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Doped semiconductor as an amorphous antiferromagnet

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The antiferromagnetic exchange interaction between shallow donors in a semiconductor at a concentration below the metal-insulator transition makes this system a model "amorphous antiferromagnet." A recent pair model for the spin susceptibility of *n*-CdS [M. Rosso, Phys. Rev. Lett. 44, 1451 (1980)] is here extended to the case of Si:P. The results are compared with experimental values for the magnetic dependence of the spin susceptibility and the specific heat. Comparison is also made with "exact" cluster calculations. In the mK range it is found that hyperfine interactions are important. In particular, they give rise to pronounced features in the extrinsic specific heat at ~2 mK. MS code no.

I. INTRODUCTION

Heavily doped, *n*-type semiconductors (as, e.g., Si:P) undergo a transition from an insulating to a metallic state when the donor concentration N_D is increased above a critical value N_C.[1,2] On the insulating side of the transition, the electrons are localized on randomly distributed donor centers. As a consequence the centers carry magnetic moments and the system may be considered as an amorphous antiferromagnet.[3–5] The electronic structure of the impurity states is well known. The resulting magnetic interaction is of antiferromagnetic type and the system may be represented by a Heisenberg Hamiltonian.

Because of the randomness, distinct clusters containing only a small number of donors may be identified at low concentrations. On this basis the following model has been formulated.[3–5] Inside a cube, let us say, a number of random points are generated, each being the site of an impurity. Each such computer-generated "sample" is divided into clusters consisting of donors coupled by exchange interactions stronger than some critical J_C. The Hamiltonian for each cluster is solved exactly for clusters up to eight donors. The exchange interactions between donors belonging to different clusters may be taken into account in a molecular field approximation, but for low concentrations such interactions bring only minor corrections. By knowing the energy eigenvalues of the separate cluster, various thermal and magnetic properties of the system easily follow. The cluster model was used by Kummer *et al.*[3] and Walstedt *et al.*[4] to study the spin susceptibility of CdS:In in the limit of zero field.

Franzén and Berggren[6] have applied essentially the same cluster model to Si:P ($N_C \simeq 3.5\times10^{18}$ cm^{-3}). Because of the many-valley character of the host conduction band the exchange interaction is then not simply H_2-like, as for CdS:In, but displays a directional and oscillatory behavior. The magnetic dependence of spin susceptibility, $\chi_s(H)$ and the extrinsic specific heat $C(H)$ were evaluated. The specific-heat values are in excellent agreement with the experimental values of Marko *et al.*[7] ($N_D = 3.5\times10^{17}$ cm^{-3}, $0.1 \lesssim T \lesssim 2.0$ K, and zero magnetic field). Qualitative agreement was found with the more recent measurements of $C(H)$ by Kobayashi *et al.*[8] ($N_D = 5.3\times10^{17}$ cm^{-3}, $0.1 \lesssim T \lesssim 1.5$ K, and $H = 0.0$, 0.97, and 3.8 T). At the time the calculations were performed, only limited experimental data for $\chi_S(H)$ were available,[9] namely for $N_D = 5.3\times10^{17}$ cm^{-3}, $H = 0.5$ T, and $1 \lesssim T \lesssim 20$ K. Agreement between theory and experiments was found excellent in this case. More recently, however, Andres[10] has determined $\chi_s(H)$ for dilute Si:P down to 2 mK using a superconducting quantum-interference device (SQUID) magnetometer. Obviously Andres's new data provide exacting demands on theory. One reason for the present report is to present a detailed comparison between theory and Andres's experiments.[11]

Another reason for this report is the striking simplification suggested by Rosso.[12] Because of the wide distribution of exchange interactions Rosso found, using perturbative arguments, that the low-lying excitations in dilute samples are due to pairs of donors far apart. Separate pairs ordered by decreasing interactions (or increasing distances

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R) then results in the distribution

$$P(R)=(3R^2/R_D^3)(1+R^3/R_D^3)^{-2}\,, \tag{1}$$

where $4\pi R_D^3/3=N_D^{-1}$. This distribution is remarkably different from the usual nearest-neighbor approximation,

$$P_{\mathrm{NN}}(R)=(3R^2/R_D^3)\exp(-R^3/R_D^3)\,, \tag{2}$$

in the sense that the long tail associated with $P(R)$ gives large R values much higher weight. This tail is essential for Rosso's excellent agreement with the experimental and theoretical cluster results for $\chi_s(0)$ in the case of CdS:In.[3-5] We will here test Rosso's approach with respect to thermal, $C(H)$, and magnetic properties, $\chi_s(H)$, of Si:P. The availability of exact cluster calculations obviously makes such a test stringent.

II. THERMAL PROPERTIES

The Hamiltonian is basically of Heisenberg type. In Si:P, however, the electrons also couple to the ^{31}P nuclear $\frac{1}{2}$ spins due to the hyperfine interaction. This interaction is of importance at very low temperatures. We therefore have

$$\hat{H}=-\tfrac{1}{2}\sum_{i\neq j}J(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_j)\hat{S}_i\cdot\hat{S}_j$$

$$+A\sum_i\hat{I}_i\cdot\hat{S}_i+g\mu_B H\sum_i\hat{S}_{z,i}\,. \tag{3}$$

Here $J(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_j)$ is the exchange interaction between two donors at sites $\vec{\mathrm{R}}_i$ and $\vec{\mathrm{R}}_j$. The evaluation of J is described in detail in Ref. 6. Furthermore, $\hat{S}_i$ is the electron spin operator, $\hat{I}_i$ the nuclear spin operator, $g=2$ the electron g factor, μ_B the Bohr magneton, and H the external field. For Si:P the hyperfine interaction constant A equals 42 G, or equivalently 5.63 mK. Thus, at lowest temperatures A should not be neglected.

Figure 1 shows the extrinsic specific heat of Si:P and its dependence on the magnetic field. Results of cluster calculations, as described in detail in Ref. 6, are given together with the experimental values of Kobayashi *et al.*[8] In the temperature range considered, the hyperfine interaction can be neglected. Using a spherically averaged expression for J, $C(H)$ has also been evaluated according to Rosso's elementary approach. Then $C(H)$ is simply

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

where $C(R,H)$ is the contribution from pairs of donors. The agreement with our considerably more elaborate cluster calculations is acceptable. As noted above there is only a qualitative agreement with experiments. Rosso's model should ideally be compared with our "exact" cluster calculations, rather than with experiments. Figure 1 also shows the results of the nearest-neighbor approximation, Eq. (1). Clearly, this approximation is less accurate at the concentration in question.

Having established that Rosso's approach works well also for thermal properties, it may now be used to study the effects of hyperfine interactions in the very low-temperature regime. Figure 2 shows the results for Si:P with $N_D=3.5\times10^{17}$ cm^{-3} and zero magnetic field. The contribution to C from the nuclear spins is indeed spectacular in the mK regime. The peak value at ~2 mK exceeds by far the maximum associated with electronic specific heat. By means of present low-temperature techniques[13] it should be possible to observe the nuclear spin contribution in Si:P.

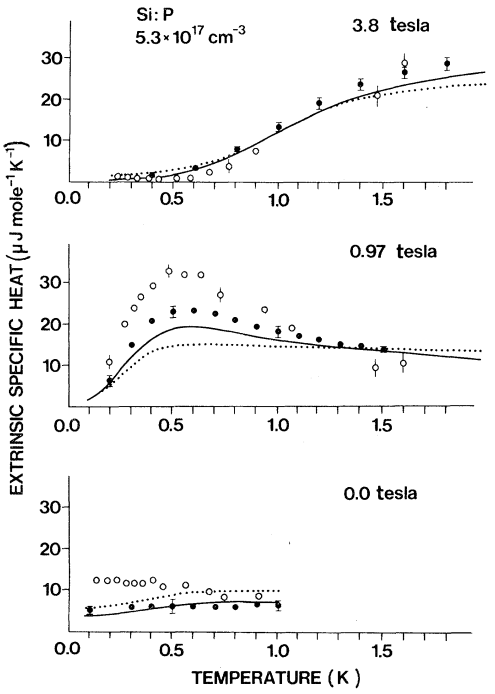

FIG. 1. Magnetic field dependence of the extrinsic specific heat of Si:P with $N_D=5.3\times10^{17}$ cm^{-3}. Open circles represent experiments (Refs. 8 and 9) and solid circles the results of cluster calculations (Ref. 6). Bars at theoretical values indicate the standard deviation for five computer generated "samples" each containing 300 impurity sites. The results of Rosso's (Ref. 12) model [Eq. (1)] are shown as solid curves. The nearest-neighbor approximation [Eq. (2)] yields dotted curves.

For $N_D = 3.5 \times 10^{17}$ cm^{-3} experimental values[7] for $C(0)$ are available for $T \gtrsim 0.1$ K, as shown in Fig. 2. In contrast to the previous case in Fig. 1, the agreement between theory and experiments is satisfactory. We also note a good agreeement between the results of cluster calculations ($A = 0$) and Rosso's approach in this temperature regime.

III. MAGNETIC PROPERTIES

The magnetization of a pair of donors is

$$M(R) = -g\mu_B \langle \hat{S}_{z,1} + \hat{S}_{z,2} \rangle \ , \tag{5}$$

where $\langle \cdots \rangle$ is the thermal average. According to Rosso's model the total magnetization is then

$$M = \frac{N}{2} \int_0^\infty dR \, P(R) M(R) dR \ . \tag{6}$$

The spin susceptibility has been obtained by numerical differentiation.

Calculations of $\chi_s(H)$ have been performed for two of Andres's[10] low-concentration samples ($N_D = 1.15 \times 10^{17}$ and 7.2×10^{17} cm^{-3}). We first omit the hyperfine interaction. Figure 3 shows the results from a cluster calculation for the higher concentration and the pair model using the distributions in Eq. (1). Above ~ 10 mK the computed $\chi_s(H)$ follows a Curie-Weiss law and the two approaches agree perfectly with each other. Because of the spin interactions there is a strong departure from free spin behavior. Below 10 mK both models predict a splitting by the magnetic field, but the numerical agreement is less satisfactory in this temperature regime. In contrast to Rosso's pair model, Eq. (1), the nearest-neighbor approximation, Eq. (2), fails completely. Even the ordering with respect to the field is incorrect, as shown in Fig. 3. For the following discussion we will consider Rosso's model adequate.

Similar results as in Fig. 3 are obtained for the other sample with $N_D = 1.15 \times 10^{17}$ cm^{-3}, but the differences at very low T are indeed much smaller depending on the fact that intercluster interactions are less important. For this concentration the nearest-neighbor approximation is also found to yield more sensible results.

In Fig. 4, finally, we study the combined effects of exchange and hyperfine interactions, and compare the results with Andres's[10] data for $N_D = 7.2 \times 10^{17}$ cm^{-3} at different fields. Above $\sim$ 20 mK there is a very good agreement between theory and experiments. Although a qualitatively correct splitting of χ_s by the applied field is obtained at low T, detailed numerical agreement with experiments is lacking. A comparison with Fig. 3 shows clearly that effects of hyperfine interactions come into play at lowest T. Very similar results as in Fig. 4 are also obtained for the sample with $N_D = 1.15 \times 10^{17}$ cm^{-3}.

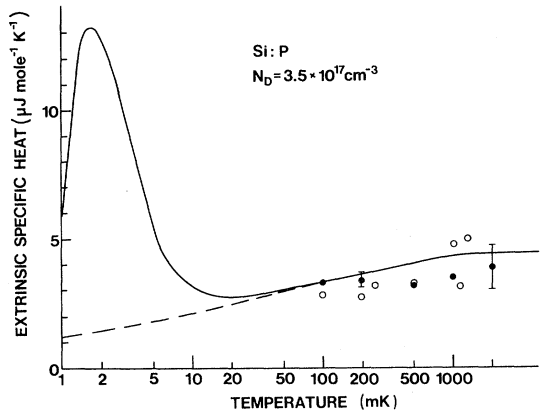

FIG. 2. Extrinsic specific heat of Si:P with $N_D = 3.5 \times 10^{17}$ cm^{-3}. The solid curve includes the effects of hyperfine interactions, while the dashed one excludes them. Both curves are obtained from Rosso's (Ref. 12) pair model. Experimental values are taken from Marko *et al.* (Ref. 7) (open circles). The results from cluster calculations (Ref. 6) neglecting hyperfine interactions are shown as solid circles. All results refer to zero magnetic field.

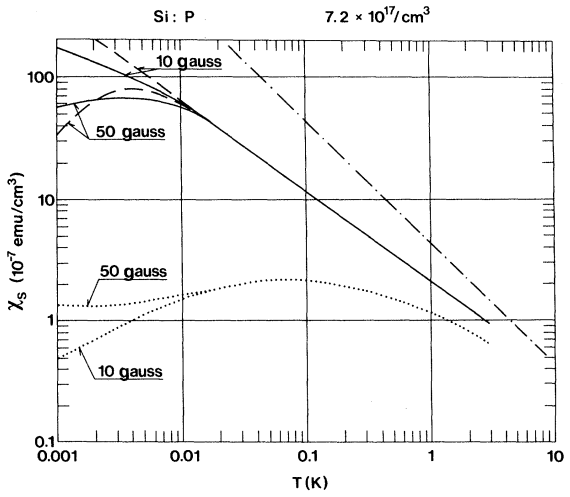

FIG. 3. Spin susceptibility of Si:P with $N_D = 7.2 \times 10^{17}$ cm^{-3} and at two different fields. Solid curves refer to cluster calculations, and dashed curves to Rosso's (Ref. 12) model [Eq. (1)]. Dotted curves represent the nearest-neighbor approximation [Eq. (2)]. The chain line refers to noninteracting spins in zero field. All results are obtained with $A = 0$.

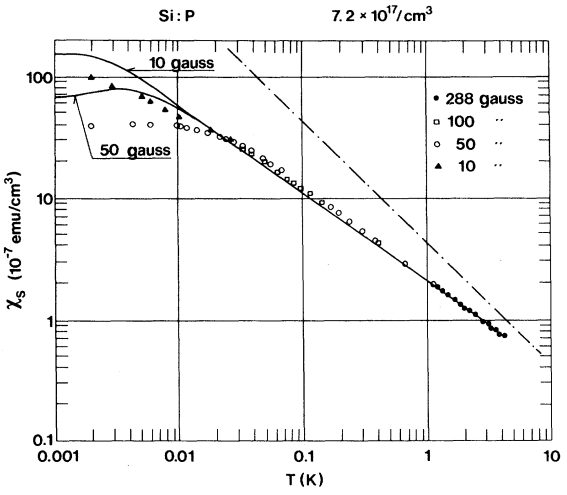

FIG. 4. Spin susceptibility of Si:P with the same N_D as in Fig. 3. The solid curves refer to Rosso's model (Ref. 12) including the hyperfine interactions. Andres's (Ref. 10) experimental data for different fields are given for comparison. The straight line refers to noninteracting spins in zero field.

We have tried to explain the disagreement at lowest temperatures by extending the model in several ways. By including four-donor clusters we have found no significant improvements. The effects of dipole-dipole interactions, hyperfine interactions with ^{29}Si nuclei in the vicinity of a ^{31}P impurity, moderate variations of the effective Bohr radius, the use of anisotropic donor wave functions, as well as other more accurate expressions for the exchange interaction[3–5] were also investigated, but with negative results. One should recall, however, that the basis of our approach is the effective-mass approximation. One may question if that approximation is good enough to give the energy levels of the system with an accuracy of $\sim 10^{-7}$ eV which would be needed at a few mK.

Note added in proof. After this article was submitted experimental data (Ref. 10) has been reported in more detail [K. Andres, R. N. Bhatt, P. Goalwin, T. M. Rice, and R. E. Walstedt, Phys. Rev. B 24, 244 (1981)] together with a theoretical analysis of the spin susceptibility similar to ours. Problems with the experimental data at very low temperatures are further discussed. Nonequlibrium effects are mentioned as one possibility.

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