Susceptibility of Si:P across the metal-insulator transition. I. Diamagnetism

A. Roy, M. Turner, and M. P. Sarachik
Department of Physics, City College of the City University of New York, New York, New York 10031
(Received 9 July 1987)

We have made static susceptibility measurements at temperatures between 1.25 and 300 K on samples of phosphorus-doped silicon with dopant concentrations in the range $0.2 < n/n_c < 1.3$, where n_c is the critical concentration for the metal-insulator transition. In this paper we discuss our results for the diamagnetism associated with the donor electrons. We find that the donor susceptibility above 60 K is diamagnetic and varies linearly with concentration. We associate the susceptibility observed at these temperatures with a diamagnetic term, $\chi_D(T,n)$, which is of the Landau-Peierls-Pauli type, but which is linear in n. Using static susceptibility data at higher concentrations obtained by other investigators, we show that the linear behavior of χ_D persists up to $\sim 3n_c$, i.e., within the entire impurity-"band" region, beyond which it reverts to the $n^{1/3}$ behavior expected for a standard band. We find that published ESR susceptibility data for similar concentrations exhibit the same concentration dependence as χ_D. Use of the ESR data has enabled us to separate out the orbital and spin contributions to the susceptibility. The average diamagnetic susceptibility per donor is found to agree with calculated values of the Larmor diamagnetism of localized electrons, and is independent of concentration over a range spanning the transition from insulating to metallic behavior; so far as the average orbital contribution of the donor electrons in the impurity "band" is concerned, it makes little difference whether the electrons are in localized or extended states. In addition to their possible implications for the nature of the impurity "band," these results are important in that they provide a baseline against which donor susceptibility can be measured in order to determine a contribution at low temperatures which may be attributed to the presence of local moments across the metal-insulator transition.

I. INTRODUCTION

The insulator-to-metal transition which occurs at zero temperature in doped semiconductors as the dopant concentration is increased beyond a critical value, n_c, has been the subject of many investigations over the years. The major focus of experimental effort has been on measuring transport properties near the transition; careful studies of the behavior of the conductivity at very low temperatures have resulted in considerable progress in our understanding of the nature of the transition. Many questions, however, remain unresolved; in particular, the magnetic behavior is not fully understood. Recent investigations of the magnetic response have concentrated on the behavior of the low-temperature paramagnetism, and the evolution of this as the transition is crossed. It seems clear that a careful study of the behavior of the dopant spins across n_c is necessary for a complete understanding of the metal-insulator transition.

Little work has been reported on the diamagnetism of doped semiconductors with concentrations near the transition. Earlier studies[1] were focused mainly on higher concentrations $n \gg n_c$, where, because of the large effects observed, it was possible to make a meaningful comparison of the results with the predictions of band theory for the orbital diamagnetism of nearly-free electrons. Reasonable agreement with the theory was found for $n > n_{CB}$, where n_{CB} is the concentration at which the Fermi level enters the conduction band. Although significant departures from band theory expectations were noted for $n < n_{CB}$, the issue was not pursued.

Inasmuch as the metal-insulator transition in doped semiconductors is believed to take place in the impurity "band",[2] i.e., $n_c < n_{CB}$, any additional insight into the nature of the impurity "band" is relevant to our understanding of the transition. In particular, the behavior of the diamagnetism of (localized or itinerant) donor electrons is dependent on the specifics of the impurity "band," and may therefore prove to be important.

Our aim is to obtain quantitative information about the magnetic response of the dopant electrons or holes at concentrations where the Fermi level is in the impurity band and, in particular, the region $0.7 < n/n_c < 1.3$. We have attempted this by means of a systematic study of the static susceptibility of Si:P over a wide range of temperature (1.25–300 K). Although static susceptibility measures both spin and orbital contributions, in contrast to ESR which measures the spin component only, it is the method of choice for precise measurements and reliable absolute values. We have obtained information, in conjunction with static and ESR susceptibility results obtained by other investigators, about the behavior of both spin and orbital contributions to the donor susceptibility in the Si:P system. In this paper we discuss our results for the magnitude and concentration dependence of the diamagnetism in the impurity "band" region. These results have enabled us to extract a low-temperature paramagnetic term in the metallic phase ($n > n_c$), which

is normally associated with local moments in the insulating phase ($n < n_c$). This low-temperature paramagnetism is the subject of the following paper (hereafter referred to as paper II).

II. BACKGROUND

Our present understanding of the metal-insulator transition (MIT) in uncompensated doped semiconductors is that it is a disorder driven transition in which the effects of correlation are important.[3] In terms of a Hubbard model as applied to the Si:P system,[4] at very low concentrations $n \ll n_c$ where the donor sites are relatively isolated, the electrons lie in singly-occupied localized states at energies of about a donor rydberg, ~ 440 K,[5] below the bottom of the conduction band. These energy levels constitute the lower Hubbard, or D_0, "band." An energy of approximately 0.95 Ry, ~ 420 K,[6] is required to place a second electron on any isolated donor site: such energy levels for double occupancy constitute the upper Hubbard, or D_- band. The electronic wave functions are of the tight-binding type; therefore wave-function overlap is expected to be small at very low concentrations. However, because of disorder, i.e., the random positions of the donor atoms on the Si lattice, some donor sites will be much closer to each other spatially than the average donor separation. This gives rise to a larger average overlap than for the ordered case at the same concentration, and causes the Hubbard bands to broaden rapidly with concentration. In addition, due mainly to clustering effects associated with the disorder,[6] the D_- band broadens much faster than the D_0 band. With increasing concentration, and therefore increasing overlap, a concentration n' (Refs. 3 and 4) is reached at which the bottom of the D_- band touches the top of the D_0 band, and thus double occupancy states are available at the Fermi level, ε_F. (For uncompensated material ε_F lies at the top of the D_0 band up to this concentration.) However, in spite of the increased wave-function overlap, the system is still an insulator: because of disorder the tight-binding wave functions are Anderson-localized up to an energy ε_c, called the mobility edge, which lies above ε_F for $n < n_c$.[3,4] The transition from insulator to metal takes place only when the concentration is high enough so that the Fermi level crosses the mobility edge. This is believed to take place at energies below the bottom of the conduction-band edge, in other words the MIT takes place in the impurity "band". The Fermi level crosses into the conduction band at concentrations much higher than n_c.

In considering the magnetic response of the Si:P system for concentrations near n_c, two important aspects of the above picture need to be kept in mind. (a) Although the electronic states are localized up to ε_c, only the singly-occupied states carry a local moment—the doubly-occupied localized states, consisting of pairs of electrons with antiparrallel spin, have no net local moment. Thus, as the concentration is increased from n' to n_c and the D_- band rapidly encroaches into the D_0 band, an increasingly significant number of the localized states will be magnetically inert in the sense that they will not carry a local moment. (b) For concentrations greater than n', the density of states at the Fermi level, $g(\varepsilon_F)$, is finite. This implies, as suggested by Mott,[4] that magnetic quantities associated with $g(\varepsilon_F)$ may be expected to vary continuously across the MIT.

Current knowledge of the concentration dependent magnetic response of the Si:P system, as obtained from experimental studies of the susceptibility that are found in the literature, and from simple theoretical considerations, is schematically summarized in Fig. 1. The metal-insulator transition, as deduced from the behavior of the zero-temperature conductivity,[7] occurs at a concentration $n_c = 3.5 \times 10^{18}$ cm^{-3} (using the Thurber[8] curve). On the basis of a variety of experimental data, Alexander and Holcomb[9] have estimated that the Fermi level enters the conduction band at $n_{CB} \approx 2 \times 10^{19}$ cm^{-3}. Figure 1 covers a concentration range corresponding to about a factor of 30 below and above n_c. This range has been divided very roughly, on the basis of available susceptibility data, into three regions: Region I, the insulator region, corresponding to the extreme insulating side of the transition ($n \lesssim 10^{17}$ cm^{-3}); region II, the impurity "band" region ($10^{17} \lesssim n \lesssim 5 \times 10^{19}$); and region III, the conduction-band region, corresponding to the extreme metallic side of the transition ($n > 5 \times 10^{19}$ cm^{-3}). Region II, which is the region of interest, is split by the MIT into regions IIA and IIB, corresponding to concentrations below and above n_c, respectively. The concentration n' referred to earlier probably falls within the upper part of region IIA, i.e., $n' \sim 10^{18}$ cm^{-3}.[10]

The susceptibility of the donor electrons consists of positive components associated with their spins, and negative components associated with their orbital motion. In the extreme insulating region (I), where wave-function overlap is negligible, the spin part is known to be de-

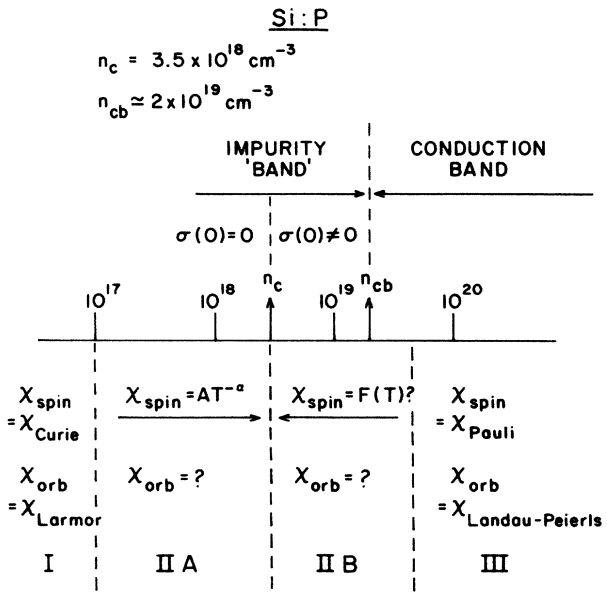

FIG. 1. Magnetic response of the Si:P system in various regions of concentration, as described in the text.

scribed[11] by the Curie law for noninteracting localized spins, each with $S=\frac{1}{2}$:

$$\chi_{\text{spin}}=\chi_{\text{Curie}}=\frac{n\mu_B^2}{\rho kT} . \quad (1)$$

The orbital part is expected to be the atomic, or Larmor, diamagnetism associated with the localized (hydrogenic) orbits:

$$\chi_{\text{orbital}}=\chi_{\text{Larmor}}=-\frac{ne^2}{6\rho m^* c^2}\langle r^2\rangle . \quad (2)$$

Since the Bohr radius of the donor electron is large, $a^*\approx 17$ Å, and the average effective mass m^* is small, the Larmor term will be much larger than that for a hydrogen atom in free space (by a factor of ~ 30). In fact, one expects it to be larger in magnitude than the Curie term for $T\geq 50$ K, so that the net susceptibility of the donor electrons is diamagnetic at high temperatures. We note that both the spin and orbital contributions in region I are proportional to the concentration n.

In the extreme metallic region (III), where the electrons are delocalized, the susceptibility exhibits the characteristics of a degenerate gas of free electrons.[12–14] The spin part of the susceptibility of a free-electron gas is the Pauli paramagnetism, and the orbital part is the Landau-Peierls (LP) diamagnetism. These terms may be combined together to give the Landau-Peierls-Pauli (LPP) susceptibility:[15]

$$\chi_{\text{spin}}+\chi_{\text{orbital}} =\chi_{\text{LPP}}=\left[1-\frac{\langle f^2\rangle}{3}\right]\frac{n\mu_B^2}{\rho kT}\frac{F'_{1/2}(\mu/kT)}{F_{1/2}(\mu/kT)} , \quad (3)$$

where $F_{1/2}$ and $F'_{1/2}$ are the Fermi integral and its derivative, μ is the chemical potential, and

$$\langle f^2\rangle=m^2\frac{2m_t+m_l}{3m_t^2m_l}\approx\left[\frac{m}{m^*}\right]^2 , \quad (4)$$

where m_t and m_l are the transverse and longitudinal effective masses. Because of the small effective mass, the LP term is larger in magnitude than the Pauli term, so that the donor susceptibility is net diamagnetic, as has been observed in this region. Using conduction band parameters,[16] $\langle f^2\rangle=12.8$, and $\chi_{\text{LP}}=-4\chi_{\text{Pauli}}$. At temperatures below the degeneracy temperature ε_F/k, χ_{LPP} is independent of temperature, and may be expressed as

$$\chi_{\text{LPP}}=\left[1-\frac{\langle f^2\rangle}{3}\right]\frac{\mu_B^2}{\rho}g(\varepsilon_F) . \quad (5)$$

Thus, both the spin and orbital parts are proportional to $g(\varepsilon_F)$ and, assuming a standard band, should vary with concentration as $n^{1/3}$.

Current knowledge and understanding of the donor susceptibility in the impurity band region (II) is confined to the low-temperature behavior of the spin component, for concentrations below n_c (region IIA). As one moves in concentration from region I to IIA, the effects of exchange interaction between the localized spins become important. This interaction is antiferromagnetic,[17] and causes the spin susceptibility to fall below the Curie value. The situation is complicated by the random positions of the donor atoms which, coupled with the exponential dependence of the exchange on interdonor separation, gives rise to an extremely broad distribution of exchange energies. However, it has proven possible to take these effects into account[18,19] and the low-temperature spin susceptibility, in agreement with experimental data,[3,20,21] is now known to be described by the behavior of the random Heisenberg antiferromagnet (RHA):

$$\chi_{\text{spin}}=\chi_{\text{RHA}}=nA(n)T^{-\alpha},\quad 0<\alpha<1 \quad (6)$$

where A and α decrease with increasing concentration. A particularly successful treatment of the properties of the RHA is the scaling calculation of Bhatt and Lee,[19] in which the spin susceptibility is shown to be that associated with pairs of localized spins, coupled hierarchically according to a renormalized distribution of exchange energies. This model will be discussed in more detail in paper II. Experiments on the nonlinear magnetization[21] have shown this description to be valid up to $n\approx 0.75n_c$, or through most of region IIA.

The behavior of the spin susceptibility as the concentration is increased from $0.75n_c$ through n_c and into region IIB is not understood. It has been observed that the temperature-dependent behavior implied by Eq. (6) apparently continues till $n\approx n_c$.[5] Whether this is a continuation of the behavior of the random Heisenberg antiferromagnet is not clear. As the concentration is increased beyond n_c, the spin part at low temperatures does not revert to the temperature-independent Pauli susceptibility expected for delocalized electrons, but continues instead to exhibit a strong temperature dependence.[12–14,22,23] The nature of this temperature dependence, whether it varies continuously across the MIT, and how far it persists into region IIB, is not known. Further discussion of these questions, which are of considerable current interest, both theoretical and experimental, is left to paper II. It should be noted here that for concentrations $n>n'$ such that $g(\varepsilon_F)$ is finite, the spin part may consist of two terms—one associated with the behavior of localized spins, such as that which gives rise to the temperature dependence in region IIA, and the other with a finite $g(\varepsilon_F)$ which could contribute a Pauli term. Attempts have been made[13,14] to describe ESR susceptibility data using such a decomposition, but without quantitative success.

Little is known about the orbital part of the donor susceptibility in region II. One may expect the Larmor diamagnetism to persist into region IIA. Alternatively, the Landau-Peierls susceptibility of region III may carry over into IIB, and possibly into IIA, for concentrations $n>n'$. At such concentrations, static susceptibility measurements may be expected to contain a χ_{LPP} term in addition to the low-temperature spin term. As in the case of ESR, however, attempts to describe the data using this decomposition have not been successful.[12] In addition, comparison of ESR with static measurements has not yielded definitive information,[14] beyond the possibility that the

orbital part is smaller than that expected on the basis of a standard band model, and that its concentration dependence may be significantly different from that expected of LP diamagnetism.

To summarize, our knowledge and understanding of the donor susceptibility in the impurity "band" region II is meager, as indicated by the question marks in Fig. 1. On the basis of our investigations, we will attempt to provide additional information in this interesting region—the low-temperature behavior in paper II, and the remainder in this paper.

III. EXPERIMENTAL PROCEDURES

The samples used in this study were cut from Czochralski-grown single crystals obtained from various sources, as listed in Table I. Sample A was a zone-floated high-purity n-type silicon sample with a room-temperature resistivity of approximately 100 Ω cm, which corresponds to a dopant concentration on the order of 10^{13} cm^{-3}. The room-temperature resistivities of the phosphorus-doped silicon samples $B-J$ were determined using the van der Pauw method;[24] a more precise determination was obtained for samples with concentrations near n_c from measurements of residual ratios $(R_{4.2}/R_{300})$ using data provided by Paalanen.[25] The phosphorus concentration for each doped sample was then obtained from the room-temperature resistivity using the calibration curve of Thurber *et al.*[8] for Si:P. Since the critical concentration on the Thurber scale is $n_c = 3.5\times10^{18}$ cm^{-3}, it can be seen from Table I that samples $B-F$ and $G-J$ are on the insulating and metallic side of the metal-insulator transition, respectively, and that the concentrations of these doped samples correspond to the range $0.2 \leq n/n_c \leq 1.3$.

The magnetic susceptibility measurements were made using a Faraday balance technique. A commercial Cahn RH microbalance was used to measure the force on a sample suspended in the superposition of a uniform field generated by a superconducting solenoid and a field gradient produced by an auxilliary superconducting coaxial coil. Measurements were obtained between 1.25 and 300 K.

To minimize surface contamination, each sample was etched with CP-4 solution immediately prior to loading it into the sample chamber. This ensured the removal of any ferromagnetic impurities that may have been introduced during cutting or storage to levels below the sensitivity limit of our magnetic measurements. After loading, the sample chamber was repeatedly evacuated and backfilled with high-purity helium gas. This process purged the samples of adsorbed oxygen that would give rise to a spurious paramagnetic signal. Thermomolecular and convective flow effects, which generate noise in the force measurement, were kept to a minimum by operating at low exchange gas pressures, and gas buoyancy effects were eliminated by observing force changes induced by reversing the direction of the field gradient.

The above procedures enabled us to obtain susceptibility measurements to a precision of 2×10^{-10} emu/g, and with a run-to-run reproducibility within 5×10^{-10} emu/g. These numbers correspond to about 0.2% and 0.4%, respectively, of the diamagnetism of silicon.

IV. RESULTS AND DISCUSSION

Figure 2 shows the measured total mass susceptibility, $\chi_T(T)$, as a function of temperature for a number of doped samples with concentrations in the range $0.7 < n/n_c < 1.3$. The measured susceptibility for the pure silicon sample is also shown in Fig. 2. As has been noted by other investigators, the susceptibility of silicon is diamagnetic and independent of temperature at low temperatures, and exhibits a modest decrease in magnitude as the temperature increases. Our measured value for the diamagnetism of silicon in the temperature-independent region is $-(115.0\pm0.5)\times10^{-9}$ emu/g; an estimate of the absolute accuracy (calibration) of our susceptibility measurements may be obtained from this number.

By subtracting the susceptibility of the pure sample from the total susceptibility, we have obtained the susceptibility associated with the donor electrons, $\chi(T)$, for each doped sample. In addition, we have divided $\chi(T)$ by the donor concentration per gram, n_g, to obtain the average susceptibility per donor atom:

TABLE I. Characteristics of the samples used for the susceptibility measurements. The concentration n_g is the donor concentration per gram.

Sample	Resistivity at 293 K (Ω cm)	Concentration n (10^{18} cm^{-3})	Concentration n_g (10^{18} g^{-1})	Source
A	100	"pure"	"pure"	Zone-float
B	0.0285	0.67	.288	Mulab
C	0.0205	1.26	.541	Mulab
D	0.0142	2.42	1.04	Mulab
E	0.0134	2.76	1.18	Virginia Semiconductors
F	0.0119	3.4	1.46	Texas Instruments
G	0.0114	3.61	1.55	Crysteco
H	0.0111	3.83	1.64	Crysteco
I	0.01037	4.27	1.83	AT&T Allentown
J	0.00991	4.6	1.97	AT&T Allentown

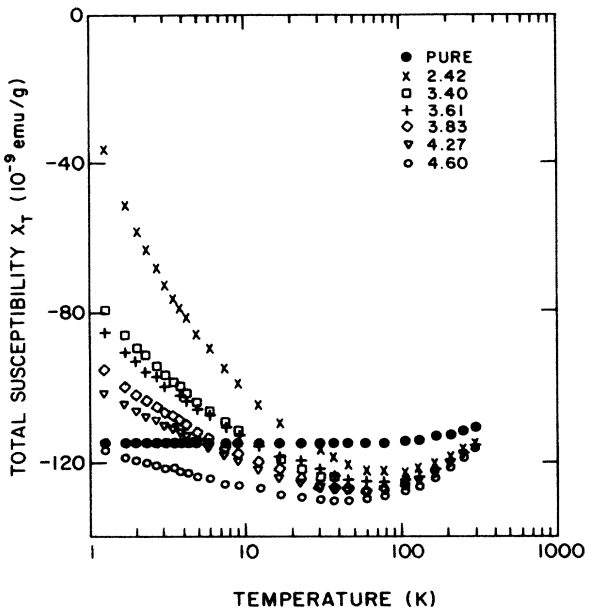

FIG. 2. Total susceptibility of Si:P as a function of temperature for the pure silicon sample and for doped samples with concentrations indicated in units of 10^{18} cm^{-3}.

$$\frac{\chi(T)}{n_g}=[\chi_T(T)-\chi_{Si}(T)]/n_g \ , \tag{7}$$

where $n_g=n/\rho$, and ρ ($=2.33$ g/cm^3) is the density of silicon. The data, so reduced, are shown in Fig. 3. The value of n_g for each sample is given in Table I.

The effects of increasing concentration are clearly evident in Fig. 3. The donor susceptibility at the lower temperatures ($T \leq 30$ K) shows a monotonic progression with concentration. For the insulating samples, the observed behavior of χ/n_g is qualitatively that expected for the random Heisenberg antiferromagnet [Eq. (6)]—the effects of the exchange interaction become more pronounced as n increases, resulting in a decrease of both the magnitude of the low-temperature paramagnetism and its temperature dependence. However, as is quite clear from Fig. 3, this behavior of χ/n_g apparently persists into the metallic phase—there is no discernible change in the behavior of the susceptibility at these temperatures as the concentration is increased beyond the critical concentration. Thus the low-temperature susceptibility of the four metallic samples of Fig. 3 continues to exhibit, on a qualitative level, the temperature- and concentration-dependent features associated with the insulating phase. This smooth variation of the magnetic response is in marked contrast with our measured residual ratios $R_{4.2\text{ K}}/R_{300\text{ K}}$ which change rapidly near the transition, and the zero-temperature conductivity which is known to change almost discontinuously.[7]

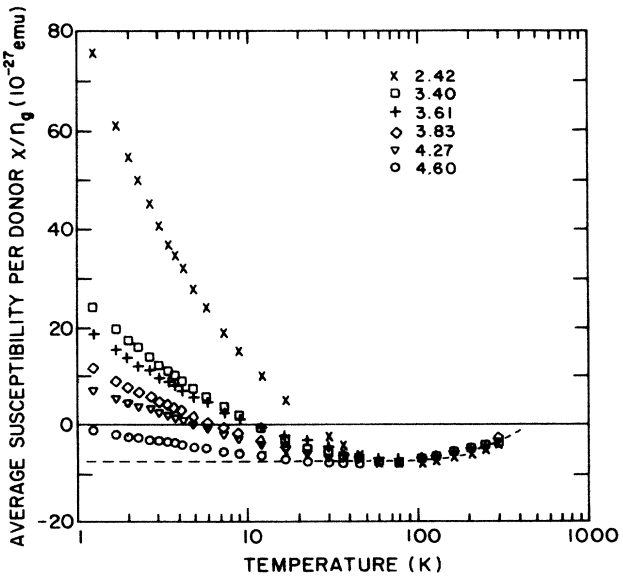

FIG. 3. Average susceptibility per donor as a function of temperature. Note that the data for all the samples tend toward a single curve for $T>60$ K. The significance of the dashed curve is explained in the text.

Figures 2 and 3 show that the donor susceptibility for samples on either side of the transition becomes diamagnetic as the temperature is raised beyond 20 K. As discussed in Sec. II, the magnitude of the orbital contribution to the donor susceptibility is known to be larger than the spin contribution in the metallic region III. For temperatures higher than 50 K, this is expected to be true even in the insulating region I. It is therefore not surprising that the donor susceptibility is observed to be net diamagnetic at high temperatures in the intermediate region II. It is important to note, however, that in this concentration range the orbital contribution evidently represents a significant portion of the donor susceptibility even at low temperatures. This is most obvious in the case of the sample with the highest phosphorus concentration, sample *J*, for which the donor susceptibility remains net diamagnetic down to the lowest temperature accessed in this experiment. In order to extract meaningful information regarding the behavior of the paramagnetism at low temperatures on the basis of these data, detailed knowledge of the diamagnetism associated with the donor electrons is clearly necessary.

The reduced data of Fig. 3 affords a direct clue to the nature of the donor electron diamagnetism. It can be seen from this figure that as the temperature is increased beyond 60 K, the values of χ/n_g tend toward a single curve for all samples independently of concentration. This striking feature of the data implies that the donor susceptibility for $T \geq 60$ K is approximately linear in the concentration. At these elevated temperatures, the paramagnetic enhancement of the susceptibility that is observed at the lowest temperatures is expected to be insignificant. For the insulating samples this is certainly the case: as can be easily seen by plotting the data on a log-log plot, the susceptibility of these samples at low temperatures falls off even faster than $1/T$ for $T \geq 5$ K.[26] The metallic samples show similar behavior (see paper II). These considerations suggest that if one writes the susceptibility within the entire temperature range as the sum of a paramagnetic and a diamagnetic term:

$$\chi(T,n)=\chi_P(T,n)+\chi_D(T,n)\ , \tag{8}$$

then for temperatures $T \geq 60$ K, the term χ_P is negligible, and the measured donor susceptibility equals the diamagnetic term χ_D. Furthermore, (i) χ_D apparently scales linearly with concentration, and (ii) the temperature dependence of χ_D is independent of concentration and, for $T \geq 60$ K, is given by the dashed curve through the data in Fig. 3. This curve, which represents an average over the χ/n_g data for all the samples, indicates that χ_D is temperature independent between 60 and 100 K, above which it steadily decreases in magnitude with increasing temperature.

These data do not enable us to directly determine the temperature dependence, if any, of the diamagnetic term χ_D below 60 K. However, the temperature dependence of χ_D above 60 K certainly resembles that expected for the LPP susceptibility of a free-electron gas with a degeneracy temperature on the order of a few hundred degrees. Although the LPP susceptibility varies with concentration as $n^{1/3}$, on the basis of the observed temperature dependence we can associate the term χ_D with diamagnetism of the "LPP type" in spite of the fact that it is linear in n.

The linearity of χ_D in concentration that is indicated by Fig. 3 can be seen more explicitly in Fig. 4, which is a plot of the measured donor susceptibility at 78 K, i.e., χ_D, as a function of concentration. The straight line is a least-squares fit to the data; the small nonzero intercept is not significant in that it lies within the uncertainties of the measurements. This figure shows clearly that χ_D does indeed vary linearly with n, in a range of concentration that covers most of region IIA, and part of region IIB. The slope of the straight line corresponds to an average diamagnetism per donor $\chi_D/n_g = -(7.5\pm0.4)\times10^{-27}$ emu.

To ascertain how far in concentration this linear behavior persists, we made use of static susceptibility data at 78 K obtained by Sasaki and co-workers[11] for Si:P samples with concentrations comparable to and higher than ours. The concentrations of these samples, which had been determined from Hall effect measurements,[27] were converted to the Thurber scale using values of room-temperature resistivity that we deduced from Ref. 27. The data of the Sasaki group along with our results at 78 K are shown in Fig. 5, plotted as a function of concentration on a double-logarithmic scale. (It should be noted that the value of the susceptibility of pure silicon obtained by Sasaki *et al.* and by our group are the same within the 0.4% uncertainty of our measurements, so that the absolute calibration of the two experiments match and therefore a meaningful comparison can be made without adjustments.) The straight lines drawn through the data in Fig. 5 have slopes of 1 and $\frac{1}{3}$ at low and at high concentrations, respectively. As indicated by the straight lines, Fig. 5 demonstrates that the donor susceptibility at 78 K ($=\chi_D$) varies linearly with concentration up to $\sim10^{19}$ cm^{-3}, or roughly three times the critical concentration, above which it exhibits the $n^{1/3}$ behavior characteristic of the LPP susceptibility of electrons in a standard band. The crossover from linear to $n^{1/3}$ behavior occurs at about 10^{19} cm^{-3}, which is approximately the concentration n_{CB} at which the Fermi level is believed to enter the conduction band. This shows that χ_D scales linearly with concentration within the entire impurity "band" region II. We note that a similar crossover from linear to $n^{1/3}$ behavior was observed by Bowers[28] in Ge:As, at a concentration corresponding roughly to three times the critical concentration for that system.[9]

The donor susceptibility at high temperatures, which we have labeled $\chi_D(T,n)$, is actually comprised of a positive spin part and a negative orbital part:

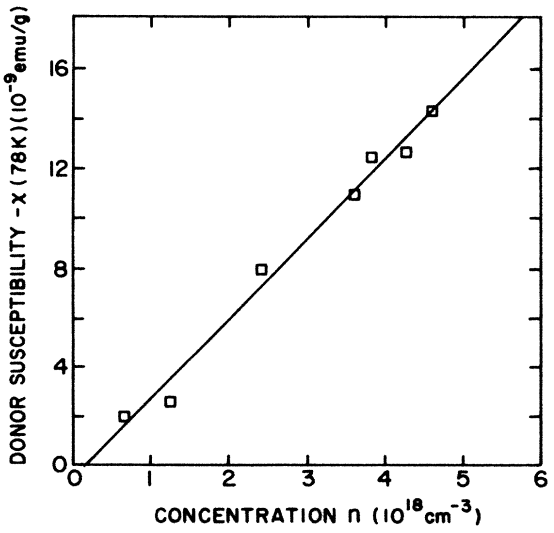

FIG. 4. Donor susceptibility at 78 K as a function of concentration,

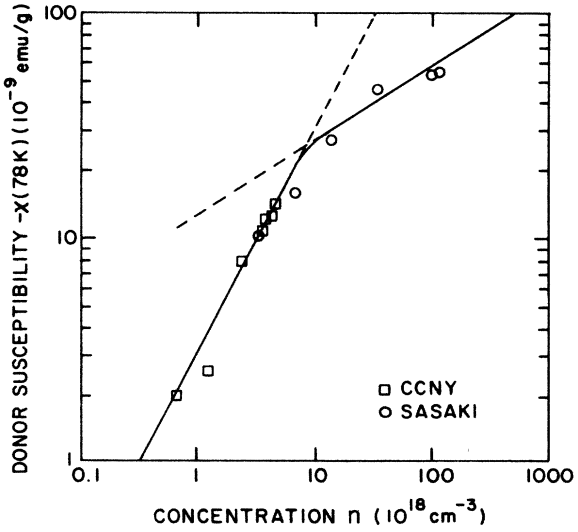

FIG. 5. Double-logarithmic plot of dopant susceptibility at 78 K versus concentration. Squares: current data. Circles: data from Ref. 12. The straight lines have slopes of 1 and $\frac{1}{3}$ at low and high concentrations, respectively.

$$\chi_D(T,n)=\chi_s(T,n)+\chi_0(T,n)\ . \tag{9}$$

The orbital term χ_0 obviously represents the dominant contribution; nevertheless χ_D must contain an admixture of a spin component associated with delocalized electrons which are present in the metallic phase at all temperatures, and which, due to thermal activation to the mobility edge, are present at these high temperatures even in the insulating phase. The overall linear dependence of χ_D on n could therefore arise either from a fortuitous adjustment of the two components, or from linearity of each individual component. Alternatively, if one associates the observed χ_D with LPP susceptibility, as appears to be appropriate in light of the observed temperature dependence, the spin and orbital terms must perforce have the same concentration dependence, which in this case is observed to be linear.

To examine this question we looked at spin-susceptibility data at 77 K obtained from ESR measurements by Ue and Maekawa[13] (UM), and by Quirt and Marko[14] (QM) for various concentrations of phosphorus in silicon. The concentrations of the UM samples were converted to the Thurber scale using the same procedures as for the samples of Ref. 12. The quoted room-temperature resistivity of the QM samples were used to determine their concentrations on the Thurber scale. As shown by Wagner and Schwerdtfeger,[29] although the results of UM and QM are self consistent, they differ in absolute value by a factor of almost exactly 2. We have scaled the results of UM down by a factor of 2. (We will comment on this choice later.) The results of these procedures are shown in Fig. 6, which is a double-logarithmic plot of the spin susceptibility at 77 K versus concentration. The straight lines through the data in Fig. 6 are identical to those in Fig. 5 except for a vertical translation, and indicate that the spin component of the donor susceptibility at 77 K follows the concentration

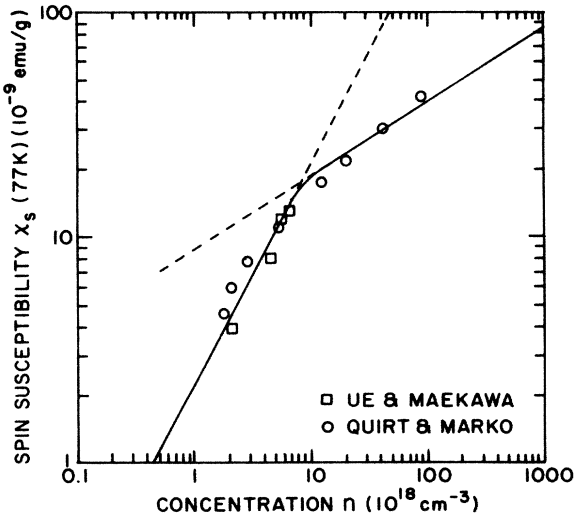

FIG. 6. Double-logarithmic plot of ESR spin susceptibility at 77 K versus concentration. Squares: data from Ref. 13. Circles: data from Ref. 14. The straight lines are the same as those of Fig. 5 except that they have been translated vertically.

dependence of χ_D, with the same crossover point from linear to $n^{1/3}$ behavior. It appears, therefore, that the observed linear behavior of χ_D from the lowest concentrations, through the metal-insulator transition to about $3n_c$, and the crossover to $n^{1/3}$ dependence for concentrations above $3n_c$, correctly describes the behavior of the individual positive and negative contributions.

As to the issue regarding the absolute values of the spin susceptibility, we note firstly that for concentrations greater than 10^{19} cm^{-3}, where $n^{1/3}$ behavior prevails, the values of QM are slightly smaller than standard band theory predictions for the Pauli susceptibility, whereas those of UM are nearly twice as large. Secondly, in the linear region below 10^{19} cm^{-3}, the UM values are higher even than those expected for the Curie susceptibility at 77 K. Although electron-electron interactions can give rise to a spin-susceptibility that is much higher than the Pauli (or Curie) value,[30] it is unlikely that these effects are significant at temperatures as high as 77 K. If anything, one may expect the spin susceptibility in this disordered system at these temperatures to be smaller than the Pauli value, owing to rapid spin-flip scattering processes.[31] Pending further investigation and in accordance with Holcomb,[9] we take the values of QM to be more accurate.

By means of a least-squares fit to the data of Fig. 6 within the linear region, we determine that the average spin susceptibility per donor at 77 K is $\chi_s/n_g = 4.3\times10^{-27}$ emu. Using our value of $\chi_D/n_g = -7.5\times10^{-27}$ emu, we then find that the average orbital susceptibility per donor is $\chi_0/n_g=\chi_D/n_g - \chi_s/n_g = -12\times10^{-27}$ emu. Thus, the ratio of the orbital to the spin susceptibility in the impurity band is $\chi_0/\chi_s=-3$, which is significantly different from the standard band expectation of -4 (see Sec. II).

It is interesting to compare the above value of the average orbital term, χ_0/n_g, with theoretical predictions for the Larmor diamagnetism of isolated donors in silicon. (i) A straightforward calculation using Eq. (2), a hydrogenic wave function with a Bohr radius of 17 Å, and an average band effective mass yields $\chi_{\text{Larmor}}/n_g = -12\times10^{-27}$ emu. (ii) On the basis of effective-mass theory, Kohn[32] offered some years ago the estimate $\chi_{\text{Larmor}}/n_g=-15\times10^{-27}$ emu. (iii) Taking the multivalley structure of the conduction-band minimum into account, Devaraj *et al.*[33] recently obtained $\chi_{\text{Larmor}}/n_g=-11\times10^{-27}$ emu. These values are comparable, and are surprisingly close to our determination of χ_0/n_g. A most striking feature of the data is that the average orbital susceptibility per donor remains the same over nearly two decades in concentration spanning the MIT, despite the fact that the ratio of localized to delocalized electrons is changing substantially. This indicates that as far as the average orbital contribution of the donor electrons in the impurity band is concerned, it makes little difference whether the electrons are in localized or delocalized (extended) states. This appears to be a confirmation of the prediction of Mooser[34] who, based on work by Baltensperger[35] on the impurity band in Si:P, showed that the orbital diamagnetism of itinerant electrons in the impurity band should be essentially the same

as that of electrons localized at isolated donor sites. We should reiterate here that only localized states with an odd occupation number (singly occupied sites or clusters with an odd number of electrons) carry a local moment. As mentioned earlier, the number of such states decreases rapidly with increasing concentration beyond n'.

We have used the fact that χ_0/n_g is a constant over a range of concentration where the ratio of localized to delocalized electrons varies appreciably to suggest that their average orbital contribution is essentially the same. A corollary to these arguments is that the average orbital susceptibility per donor due to localized electrons and due to delocalized electrons must each separately be independent of concentration. One would not expect this to be evident unless the contribution to the susceptibility due to the delocalized electrons is independent of temperature at 78 K. This is consistent with the conjecture, made earlier on the basis of the observed temperature dependence of χ_D, that the degeneracy or Fermi temperature is well above 78 K. This would imply, then, that χ_D is independent of temperature below this temperature, so that the value of χ_D at all temperatures $T<60$ K is approximately the same as that at 78 K, namely -7.5×10^{-27} emu/donor, as indicated by the continuation of the dashed curve to temperatures below 60 K in Fig. 3.

We should consider other possible mechanisms that could give rise to this observed behavior. Linear dependence could, in principle, be associated with electrons in extended states at temperatures above the degeneracy temperature of the electron gas. If so, then the susceptibility at high temperatures should be consistent with the LPP expression for a free-electron gas, Eq. (3), which, with increasing temperatures above ε_F/k, describes the transition from degenerate to classical statistics (linear in n). We find, however, that a rigorous application of free-electron theory, using Eq. (3) in conjunction with tables provided in Ref. 36, cannot simultaneously reproduce both the concentration dependence and the temperature dependence between 70 and 300 K that is seen in Fig. 3. In addition, it is unlikely that the electron gas is, in fact, nearly nondegenerate at temperatures around 80 K since the Fermi temperature is believed to be on the order of 80 K or higher in these materials.

We conclude that the susceptibility is associated with an electron system that is degenerate below 100 K. As discussed in Sec. II, within our present picture of the nature of the metal-insulator transition in Si:P, the density of states at the Fermi level, $g(\varepsilon_F)$, is finite for concentrations $n>n'$, where $n'<n_c$. Furthermore, in the context of magnetic susceptibility, this quantity is the thermodynamic density of states, which is expected to vary smoothly across the transition.[37] A possible implication of our current findings is that the susceptibility over our entire measured range of concentration n across the transition could derive from a LPP-type susceptibility, Eq. (5), where the observed linear dependence results from a linear dependence of the density of states on donor concentration. A similar suggestion based on specific-heat studies has been advanced by Mael *et al.*[38] for MoGe alloys. One should keep in mind, however, that the spin susceptibility in general involves a Fermi-liquid correction, so that the above implication holds only if this correction varies smoothly across the transition, or introduces at most a small discontinuity.

Irrespective of the possible reasons for the unexpected concentration dependence of the various contributions to the susceptibility or, for that matter, whether we have made a correct separation into positive and negative terms, it is important to note that if one makes the reasonable assumption that the net measured diamagnetism is independent of temperature at low temperatures (as would surely be true for a degenerate system), then using this as a baseline allows one to make a reliable determination of the term χ_P which one normally associates with local moments in insulating samples, and which clearly persists for metallic samples. This is the subject of the following paper (paper II).

ACKNOWLEDGMENT

We gratefully acknowledge numerous valuable discussions with Y. Yafet of AT&T Bell Laboratories. We would like to thank M. A. Paalanen, also of AT&T, for providing samples *I* and *J*, and M. Levy and L. L. Isaacs of City College for help with the experimental work. This work was supported by the U.S. Department of Energy under Grant No. DE-FG02-84ER45153. Partial support for one of the authors (M.T.) was provided by the Professional Staff Congress (PSC)–CUNY Research Award Program.

[1]For reviews of earlier work, see R. Bowers, J. Phys. Chem. Solids **8**, 206 (1959); D. F. Holcomb, in *The Metal-Nonmetal Transition in Disordered Systems,* edited by L. R. Friedman and D. P. Tunstall (Scottish Universities Summer School in Physics Publications, Edinburgh, 1978), p. 251.

[2]N. F. Mott, in *Localization and Interaction,* edited by D. M. Finlayson (Scottish Universities Summer School in Physics Publications, Edinburgh, 1986), p. 29.

[3]R. F. Milligan, T. F. Rosenbau, R. N. Bhatt, and G. A. Thomas, in *A Review of Electron-Electron Interactions in Disordered Systems,* edited by A. L. Efros and M. Pollak (North Holland, New York, 1985); N. F. Mott and J. H. Davies, Philos. Mag. **42**, 845 (1980); N. F. Mott, in *The Metal-Nonmetal Transition in Disordered Systems,* Ref. 1, p. 149.

[4]N. F. Mott, *Metal Insulator Transitions* (Taylor and Francis, London, 1974).

[5]K. Andres, R. N., Bhatt, P. Goalwin, T. M. Rice, and R. E. Walstedt, Phys. Rev. B **24**, 244 (1981).

[6]R. N. Bhatt and T. M. Rice, Phys. Rev. B **23**, 1920 (1981); Philos. Mag. B **42**, 859 (1980).

[7]T. F. Rosenbaum, R. Milligan, M. A. Paalanen, G. A. Thomas, R. N. Bhatt, and W. Lin, Phys. Rev. B **27**, 7509 (1980).

[8]W. R. Thurber, R. L. Mattis, Y. M. Liu, and J. J. Filliben, J. Electrochem. Soc. **127**, 1807 (1980).

[9]M. N. Alexander and D. F. Holcomb, Rev. Mod. Phys. **40**, 815 (1968); see also D. F. Holcomb, in *Localization and Integration,* Ref. 2, p. 313.

[10]We should emphasize that, of all the concentrations that we have attached labels to, only n_c can be determined to some degree of accuracy, and, to a lesser extent, n_{CB}. The concentrations that define the three regions of magnetic behavior are, and probably can be, only approximate.

[11]E. Sonder and D. K. Stevens, Phys. Rev. **110**, 1027 (1958); see also Ref. 1.

[12]W. Sasaki and J. Kinoshita, J. Phys. Soc. Jpn. **25**, 1622 (1968); S. Ikekata, T. Ema, S. Kobayashi, and W. Sasaki, *ibid.* **50**, 3655 (1981).

[13]H. Ue and S. Maekawa, Phys. Rev. B **3**, 4232 (1971).

[14]J. D. Quirt and J. R. Marko, Phys. Rev. Lett. **26**, 318 (1971); Phys. Rev. B **5**, 1716 (1972); **7**, 3842 (1973).

[15]A. H. Wilson, *The Theory of Metals,* 2nd ed. (Cambridge University Press, London, 1958).

[16]G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).

[17]C. Herring and M. Flicker, Phys. Rev. **134**, A362 (1964).

[18]M. Rosso, Phys. Rev. Lett. **44**, 1541 (1980); P. H. Thomas and M. Rosso, Phys. Rev. B **34**, 7936 (1986).

[19]R. N. Bhatt and P. H. Lee, Phys. Rev. Lett. **48**, 344 (1982); J. Appl. Phys. **52**, 1707 (1981).

[20]C. T. Murayama, W. G. Clark, and J. Sanny, Phys. Rev. B **29**, 6063 (1984).

[21]M. P. Sarachik, A. Roy, M. Turner, M. Levy, D. He, L. L. Isaacs, and R. N. Bhatt, Phys. Rev. B **34**, 387 (1986); A. Roy, M. P. Sarachik, and R. N. Bhatt, Solid State Commun. **60**, 513 (1986).

[22]S. Ikehata and S. Kobayashi, Solid State Commun. **56**, 607 (1985).

[23]M. A. Paalanen, S. Sachdev, R. N. Bhatt, and A. E. Ruckenstein, Phys. Rev. Lett. **57**, 2061 (1986).

[24]L. J. van der Pauw, Phillips Res. Rep. **13**, 1 (1958).

[25]M. A. Paalanen (private communication).

[26]A. Roy, M. Levy, M. Turner, M. P. Sarachik, and L. L. Isaacs, in *Disordered Semiconductors,* edited by M. A. Kastner, G. A. Thomas, and S. R. Ovshinsky (Plenum, New York, 1987), p. 65.

[27]C. Yamanouchi, K. Mizuguchi, and W. Sasaki, J. Phys. Soc. Jpn. **22**, 859 (1967).

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

[29]H. J. Wagner and C. F. Schwerdfeger, Solid State Commun. **30**, 597 (1979).

[30]A. M. Finkelstein, Z. Phys. B **56**, 189 (1984); C. Castellani, C. DiCastro, P. A. Lee, M. Ma, S. Sorella, and E. Tabet, Phys. Rev. B **30**, 1596 (1984); **33**, 6169 (1986); C. Castellani, G. Kotliar, and P. A. Lee, Phys. Rev. Lett. **59**, 323 (1987).

[31]J. S. Helman, Phys. Kondens. Mater. **6**, 297 (1967).

[32]W. Kohn, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.

[33]T. V. Devaraj, B. Sukumar, and K. Navaneethakrishnan, Solid State Commun. **61**, 727 (1987).

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

[35]W. Baltensperger, Philos. Mag. **44**, 1355 (1953).

[36]J. McDougall and E. S. Stoner, Philos. Trans. R. Soc. London, Ser. A **237**, 67 (1939).

[37]P. A. Lee, Phys. Rev. B **26**, 5882 (1982).

[38]D. Mael, S. Yoshizami, and T. H. Geballe, Phys. Rev. B **34**, 467 (1986).