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Absolute Spin Susceptibilities and Other ESR Parameters of Heavily Doped *n*-Type Silicon. II. A Unified Treatment*

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Spin susceptibility, g-value, and ESR linewidth data are presented for (Si:P) samples having impurity concentrations $10^{18} < N_D < 10^{19}$ donors/cm^3. These results and those previously obtained for $N_D > 10^{19}$ donors/cm^3 samples are compared with the predictions of alternative simple models of the semiconductor-metal transition in heavily doped semiconductor materials. At low concentrations ($N_D < 3\times 10^{18}$ donors/cm^3) our samples behave as semiconductors in transport experiments and are characterized by Curie–Weiss-law spin susceptibilities. Near the upper limit of our sample impurity concentration range ($N_D \sim 10^{20}$ donors/cm^3), transport measurements indicate metallic properties and spin susceptibilities which follow the Pauli-law expression with an effective mass which is slightly smaller than that usually associated with the silicon conduction band. A good representation of the experimental spin susceptibilities of samples having intermediate impurity concentrations can be achieved through an expression which is the sum of two terms: one of which is of the Curie–Weiss form and the other of the Pauli type. An analysis of previously published Hall carrier-density data is offered which would appear to allow the identification of these two components with nonconducting (or partially localized) and conducting extrinsic electrons, respectively. The inferred presence of partially localized electrons even in samples with $N_D > 10^{19}$ donors/cm^3 is discussed with respect to previously published magnetoresistance and Knight-shift data.

I. INTRODUCTION

In a previous publication[1] (henceforth referred to as I) we have presented electron-spin resonance (ESR) data for samples of silicon heavily doped with phosphorus (Si : P) which can be reasonably well understood in terms of a rigid-band Pauli susceptibility model and the assumption that the Fermi energy lies in the silicon host conduction band[2] when the impurity concentrations N_D exceed approximately 2×10^{19} donors/cm^3. However, evidence was also presented for the existence of small but consistent deviations from Pauli-law behavior in these "metallic" ($N_D > 10^{19}$ donors/cm^3) samples. The relative magnitude of the postulated "non-Pauli" susceptibility component was a decreasing function of the donor impurity concentration and, because of experimental accuracy limitations, its presence or absence could not be conclusively demonstrated for samples with concentrations in excess of $N_D = 4\times 10^{19}$ donors/cm^3.

In the present work we shall both reexamine these previous results and present similar data obtained for samples having impurity concentrations $N_D < 10^{19}$ donors/cm^3. One of our purposes will be to consider the possibilities available for the construction of a general model which is capable of offering a consistent semiquantitative understanding of the observed magnetic susceptibility and transport properties of this heavily doped semiconductor system.

Historically there have been two generic approaches to the construction of such models. One of these, the "band" model assumes that, at suitably high-impurity concentrations, all extrinsic electrons are delocalized and may be considered to occupy some sort of "conduction-band" state. In this view, all extrinsic electrical and magnetic properties of such a material may be attributed to the same group of delocalized electrons. Any anomalous experimental properties are interpreted in terms of the structure of the associated "band." An example of this approach may be found in the work of Jérome[3,4] in which the experimental susceptibility of a single Si : P sample was interpreted in terms of the temperature-dependent degeneracy of electrons in narrow conduction-band states. An alternative view, often called the inhomogeneity model, explains these same properties by assuming the simultaneous existence within a sample of localized and delocalized extrinsic electrons. The term "inhomogeneity" arises from the association of these two groups of electrons with spatial regions of the samples which, because of the random placement of donors, have local impurity concentrations which are, respectively, less than and greater than the critical values required for complete delocalization. A specific form of this model proposed by Mikoshiba[5] assumes that the magnetic response of the "metallic" electrons is in accord with a Pauli-law susceptibility. The electrons in nonconducting "localized" states in this model contribute to the spin susceptibility according to a Curie-law expression and as a result dominate the magnetic response of these samples at low temperatures. In this view, the temperature dependence of the extrinsic low-temperature magnetic properties is not primarily associated with those electrons responsible for the electrical conduction process. This interpretation contrasts strongly with the fundamental assumption of the alternative "band" approach.

It is possible, on the basis of the available ESR and electrical-transport data, to judge the relative merits of these two general approaches. Specifically we shall show in the latter sections of this work that a simple "band" approach is not consistent with our observations. On the other hand, a generalized version of the alternative inhomogeneity model does offer an excellent representation of the observed spin susceptibilities. Further, if a slight change is made in the usual interpretation of the room-temperature Hall-coefficient data, this model is consistent with the corresponding electrical-transport results available for samples with impurity concentrations $N_D > 10^{18}$ donors/cm^3.

The remainder of this paper will begin (Sec. II) with a discussion and evaluation of the experimental electrical-transport data appropriate to the samples under consideration. Section III will contain a brief description of our experimental ESR procedures and is followed (Sec. IV) by a presentation of the resulting data and a brief comparison with the predictions of the simple models. In Sec. V we will discuss the ESR and electrical-transport data in general terms and with respect to a specific form of the inhomogeneity model. Finally, the main experimental and interpretative conclusions of this work will be summarized in Sec. VI.

II. ELECTRICAL-TRANSPORT PROPERTIES

It is the purpose of the present section to establish, as explicitly as possible, the electronic-transport properties of the Si : P samples considered in our study. Specifically we shall estimate from the available data, the ratio of the dc electrical carrier density (n) to the donor impurity density (N_D) as a function of N_D and the temperature T. This information is essential to allow the formulation of a model for these systems which is both physically reasonable and in accord with the observed experimental results.

The ratio n/N_D has been generally used as an indicator of the semiconductor-metal (SM) transition in Si : P and similar materials. Thus, if n is measured at very low temperatures, the ratios $n/N_D \approx 0$ and 1 are assumed to define samples, respectively, on the semiconducting and "metal" sides of an SM transition.

In practice, n is determined from measurements of the Hall coefficient R_H and the equation

$$n = A/R_H ec \ , \tag{1}$$

where e and c, respectively, represent the charge of an electron and the velocity of light. The factor A is a function of the dominant mechanism of momentum relaxation, the statistics, the magnetic field, and the structural details of the conduction band. For electrons occupying silicon conduction-band states, A may be written as[6]

$$A = \frac{3K(K+2)}{(2K+1)^2}\, r \ . \tag{2}$$

In this expression $K = m_l^* \tau_t / m_t^* \tau_l$, where $m^*_{l(t)}$, $\tau_{l(t)}$, represent, respectively, the longitudinal (and transverse) principal components of the silicon conduction-band effective-mass and momentum-relaxation-time tensors. Magnetoresistance measurements by Tufte and Stelzer[7] indicate that $3 \leq K \leq 5$, and the later work of Sasaki and Kinoshita[8] gives a value of $K = 4.7$. The first factor on the right-hand side of Eq. (2) is not strongly sensitive to the exact value of K, and the result $A = 0.87r$, calculated on the basis of $K = 4.7$, will be used in the following discussion. The factor r has been calculated in the low-field limit, assuming the applicability of classical statistics, for situations in which the dominant scattering of electronic carriers arises from ionized impurities, acoustic phonons, and neutral impurities. In these three cases r takes the values 1.93, 1.18, and 1.0, respectively.[6] On the other hand, if degenerate statistics are applicable, r is, in all cases equal to one. The value $A = 1$ is unambiguously valid, independent of temperature and concentration, in the limit of infinite magnetic field. Unfortunately, the magnitude of the field necessary[6] to guarantee that $A = 1$ is too large ($B \gtrsim 10^6$ G) to be experimentally feasible in the case of Si : P. In the absence of complete degeneracy and at low magnetic fields, A would be expected to be a function of the sample concentration and temperature.

The donor concentrations N_D in the two most complete sets[9,10] of Si : P low-temperature electrical-transport data available have been established from room-temperature measurements of R_H, with the assumptions $n(300\ \text{K}) = N_D$ and $A = 1$. On

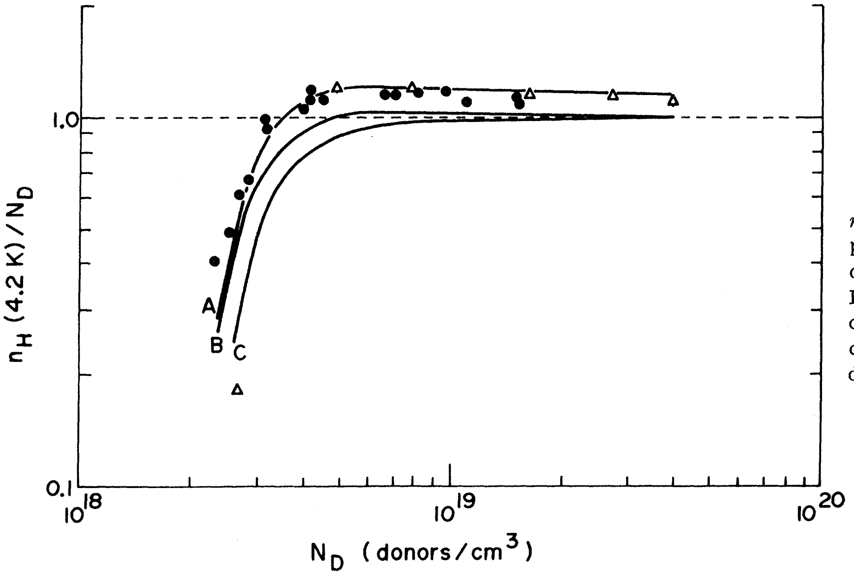

FIG. 1. Relative carrier density n/N_D at $T=4.2$ K for various interpretations of Hall-effect data. The data points are based on Fig. 2(b) of Ref. 11 and correspond to the results of Ref. 9 (triangle) and Ref. 10 (circle), respectively. The curves are discussed in the text.

the basis of the discussion above, the latter assumption is only approximately correct and has led to some confusion in the interpretation of previous experimental results. For example, as noted by Holcomb and Rehr,[11] this procedure when used with low-temperature values of R_H leads to experimental "carrier densities" at $T=4.2$ K which for some samples exceed the reported concentrations N_D by more than 20%. Such a result is obviously nonphysical and indicates that a more consistent method of determining n is necessary before these results can be treated in quantitative detail. Figure 1 is based on Fig. 2(b) of Ref. 11 which presents the previous experimental data.[9,10] The actual quantity plotted is the ratio $R_H(300\text{ K})/R_H(4.2\text{ K})$ which corresponds to $n(4.2\text{ K})/N_D$ only if the factor A of Eq. (1) is independent of temperature.

Unfortunately, the factor A can be calculated easily only in the extreme cases of very low and very high sample impurity concentrations. In these cases classical and degenerate Fermi statistics, respectively, apply most unambiguously, and the dominant scattering mechanisms are most clearly understood. However, at $T=300$ K neither of these statistical extremes is obtained in the concentration range of interest. Thus even on the basis of the conventional assumption that all electrons are in conduction-band states, the Fermi level at this temperature lies below the band edge for samples with $N_D \lesssim 10^{19}$ donors/cm^3. More specifically, this Fermi level varies from approximately $-3kT$ when $N_D=2\times10^{18}$ donors/cm^3 to $\sim 2kT$ when $N_D=10^{20}$ donors/cm^3 (in this case the zero of energy is taken at the bottom of the conduction band). Although the partial degeneracy which exists in these cases should reduce the scattering factor r, the extreme degeneracy limit $r=1$ is not expected to be valid at room temperature. However, at liquid-helium temperatures, the assumption of degeneracy is reasonable and the values $r=1$ and therefore $A=0.87$ should be appropriate.

Combining this value for A at low temperature with the assumption that $A=1$ at 300 K, the ratio "n"$/N_D$ at 4.2 K takes the form indicated by the curve B in Fig. 1. This curve is weighted to correspond with the data of Chapman *et al.*[9] because of the much greater experimental scatter evident in the alternate study.[10] Although this correction almost eliminates the disconcerting condition that $n(4.2\text{ K})/N_D>1$, it should not be accepted unequivocally, because the assumption that $A=1$ at 300 K cannot be justified except as a first approximation.

Recently Reimann and Walton[12] have attempted to determine experimentally r and hence A for a similar set of samples through the combined use of Faraday rotation, dispersion, and Hall-coefficient data. For samples with donor concentrations between 10^{18} and 10^{19} donors/cm^3, these workers found $1.3<A<1.5$ at 300 K. Values of $A>1$ seem reasonable since the anticipated dominant ionized impurity scattering mechanism would, for classical statistics, give a value $r=1.93$. The onset of partial degeneracy in these samples might be expected to lower this last value into accord with the Reimann and Walton experimental numbers.[13] Unfortunately, however, it is, at present, difficult to completely accept the Reimann and Walton results in the absence of further published detail concerning measurement techniques and the interpretation of data under conditions of varying degrees of degeneracy. This information would seem essential in view of the extremely anomalous 77-K results reported by these same authors.[12]

In any case, the concentration values obtained assuming $A(300\text{ K}) = 1$ in the two cited[9,10] low-temperature studies are significantly lower in the $10^{18} \leq N_D \leq 10^{19}$ donors/cm^3 sample range than would be deduced from the reported resistivities and the so-called "Irvin curve." The latter curve[14] gives the relationship between the room-temperature resistivity $\rho(300\text{ K})$ and the donor impurity concentration N_D of n-type silicon. It was constructed on the basis of a compilation of data obtained through the use of standard dc transport techniques and from methods which directly measure the donor impurity concentration. The disagreement with the Irvin curve is most evident in the results reported by Yamanouchi *et al.*[10] The absolute values of these reported concentrations are sometimes only about 50% of those which would be inferred from the reported values of $\rho(300\text{ K})$ and the Irvin curve. This discrepancy is almost certainly responsible for the different values given[15,16] for the concentration at which the "hyperfine" ESR lines disappear. Maekawa and Kinoshita[16] have estimated this concentration to be $\approx 7\times10^{17}$ donors/cm^3, presumably using samples and concentration measurement techniques similar to those used by Yamanouchi *et al.*[10] On the basis of the Irvin-curve method of estimating N_D and our own ESR and resistivity measurements, we have found that these lines vanish at a significantly higher concentration $N_D \approx 1\times10^{18}$ donors/cm^3. This value is in good agreement with previous measurements.[15]

The sample concentrations quoted in the alternative low-temperature experimental study by Chapman *et al.*[9] differ to a much lesser extent from the corresponding Irvin-curve values. Further it is important to note that the Hall-coefficient and resistivity data presented in the Chapman study are in good agreement with the corresponding results as reported by Logan *et al.*[17] and Omel'yanovskii *et al.*[18] In all three of these studies[9,17,18] the donor concentrations were determined through the assumed validity of $N_D = [R_H ec]^{-1}$ at room temperature. The discrepancies between the values obtained for N_D in these studies and by nuclear activation techniques[19] were significant only in the $10^{17} < N_D < 10^{19}$ donors/cm^3 concentration range. These differences could be resolved if values of A between 1.0 and 1.3 were appropriate in this range (see Ref. 13). The Irvin curve represents a compromise between the results of these two different experimental approaches and in our estimation provides, at present, the most reliable method of establishing the values of N_D. Use of the resistivity data and the Irvin chart would result in a 10 to 20% upward revision of the donor concentrations reported in the Chapman work for samples with $N_D \lesssim 10^{19}$ donors/cm^3. As shown by curve C in Fig. 1, these changes would have at least two noteworthy effects. The first of these would be to shift upward the value $N_D{}^C \approx 3\times10^{18}$ donors/cm^3 previously deduced[2] for the critical concentration $N_D{}^C$ commonly associated with the SM transition in Si : P. The only immediate significance of this small change would appear to lie in the fact that it worsens slightly the agreement between measured and calculated values of this critical concentration.[20-22] However, such an increase in the value of $N_D{}^C$ would bring the experimental value of $a_H(N_D{}^C)^{1/3}$ (here a_H is the "atomic radius" appropriate to a given impurity-semiconductor system) into better agreement with the results for germanium and other semiconductors.[2]

Second the reinterpretation of the Hall-coefficient measurements, in terms of proposed increases in N_D and the factor A at 300 K, would indicate that the quantity n/N_D in Si : P at 4.2 K increases more slowly as the donor concentration rises through $N_D{}^C$ than has been previously believed.[11] The more gradual nature of this transition is similar to the corresponding behavior observed in Ge and other semiconductors and would lessen agreement with the results of the Holcomb and Rehr percolation calculation. Unfortunately because of the small number of samples studied in the critical concentration range, it is not possible to estimate the width (in concentration) of the Si : P SM transition on the basis of the data obtained by Chapman and his co-workers.[9] Previous conclusions[11] in this regard have been based largely on the data of Yamanouchi *et al.*[10] which exhibit large experimental scatter, particularly in the neighborhood of the critical-concentration region. An experimental clarification of this situation might enable more definitive conclusions to be drawn with regard to the effect of the random impurity distribution upon the predicted[20] discontinuous nature of the SM transition for a regular lattice.

In any case the $N_D < 10^{19}$ donors/cm^3 samples in the present investigation were specifically chosen to facilitate the study of the critical-concentration region. These samples have impurity concentrations of $N_D = 1.8\times10^{18}$, 2.3×10^{18}, 3.4×10^{18}, and 5.9×10^{18} donors/cm^3 [based on the Irvin curve and our own measurements of $\rho(300\text{ K})$]. In a commonly used notation, these will be denoted, respectively, as samples (1.8–18), (2.3–18), (3.4–18), and (5.9–18). For the purposes of our discussion it will be useful to classify each of these samples into one of three categories; "semiconducting," "metallic," and "transition" on the basis of their respective experimental carrier density behaviors. The properties characteristic of each of these categories will become clear in the course of the dis-

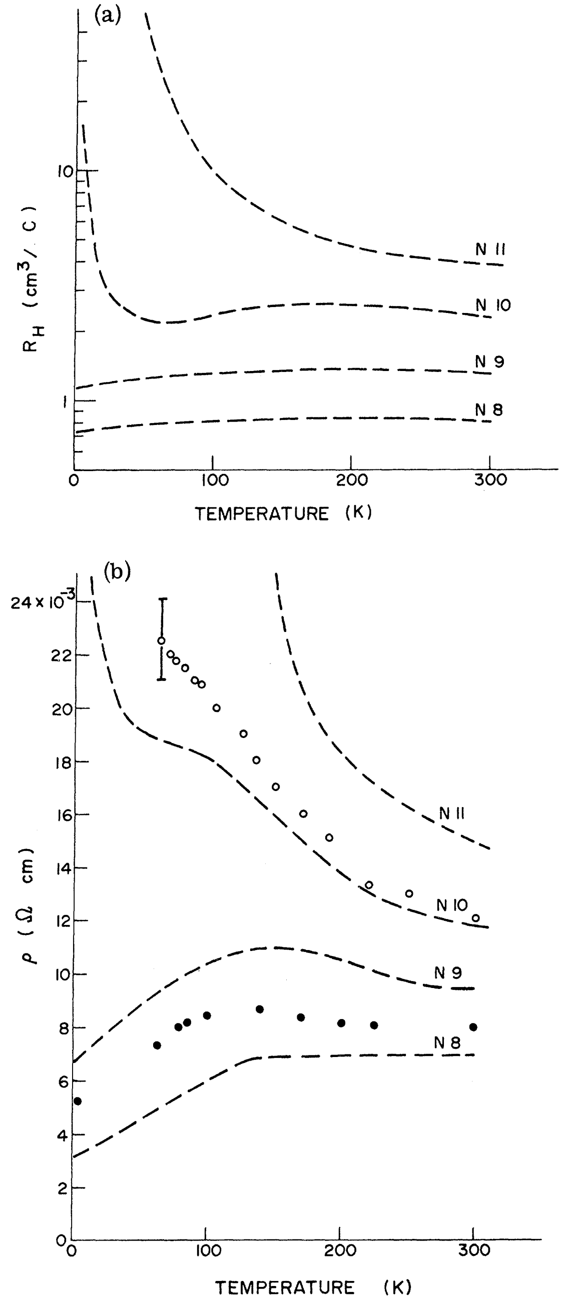

FIG. 2. Temperature dependence of the resistivity (ρ) and Hall coefficient (R_H). The dashed curves are based on the data of Ref. 9. Experimental results for samples (3.4–18) and (5.9–18) are represented by open and closed circles, respectively.

cussion below. In the absence of complete measurements of the Hall effect in our own samples, we will utilize the results of Chapman *et al.*[9] [as presented in Figs. 2(a) and 2(b)]. Insofar as possible, we make suitable identifications with our samples.

A. Semiconducting (*S*-Type) Samples

From the data presented in Figs. 2(a) and 2(b), there is no evidence of significant low-temperature carrier densities in samples with $\rho(300\ \text{K}) > 0.016$ Ω cm. More precisely n/N_D appears to be negligibly small when $T < 50$ K, increasing to a value $\lesssim 0.2$ at 77 K. This dependence of n upon T clearly places these samples on the low-concentration or semiconductor side of the SM transition. Accordingly, we describe samples (1.8–18) and (2.3–18) as "semiconducting" or *S*-type samples.

B. Metallic (*M*-Type) Samples

Samples (5.9–18) and all previously considered[1] samples with $N_D > 10^{19}$ donors/cm^3 have been denoted as "metallic" or *M* type because the nearly flat experimental R_H-vs-T curves obtained in these cases [Fig. 2(b)] indicate that the corresponding conduction electron densities are essentially temperature independent. Unfortunately, quantitative considerations of these results are complicated by the fact that the electronic carriers in most of these samples are not completely degenerate at 300 K. This circumstance, as previously discussed, leads to some uncertainty as to the correct room-temperature values of the Hall scattering factor A.

The small decrease observed in R_H as the temperature is lowered may be ascribed[23] to a reduction in the value of A as a result of the increasing degeneracy. Although the low-temperature carrier densities of *M*-type samples are generally assumed to be approximately equal to N_D, it will be useful, for our later discussions, to make an explicit estimate of the experimental low-temperature ratio n/N_D. On the basis of the Irvin curve, the Chapman sample *N*9 has a donor concentration $N_D = 5.4\times10^{18}$ donors/cm^3 [which corresponds to a value $A(300\ \text{K}) = 1.10$]. At temperatures below approximately 20 K, complete degeneracy should be approached and a value $A = 0.87$ is applicable. These values of A, together with the Hall-coefficient data in Fig. 2 give a ratio $n(4.2\ \text{K})/N_D = 0.93$ for this sample. This result is in accord with our general expectation that the low-temperature carrier densities of sample (5.9–18) and our other *M*-type samples lie no more than a few percent below the corresponding values of N_D. The differences between n and N_D in $N_D > 10^{19}$ donors/cm^3 samples at low temperatures are too small to be directly observed in Hall-effect studies. However, it is important to note that if a larger value of A is correct at 300 K (as implied by the nuclear activation results[19] and the measurements of Reimann and and Walton[12]) in the $N_D < 10^{19}$ donors/cm^3 samples, a correspondingly smaller ratio $n(4.2\ \text{K})/N_D$ would result. This reduction would not exceed 10%.

C. Transition (T-Type) Samples

The room-temperature resistivity and R_H values of sample (3.4–18) nearly agree within experimental error with the corresponding results reported by Chapman *et al.* for their sample $N10$. A similarity of the ρ-vs-T behavior is also noted between these two samples [Fig. 2(a)]. We thus feel justified in assuming an identity between these samples for the purposes of the following transport property discussion. From Fig. 2(b) it can be seen that the carrier density in the Chapman sample $N10$ has a temperature dependence which is intermediate to the extreme S- and M-type forms of behavior. Specifically, the relative carrier density n/N_D is strongly dependent upon T at low temperatures. This relative density rises from nearly zero below 4.2 K (similar to S type) to a value near unity at ~20 K (characteristic of M type). We shall refer to this "transitional" behavior as "T type."

In the absence of our own Hall-coefficient measurements and a complete knowledge of $A(T)$, we have been content to estimate the conducting electron densities $n(T)$ appropriate to sample (3.4–18) from a determination of the lower bound of $n(T)$ for sample $N10$.

Our procedure assumes the value $A(300\text{ K}) = 1.2$ necessary to reconcile the Hall-effect measurements with the Irvin curve and a value $A = 0.87$ at low temperatures. This approach gives lower limits of approximately 10% and 50% for the relative carrier densities at 4.2 and 10 K, respectively. It must be recognized that these results are only qualitative because of both the uncertainty involved in identifying sample (3.4–18) with the Chapman sample $N10$ and the neglect of "two-band" conduction effects.[24] Nevertheless, it is clear that a change does occur in the low-temperature electrical properties of sample (3.4–18) which is consistent with such a carrier density variation. The general trend of the Hall-effect data indicates $n/N_D \approx 1$ for temperatures $\gtrsim 20$ K.

III. EXPERIMENTAL ESR PROCEDURES

The ESR measurements discussed in this paper were performed on powdered Si : P samples at temperatures ranging from 1.1 to 77 K. Details of sample preparation and the modulation-switching technique used in the measurement of relative spin susceptibilities have been given in I. Using the double-sample modulation-switched (DSMS) cavity and the previously described procedures, we have obtained experimental values for the spin susceptibilities χ_s, the ESR linewidths $\Delta H_{\text{p-p}}$ and the g factors for our samples at the temperatures 1.1, 4.2, and 77 K.

The long-term temperature stability required for the application of the DSMS cavity technique precluded its use at temperatures between 4.2 and 77 K. Susceptibilities at these intermediate temperatures were instead measured by a simpler but slightly less accurate method. This procedure was based on the nearly simultaneous observation of the ESR signals which arise from the Si : P sample and from a small piece of annealed, neutron-irradiated LiF (LiF : Li).[25] The signal from the latter material has been shown to originate from microscopic globules of lithium metal which has been shown to have[26,27] a temperature-independent spin susceptibility in the 1.1–77 K temperature range.

The Si : P powder and a piece of LiF : Li were contained in the same sealed cylindrical Lucite sample capsule which was ground flat on one side and affixed with thermally conducting grease to the bottom face of a TE_{102} rectangular X-band cavity. This resonant cavity was enclosed within a stainless-steel can which could be removed to allow sample replacement. A brass flange, attached to the waveguide above the cavity iris, provided thermal contact with the stainless-steel can and hence with the liquid-helium bath in which the entire assembly was immersed. Soldered to the outside of the bottom plate of the cavity was a large brass block in which were embedded a carbon resistance thermometer and a heater. The former of these was located immediately below the cavity bottom plate and the latter at the extreme bottom of the brass block. Using the heater, temperatures up to 30 K could be maintained with excellent stability, for as long as 30 min. The stability decreased with increasing temperature, and thermal equilibrium between the sample and the thermometer cannot be assumed for $T > 30$ K. Because of the placement of the sample and thermometer relative to the heater, the measured temperature might be expected to exceed slightly that of the sample. The carbon resistor was calibrated by comparison with a precision germanium resistance thermometer. The accuracy with which the sample temperature could be measured was estimated to be 5% for $T < 30$ K and ≈10% for temperatures above this limit.

The magnetic field separations and linewidths of the LiF : Li and Si : P ESR lines allow a relatively simple separation of their individual contributions to the observed combined spectra. As described in I, our spectrometer yields a digital output signal which is proportional to the derivative with respect to the magnetic field H of the absorptive component $\chi''(H)$ of the complex magnetic susceptibility. The paramagnetic spin susceptibility χ_s has been shown[27] to be proportional to $g\int_0^\infty \chi''(H)\,dH$; thus the relative spin susceptibilities of the Si : P and LiF : Li samples at a given temperature could be measured by a comparison of their respective doubly integrated ESR signals.[28] This comparison when combined with the known temperature independence of the LiF : Li spin susceptibility yielded the temperature dependence of χ_s for the Si : P samples. These temperature dependences were taken together with the absolute values χ_s(77 K) and χ_s (4.2 K) determined for Si : P by DSMS cavity techniques, to establish absolute values of χ_s at intermediate temperature points.

As discussed in I, although an error estimate of 10% seems appropriate to the absolute spin-susceptibility values obtained by the DSMS cavity technique, relative susceptibility ratios such as $\chi_s(77\text{ K})/\chi_s(4.2\text{ K})$ may be specified to a somewhat better accuracy. In successive measurements at a given temperature, the ratio of the Si : P sample's susceptibility to that of the LiF : Li exhibited a standard deviation which was less than 5%. This would suggest that in the absence of a systematic error, a ratio of the form $\chi_s(T_1)/\chi_s(T_2)$ could be specified to an accuracy of ≈7%. The ratios $\chi_s(77\text{ K})/\chi_s(4.2\text{ K})$ obtained by this technique agreed well within experimental error with the values obtained for this quantity by the DSMS cavity technique. The latter results were obtained by comparison with LiF : Li, $CuSO_4 \cdot 5H_2O$, and DPPH standards and were based on the unambiguous separation of the Si : P and "standard" samples' ESR signals as discussed in I. The consistency of the results obtained by these two methods would appear to substantiate the reliability of the technique used at intermediate temperatures.

The peak-to-peak linewidth ($\Delta H_{p\text{-}p}$) results presented in I have been extended to include data points between 4.2 and 77 K for samples with $N_D < 10^{19}$ donors/cm^3. The techniques used in these measurements are standard and have been discussed in I.

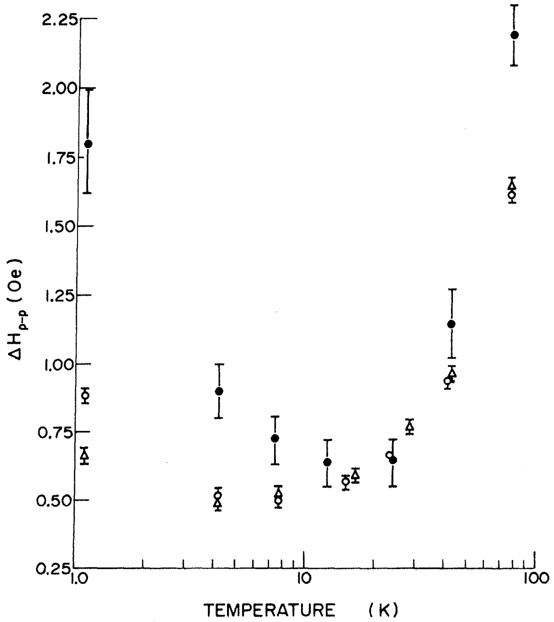

FIG. 3. Experimental peak-to-peak linewidth $\Delta H_{p\text{-}p}$ as a function of the temperature for samples (1.8–18) (closed circle); (2.3–18) (open circle); (3.4–18) (triangle).

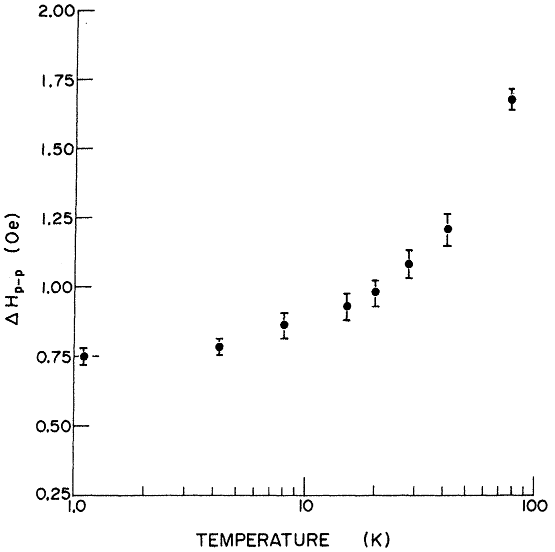

FIG. 4. Experimental peak-to-peak linewidth $\Delta H_{p\text{-}p}$ as a function of the temperature for sample (5.9–18).

IV. EXPERIMENTAL ESR RESULTS

A. Linewidths and *g* Values

In I we have reported the peak-to-peak linewidth and *g* values observed at 1.1, 4.2, and 77 K for Si : P samples with $N_D \geq 2.3\times10^{18}$ donors/cm^3. We have now extended these measurements to intermediate temperature points and to include a $N_D = 1.8\times10^{18}$ donors/cm^3 sample.

The *g*-value data may be summarized as follows:

(i) Within experimental accuracy (~± 1 part in 4×10^4), the *g* values are independent of concentration and temperature when $1.1 \leq T \leq 77$ K and $N_D \leq 4\times10^{18}$ donors/cm^3.

(ii) A slight increase of *g*, barely within our experimental sensitivity, can be observed in the *M*-type sample (5.9–18) when the temperature decreases. This dependence becomes significant in slightly more concentrated samples.

(iii) The differences between the *g* values of sample (5.9–18) and of our $N_D = 1.3\times10^{19}$ donors/cm^3 sample are at the limits of our sensitivity. However, when N_D exceeds $\sim 2\times10^{19}$ donors/cm^3, it is clear that the *g* values are decreasing functions of the impurity concentration at all temperatures.

Our more complete temperature-dependence data for $\Delta H_{p\text{-}p}$ in $N_D < 10^{19}$ donors/cm^3 samples are presented in Figs. 3 and 4. The first of these figures contains data specifically pertaining to our *S*- and

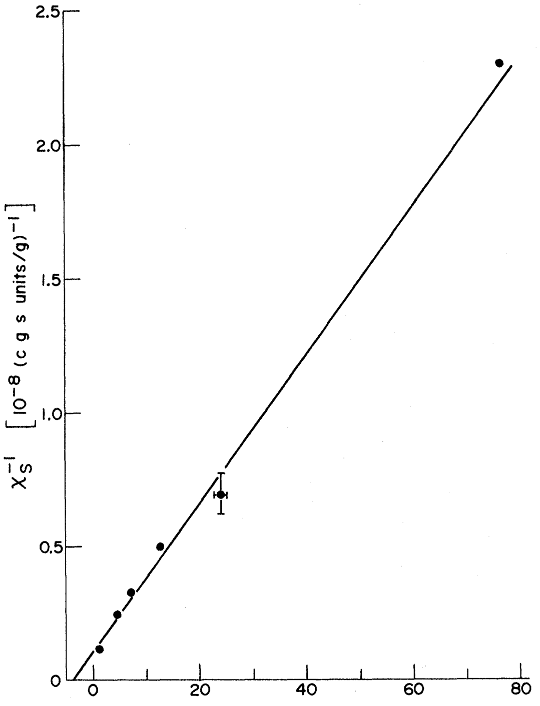

FIG. 5. Experimental inverse spin susceptibility χ_s^{-1} as a function of temperature for sample (1.8–18). The solid line in this figure represents the dependence of χ_s on T expected on the basis of the two-component susceptibility model discussed in the text.

T-type samples, while Fig. 4 is concerned only with our M-type sample (5.9–18) results. The linewidths in the latter sample increase monotonically with temperature. This result is in contrast with the observed behavior in S- and T-type samples where a definite minimum appears in the experimental linewidths as a function of T. This minimum has been previously reported[16] and interpreted as a characteristic of samples on the semiconducting side of the SM transition. The temperature at which this minimum occurs is observed to decrease with increasing N_D. The observed broadening of the ESR lines on the low-temperature side of the minimum would appear to be the result of incomplete motional or exchange averaging of local effective fields. The decreasing prominence of the minimum in the linewidth-vs-temperature data as the concentration N_D was increased is indicative of a corresponding decrease in the extent of the localization associated with the extrinsic electrons at the low-temperature extreme.

We have also found, in accord with previous results,[16] that at low temperatures the experimental linewidths achieved their minimum values at the concentration ($N_D = 3.4\times10^{18}$ donors/cm^3) most closely associated with the SM transition in the electrical-transport properties.

It is also worthy of note that the linewidths observed at 77 K for our three most concentrated $N_D < 10^{19}$ donors/cm^3 samples are all essentially identical and commonly separated from the larger value obtained for sample (1.8–18). This behavior may be related to the significantly larger relative carrier densities (n/N_D) in the former group of samples at 77 K.

We have not analyzed our $N_D < 10^{19}$ donors/cm^3 sample linewidths in a manner which would allow an extraction of the spin-lattice relaxation rates. In addition to the complications associated with the incomplete motional narrowing, the narrow linewidths observed in these samples make inapplicable the approximate procedure used in I to extract the "true" lifetime linewidths from the broader experimental $\Delta H_{p\text{-}p}$ values.

B. Spin Susceptibilities, Experimental Results, and Models

The inverse of the measured susceptibility χ_s^{-1} is plotted as a function of the temperature in Figs. 5–8 for each of our four $N_D < 10^{19}$ donors/cm^3 samples. This particular form of data presentation was chosen to simplify the extraction of anticipated Curie- or Curie–Weiss-law susceptibility components from our experimental results.[29]

The general form of our data in this temperature range is clearly inconsistent with the simple band model in which the temperature dependence of χ_s is assumed[3,4] to arise from the changing degeneracy of the electrons in a narrow conduction

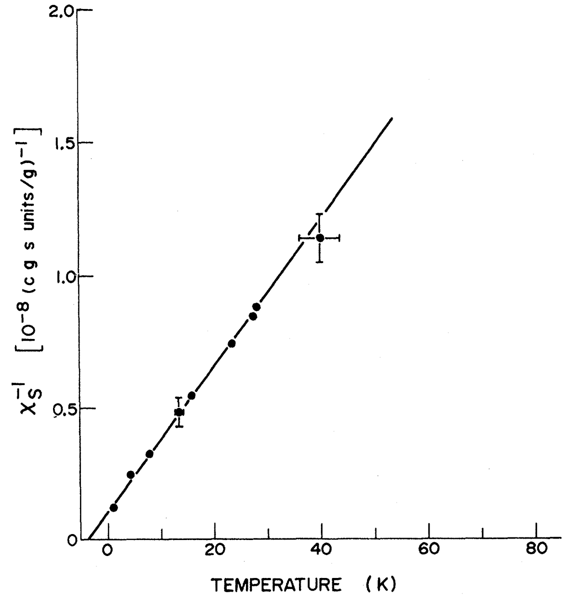

FIG. 6. Same caption as Fig. 5 except for sample (2.3–18).

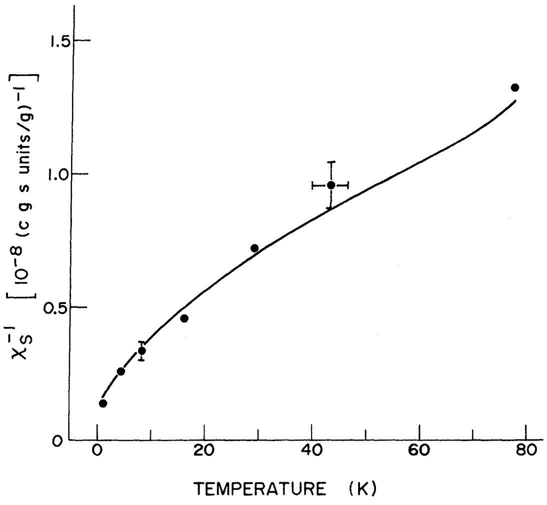

FIG. 7. Same caption as Fig. 5 except for sample (3.4–18).

band as a function of the temperature. The slope of the characteristic χ_s^{-1}-vs-T curve predicted by this model is an increasing function of temperature. An opposite behavior is observed in our experimental results and we must conclude that this approach, at least in its simple tractable form, cannot offer a satisfactory representation for the Si : P spin susceptibilities.[30]

On the other hand, we have been able to reproduce our experiemental results by a simple phenomenological approach, which is a generalization of the earlier inhomogeneity model suggested by Mikoshiba.[5] The spin susceptibility in our two-component model is assumed to be a simple sum of Curie–Weiss-law and Pauli-law susceptibility components and can be written as

$$\chi_s = \chi_{\mathrm{CW}} + \chi_{\mathrm{P}} \ . \tag{3}$$

The Curie–Weiss susceptibility component can be written explicitly as

$$\chi_{\mathrm{CW}} = C/(T-\theta) \ , \tag{4}$$

where C and θ, respectively, represent the Curie constant and the Curie-Weiss temperature. We shall assume that an extrinsic density of N_{CW} electrons per unit volume contribute to this component of the susceptibility. The Pauli-law component in Eq. (3) may be written as

$$\chi_P = \frac{\mu_B^2 N_P}{\delta k T}\,\frac{F'_{1/2}(\xi/kT)}{F_{1/2}(\xi/kT)} \tag{5}$$

and corresponds to the susceptibility contribution from N_P, the number of Pauli-law electrons per unit volume. In this equation μ_B represents the Bohr magneton, δ is the Si mass density, and k is the Boltzmann constant, while $F_{1/2}(\xi/kT)$ and $F'_{1/2}(\xi/KT)$, respectively, denote the Fermi integral[31] and its first derivative evaluated at the Fermi level ξ.

The use of Eq. (3) may be partially justified by its correspondence with the observed temperature dependences of the samples at the extremes of the studied concentration range. As shown in Fig. 5, the χ_s data of our most dilute sample (1.8–18) follow a Curie–Weiss law, while our most concentrated sample (1.05–20) has been shown (in I) to exhibit, within experimental error, a temperature-independent susceptibility characteristic of the Pauli law.

In order to determine the parameters C, θ, N_D, and ξ appearing in Eqs. (4) and (5), certain additional assumptions were made. Equation (3) was fitted to the experimental data subject to the constraints imposed by these assumptions which are outlined below.

(i) The appropriate Curie constant for each sample was determined in a manner consistent with the observed susceptibilities of the S-type samples. In the latter cases C and θ could be obtained directly from the straight-line forms of the experimental data and on the basis of the reasonable assumption that at low temperatures N_p, $\chi_p = 0$. For these samples C was found to be equal to approximately one-half of the value C_R calculated from the standard expression[31] appropriate to $N = N_D$ electrons of spin $\frac{1}{2}$ in a regular lattice:

$$C_R(N) = N\mu_B^2 g^2/4\delta k \ . \tag{6}$$

On the basis of this result, the relationship be-

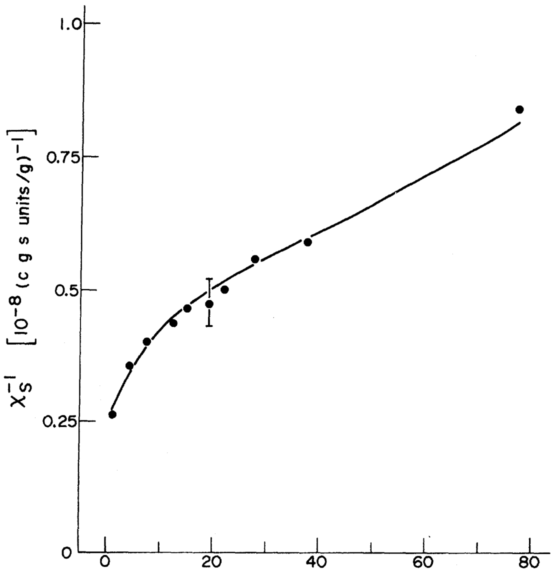

FIG. 8. Same caption as Fig. 5 except for sample (5.9–18).

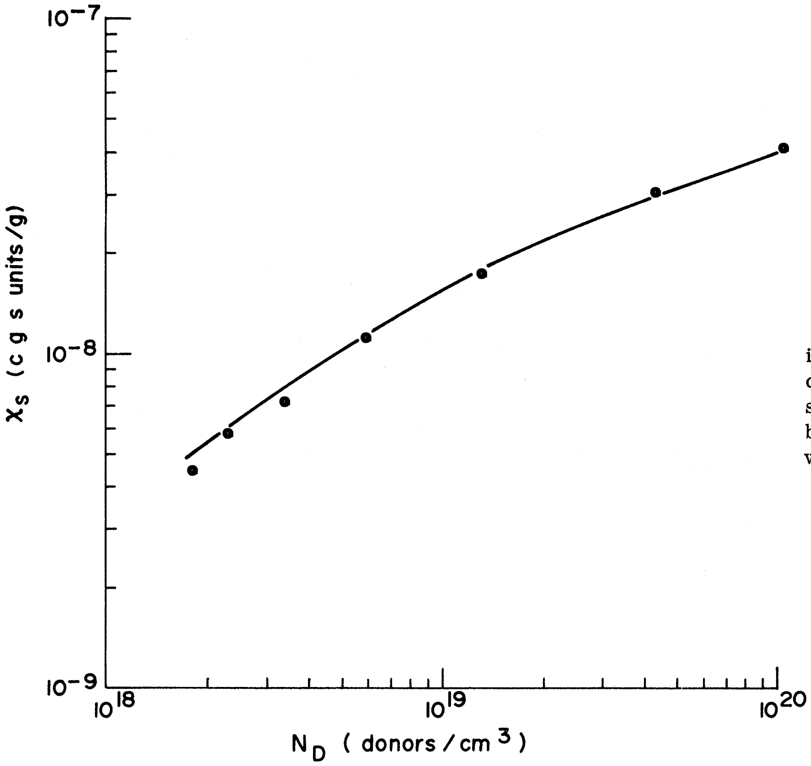

FIG. 9. Experimental spin susceptibility χ_s at $T = 77$ K as a function of donor concentration N_D. The solid curve represents the corresponding Pauli susceptibility of N_D electrons per unit volume with effective mass $m^* = 0.9m_0$.

tween C and the corresponding electron density N_{CW} was defined by

$$C \equiv \tfrac{1}{2} C_R(N_{\mathrm{CW}}) \ . \qquad (7)$$

(ii) The χ_P component was calculated by Eq. (5) using linear interpolation between the tabulated values of the Fermi integrals[32] and the standard $T = 0$ approximation when ξ/kT exceeded the tabulated range of arguments. The Fermi level was determined through the use of the standard "rigid-band" expression

$$N_P = 4\pi\left(\frac{2m^*kT}{\hbar}\right)^{3/2} F_{1/2}\left(\frac{\xi}{kT}\right) \ . \qquad (8)$$

The effective mass $m^* = 0.9m_0$ (m_0 is the free electronic mass) was determined by fitting Eq. (5) to the experimental susceptibilities measured at 77 K for our most heavily doped samples. This procedure seems reasonable inasmuch as it was shown in I that, for samples with $N_D > 10^{19}$ donors/cm^3, deviations from Pauli-law behavior were small even at low temperatures. Further, these deviations should become less significant with rising temperature if they follow a Curie- or Curie–Weiss-law form of behavior. As shown in Fig. 9, the agreement between the experimental data and the Pauli susceptibility calculated for $N_P = N_D$ and $m^* = 0.9m_0$ is excellent at high concentrations and persists to a lesser extent even to the most dilute samples studied. For the S-type samples, which behave essentially as Curie–Weiss materials, this agreement between χ_P and the experimental susceptibilities would seem to be fortuitous. However, the correspondence at larger values of N_D can be considered as a justification for both the use of a Pauli susceptibility term in Eq. (5) and the choice $m^* = 0.9m_0$. The discrepancy between the latter value and the effective mass $m^* = 1.06m_0$ calculated on the basis of peizoresistance[33] and cyclotron resonance data[34] may in part be due to the 10% uncertainty in the absolute susceptibility calibration. Such an error does not strongly affect the experimental χ_P temperature dependence which is the dominant factor in determining $\chi_P/\chi_{\mathrm{CW}}$.

(iii) The concentration N_P is subject to the requirement that $N_P + N_{\mathrm{CW}} = N_D$. The Pauli susceptibility χ_P should not be very sensitive to errors in the estimated values of N_{CW}, since it varies approximately as $N_P^{1/3}$.

A successive approximation technique was used to match Eq. (3) to the χ_s data obtained for T- and M-type samples, subject to the constraints stated above. The values for θ, N_{CW}/N_D and N_P/N_D determined in this way for each sample are listed in Table I, and the corresponding "two-component" susceptibilities are represented by the solid curves in Figs. 5–8. The errors quoted in Table I for samples with concentrations $N_D < 10^{19}$ donors/cm^3 correspond to the extremal fits within the limits of experimental error. The quoted values for $N_{\mathrm{CW}}/$

TABLE I. Values of parameters for best fit of two-component susceptibility model to χ_s data.

Sample	N_P/N_D	N_{CW}/N_D	θ(K)
1.8–18			-2.5 ± 1
2.3–18			-3.0 ± 1
3.4–18	0.65 ∓ 0.07	0.35 ± 0.07	-2.6 ± 1
5.9–18	0.86 ∓ 0.05	0.14 ± 0.05	-3.7 ± 1.6
1.3–19	0.98	0.02	-6
2.1–19	0.98	0.02	-7
4.3–19	0.99	0.01	-9
1.05–20	0.99	0.01	-12

N_D for the M- and T-type samples are subject to the validity of the assumption Eq. (7). The results for $N_D > 10^{19}$ donors/cm^3 are exact solutions for the two-parameter fit through the three experimental data points at 1.1, 4.2, and 77 K. However, since the possible experimental error is comparable in magnitude to the total change in χ_s as a function of temperature, a wide variation of the parameters is possible. Thus the parameters listed for these samples in Table I should be regarded as approximate.

V. DISCUSSION

A. Experimental S-, T-, and M-Type Sample Results

The two-component model which has been applied to our spin susceptibility data in Sec. IV is a generalization of the earlier inhomogeneity proposal of Mikoshiba.[5] Our modifications of this latter model consist of replacing its Curie-law susceptibility component by one of the Curie–Weiss form and of eliminating, for the sake of generality, rigorous identifications between, respectively, conducting and Pauli-law electrons, and nonconducting and Curie–Weiss electrons. It would seem that these identifications are in fact justified in the extreme cases of dilute S-type and concentrated M-type samples. However, in samples of intermediate impurity concentrations, the experimental transport and spin-susceptibility data are not such as to establish unambiguously the inhomogeneity model as applicable. In discussing this situation, we shall follow a format similar to that of Sec. II in which the relatively straightforward results obtained at the extreme concentrations are considered prior to a treatment of the T-type data.

1. S-Type Samples

The experimental results of Secs. II and IV indicate that samples (1.8–18) and (2.3–18) can be characterized by negligible relative carrier densities n/N_D and a Curie–Weiss-law susceptibility when $T < 50$ K. At higher temperatures these samples exhibit small but significant carrier density and deviations from the low-temperature Curie–Weiss susceptibility behavior. These deviations are more pronounced in the more concentrated sample (2.3–18). It seems plausible for these samples to associate a Curie–Weiss spin susceptibility with nonconducting and hence presumably partially "localized" electrons. At temperatures below the carrier generation threshold, these materials, because of the antiferromagnetic interaction[34] between unpaired neighboring electrons, are prototype disordered or amorphous antiferromagnets. Hence the Curie–Weiss susceptibility observed in our S-type samples might be interpreted as a characteristic of such systems. As noted above, the Curie constants determined empirically for these samples are only about one-half of the values predicted by the regular lattice expression for C_R [the ratios C/C_R are 0.62 and 0.56 for samples (1.8–18) and (2.3–18), respectively]. Further, the values of θ obtained for these samples are approximately one order of magnitude larger than the Curie–Weiss temperatures calculated on the basis of an expression appropriate to a regular face-centered-cubic lattice[35] and a previous estimate[36] of donor pair exchange energies. Both of these differences from the regular lattice results are such as to reduce the low-temperature spin susceptibility and may presumably be at least partly attributed to the random spatial distribution of the impurity atoms. This reduction has been qualitatively anticipated by Mott[37] who argued that in a random array of spins, the environment at a given site will tend to be dominated by the nearest neighboring impurity. This situation leads to pairing of some very strongly coupled neighboring spins into nonmagnetic states[34,36] and consequently to a reduction in the magnetization relative to that of an ordered array with the same mean spin density. Such randomness-related effects complicate, and at present, prevent a quantitative analysis of these results in terms of Hubbard-model[38] parameters such as has recently been attempted by Epstein *et al.*[39] in the case of a "one-dimensional" regular lattice system.

The data show no significant evidence of the existence of an antiferromagnetic ordering transition in the temperature range observed. For a regular lattice antiferromagnet, the transition temperature T_N is generally $\geq \frac{1}{3}|\theta|$.[35] If this empirical rule were applicable to the present random-lattice case, the values of T_N should exceed the 1.1-K lower-temperature limit of our observations. Both upward and downward randomness-induced shifts of T_N have been predicted.[40–42] Our results appear to be in conflict with the former alternative,[42] but accuracy limitations and the experimental restriction to temperatures $T \geq 1.1$ K prevented definitive examination of this critical behavior.

2. M-Type Samples

In spite of the limited temperature-dependence data available for the spin susceptibilities of our $N_D > 10^{19}$ donors/cm^3 samples, there would appear to be little doubt that the general two-component model can be used to represent the M-type sample experimental results. However, if an underlying physical basis is to be presumed for this model, it is necessary to establish an interpretation of the corresponding dc transport data which is consistent with the existence of these two magnetic components. We have shown that, for S-type samples where $n/N_D \approx 0$, the identification of a Curie–Weiss susceptibility with the nonconducting electrons ($N_{\rm CW} = N_D - n$) and a Pauli susceptibility with the conducting electrons ($N_P = n$) is quite successful. Unfortunately, in M-type samples, the complexities of transport property measurement and interpretation make it difficult to specify the relative carrier density n/N_D to an accuracy greater than a few percent. Further, because of both the small number (three) of temperature points taken per sample and the weak temperature dependence of χ_s, the values of $N_{\rm CW}/N_D$ listed in Table I for the $N_D > 10^{19}$ donors/cm^3 samples should be considered uncertain to at least a factor of 2. Thus although it is generally assumed that $n/N_D = 1$ for M-type samples, it is difficult to prove that the nonconducting electron densities $N_D - n$ in $N_D > 10^{19}$ donors/cm^3 samples are not sufficiently large to correspond to the deduced Curie–Weiss densities. In the case of sample (5.9–18), however, the more extensive set of experimental data and the larger temperature dependence of χ_s permits the density $N_{\rm CW} = 0.14 N_D$ to be specified with an uncertainty of perhaps 40%. This result is significantly larger than the nonconducting electron densities deduced in previous interpretations of Hall-effect data assuming $A(300\ {\rm K}) = 1$ but only slightly exceeds (allowing for the experimental error limits) the values calculated in Sec. II assuming the validity of the Irvin curve (as indicated by the curve C in Fig. 1).

3. T-Type Samples

As indicated in Sec. II, the T-type sample (3.4–18) can be distinguished from all other samples used in the present study by the strong temperature dependence of its carrier density in the 1.1–77-K experimental region. This behavior is such as to suggest that a semiconductor-to-metal transition might occur in this sample with rising temperature. An effect of this nature has been observed in other materials[39] and in the present case might be attributed to the elimination of previously occupied partially localized states by the screening produced by the initial thermally generated carriers. The methods used in Sec. II to estimate n/N_D for this sample are particularly crude. Nevertheless there is little doubt that this quantity rises from a value < 0.1 at $T \sim 1$ K to approximately unity at a temperature ~ 20 K.

It is very difficult to reconcile these carrier densities with the spin component densities $N_{\rm CW}$ and N_P derived from the χ_s data and listed in Table I. The fact that $N_P = 0.65 N_D$ greatly exceeds the low-temperature carrier density need not be regarded as physically unreasonable. The criterion for participation in the dc conductivity differs from that for Pauli-like temperature dependence of the susceptibility. The latter may be satisfied by delocalization of the electrons within a large "cluster" of impurities, whereas the former requires connectivity of the clusters. An alternative explanation in terms of possible exchange enhancement does not seem viable in view of the observed lack of such enhancement in our most concentrated samples.

However, the strong temperature dependence of n prevents its direct identification with the temperature-independent parameter N_P. Therefore, it appears that little physical significance may be attached to the two-component model, with fixed temperature-dependent values of $N_{\rm CW}$ and N_P, deduced from the sample (3.4–18) experimental χ_s data. This circumstance underlines the dangers inherent in the application of an empirical model to a limited number of the experimental properties of any system.

B. General Considerations

It has been seen that at the extreme low and high impurity-concentration limits of the present study, the experimental spin susceptibilities may be represented, respectively, by the standard Curie–Weiss- and Pauli-law expressions. Similarly at these limits of N_D the respective assumptions (at low temperatures) of negligible densities of conducting and nonconducting extrinsic electrons seem well founded. In these extreme cases the inhomogeneity model identifications of nonconducting electrons with $\chi_{\rm CW}$ and of conducting electrons with χ_P would appear to be firmly established. The two-component model does offer a method of representing the experimental spin susceptibilities for samples of intermediate impurity concentrations. However, it is difficult, in view of the existing electrical-transport data, to make the inhomogeneity model identifications which would allow a simple physical interpretation of the two-component susceptibilities empirically deduced for these samples.

There are a number of alternative approaches available to us which allow these results to be understood within the confines of a general two-component approach. In our opinion the simplest and most likely of these possibilitites involves the assumption of a small error in the sample impurity concentration values as deduced from the Irvin curve in the $10^{18} < N_D < 10^{19}$ donors/cm^3 sample range. More specifically an upward shift of 5 or 10% in the impurity concentration assumed for sample (5.9–18) will, when combined with the preceding analysis of the low-temperature Hall carrier density data, give a value of $N_D - n$ for this sample which is, within experimental error, equal to the value deduced for N_{CW}. This shift then allows the inhomogeneity model to be consistent with the experimental electrical-transport and spin-susceptibility data appropriate to all of our M-type samples. An error in the Irvin curve of this magnitude and sign is not unexpected. As discussed in Sec. II, the available neutron-activation data,[19] the recent results of Reimann and Walton,[12] and our simplistic calculations[13] of A(300 K) indicate that such a revision of the sample impurity concentration values is reasonable. The proposed impurity concentration changes would be much smaller in the $N_D > 10^{19}$ donors/cm^3 sample region where the spin susceptibility data are compatible with the electrical-transport data and the inhomogeneity interpretation is within experimental error.

A realistic inhomogeneity model appropriate to our T-type sample should take some account of the strong temperature dependences observed for the corresponding nonconducting and conducting electronic densities. Presumably the quantities N_{CW} and N_P should follow the observed values of $N_D - n$ and n, respectively. Because of the limited accuracy of the available $n(T)$ data, we have not constructed such a model for our sample (3.4–18). Nevertheless it seems clear that the nearly Curie–Weiss experimental behavior observed for this sample requires a nonconducting electron density of at least $0.2N_D$ in the 15–30-K temperature range. Nonconducting electron densities of the magnitude required by this inhomogeneity model are not unreasonable in view of the available Hall-coefficient data and the uncertainty in the impurity concentration. If a smaller value of N_{CW} is used, a very sharply defined "plateau" appears in the χ_s^{-1}-vs-T curve. Such a structure is not supported by the experimental data which exhibit a gradual change in slope as a function of T. Although the data in the temperature range $T < 77$ K do not exhibit a plateau such as that predicted by Mikoshiba[5] and reported experimentally by Ue and Maekawa,[29] extension to higher temperature (and thus lessened degeneracy) would presumably reveal such behavior.[30]

It is common to associate the nonconducting, Curie–Weiss electrons of the inhomogeneity picture with the low-energy (E) portion of the one-electron density-of-states curves $D(E)$ which have been drawn[43] in reference to the properties of heavily doped semiconductors. We have sketched curves of this type relevant to our own samples in Fig. 10. The state density appropriate to S-type samples is illustrated in Fig. 10(a). The low-lying partially localized states in this picture are separated from the relatively normal conduction-band levels by a local minimum and "pseudogap"[44] in the density-of-states curve. These partially localized states are present at energies at least as high as the Fermi level, and dc current carriers can be generated only by excitation across this "pseudogap." The existence of this structure has been previously deduced[44] from tunneling data. The $D(E)$ curve sketched in Fig. 10(b) corresponds to our T-type sample (3.4–18) at liquid-helium temperatures. In this case a larger number of states exist at energies in the range associated with the "pseudogap" in S-type samples. As the

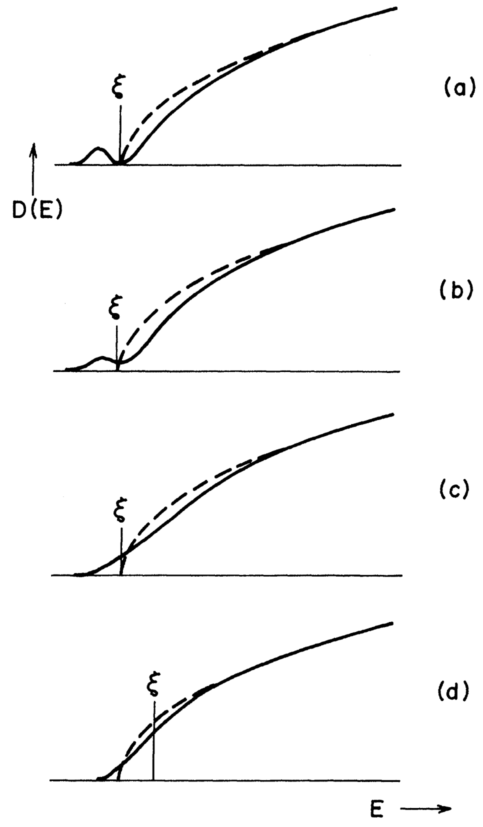

FIG. 10. A schematic plot of the density of one-electron states $D(E)$ as a function of energy E. (a) corresponds to an S-type (semiconducting) sample, while (b) and (c) represent a T-type (transition) sample at low and high temperatures, respectively. The density of states in (d) is appropriate to a relatively dilute M-type (metallic) sample. The vertical lines are indicative of the corresponding Fermi levels.

temperature is raised, the resultant excitation of carriers screens out some low-energy nonconducting states leaving at high temperatures only a small "tail" of these states appended to the normal conduction-band $D(E)$ curve. This situation is illustrated in Fig. 10(c). In this view, the "tail" may be assumed to exist at nearly all temperatures of interest in our M-type samples [see Fig. 10(d)]. In accord with the N_{CW}/N_D values listed in Table I, the number of states in these Curie–Weiss "tails" is assumed to be a monotonically decreasing function of N_D. At very high concentrations ($N_D \sim 10^{20}$ donors/cm^3) screening of the impurity potentials should eliminate "localized" states, although a tail is expected to remain on the density-of-states curve.[43]

In this picture, the Fermi levels in all M-type samples lie at energies which correspond to "conduction-band" states. The conflict between this result and the Alexander–Holcomb proposal[45] that the Fermi level enters the silicon host conduction band at an impurity concentration $N_D \sim 2\times 10^{19}$ donors/cm^3 may be resolved by a more detailed consideration of these electronic states.[46]

In the preceding paragraphs we have offered a representation of the properties of our Si : P samples in terms of an inhomogeneity model. As indicated, prior to this discussion, this simple approach appears to be consistent with the experimental electrical-transport and spin-susceptibility data only if a small error exists in the concentration values as determined by the standard Irvin-curve method. Obviously a detailed study of the Hall coefficient and conductivity properties of similar samples is essential to the resolution of this question. Such a study could more precisely establish the extent to which the inhomogeneity model offers a representation of heavily doped semiconductor systems.

If, on the other hand, our nominal impurity concentrations are in fact correct, the resultant inequality $N_{\mathrm{CW}} > N_D - n$ in the sample (5. 9–18) data requires additional assumptions if a physical interpretation is to be attached to the deduced two-component susceptibilities. For example, this inequality of N_{CW} and $N_D - n$ could be understood as the result of an enhancement of the Curie–Weiss susceptibility component of the localized electrons through an interaction with the conducting-electron component. This enhancement could be qualitatively similar to that observed in connection with dilute Pd : Fe alloys.[47] Alternatively, it is conceivable that dc current carriers exist in these samples which may be characterized by a spin susceptibility which is roughly of the Curie–Weiss form. There is some theoretical reason[48] to expect that electrons in the conducting states initially formed at the semiconductor-to-metal transition may have a net magnetic behavior which is intermediate to the extreme Pauli and Curie–Weiss forms. A small number of these electrons in our M-type samples could be consistent with the experimental data. However, these more complicated alternatives should receive more detailed consideration only if a clarification of the experimental electrical-transport situation demonstrates that the simple inhomogeneity model is in fact inappropriate to the Si : P problem.

C. Magnetoresistance

In this subsection we wish to consider the relationship between the spin-susceptibility data presented above and the large body of magnetoresistance data available for heavily doped semiconductors. An excellent review of this latter field has been contributed by Khosla and Fischer[49] in the course of their analysis of the CdS : In system. These authors have matched an empirical expression containing two terms with four adjustable parameters to their experimental data. One of these terms represented a positive magnetoresistance and was associated with the "shrinking" or increased localization of the extrinsic electron wave functions which can be produced by an increase in the applied magnetic field.[50] The second term, which had a negative sign, was of the form suggested by Appelbaum's calculation,[51] to third order in the s-d interaction, of the scattering of conduction electrons by "localized moments." The positive magnetoresistance component was observed to disappear near the upper limit of the CdS : In concentration range, presumably because of the insensitivity of the resulting conduction-band-like wave functions to even very large magnetic fields. The negative component, however, persisted to the highest experimental impurity concentration ($N_D = 1.2\times 10^{19}$ donors/cm^3), attaining its maximum size at the concentration $N_D \sim 1.5\times 10^{18}$ donors/cm^3 which has been associated with the semiconductor-to-metal transition in this material. Although all data were represented, within experimental accuracy, by the four-parameter expression, no explicit identification has been made of the localized spins required to justify the chosen form of the negative magnetoresistance component.

There are several indications that these "localized moments" may be associated with the electrons responsible for the Curie–Weiss portion of our two-component decomposition of χ_s. As has been noted by Lass,[52] the empirical B_2 coefficients of the Khosla and Fischer model, which should be proportional to the magnetization of the localized spin scattering centers, generally exhibit a temperature dependence of the form $B_2 \propto [T-\theta]^{-1}$. The constants θ in these Curie–Weiss-like proportionalities are similar (to within a factor $\lesssim 2$) to the values of the Curie–Weiss temperatures deduced in our susceptibility analysis for corresponding Si : P samples. Furthermore the magnetoresistance values of θ exhibit a concentration dependence which is comparable to that observed in our spin susceptibility results. The decrease in the magnitude of the negative magnetoresistance with increasing concentration on the "metallic" side of the semiconductor-to-metal transition parallels the observed decline in the relative and absolute magnitude of the corresponding Curie–Weiss susceptibility terms. Similar conclusions as to the Curie–Weiss behavior of the postulated localized moments have been reached by Toyozawa[53] and Halbo and Sladek[54] for *n*-type Ge and GaAs samples, respectively. A direct comparison of magnetoresistance and spin-susceptibility data for the Si : P system would be most useful. Khosla and Fischer[55] have measured the magnetoresistance for a number of Si : P samples and have been able to represent them by a four-parameter expression identical to that used in their CdS : In work. However, in the Si : P case, the values extracted for the coefficients B_2 do not exhibit any consistent temperature-law dependence. This result is in contrast to the behavior of the CdS : In samples and could be due to the relatively larger experimental uncertainty in the Si : P data introduced by the much smaller magnitude of the negative magnetoresistance in this material. In any case, a detailed comparison of these data is not feasible at the present time. Nevertheless, estimates[55] made of the required densities of localized spin scattering centers are in rough accord with the values of N_{CW} listed in Table I.

In our opinion, the general properties of the "localized spins" deduced from the magnetoresistance data are such as to permit their direct identification with the Curie–Weiss portion of our two-component spin susceptibility interpretation.

It is worthwhile to comment on one aspect of the magnetoresistance results which is suggestive of further experiments. Such a possibility arises from the localizing effects of applied magnetic fields on the extrinsic electronic wave functions. The resulting field dependence of the experimental parameters R_H and ρ might be expected to have counterparts in the ratios N_{CW}/N_D and N_P/N_D which can be extracted in a two-component decomposition of the experimental spin susceptibilities. This procedure would require ESR measurements at widely separated microwave frequencies. A correlation of the resulting two-component densities N_P and N_{CW} with the corresponding Hall-coefficient and mobility data could serve as a useful check on the various interpretations of Si : P data which have been offered in this work and elsewhere.

VI. SUMMARY AND CONCLUSIONS

Our studies of the heavily doped Si : P system have confirmed that a rather fundamental transition occurs in the experimental ESR properties as a function of the phosphorus impurity concentration. This change can be associated with a similar discontinuity in the electrical-transport properties which is generally designated as a semiconductor-to-metal transition. The magnetic spin susceptibilities of samples on the low-concentration (semiconducting) side of this transition follow a standard Curie–Weiss form in the absence of an appreciable density of thermally generated carriers. At the extreme high-concentration end of our sample range, the experimental susceptibilities may be described by a Pauli expression appropriate to a conduction band with m^* slightly smaller than the value which is generally associated with the density-of-states effective mass for the host conduction band. In our most concentrated sample all extrinsic electrons, to within at most a few percent, may be assumed to act as dc current carriers at all temperatures. The spin susceptibility of samples having intermediate impurity concentrations may be represented self-consistently by the sum of a Curie–Weiss- and a Pauli-law term. However, an association of these susceptibility components with localized and delocalized electrons, respectively (inhomogeneity model), requires a small upward shift in the concentration values assumed, on the basis of the Irvin curve, for samples in or near the transition concentration region. There is some independent justification for this shift, which has the effect of reducing the sharpness of the semiconductor-to-metal transition more or less in accord with observations for other heavily doped semiconductor materials.

The Curie–Weiss (or at least non-Pauli) component of χ_s persists for sample concentrations at least as high as $N_D \approx 2\times 10^{19}$ donors/cm^3 and correlates well both in form and magnitude with the "localized spin" susceptibility deduced from magnetoresistance studies of comparable semiconductor systems.

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[30] At higher temperatures however, a temperature dependence arising from decreasing degeneracy of the conduction electrons is to be expected. This effect has been observed by Portis *et al.* [Phys. Rev. **90**, 988 (1953)]. Direct comparison with their result is made difficult by the difference between the temperature ranges studied and uncertainty about the impurity concentration of their sample.

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