Magnetic Behavior of an $S = \frac{1}{2}$ Amorphous Antiferromagnet

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The magnetic behavior of bound shallow donors in CdS, a model $S = \frac{1}{2}$ amorphous antiferromagnet, has been measured by a Faraday rotation technique down to $T \sim 50$ mK. The susceptibility, χ, *and* $d\chi/dT$ *as well* increase monotonically with decreasing T with no sign of an ordering transition even though the *median* exchange interaction of a spin is ~ 7 K. The results agree with a hydrogeniclike exchange model which is solved in terms of exactly diagonalized weakly interacting clusters.

A semiconductor lightly doped with shallow donors is an example of a simple and rather well-characterized $S = \frac{1}{2}$ amorphous antiferromagnet. The amorphous character follows from the large donor orbits, random placement, and low concentration. The exchange interaction between neutral donors, J_{ij}, is essentially hydrogenic resulting in a well-described distribution of antiferromagnetic interactions which fall off basically exponentially with their separation.[1] Such a system has the essential element of "frustration" of competing interactions characteristic of spin-glasses,[2] but differs in having exchange couplings of consistently negative sign and *short range* in contrast to the $1/r^3$ behavior of Ruderman-Kittel-Kasuya-Yosida (RKKY) systems. An intriguing question is whether or not these systems undergo a spin-glass transition to an ordered state at finite temperature.[3]

In RKKY systems, a discontinuity in $d\chi/dT$ (usually a cusp at low fields) has been used by many as an earmark of such a proposed transition. By contrast, no such discontinuity in $d\chi/dT$ has been observed in experiments on a variety of homogeneous random amorphous antiferromagnets[3-6] at temperatures well below the antiferromagnetic Curie-Weiss Θ extracted from the high-temperature behavior of χ. Even more striking in these systems is the monotonic *increase* in $|d\chi/dT|$ with decreasing T, with χ tending towards infinity. Our current experiments on donors in CdS, extended to temperatures two orders of magnitude lower than Θ, show a similar behavior for χ (see Fig. 1). These observations are in good quantitative agreement with a modified hydrogenic exchange model which is solved in terms of exactly diagonalized clusters with the intercluster interaction treated in a molecular-field approximation. For spins $S = \frac{1}{2}$ this approach has the important advantage over, e.g., Monte Carlo techniques,[7] of being quantum mechanical. Of course, the condition for a division into clusters is that the intercluster interaction be less than $k_B T$. The special feature of the short-range interaction (as compared to RKKY) is that this condition persists down to a temperature two orders of magnitude lower than the median value of the closest-neighbor exchange interactions. Unusual percolative properties are also found as will be seen below.

We study the spin polarization of donors in CdS by means of the Faraday rotation,[8] Φ, to which it is related by a constant of proportionality (apart from a small, temperature-independent background rotation η). Thus

$$\Phi = \eta + \Phi_{sat} \langle \sigma_z \rangle_{av}, \tag{1}$$

where $\langle \sigma_z \rangle_{av} = N^{-1} \sum_i \langle \sigma_{zi} \rangle$ and Φ_{sat} is the limiting rotation when the spins are saturated ($\langle \sigma_z \rangle_{av} \to 1$). The measurements were done at $\lambda = 4880$ Å using an argon-ion laser. The near-resonant character of this wavelength, which is only 5 meV below the (I_2) exciton bound to the neutral donor in CdS, leads to a highly selective response to the donor spins.[8] This point has been further corroborated by measurement of Φ as a function of λ.[9]

The measurements were done at temperatures 50 mK $\leq T \leq 2$ K in a SHE Corporation He^3/He^4 dilution refrigerator. Light was coupled into and out of the system by means of Bell Laboratories epoxy-coated glass fibers. Samples, typically 1 mm (or less) thick, were mounted between crossed polarizers and inserted between input and output light fibers. Light propagation and magnetic field were oriented along the c axis of the crystal. The sample assembly was immersed in superfluid He^4 inside a specially designed chamber, and temperatures were measured with a calibrated Ge thermometer. Optical power ranged from 30 to 1000 nW and was varied to ensure that Φ was independent of power, i.e., that sample heating was negligible. Magnetic fields were generated by a superconducting solenoid

which was calibrated with an NMR probe.

A series of samples in the concentration range $8.5\times10^{16} \leq c \leq 1\times10^{18}$ In donors/cm^3 was studied. For $c \leq 2.5\times10^{17}$/cm^3 Hall and resistivity data showed clear evidence for carrier freezeout at low temperatures, giving assurance that in this regime we are dealing with localized spins. A low-concentration sample ($c \sim 8\times10^{16}$/cm^3) was chosen for the analysis presented. In Fig. 1 we plot the inverse donor "susceptibility" $(R-a)^{-1}$ as a function of temperature, where $R=(d\Phi/dH)_{H=0}$ and $a=d\eta/dH$.[10] It is seen that χ^{-1} bends downward as $T\to0$ in a fashion common to many of these systems.[3-5] Similar behavior was observed at $c\sim2\times10^{17}$/cm^3. In addition, there is an apparent Curie-Weiss temperature Θ which is a few tenths of a kelvin in Fig. 1. The model presented below suggests that the actual Θ is much larger than this. The short-range coupling between randomly distributed donor spins gives rise to a very broad distribution of "closest-neighbor" exchange interactions. In the present case, calculations using wave functions described below indicate that this distribution peaks in the vicinity of $|J_{ij}|/k_B \sim 7$ K, but has wings which extend beyond 100 K and below 0.1 K. Thus the true intercept of χ^{-1} vs T would only emerge in measurements taken at $T\sim100$ K or higher.[11] The extent of this exchange distribution is also reflected by the magnetization data at $T\sim80$ mK shown in Fig. 2, where we see that saturation is far from complete in a field of 15 kG. The curves drawn in Figs. 1 and 2 are from calculations described below.

For N spins in a field H, the Hamiltonian is

$$\mathcal{H}=-g\mu_B H\sum_i^N S_{iz}-\sum_{i>j}^N J_{ij}\vec{S}_i\cdot\vec{S}_j. \qquad (2)$$

where $J_{ij}<0$. An approximate solution to the Hamiltonian is generated in a computer simulation as follows. Random spatial distributions of $N=324$ donor spins are generated in a cubic volume and an exchange interaction matrix is established assuming periodic boundary conditions. The sample Hamiltonian which results is then solved with use of a cluster approximation. We set a clustering threshold Δ, where $|J_{ij}|>\Delta$ for spins i and j to be included in the same cluster.[12] The sub-Hamiltonians of the clusters so determined are then diagonalized exactly and the magnetization of the system is calculated with use of the cluster eigenstates, taking account of the intercluster exchange in a molecular-field approximation. The molecular field h_i acting on cluster (or spin) i is assumed parallel to the applied field and taken to be $h_i=\langle\sigma_z\rangle_{av}F_i/2$, where $F_i=(g\mu_B n_i)^{-1}\sum_{jk}{}'J_{jk}$ is a molecular-field constant for cluster i containing n_i spins. The prime indicates that the summation is taken over spins j in cluster i and spins k not in cluster i. The low-field polarization if cluster i is thus given by $\chi_i(H_0+h_i)$, where h_i must be determined self-consistently. A certain fraction of the spins re-

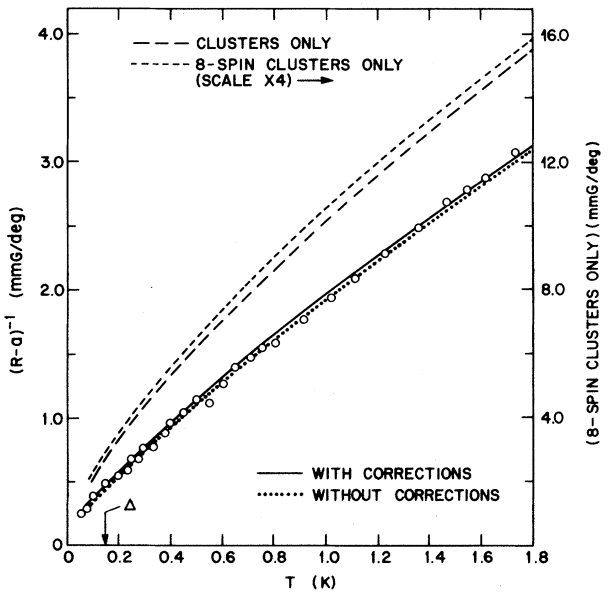

FIG. 1. Faraday-rotation susceptibility data presented as $(R-a)^{-1}$ vs T. Calculated curves (see text) with and without molecular-field corrections are shown as well as partial results from clusters alone and from eight-spin clusters alone. The cluster threshold Δ is indicated.

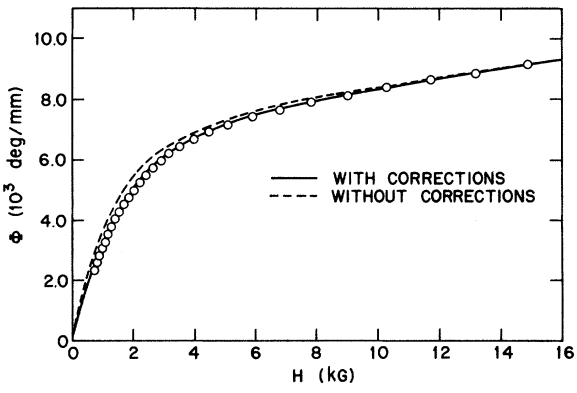

FIG. 2. Faraday-rotation saturation curve at T = 80 mK. Calculated curves (see text) with and without molecular-field corrections are also shown.

main isolated, and their subthreshold exchange couplings are treated in the same fashion. In the calculations presented the cluster threshold was set at $\Delta/k_B = 0.15$ K. At this level, 9% of the spins remain isolated, with the remainder grouped into clusters. Clusters larger than $n = 8$ spins (our practical limit for diagonalization) are subdivided by "breaking" the weakest bonds possible. These bonds are, of course, included in the molecular-field treatment. The fraction of bonds above threshold so treated was ~14%. The molecular-field approximation used gives only a rough estimate of the actual corrections. Nonetheless we might reasonably expect the results to be accurate if the estimated corrections are small.

The magnitude of J_{ij} as a function of separation r_{ij} is estimated from hydrogenic wave functions (appropriately scaled to the case of donors in CdS), with use of the exchange splittings for the hydrogen molecule calculated by Kolos and Wolniewicz.[13] Their results approach the asymptotic expression given by Herring and Flicker[1] for large r_{ij}. In the uncompensated dilute limit, the effective mass of $m^* \sim 0.18$ and dielectric constant $\epsilon \sim 9$ give a Bohr radius $a_H \sim 25$ Å and an effective Rydberg (Ry) of ~31 meV. However, an inevitable degree of self-compensation in CdS along with other effects lowers the ionization energy (Ry) by approximately 45% at concentration levels considered here.[14] The corresponding effect on J_{ij} will be less drastic and so as a rough estimate we adopt an intermediate value of ~24 meV for Ry and $a_H = 28$ Å ($a_H \propto \mathrm{Ry}^{-1/2}$).

For the neutral-donor concentration $n = N_D - N_A$ we take $n = 8 \times 10^{16}$ cm^{-3} from Hall data. With $g = 1.79$ (Ref. 8) and the parameters given above, we have carried out explicit calculations using five spatial distributions of $N = 324$ spins. By selecting $\Phi_{sat} = 2.2 \times 10^4$ deg/mm for this concentration we obtain excellent agreement with the observed χ^{-1} vs T data of Fig. 1 as well as the magnetization curve of Fig. 2. The corresponding value for Φ_{sat}/n is in reasonable agreement with other estimates of the Faraday rotation per fully aligned spin.[8] Equally good fits can be obtained with appropriate adjustment of the parameters within a 25% range of the values quoted. However, apart from the apparent quantitative success of the model, we emphasize that it yields the correct qualitative features of the data (including higher-temperature behavior not discussed) with any reasonable set of parameter values.

The calculated curves in Figs. 1 and 2 are presented both with and without molecular-field corrections in order to assess their importance. These corrections are not significant except at the lowest temperatures in Fig. 1 and at low fields in Fig. 2 where the fit is least good. We conclude that our solution of the model Hamiltonian is reasonably accurate over the range of fields and temperatures involved.

A common feature of susceptibility behavior in amorphous antiferromagnets is the steadily decreasing slope of χ^{-1} as T increases (Fig. 1). This feature has been attributed to a minority of "free" spins in some models.[15] However, our analysis shows that clusters alone (large dash line in Fig. 1) give this same characteristic behavior and that their contribution far exceeds that of the isolated spins. Nor is the cluster χ dominated by odd-spin clusters as might be suggested by the three-spin cluster model of Marko and Quirt.[4] Large even-numbered-spin clusters also undoubtedly behave as "paramagnetic particles," such that they have low-lying magnetic states within $k_B T$ of the ground state. For example, the present results yield a substantial incidence of triplet ground states among even-spin clusters (except pairs). To illustrate these points we have also plotted in Fig. 1 the χ^{-1} of eight-spin clusters. Their behavior is remarkably close to that of clusters as a whole; their susceptibility contribution per spin is very near the average for all clusters. Regarding the downward curvature of χ^{-1}, we make the following brief comments. For any cluster, $\chi = (g^2 \mu_B^2 / 3k_B T) \sum_i S_i(S_i+1)P_i$, where S_i and P_i are the spin and occupancy factor, respectively, of the ith eigenstate of a cluster. In general, the lower-lying states will have lower values of S_i. The downward curvature of χ^{-1} therefore is an expression of the relatively gradual decrease of $\sum_i S_i(S_i+1)P_i = \langle \vec{S} \cdot \vec{S} \rangle$ with decreasing T which results from the low-lying magnetic states noted earlier. This behavior of $\langle \vec{S} \cdot \vec{S} \rangle$ will be treated in greater detail elsewhere.

It is interesting to consider this system from the standpoint of percolation. Even though the median exchange coupling is ~7 K, the cluster decoupling procedures described above have revealed that this system only approaches percolation when the threshold Δ is set at ~0.1 K. This behavior, connected with the short-range interaction, is in sharp contrast with that of an RKKY system, where both percolation and the spin-glass ordering temperature occur in the neighborhood of the exchange distribution peak. Thus one can-

not rule out the possibility that the present system may yet undergo a spin-glass–like transition at temperatures below those studied here.

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[5]See Hudgens, Ref. 1. While a maximum is observed in χ vs T for some samples of amorphous Ge and Si, these systems are inhomogeneous and the interactions are not well characterized.

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[10]A fit of the model described to higher-temperature measurements gives $a \sim -0.01$ deg/G·mm. We adopt this value tentatively for the sake of Fig. 1, where it gives a correction $< 3\%$. We also note that a has the opposite sign from the value stated in Ref. 8. Further experiments are necessary before we come to a firm conclusion about the sign and magnitude of a.

[11]In Ref. 8, data on a similar sample for $1.6\ \mathrm{K} \leq T \leq 2.3$ K led to an estimate $\langle\Theta\rangle \sim 0.3$ K. Subsequent data at higher temperatures showed this to be an underestimate. For similar reasons, $\langle\sigma_z\rangle$ was *overestimated* by a factor ~ 2 at 1.6 K and the spin-flip cross section was *underestimated* by a factor ~ 4.

[12]It is important to note the distinction between our clusters of fixed size and the spin-glass clusters discussed by D. A. Smith [J. Phys. F 5, 2148 (1975)] of which the size increases with decreasing temperature.

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Self-Polarization at the Order-Disorder Phase Transition in NH_4Cl and NH_4Br

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Spontaneous or self-polarization current peaks were observed in NH_4Cl and NH_4Br, when the samples were thermally cycled through their order-disorder phase transition. In NH_4Cl, but not NH_4Br, these peaks can be modulated by an externally applied electric field. It is expected that this difference is due to the ferromagneticlike order in NH_4Cl and the antiferromagneticlike order in NH_4Br.

In this paper we report our observations on the spontaneous or self-polarization current peaks in NH_4Cl and NH_4Br, when the samples are thermally cycled through their low-temperature phase transition. The words "spontaneous" and "self" are used here to mean that the currents are the result of the rearrangement of charges in the sample that occurs during the phase transition and not due to an externally applied electric field. An earlier observation of this effect in NH_4Cl has been reported by Kessler.[1] Our results confirm his, but we have studied additional features of this self-polarization and have observed a significant difference in the behavior of NH_4Cl as compared to NH_4Br.

NH_4Cl and NH_4Br show low-temperature phase transitions at 243 and 235 K, respectively. In the low-temperature phase, the NH_4 tetrahedra order ferromagnetically for NH_4Cl and antiferromagnetically for NH_4Br. In the ordered state, NH_4Cl is piezoelectric while NH_4Br is not.[2] Since the transition is associated with the preferred orientation of the NH_4 ions and our results show a self-polarization peak at the transition temperature, it is expected that this peak is related to the orientation or disorientation of the NH_4 ions

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