equivalent data are shown in Fig. 10 for a Si:P sample, where M_{free} was calculated using the values $g=2$ and $J=\frac{1}{2}$ appropriate to phosphorus donors.

It is apparent from the data of Fig. 9 that a fairly small fraction of the free moment magnetization is available, and that this fraction is smaller for the samples with

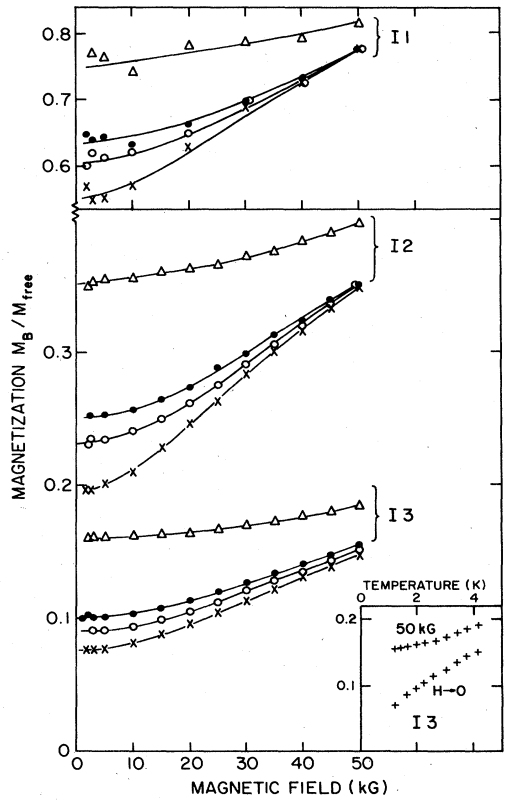

FIG. 9. M_B/M_{free} as a function of magnetic field, where M_B/M_{free} is the magnetization of the boron relative to the magnetization of an equal number of noninteracting moments (see text). Data are shown for three concentrations at ×, 1.25 K; ○, 1.7 K; ●, 2 K; △, 4.2 K. Curves are drawn to guide the eye. Note the broken scale. The inset shows M_B/M_{free} as a function of temperature at 0 and 50 kG for sample I3.

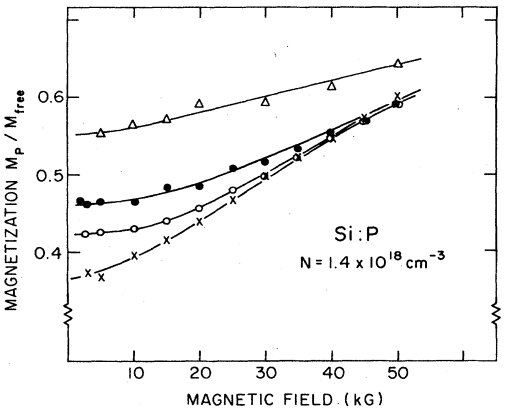

FIG. 10. M_P/M_{free} as a function of magnetic field for Si:P with concentration $N=1.4\times10^{18}$ cm^{-3}. Data are plotted for ×, 1.25 K; ○, 1.7 K; ●, 2 K; △, 4.2 K. Curves are drawn to guide the eye.

higher concentration, where the boron atoms are closer together and more strongly coupled by exchange. Comparison of sample I2 of Fig. 9 with data for the same concentration of phosphorus atoms in silicon shown in Fig. 10 indicates that an appreciably larger fraction is available in Si:P, thereby supporting our earlier contention that exchange and cluster formation are considerably more important in Si:B.

The data of Fig. 9 show that, for a given impurity concentration, neighboring magnetic moments are decoupled by raising either the magnetic field or the temperature (or both), thus causing an increase in the fractional moment M_B/M_{free}. Field energies at 50 kG clearly exceed thermal energies at 2 K but not at 4.2 K. Thus, at 1.25, 1.7, and 2 K the fractional moment approaches the same value as the magnetic field is raised to 50 kG, so that the field has decoupled moments whose exchange energies exceed 2 K, whereas raising the temperature to 4.2 K at this field uncouples additional magnetic centers.

SUMMARY AND CONCLUSIONS

We have measured the susceptibility between 1.25 and 300 K and the magnetization to 50 kG of a series of Si:B samples spanning the metal-nonmetal transition.

Delocalized holes contribute a positive susceptibility which unexpectedly decreases with increasing boron concentration. This is in contrast to the negative susceptibility observed in other doped semiconductors such as Si:P, Ge:P, and Ge:B. Following calculations by Gel'mont and McLure[28] for heavy and light holes in p-type semiconductors, the positive susceptibility of delocalized holes in Si:B can be attributed to the heavy holes whose role appears to become increasingly important as the M-NM transition is approached.

The localized holes contribute a term at low temperatures whose temperature dependence is weaker than a Curie law, and follows a power-law dependence $\chi\sim T^{-\alpha}$ with $\alpha<1$, as has been found over an extended temperature range[11,12] for Si:P. The departure from T^{-1} behavior has been ascribed to antiferromagnetic pairing of increasing numbers of neighboring local magnetic moments as the temperature is lowered and thermal energies fall below exchange energies of the randomly distributed boron atoms. The exponent α is smaller for Si:B than for Si:P, suggesting that exchange plays a more important role in Si:B.

The impurity magnetization of insulating Si:B is not saturated at 50 kG and 1.25 K, and the fraction of the magnetization available is small relative to the value expected for an equivalent number of free noninteracting moments, indicating that an appreciable number of boron atoms experience exchange fields in excess of 50 kG. The fraction of available magnetization decreases with increasing boron concentration, and increases with temperature and magnetic field, as expected. It is smaller than the corresponding fraction for Si:P, indicating again that exchange is more important in Si:B.

A more complete understanding of the magnetic behavior of doped semiconductors, particularly near the M-NM transition and in the "just-metallic" range of composition, will require further theoretical work and additional measurements at higher magnetic fields and lower temperatures. For p-type materials, theoretical work is needed to determine the behavior of acceptors and to elucidate the role of spin-orbit coupling.

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APPENDIX: SUSCEPTIBILITY OF ACCEPTOR PAIRS

The Hamiltonian for a system of two holes at sites 1 and 2 is taken to be

$$H=E_{sl}(\boldsymbol{l}_1\cdot\mathbf{s}_1+\boldsymbol{l}_2\cdot\mathbf{s}_2)+E_{ss}(\mathbf{s}_1\cdot\mathbf{s}_2)\ , \tag{A1}$$

where $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$ are the orbital-angular-momentum operators and $\mathbf{s}_1$ and $\mathbf{s}_2$ are the spin operators on sites 1 and 2. E_{sl} gives the magnitude of the spin-orbit exchange on a single site, and E_{ss} denotes the spin-spin exchange between two sites. The spin-orbit interaction in Si:B is $\sim$500 K, and although they encompass many decades, studies on Si:P indicate that at low concentrations typical median spin-spin exchange energies are $\sim$10 K. We therefore proceed on the assumption that $|E_{sl}|\gg|E_{ss}|$, so that each hole is locked into a state of total angular momentum $j_1=j_2=\frac{3}{2}(\mathbf{j}_i=\boldsymbol{l}_i+\mathbf{s}_i,\ i=1,2)$, since the localized holes have an orbital angular momentum characterized by $l_1=l_2=1$.

Thus, the states for the two-hole system can be charac-

terized by the square of the total angular momentum $\mathbf{J}=\mathbf{j}_1+\mathbf{j}_2$, and by the corresponding magnetic quantum number M, with J taking the values 3, 2, 1, and 0. For these states the spin-orbit part of the Hamiltonian is easily evaluated to be just E_{sl}, since

$$\boldsymbol{l}_i\cdot\mathbf{s}_i=(\mathbf{j}_i^2-\boldsymbol{l}_i^2-\mathbf{s}_i^2)/2\ ,\quad i=1,2$$

is diagonal in the above representation and has an eigenvalue of $\frac{1}{2}$.

The spin-exchange part of the Hamiltonian can be evaluated with the help of the Wigner-Eckart theorem as follows. We express the expectation value of s_i, $i=1,2$, in the $|\,j_i m_i\,\rangle$ representation:

$$\langle j_i m_i\,|\,\mathbf{s}_i\,|\,j_i m_i'\,\rangle=\langle j_i||s_i||j_i\rangle\langle j_i m_i\,|\,\mathbf{j}_i\,|\,j_i m_i'\,\rangle \tag{A2}$$

where $\langle j_i||s_i||j_i\rangle$ is a proportionality constant independent of m_i or m_i', and m_i is the magnetic quantum number corresponding to j_i. This proportionality constant can be evaluated by noting that

$$\langle j_i m_i\,|\,\mathbf{s}_i\cdot\mathbf{j}_i\,|\,j_i m_i\rangle=\langle j_i||s_i||j_i\rangle j_i(j_i+1)\ ,$$

and also

$$\langle j_i m_i\,|\,\mathbf{s}_i\cdot\mathbf{j}_i\,|\,j_i m_i\rangle=[j_i(j_i+1)-l_i(l_i+1)+s_i(s_i+1)]/2\ ,$$

so that for $j_i=\frac{3}{2}$, $l_i=1$, and $s_i=\frac{1}{2}$, we obtain

$$\langle j_i||s_i||j_i\rangle=\tfrac{1}{3}\quad\text{for } i=1,2\ . \tag{A3}$$

The expectation value of $\mathbf{s}_1\cdot\mathbf{s}_2$ between the states $|\,JM\,\rangle$ can then be written as

$$\begin{aligned}\langle JM\,|\,\mathbf{s}_1\cdot\mathbf{s}_2\,|\,JM\rangle&=\sum_{m_1,m_2}\sum_{m_1'm_2'}\langle j_1m_1j_2m_2\,|\,JM\rangle\langle JM\,|\,j_1m_1'j_2m_2'\rangle\langle j_1m_1'\,|\,\mathbf{s}_1\,|\,j_1m_1\rangle\cdot\langle j_2m_2'\,|\,\mathbf{s}_2\,|\,j_2m_2\rangle\\&=\tfrac{1}{9}\sum_{m_1,m_2}\sum_{m_2',m_1'}\langle j_1m_1j_2m_2\,|\,JM\rangle\langle JM\,|\,j_1m_1'j_2m_2'\rangle\langle j_1m_1'\,|\,\mathbf{j}_1\,|\,j_1m_1\rangle\cdot\langle j_2m_2'\,|\,\mathbf{j}_2\,|\,j_2m_2\rangle\\&=\tfrac{1}{9}\langle JM\,|\,\mathbf{j}_1\cdot\mathbf{j}_2\,|\,JM\rangle\ .\end{aligned} \tag{A4}$$

Noting that $\mathbf{j}_1\cdot\mathbf{j}_2$ is diagonal in the $|\,JM\,\rangle$ representation, with $\mathbf{j}_1\cdot\mathbf{j}_2=(\mathbf{J}^2-\mathbf{j}_1^2-\mathbf{j}_2^2)/2$, we obtain

$$\langle JM\,|\,\mathbf{s}_1\cdot\mathbf{s}_2\,|\,JM\rangle=\tfrac{1}{18}[J(J+1)-j_1(j_1+1)-j_2(j_2+1)]\ . \tag{A5}$$

This result was checked by evaluating $\langle JM\,|\,\mathbf{s}_1\cdot\mathbf{s}_2\,|\,JM\rangle$ using Clebsch-Gordan coefficients to express the states $|\,JM\,\rangle$ as linear combinations of the states which diagonalize the operators $\boldsymbol{l}_i^2$, l_{iz}, $\mathbf{s}_i^2$, and s_{iz}, $i=1,2$.

The energy E_J of state J is thus given by

$$E_J=E_{sl}-5E_{ss}/12+E_{ss}J(J+1)/18\ . \tag{A6}$$

The corresponding energy-level diagram is shown in Fig. 11(a).

The low-field susceptibility can now be deduced in a straightforward way as detailed below. The equilibrium population in state J,m_J is given by

$$N_{J,m_J}/N=\exp(-E_{J,m_J}/kT)\Big/\sum_{J=0}^{3}\sum_{m_J=-J}^{J}\exp(-E_{J,m_J}/kT)\ , \tag{A7}$$

where the energy of the J,m_J level in a magnetic field H is

$$E_{J,m_J}=E_J+m_Jg\mu_BH\ .$$

The magnetization for N atoms per unit volume is

$$M=\sum_J\sum_{m_J}m_Jg\mu_BN_{J,m_J}=Ng\mu_B\sum_J\sum_{m_J}m_J\exp(-E_{J,m_J}/kT)\Big/\sum_J\sum_{m_J}\exp(-E_{J,m_J}/kT)\ . \tag{A8}$$

When $\mu_BH\ll kT$, the exponential can be expanded,

$$\exp(-E_{J,m_J}/kT)=\exp(-E_J/kT)(1+m_Jg\mu_BH/kT)\ ,$$

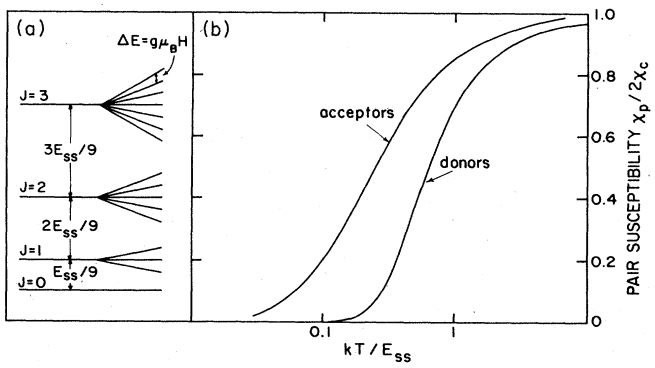

FIG. 11. (a) Energy-level diagram for acceptor pairs for $|E_{sl}|\gg|E_{ss}|$. (b) The ratio of susceptibility of paired to uncoupled magnetic moments as a function of kT/E_{ss}.

and the magnetization at low fields reduces to

$$M=Ng\mu_B\frac{\sum_{J=0}^{3}\exp(-E_J/kT)\sum_{m_J=-J}^{J}m_J(1+m_Jg\mu_BH/kT)}{\sum_{J=0}^{3}\exp(-E_J/kT)\sum_{m_J=-J}^{J}(1+m_Jg\mu_BH/kT)}=Ng^2\mu_B^2H\frac{\sum_{J=0}^{3}J(J+1)(2J+1)\exp(-E_J/kT)}{\sum_{J=0}^{3}(2J+1)\exp(-E_J/kT)}\,. \tag{A9}$$

Inserting the values of E_J given in Eq. (A6) and performing the summations, one obtains, for the low-field susceptibility,

$$\chi_p=\left.\frac{\partial M}{\partial H}\right|_{H\to0}=1.6\chi_c(x+5x^3+14x^6)/(1+3x+5x^3+7x^6)\,, \tag{A10}$$

where $x=\exp(-E_{ss}/9kT)$ and $\chi_c=5Ng^2\mu_B^2/4kT$, the susceptibility of an individual $J=\frac{3}{2}$ acceptor.

For donors $j_i=s_i=\frac{1}{2}$, and the total angular momentum of a pair is given by a ground state $J=0$ and a triply degenerate state $J=1$, which is higher in energy by the full amount E_{ss}. The susceptibility in this case is

$$\chi_p=(2Ng^2\mu_B^2/kT)/[\exp(E_{ss}/kT)+3]=8\chi_c/[\exp(E_{ss}/kT)+3]\,, \tag{A11}$$

where here $\chi_c=Ng^2\mu_B^2/4kT$, the susceptibility of a single $J=\frac{1}{2}$ donor.

The ratio of the susceptibility χ_p of a pair to the susceptibility $2\chi_c$ of two individual uncoupled moments is shown in Fig. 11(b) for acceptors and donors.

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