Specific-heat studies of heavily doped Si:P†

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The extrinsic specific heats of several samples of phosphorus-doped silicon have been measured at temperatures $0.06 < T < 1.6$ K. The phosphorus concentrations of the samples range from $N_D = 3.5 \times 10^{17}$ to 1.05×10^{20} donors/cm^3. The results obtained for the semiconducting, amorphous antiferromagnet samples with $N_D < N_D^C \sim 3 \times 10^{18}$ donors/cm^3 compare favorably with expectations on the basis of a short-range-order-dominated cluster theory. No evidence was found for the existence of specific-heat anomalies which would be associated with ordering in these materials. Our more concentrated metallic samples (i.e., with $N_D > 5.9 \times 10^{18}$ donors/cm^3) exhibited specific heats which were equal to, within experimental error, the theoretical values anticipated from a rigid conduction band characterized by the accepted density-of-states effective mass $m^* = 1.06 m_0$. In a dilute metallic sample, having $N_D = 5.9 \times 10^{18}$ donors/cm^3, deviations from the rigid-band results were observed. These deviations were quantitatively explained in inhomogeneity-model terms in a manner consistent with earlier interpretations of the spin-susceptibility and Hall-carrier-density data. Ambiguities in this description are discussed and related to other experiments and the alternative Brinkman-Rice-like interpretation of these results.

I. INTRODUCTION

Heavily doped semiconductors such as phosphorus-doped silicon (Si : P) have often been used in experimental studies of the semiconductor-to-metal (SM) transition.[1,2] Although the spatial disorder of the impurity systems introduces complications, the observed SM transitions are of particular interest in that they are not accompanied by significant changes in lattice structure. As a result the heavily-doped-semiconductor data should offer insight into either the correlation- (Mott[3]) or disorder-induced (Anderson[4]) transition processes, or both.

At present the available experimental data are generally well understood only for samples having impurity concentrations either very much smaller or very much larger than the critical transition concentration N_D^C. In the former case, quantitative interpretation is possible in terms of the properties of extrinsic electrons which do not interact with each other and are each individually bound and localized to the randomly distributed donor impurity sites. At impurity concentrations $N_D > 10^{16}$ donors/cm^3, antiferromagnetic exchange becomes a significant and dominant form of mutual localized electron interaction.[5] This fact, taken together with the spatial disorder allows such samples with $N_D < N_D^C$ to be considered as prototype amorphous antiferromagnets.[6-8] At the other extreme of concentration, the properties of samples with $N_D \gg N_D^C$ fit quite well with expectations in terms of the rigid-band "metallic" picture in which the N_D extrinsic electrons per unit volume occupy states in an only slightly modified conduction band of the host semiconductor. It is important to note however that in the case of both amorphous antiferromagnet and metallic samples, the proposed simple models become increasingly unsatisfactory as N_D approaches N_D^C.

Interest in the amorphous antiferromagnet samples has recently been confined to two experimental observations.[7] Firstly, an anomalous decrease occurs in the ratio (C/C_R) of the experimental (C) and "regular impurity superlattice" $(C_R = N_D \mu_B^2 g^2 / 4\delta k)$ Curie constants appropriate to the Curie-Weiss-law magnetic spin susceptibilities of these materials. In the expression for C_R, μ_B represents the Bohr magneton, g the electronic g factor, δ the mass density, and k the Boltzmann constant. A similar result has been noted[9] in a "one-dimensional" experimental system and has been attributed to the onset of electron delocalization. The localized electron-"cluster" approach is not applicable under these conditions and hence has been unable to reproduce this experimental effect. Secondly, no evidence of antiferromagnetic ordering in these materials has been observed even at temperatures as low as $\Theta/3$ (where Θ is the experimental "paramagnetic" Curie-Weiss temperature). This absence appears to be a general property of amorphous antiferromagnets and has been tentatively attributed[10,11] to a randomness-induced shift of the spin-wave excitation spectrum to lower energies.

The principal problem associated with models of metallic samples, on the other hand, has involved their reconciliation with the experimental magnetic susceptibility, magnetoresistance and NMR data. Particularly significant deviations

from rigid-band expectations were noted[12] in both the magnitudes and temperature dependences of the experimental magnetic spin susceptibilities, χ_s. These deviations persisted even at impurity concentrations which exceeded N_D^C by one order of magnitude or more. The "inhomogeneity model" has been introduced[7,13] in an attempt to resolve these difficulties. This model assumes the existence in metallic or "M-type" samples of a concentration-dependent density, N_{CW}, of at least partially localized electrons which add a Curie-Weiss-law component to the total magnetic susceptibility. Unfortunately, uncertainties in the estimates of N_{CW} and the low-temperature carrier density have so far prohibited a definitive quantitative check of this model with magnetic and transport data. Nevertheless some consistency has been achieved with both sets of results[7] as well as with the Khosla-Fischer mechanism[14] of negative magnetoresistance. However in spite of the fact that a simple argument can be made (see the Appendix) for the anisotropy-induced existence of localized electrons in M-type Si:P, theoretical objections still remain[2] against the presence of the required numbers of these electrons. Moreover, further skepticism toward the inhomogeneity model would seem to be justified on the basis of the apparent absence[15] of a magnetic-field dependence in the specific heat of an Si:P sample with $N_D = 5.9\times10^{18}$ donors/cm^3.

The present paper will be primarily concerned with the results of our own specific-heat measurements carried out on Si:P samples in a negligible magnetic field and at very low temperatures. It is our intention to utilize the results obtained for amorphous antiferromagnet ($N_D < N_D^C$) samples to further test the predictions of the cluster model and to continue the search for critical ordering behavior in these materials. Our studies of the metallic ($N_D > N_D^C$) samples, on the other hand, have been directed toward filling a substantial gap in the available experimental knowledge and hopefully will allow further inference to be drawn with regard to the suitability of the "inhomogeneity model" and other descriptions of these systems. Experimental data are presented in Sec. II. These results will be discussed and related to previous work and models in Sec. III.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The specific heats of single-crystal samples of Si:P with $9\times10^{15} < N_D < 1.05\times10^{20}$ donors/cm^3 were measured using a previously described[16] heating-pulse decay method. Our measurements were carried out with the aid of a He^3-He^4 dilution refrigerator at temperatures $0.06 < T < 1.6$ K which were determined through calibrated-resistance thermometry.

Since we are interested primarily in the impurity-related properties of these samples, extrinsic specific-heat values C_e were abstracted from the raw sample data by subtraction of the Debye law ($\Theta_D = 640$ K) contribution of the silicon host lattice. This subtraction procedure, of course, leads to reduced accuracy near the upper limit of our experimental temperature range. Our results are presented in $\ln C_e$-vs-$\ln T$ form in Figures 1–7 using the usual[7,14] notation (A-B) for a sample having $N_D = A\times10^B$ donors/cm^3. Data are not included for our most dilute sample (9-15) since in this case the observed specific heats were indistinguishable at all temperatures from the sum of the silicon host and experimental addenda contributions. This null result, taken together with the monotonic dependence of C_e upon N_D, provides some justification for our assumption that no significant portions of the reported extrinsic specific heats arise from unintentional impurities or lattice defects. This assumption is implicit to the data analyses offered in Sec. III.

III. DISCUSSION OF RESULTS

A. General

The extrinsic specific-heat data presented in Figs. 1–7 confirm the general result of earlier investigations of heavily doped semiconductors in which distinctly different experimental behavior was noted for respectively semiconducting (S-type)[7] and metallic (M-type) samples. In the present case the very weak temperature dependence of C_e in a dilute S-type Si:P sample (Fig. 1) steepens with increasing N_D. However only at impurity concentrations well above $N_D^C \sim 3\times10^{18}$ donors/cm^3 does a characteristically metallic linear temperature dependence obtain (Figs. 5–7). The S- and M-type results will be treated separately in the following two subsections. Our conclusions and a brief summary will be presented in the final subsection (IIID) of this work.

B. S-type samples

Many aspects of amorphous antiferromagnet, S-type doped semiconductors can be treated quantitatively,[8,17–21] if the impurity concentration is low enough to allow a simple perturbation treatment of the mutual donor exchange problem. These theoretical methods concentrate on the relatively straightforward short-range-order aspects of these systems even at very low temperatures. The most recent application of these methods has been in calculating the Si:P magnetic spin susceptibilities using the simple expressions derivable for the energy eigenvalues and average magnetizations of "clusters" of three exchange-coupled spins.[8] This version of the cluster model treated the N_D donor

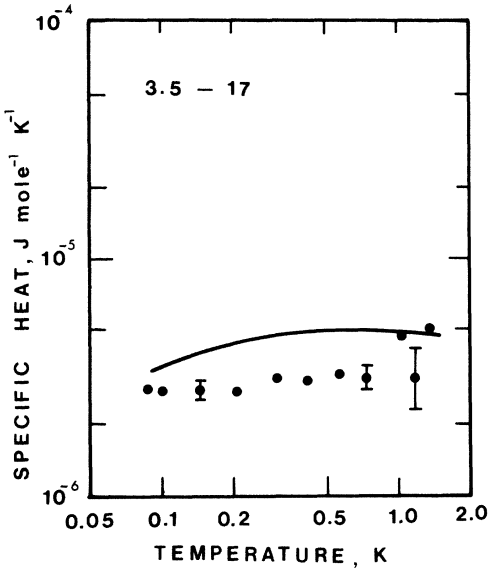

FIG. 1. Extrinsic specific heat (C_e) as a function of temperature for sample (3.5-17): circles show experimental data; the line is the cluster model. The specific heat in this figure and in Figs. 2–7 is measured in JK^{-1} per mole of Si. In this figure, and in Figs. 2–7, the lattice specific heat subtracted was $6.9\times 10^{-6} T^3$ J K^{-1} mole^{-1}.

spins per unit volume as $N_D/3$ noninteracting three-spin clusters, each chosen to include randomly selected donors and their first and second nearest neighbors. Distribution functions were derived for the three possible intracluster exchange constants J_{12}, J_{13}, J_{23} using the relationship between the exchange constant and interdonor separation deter-

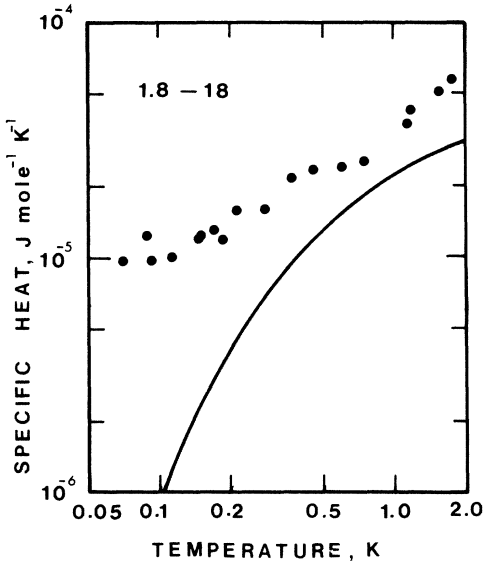

FIG. 2. Extrinsic specific heat as a function of temperature for sample (1.8-18): circles show experimental data; the line is the cluster model.

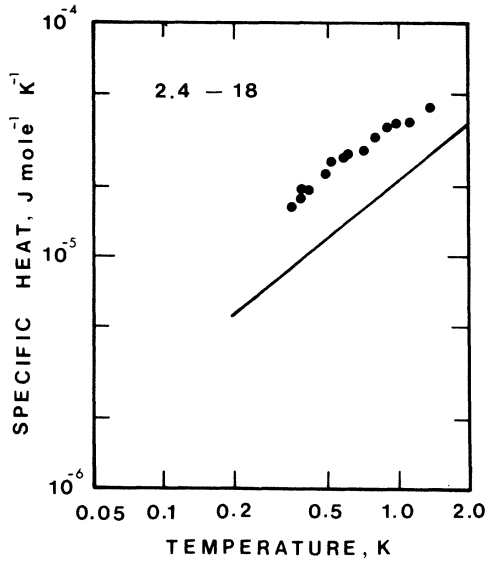

FIG. 3. Extrinsic specific heat as a function of temperature for sample (2.4-18): circles show experimental data; the line is the cluster model.

mined by Cullis and Marko.[8,17] These distributions were combined with the general expression for the average cluster magnetization to give theoretical spin susceptibilities χ_s which were in accord in many respects with experimental observations. As noted in Sec. I, the only significant failure of this calculation has been in its inability to reproduce the observed falloff in the Curie constant ratio, C/C_R, as N_D approaches N_D^C.

We have now extended the cluster approach to calculate the extrinsic specific heats of S-type Si : P. This calculation is straightforward and involves differentiation with respect to T of the average extrinsic energy derived through the combined use of the cluster distributions and the expression for the average energy of a given cluster:

$$E = \frac{\sum_{i=1}^{3} E_i w_i\, e - E_i/kT}{\sum_{i=1}^{3} w_i\, e - E_i/kT} \quad . \tag{1}$$

In this expression,

$$E_1 = -\tfrac{1}{4}(J_{12}+J_{13}+J_{23}) - (J_{12}^2+J_{13}^2+J_{23}^2 - J_{12}J_{13} - J_{23}J_{13} - J_{13}J_{23})^{1/2} \quad ,$$

$$E_2 = -\tfrac{1}{4}(J_{12}+J_{13}+J_{23}) + (J_{12}^2+J_{13}^2+J_{23}^2 - J_{12}J_{13} - J_{23}J_{13} - J_{13}J_{23})^{1/2} \quad ,$$

$$E_3 = \tfrac{1}{4}(J_{12}+J_{23}+J_{31}) \quad ,$$

and $w_1 = 2$, $w_2 = 2$, $w_3 = 4$ represent the degeneracies associated with these energy levels at zero magnetic field.

The calculated specific heats have been represented by the solid curves in Figs. 1–3. The

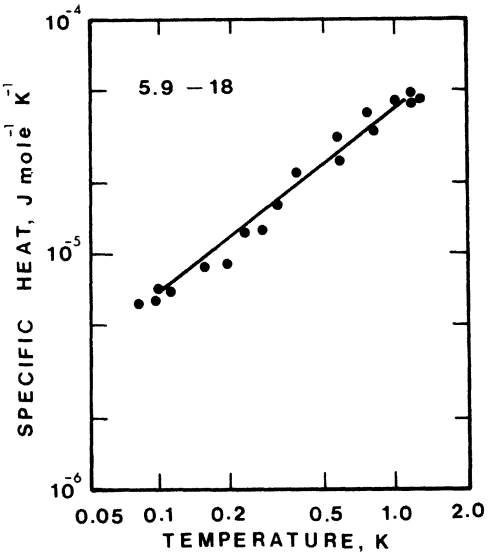

FIG. 4. Extrinsic specific heat as a function of temperature for sample (5.9-18): circles show experimental data; the line is the inhomogeneity model with $N_L = 0.08N_D$ and $m^* = 1.06m_0$.

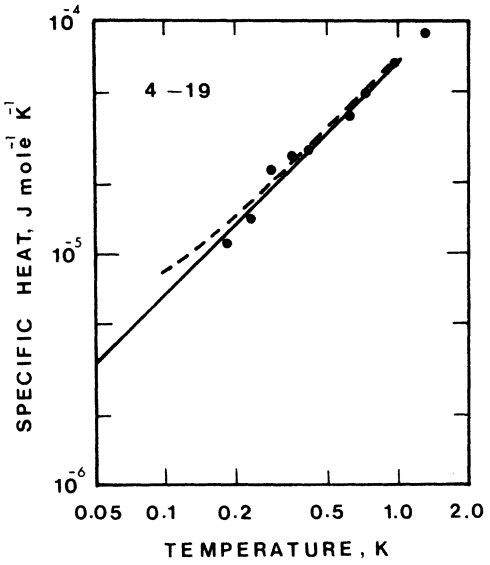

FIG. 6. Extrinsic specific heat as a function of temperature for sample (4-19): circles show experimental data; the solid line is the inhomogeneity model with $N_L = 0$ and $m^* = 1.06m_0$; the dashed line is the inhomogeneity model with $N_L = 0.005N_D$ and $m^* = 1.06m_0$.

agreement between the calculated and measured results is reasonably good, particularly with regard to the temperature dependences. Even the faster than observed falloff of C_e with decreasing temperature at $T \leq 0.3$ K in samples (1.8-18) and (2.4-18) can be understood in terms of the artifical remaining twofold degeneracy of the cluster ground state. This shortcoming of the cluster approximation leads to a predicted infinite-temperature entropy $S_\infty = \int_0^\infty (C_e/T)\,dT$ equal to only two-thirds of the value, $N_D k \ln 2$, expected in the realistic presence of degeneracy-lifting interactions. A simple estimate indicates that typical intercluster coupling

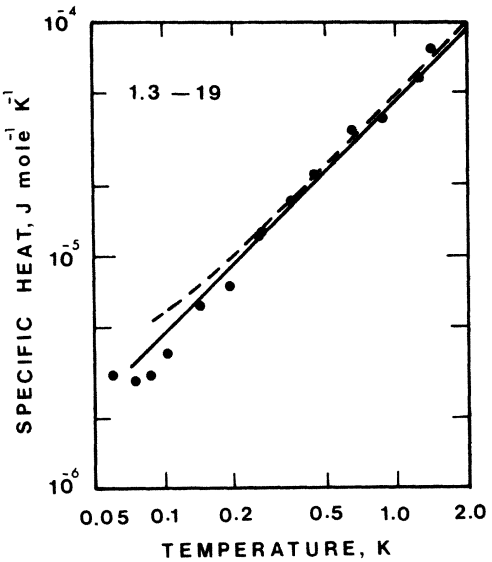

FIG. 5. Extrinsic specific heat as a function of temperature for sample (1.3-19): circles show experimental data; the solid line is the inhomogeneity model with $N_L = 0$ and $m^* = 1.06m_0$; the dashed line is the inhomogeneity model with $N_L = 0.01N_D$ and $m^* = 1.06m_0$.

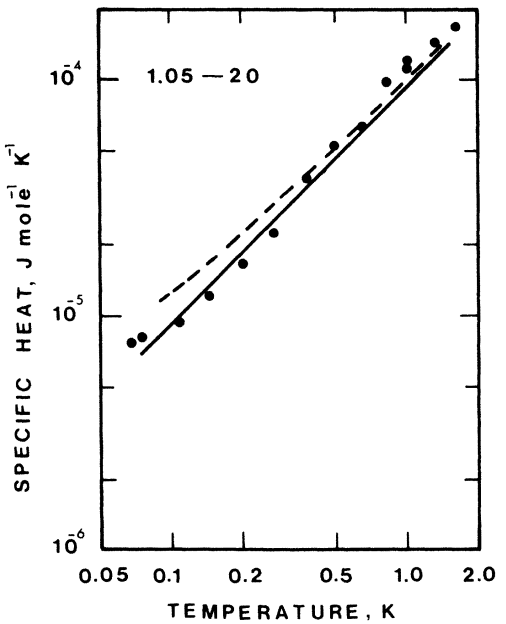

FIG. 7. Extrinsic specific heat as a function of temperature for sample (1.05-20): circles show experimental data; the solid line is the inhomogeneity model with $N_L = 0$ and $m^* = 1.06m_0$; the dashed line is the inhomogeneity model with $N_L = 0.005N_D$ and $m^* = 1.06m_0$.

energies (which would serve to life the degeneracy in our model) are on the order of 0.1 K (in temperature units) in a $N_D \sim 2\times 10^{18}$ donors/cm^3 sample. As a result, it is not surprising that neglect of these interactions in our model leads to an underestimate of the actual extrinsic specific heat at temperatures $T \lesssim 0.3$ K.

As in the case of the spin-susceptibility calculations,[8] the low-concentration agreement between the cluster model and measured specific-heat magnitudes worsens as N_D approaches N_D^c. It should be noted however that while our model *overestimates* χ_s by a factor 2 for samples (1.8-18) and (2.4-18), it *underestimates* C_e by a similar factor.

In any event, the general form of the S-type-sample specific-heat data is consistent with the dominance of the short-range portions (nearest and next-nearest neighbor) of the mutual spin-spin interactions. The data contain no evidence of low-temperature maxima or specific-heat "anomalies" which could be associated with the predicted[22,23] antiferromagnetic ordering transitions in "amorphous" spin systems. As noted above, the apparently universal absence of such ordering phenomena in amorphous antiferromagnets has been attributed by Egami *et al.*[10,11] to the appearance of a peak at very low energy in the disordered system spin-wave spectrum. If this explanation is correct, our results would seem to imply that the specific-heat anomalies associated with the low-energy peaks must occur below $T = 0.07$ K at least in samples (3.5-17) and (1.8-18). In order to investigate this possibility further, we have evaluated S_∞ for sample (1.8-18) assuming: (i) the specific heat at $T < 0.07$ K can be obtained from a straight-line extrapolation of the data in Figs. 1–3; and (ii) the slope dC_e/dT at $T > 1$ K is equal to the corresponding calculated cluster-model value. Unfortunately, the precision and extent of the sample (3.5-17) and (2.4-18) data did not allow meaningful estimates of S_∞ to be made in these cases. In the case of sample (1.8-18), however, S_∞ was found to be equal to (within 5%) the maximum spin entropy, $N_D k \ln 2$. Although further measurements would be useful in order to check our extrapolations, this apparent equality would appear to rule out the presence of a significant low-energy excitation peak in this dilute amorphous antiferromagnet system. Further theoretical work would appear to be necessary to establish whether the observed absence or ordering is simply the result of spatial disorder or, instead, represents a more fundamental property of sufficiently isotropic, antiferromagnetically coupled spin-$\frac{1}{2}$ systems.[24]

C. *M*-type samples

An important feature of the experimental M-type-sample data of Figs. 4–7 is the fact that a "metallic" linear temperature dependence is achieved only when the impurity concentration is raised above $\sim 10^{19}$ donors/cm^3. At lower concentrations, therefore, a simple rigid-conduction-band model cannot offer a satisfactory representation of our experimental results. This situation is similar to that already noted for the spin susceptibilities of these samples and as in this previous case our initial approach to the data will be in "inhomogeneity model" terms. Unfortunately however the guidelines for applying this model to the specific-heat data are much more ambiguous than in the spin-susceptibility case. A particular difficulty arises from the absence of an obvious functional form for the "localized electron" specific-heat contribution. In the general spirit of the earlier treatment, we have taken an empirical approach in this matter based upon our lower-concentration or S-type-sample data. Thus we have set the specific-heat contribution of a density of N_L localized electrons equal to the experimental C_e for an S-type sample of concentration $N_D = N_L$. In practice, the necessary S-type C_e-vs-T data were obtained from a straight-line interpolation of the sample (3.5-17) and sample (1.8-18) data on a $\ln C_e(T)$-vs-$\ln N_D$ plot. It was found (see Fig. 4) that a good representation of the experimental sample (5.9-18) data could be achieved with an assumed localized electron density $N_L = 5\times 10^{17}$ donors/cm$^3 = 0.08 N_D$ and an effective mass $m^* = 1.06 m_0$ (where m_0 is the mass of a free electron). The latter value is equal to the density-of-states effective mass deduced from cyclotron-resonance data.[25] Furthermore, our data for more concentrated $N_D > 10^{19}$ donors/cm^3 samples are consistent (see Figs. 5–7) with the same $m^* = 1.06 m_0$ conduction-electron effective mass and localized electron densities which are either negligible or no larger than 1%.

The effective mass deduced above is significantly larger than the $m^* = 0.9 m_0$ value obtained from the spin-susceptibility data.[7] It would seem likely that the major portion of this discrepancy arises from an error in the difficult "absolute calibration" step of the χ_s measurement procedure.[12] It should be noted that such a measurement error would not significantly change the densities of localized or (in the earlier terminology[7]) Curie-Weiss-law electrons deduced on the basis of spin-susceptibility data. These densities N_{CW} were determined chiefly from the low-temperature T dependence of χ_s and hence were relatively insensitive to small absolute calibration errors.

As in the case of the spin susceptibility, only the sample (5.9-18) specific-heat results, because of their considerable "nonmetallic" character, can offer a satisfactory test of the inhomogeneity model. The density of localized electrons, $N_L = 0.08 N_D$, deduced for this sample is consistent with the earlier

estimate[7] of the corresponding non-current-carrying extrinsic electron density $N_D - n = 0.07N_D$ (where n is the Hall carrier density). However N_L and $N_D - n$ are both only equal to approximately half of the Curie-Weiss-law electron density $N_{CW} = 0.14N_D$ deduced from the χ_s data. The value of N_{CW} was determined by assuming the Curie constant appropriate to a given localized electron density is given by $C(N_{CW}) = \frac{1}{2} C_R(N_{CW})$. This assumption was based upon the observed relationships between the experimental and regular-impurity-superlattice Curie constants of samples (1.8-18) and (2.4-18). However a recent reevaluation[8] of the early data of Sonder and Stevens[26] has shown that $C = C_R$, in agreement with theory, for samples with $N_D < 10^{18}$ donors/cm^3. As a result, a consistent application of the inhomogeneity model to sample (5.9-18) would appear to require the use of the $C(N_{CW}) = C_R(N_{CW})$ equality since in this case the deduced density $N_{CW} = 0.07N_D$ is less than 10^{18} donors/cm^3. With this alteration, equality, to within experimental error, is achieved between the quantities N_L, $N_D - n$, and N_{CW} in accord with a simple inhomogeneity-model picture of sample (5.9-18).

Nevertheless, even leaving aside questions of experimental uncertainty, this agreement cannot be taken as a conclusive vindication of the inhomogeneity approach in heavily doped semiconductors. Our major misgivings about our results concern the fact that the model parameters are not deduced in a completely equivalent manner from the alternative specific-heat and spin-susceptibility sets of data. For example, the spin susceptibility expected from $N_{CW} = 0.07N_D$ localized electrons in sample (5.9-18) is *not* equal to expectations from an S-type sample having an impurity concentration $N_D = N_{CW}$. In the latter case, a Curie-law behavior (i.e., $\Theta = 0$) would be observed as opposed to the characteristic Curie-Weiss temperature $\Theta = 3.5$ K deduced for the localized component of the inhomogeneity-model spin susceptibility.[7] In view of the uncertainties involved in assigning the forms of the localized electron contributions in M-type samples, this discrepancy need not necessarily detract from our demonstration that the χ_s, C_e, and low-temperature carrier-density data are all at least semiquantitatively consistent with an inhomogeneity-model picture. This ambiguity in the characterization of the localized electron component does however confuse matters with regard to the prediction of other experimental results such as the magnetic field dependence of C_e. Thus on the basis of the assumption that the postulated $N_L = 5 \times 10^{17}$ localized electrons/cm^3 of sample (5.9-18) each behave as isolated electrons, Hedgcock, Heiniger, and Paoli[15] have calculated that the extrinsic specific heat of this sample at $T = 1.5$ K should increase by an amount $\Delta C_e \sim 3 \times 10^{-5}$ J/kg mole when a 28.5-kOe magnetic field is applied. The failure of these workers to experimentally observe such a change[15] would appear to argue against the proposed concentration of localized electrons and hence against the validity of the inhomogeneity interpretation. However, on the basis of the previously reported spin-susceptibility results, it is not at all clear that the "isolated electron" value of ΔC_e is appropriate. Thus, the isolated-electron picture leads to a Curie-law temperature dependence for the localized electron magnetization, in contrast to the experimentally deduced Curie-Weiss form. As a result, since $\Delta C_e \propto T\partial^2 M/\partial T^2$ (where M is the magnetization) consistency with the experimental results would seem to require that the specific-heat change calculated by Hedgcock *et al.* be reduced by a factor $T^2/(T+\Theta)$. Putting in the deduced value[6] $\Theta = 3.5$ K leads to an expected change, $\Delta C_e = 0.3 \times 10^{-5}$ J/kg mole, which is at or below the sensitivity of the reported measurements. In our opinion, a definitive specific-heat field-dependence test of the inhomogeneity-model picture of sample (5.9-18) requires measurements at fields on the order of 100 kOe and perhaps at temperatures $T < 1.5$ K. Under the latter conditions, any of the reasonable choices for the sample inhomogeneity parameters should lead to an observable field-dependent component of C_e. The absence of a field dependence in these circumstances would be completely inconsistent with the inhomogeneity-model interpretation and would appear to imply a need for a completely bandlike theory of M-type doped semiconductors.

The only theory of the latter general form which has been developed in any detail has been based on considerations of the properties of a "correlated electron gas." In this approach to the SM transition, Brinkman and Rice[27] have found that correlation leads to an increase in the overall density of states, and hence effective mass, at the Fermi energy. This circumstance, in turn, leads to "enhanced" spin susceptibilities and specific heats. These ideas have been applied with some apparent success to the metallic phases of several transition-metal oxides[28] and have been adapted by Mott,[2,6] with the introduction of the spin-polaron concept, to provide a qualitative interpretation of the sample (5.9-18) χ_s data. Berggren[29] has also recently calculated χ_s for M-type Si:P on a similar basis, obtaining larger-than-observed enhancements. Thus far however all applications of the Brinkman-Rice theory have failed to incorporate the spatial randomness of the donor impurity distribution. It is important to note that this randomness is the source of electron localization in the alternative inhomogeneity descriptions of M-type doped semiconductors.

It is illustrative to express the experimental

sample (5.9-18) χ_s and C_e results as enhancements of the values expected from N_D electrons in a rigid band characterized by an effective mass $m^* = 1.06m_0$. These enhancements $\eta_\chi \equiv \chi_s/\chi_s$(rigid band) and $\eta_{C_e} \equiv C_e/C_e$(rigid band) are plotted as functions of T (the η_χ data for $T < 1.1$ K were obtained by extrapolation and hence should be regarded as very approximate). It can be seen that substantial enhancements of the spin susceptibility appear at temperatures $T \sim 10$ K, at which, by reasonable extrapolation, $\eta_{C_e} \sim 1$. The observed inequality $\eta_\chi > \eta_{C_e}$ was also apparent in other experimental systems[28] to which the Brinkman-Rice theory[27] has been applied. We know of no correlated-electron-gas theory which quantitatively reproduces or accounts for these nonequivalent enhancements. Considerations of this anomaly would seem to be necessary, before theories of this kind can be further compared with experiment.

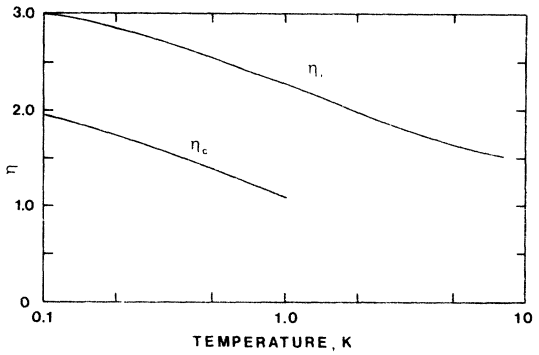

FIG. 8. Sample (5.9-18) spin-susceptibility enhancement (η_χ) and specific-heat enhancement (η_{C_e}) as functions of temperature.

D. Summary and conclusions

The extrinsic specific-heat data presented in this paper corroborate earlier evidence for the utility of simple models of heavily doped semiconductors having impurity concentrations either very much smaller or very much larger than N_D^c. The short-range-oriented cluster and rigid-band models, respectively, were shown to be appropriate to these concentration regimes.

No quantitative attempt has been made to explain the deviations from cluster-model predictions as N_D approaches N_D^c from below. Instead we have shown that, as in the case of the spin susceptibility, the cluster approach generally reproduces the observed specific-heat temperature dependences of all S-type samples. An additional proof of the dominance of short-range interactions was found in the demonstrated absence of the specific-heat anomalies normally associated with long-range ordering.

The deviations from rigid-band metallic behavior of our M-type-sample specific-heat results are smaller than in the case of the reported spin susceptibilities and the expected host effective-mass value, $m^* = 1.06m_0$, is obtained. In fact a non-rigid-band specific-heat component was unequivocal only in a sample with $N_D = 5.9 \times 10^{18}$ donors/cm^3. Nevertheless, experimental accuracy was such that the localized electron contributions, deduced on the basis of an inhomogeneity-model approach to the χ_s and electrical transport data, could be consistent with our data for all M-type samples. In sample (5.9-18), where the deviations from rigid-band behavior are most pronounced, a set of inhomogeneity-model parameters has been derived which appears to be simultaneously consistent with the available C_e, χ_s, and carrier-density data. However uncertainties as to the form of the specific-heat contributions expected from localized electrons in otherwise "metallic" samples presently prevent this consistency from being taken as a proof of the validity of the inhomogeneity approach. On the other hand, a Brinkman-Rice-type description of the M-type samples is at present very unsatisfactory because of its underlying artificially "crystallized" donor distribution as well as its failure, thus far, to quantitatively account for the different observed enhancements in the quantities C_e and χ_s. Further quantitative considerations of the correlated-electron-gas theory are needed relative to realistic heavily-doped-semiconductor materials.

In our opinion the successes of the inhomogeneity approach are sufficient to justify further experimental and theoretical studies of its validity. Particular attention should be given to the experimental properties of M-type samples at high magnetic fields and low temperatures as well as to the nature of the postulated localized electrons. Our simple argument (Appendix) for the existence of these electrons is based on the anisotropy of the electron-electron interactions in many-valleyed semiconductors. As a result this argument may not apply to all semiconductor systems in which the existence of localized electrons has been inferred. It also ignores the important question of localized-electron–conduction-electron interactions which may[2] or may not suppress local moment formation according to the effectiveness of higher-order effects in inducing a depression of the Kondo temperature.[30]

APPENDIX

The Holcomb-Rehr percolation calculation[31] is one of the few treatments of the SM transition in doped semiconductors in which the randomness of the donor spatial distribution receives explicit consideration. In that work, an electron, initially associated with a given donor site, is assumed to be a current carrier if this donor is a member of

an infinite chain of donors constituted such that each member is separated by a distance $\lesssim R_{max}$ from at least one other member of the chain. R_{max} was chosen empirically so that the concentration $N_D^c(R_{max})$ at which a sudden jump in the calculated carrier density occurs is equal to the experimental value of N_D^c. In Si : P it was found that $R_{max} = 60$ Å. However the critical quantity with respect to delocalization is the magnitude of interdonor interaction energy. It is therefore more relevant to note, using the known $J(|\vec{R}|)$ relationship,[8,17] that the Holcomb-Rehr result implies a minimum critical exchange constant $J_{min} = 4\times 10^4$ MHz for participation in the conduction process. If the exchange constant is spatially isotropic, there is little practical purpose to our distinction between the critical distance and exchange constant. However, at least in noncentrosymmetric or "multivalley" semiconductors the exchange constant has a strong dependence upon the direction of the interdonor separation vector. For donors in silicon we can write[17]

$$J(R) = G(|\vec{R}|)\left(\sum_{j=1,2,3} \cos\vec{k}_j \cdot \vec{R}\right)^2 , \qquad \text{(A1)}$$

where $G(|\vec{R}|)$ is an extremely long expression defined by inspection from Eq. (11) of Ref. 17 and k_1, k_2, and k_3 represent any three orthogonal vectors connecting the origin in reciprocal space to the six equivalent conduction-band minima. We have examined the possibility that localized electrons in M-type samples can arise from donor sites whose nearest neighbors are positioned such that $J < J_{min}$. Thus Eq. (A1) was evaluated for a relatively fine grid of directions for the vector $\vec{R}$. For each value of $|\vec{R}|$ our program noted the fraction of directions $\gamma(|\vec{R}|)$ for which $J(\vec{R}) < J_{min}$. Using the usual expression for the probability $P(|\vec{R}|)$ of finding a nearest neighbor at a distance $|\vec{R}|$, we have calculated the localized electron density according to

$$N_L = N_D \sum_{|\vec{R}|} P(|\vec{R}|)\gamma(|\vec{R}|) . \qquad \text{(A2)}$$

Our results are plotted in Fig. 9 as a function of N_D along with the most consistent estimates of N_L on the basis of the χ_s and C_e data. It can be seen

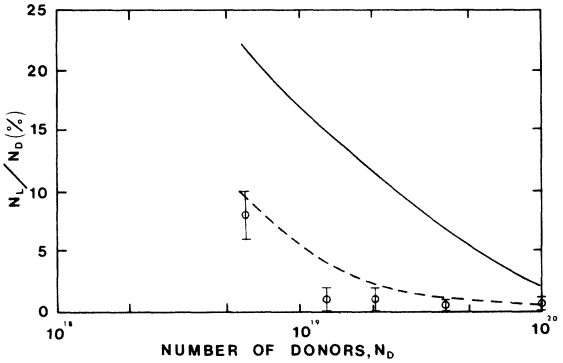

FIG. 9. Percentage of localized centers is shown as a function of concentration: the circles are values deduced from χ_s and C_e data; the solid line is calculated with $J_{min} = 4\times 10^4$ MHz; the dashed line is calculated with $J_{min} = 8\times 10^3$ MHz.

that our simple calculation actually overestimates the experimentally deduced values of N_L. This could be due to either an error in the choice of J_{min} [for example, much better agreement is achieved (see Fig. 9) if J_{min} is set equal to the value, 8×10^3 MHz, associated with the critical separation according to the modified Mott[32] criterion $N_D^{1/3}a^* = 0.22$, where a^* is the donor Bohr radius] or from the extreme simplicity of our approach. With regard to the latter defect, it should be noted that our calculation completely neglects the possibility of exchange interactions with second or third nearest neighbors which exceed J_{min}. This would lead to a fractional lowering of the curves in Fig. 9 which increases with N_D in accord with the requirements of the experimental data. In any case it is the point of our exercise to show that simple considerations based on the randomness of the donor distribution and anisotropy predict localized electron concentrations at least as high as those experimentally deduced. Our treatment does not account for interactions with the "conduction electrons" nor does it explain the deduced existence of localized moments in centrosymmetric semiconductors such as CdS. In the latter case however it is possible that localization can occur in a similar way through exchange-constant anisotropies associated with the extremely anisotropic donor-wavefunction envelopes.

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