Small-cluster calculations of the localized-moment contribution to the specific heat of heavily doped Si:P

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(Received 5 August 1993)

The localized-moment contribution to the specific heat of Si:P in the vicinity of the metal-insulator transition has been calculated as a function of temperature and magnetic field. The magnetic susceptibility has also been obtained and compared with available experimental data. Small clusters of spins are used in the calculations. The specific-heat predictions are in fairly good agreement with experimental data in fields up to 5.7 T for $n/n_c < 0.2$. At higher concentrations a reduced number of effective spins must be used in order to obtain reasonable agreement with experiment.

INTRODUCTION

Measurements of the thermodynamic response functions, such as low-temperature specific heat[1] and magnetic susceptibility,[2] for systems such as Si:P in the vicinity of the metal-insulator (MI) transition have provided information on the electronic states of these systems. Calculations which attempt to explain the observed properties on both sides of the transition generally do so in terms of localized and delocalized electron states.

Experiments carried out in the presence of high magnetic fields permit additional information to be obtained about the nature of the electronic structure. For Si:P, specific-heat measurements in strong magnetic fields have been made by Kobayashi *et al.*[3] and Lakner and Löhneysen.[4] Schottky-type specific-heat peaks, which are attributed to localized moments, have been observed.

Various approaches have been used in attempting to explain the observed behavior of the thermodynamic response functions. In a scaling approach involving numerical procedures with large arrays of spins, Bhatt and Lee[5] have calculated the low-field magnetic susceptibility χ for Si:P on the insulating side of the transition. Spin pairs with exchange couplings much greater than $k_B T$ become "frozen" in the ground singlet state and are successively discarded with renormalization of the magnetic field as T is lowered. The effective number of free spins at a given temperature and concentration can be found in this way, and hence χ can be obtained.

Fairly recently, Eto and Kamimura[6] have carried out multiconfiguration self-consistent-field calculations for the susceptibility and specific heat of Si:P near the MI transition. Averages were taken for six spins, distributed randomly in a sphere at the appropriate concentration. Both spin-singlet and spin-triplet ground states were shown to occur. The predictions are in general agreement with the specific-heat results of Kobayashi *et al.*[3]

In the present paper a small-cluster model is used to fit the available specific-heat curves as a function of temperature and magnetic field. The approach may be expected to work fairly well in the dilute limit $n/n_c \ll 1$. At higher concentrations, cluster-cluster interactions become important and will lead to failure of the model. In designing more elaborate approaches, it is of interest to know how well the predictions of the simple cluster model agree with the high-field experiments, and to establish the concentration range in which serious discrepancies start to occur. Information of this kind may be obtained from the results presented below.

THEORETICAL CALCULATIONS

For a system of N localized spin $\mathbf{S}_j$, interacting via the exchange interaction, in a magnetic field $\mathbf{B}$, the Hamiltonian is

$$\mathcal{H} = \gamma \hbar B \sum_{j=1}^{N} S_{zj} + \sum_{i>j=1}^{N} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \ . \tag{1}$$

The dipolar and hyperfine interactions are regarded as unimportant for the present purposes. J_{ij} is the exchange coupling between spins i and j and, ignoring the many-valley character of Si, is given by the asymptotic Herring-Flicker[7] form

$$J_{ij}(R) \simeq 0.3 (R/a_H^*)^{5/2} e^{-2R/a_H^*} \ . \tag{2}$$

a_H^* is the effective hydrogenic radius of the impurity centers, and R is the separation between spins i and j. The distribution of R values for nearest-neighbor spins is given by the Poisson distribution

$$P(R)dR = 4\pi R^2 n e^{-(4/3)\pi R^3 n} dR \ , \tag{3}$$

where $n = N/V$, and V is the volume of the sample.

In order to simplify the calculation, clusters of one, two, or three spins have been considered. Figure 1(a) shows the singlet-triplet energy-level diagram for a pair of spins in a magnetic field B. In low fields the ground state is a singlet state, but for high fields the lowest triplet state may cross the ground-state level, depending on the magnitude of the exchange coupling for the particular spin pair. Andres *et al.*[2] have carried out similar susceptibility calculations for the pair model in a somewhat different approach, using an empirical form for the distribution of J values.

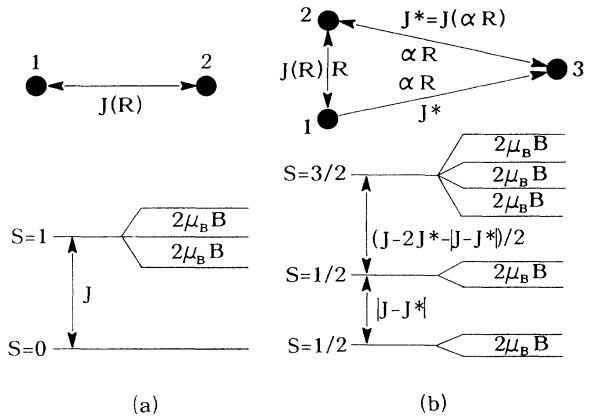

FIG. 1. Energy-level diagram for the (a) spin pair and (b) spin triad in a magnetic field B. J is the exchange coupling between a pair of spins, and $\propto$ is a parameter which is a little greater than unity.

Figure 1(b) shows the energy-level diagram for three spins in a field B.[8] The ground state is a doublet in contrast to the pair singlet ground state. In calculations related to electron paramagnetic resonance (EPR) spectra, New and Castner[9] have examined the most probable topological arrangement for three spins. They used Monte Carlo calculations for donors on a diamond lattice in a cubic box of volume roughly two orders of magnitude greater than the characteristic volume of a cluster determined using Poisson statistics. Using the pair exchange interaction $J_{ij}(R_{ij},k_0)$ for many-valley semiconductors, the donors were grouped into clusters using a small cutoff exchange coupling J_c, which fixed the mean cluster size (obtained from Poisson statistics) for the particular donor concentration. They identified those triads with $J_{13}\simeq J_{23}\ll J_{12}$ as the most probable ones. In our calculations we have, for simplicity, chosen an isosceles triangle shape for triads, with the ratio of side to base length given by a parameter α, as shown in Fig. 1(b).

Using the energy levels shown in Figs. 1(a) and 1(b) together with Eqs. (2) and (3), we have evaluated the partition function Z for the system of localized spins. Numerical integration procedures are used in the calculation. For spin pairs, we have

$$\ln Z=\frac{N}{2}\int_0^\infty dR\,P(R)\ln Z(R)\,, \tag{4}$$

where $Z(R)$ is the pair partition function for spin separation R. A similar expression applies to the triad case. For the spin pairs there are no adjustable parameters in the model, if we take the effective radius a_H^* as fixed ($\sim$15 Å). In the case of the triad model, there is one adjustable parameter α. From $\ln Z$, the heat capacity C_H and the magnetic susceptibility χ may be calculated in the usual way.

RESULTS AND DISCUSSION

Figure 2 shows the low-field magnetic-susceptibility predictions for the single-spin, pair, and triad models. The experimental results of Andres *et al.*[2] are shown for comparison. The single-spin model, which predicts Curie law behavior over the entire temperature range, shows significant departures from the observation below 1.0 K. The agreement with experiment for the pair and triad models is seen to be acceptable for $n/n_c\leq 0.2$ at temperatures above approximately 100 mK. At higher concentrations the pair and triad calculations show departures from the experimental results. In this region the pair model gives values which are too low, while the triad model gives values which are higher than the measured values. The presence of the doublet ground state for the single-spin and triad models clearly leads to an overestimate of the susceptibility at low temperatures. The more elaborate Bhatt-Lee model is preferable for these higher concentrations. A combination of pair and triad models could be used to obtain better fits to the data at the expense of introducing an additional parameter. In the present calculations, the "freezing out" of spins in the singlet ground state for the pair model is accomplished in a continuous way as T is lowered.

In Figs. 3 and 4 the specific-heat predictions are compared with experimental data for particular n/n_c values as a function of temperature in various fields. The experimental curves are taken from the results of Kobayashi *et al.*[3] and Lakner and Löhneysen.[4] The phonon contri-

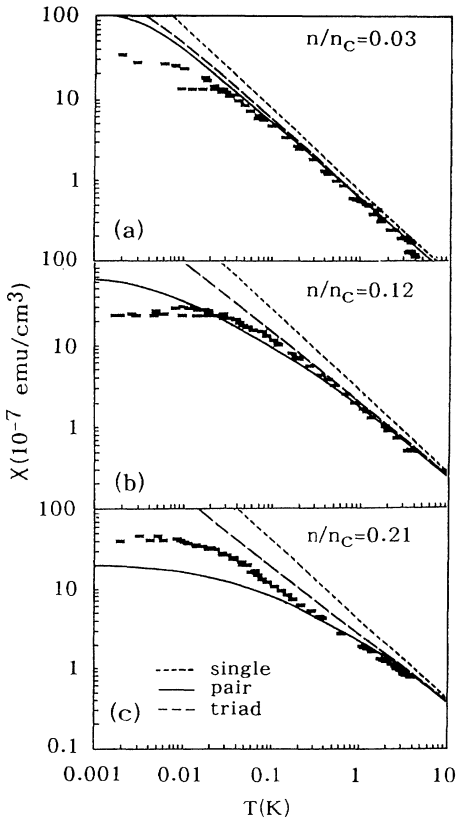

FIG. 2. Low-field magnetic-susceptibility predictions for Si:P as a function of temperature and concentration for the single-spin, pair, and triad models. The experimental data at 50 G are taken from Andres *et al.* (Ref. 2).

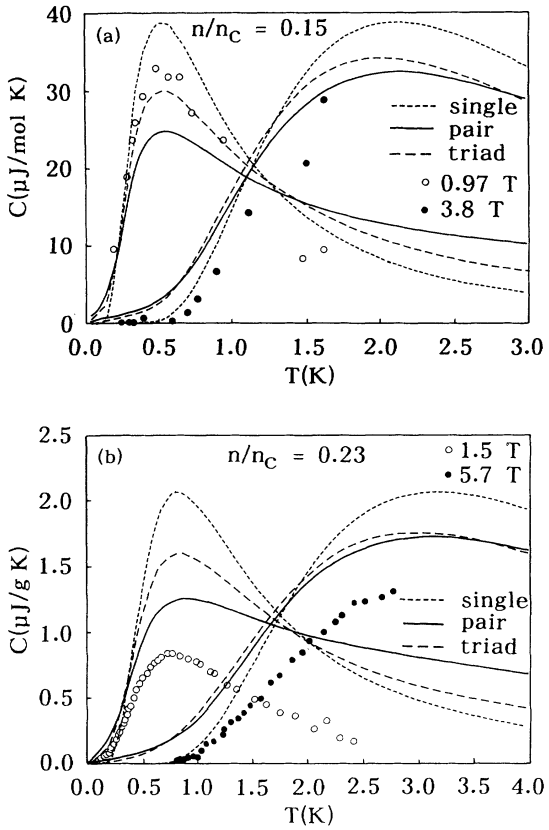

FIG. 3. Specific-heat predictions for Si:P as a function of concentration, temperature, and magnetic field for the single-spin, pair, and triad models. The experimental data of (a) are taken from Kobayashi *et al.* (Ref. 3), while those of (b) are taken from Lakner and Löhneysen (Ref. 4).

bution (γT^3) has been subtracted from the measured specific heats. For $n/n_c = 0.15$, the agreement between the triad model, with $\alpha = 1.25$, and the experimental results of Kobayashi *et al.* is acceptable at the two field values shown in Fig. 3(a). The pair-model peaks are broader and flatter than the experimental curves.

For the triad model, changing α from 1.0 (equilateral triangle) to 1.1 produces an increase of 15–20 %, depending on n/n_c, in the amplitude of the specific-heat peak. Thereafter, further increases in α produce only fairly small changes ($\lesssim 5\%$) in the peak amplitude. The high-temperature tail of the curves becomes somewhat stretched out, compared to the low-α value curves, but overall the change in shape is not very significant. For $\alpha > 1.6$, the curves effectively correspond to those of a pair of spins and a single spin, averaged over all pair separations. We arbitrarily chose $\alpha = 1.25$ for all the triad curves as a reasonable intermediate value between 1.1 and 1.6.

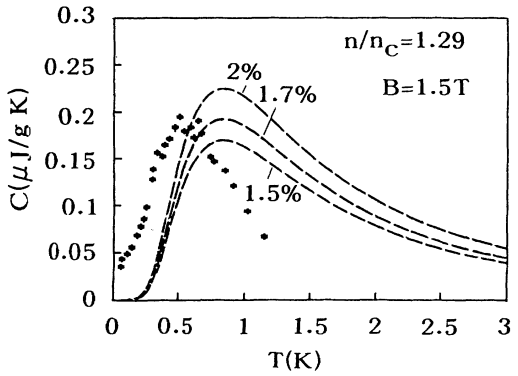

FIG. 4. Specific-heat predictions for the triad model with a reduced number of effective spins compared with the experimental results of Lakner and Löhneysen (Ref. 4) for a sample on the just-metallic side of the transition.

For $n/n_c = 0.23$ the theoretical curves, shown in Fig. 3(b), are somewhat higher than the experimental data. As is the case with the susceptibility results, neither the simple pair model with no adjustable parameters nor the triad model with one parameter α is able to provide quantitative fits to the experimental points. The shapes of the triad model plots appear to be closer than the single-spin or pair model shapes to those of the experimental curves. Scaling n by a factor of roughly 0.5 would bring the curves into fairly close agreement with experiment.

Schottky fits for single spins require that the effective number of spins is a function of the applied field[4] in order to fit the experimental observations. The predicted amplitude of the single-spin Schottky specific-heat peak is the same in all fields for a given spin concentration, while the pair and triad models give rise to field-dependent peak amplitudes. This feature supports the cluster-model approach.

Figure 4 shows the experimental results[4] for $n/n_c = 1.29$ with $B = 1.5$ T. The fitted curve is based on the triad model, with n scaled by the factors shown in the figure for insertion in Eqs. (3) and (4). Neither the shape nor peak position is in very close agreement with experimental points. Nevertheless, it is highly probable that the observed peak is due to the presence of localized moments on the metallic side of the transition. This is consistent with the so-called two-fluid-model ideas[10–12] and the recent work of Bhatt and Fisher.[13] The scaling in the number of effective spins may be explained as being the result of the presence of much larger clusters than those that have been considered here. Alternatively, cluster-cluster interactions may be invoked to justify the scaling that is required for $n/n_c > 0.2$. It should be emphasized that the effective n value is used in obtaining the partition function and hence the plotted curves. If the actual n value is used to obtain the specific heat, followed by scaling in amplitude, the shapes and positions of the curves are in poor agreement with experiment.

More elaborate cluster calculations along the lines of those of Eto and Kamimura[6] should provide a better description for samples with $0.2 < n/n_c \lesssim 1.0$ than the simple cluster models. The presence of both spin-singlet and spin-triplet ground states appears to be a desirable feature in accounting for the specific-heat observations. With the simple cluster-model approach, a combination of pairs and triads could be used in the calculations. This would, however, involve the introduction of a further parameter, which could be regarded as a fitting parameter. We have not carried out such procedures.

CONCLUSION

Cluster-model calculations, involving spin pairs and spin triads, have been carried out for the low-temperature magnetic susceptibility and specific heat of heavily doped Si:P in the vicinity of the metal-insulator transition. For $n/n_c < 0.2$, the low-field susceptibility and specific-heat predictions in fields up to 5.7 T are in fair quantitative agreement with experiment. At high concentrations it becomes necessary to introduce a reduced effective number of spins in order to bring the predictions into approximate agreement with experiment. The need for this scaling of n may be interpreted as the result of large clusters and cluster-cluster interactions, which give rise to a reduced susceptibility and specific-heat contribution from regions in the sample in which the localization length is becoming large.

For samples just on the metallic side of the transition, the cluster-model predictions require substantial scaling of n in order to bring them into agreement with experiment. The results are consistent with the presence of a small number of localized spins on the metallic side of the transition.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support provided by the Foundation for Research Development and the University of the Witwatersrand Research Committee.

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