Measurement of the Spin-Glass Order Parameter in Amorphous $Gd_{0.37}Al_{0.63}$

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Amorphous films of composition $Gd_{0.37}Al_{0.63}$ are found to exhibit a transition to a spin-glass state below 16 K. The magnetic properties show thermal hysteresis and relaxation below the spin-glass transition. The susceptibility maximum at 16 K, when measured in dc fields $\leq$10 Oe, sharpens into an asymmetric cusp, consistent with the Edwards-Anderson picture of the transition as one into a random, but rigid, state. Using the theory of Sherrington and Kirkpatrick, we extract the spin-glass order parameter from the observed cusp, and find deviations from simple mean-field behavior.

The term "spin-glass" was coined[1] to describe the metastable magnetic state observed at low temperatures in some simple solid-solution alloys (e.g., $Au_{1-x}Fe_x$ or $Cu_{1-x}Mn_x$, with x in the range 10^{-3} to 10^{-1}). Recent interest in the phenomenon has been stimulated by the observation[2] that the susceptibility, when measured by ac techniques in fields $H \lesssim 200$ Oe, has a sharp maximum reminiscent of a conventional second-order transition to a phase with periodic long-ranged order. However, dc measurements using[3] $H \approx 1$ Oe on $Cu_{1-x}Mn_x$ ($x = 10^{-4}$) with a susceptibility plateau below ≈ 0.2 K and with $H \approx 160$ Oe on a $Au_{1-x}Fe_x$ ($x = 5\times10^{-3}$) with a susceptibility maximum at $T_{max} \approx 5$ K fail to reveal a sharp cusp in the susceptibility. Tholence and Tournier[5] have proposed that such cusps are artifacts of the ac technique.

In this Letter, we show that such cusps are not artifacts of the measurement technique by reporting d.c. measurements of the susceptibility of a new type of spin-glass material with a much higher density of magnetic constituent—amorphous films of $Gd_{0.37}Al_{0.73}$. A susceptibility maximum with $T_{max} \approx 16$ K is observed in fields of 3 and 2 kOe which sharpens into a cusp when measured in fields of 10.0 to 0.1 Oe. Below 16 K in low fields, relaxation effects associated with spin-glasses[1] are also observed.

Edwards and Anderson[6] have proposed that the transition from paramagnet to spin-glass is a second-order transition to a random state. To detect the presence of such a state they introduce a new type of order parameter, q, which has the interpretation[7,8]

$$q(T) = \langle |\langle S_i\rangle_T|^2\rangle_r. \tag{1}$$

In (1), the thermally averaged local moment, $\langle S_i\rangle_T$, is squared to remove any dependence on the local orientation before carrying out spatial averaging, denoted by the angular brackets $\langle\ \rangle_r$. The susceptibility χ, provides an experimental probe of q, since[8]

$$\chi(T) = \{C(T)[1-q(T)]\}\{T-\theta(T)[1-q(T)]\}^{-1}, \tag{2}$$

where both $C(T)$ and $\theta(T)$ are temperature-independent in the mean-field theory of Ref. 8, and should be slowly varying close to the spin-glass transition temperature, T_{SG}, in real materials. Since q vanishes for $T \geq T_{SG}$, (2) predicts an asymmetry in the temperature dependence of χ above and below T_{SG}.

The susceptibility data obtained from $Gd_{0.37}Al_{0.63}$ films at fields below 10 Oe is consistent with the second-order phase transition picture. When q is extracted from the data with the use of (2), small deviations from the mean-field-theory predictions of Refs. 6–8 are observed. It does not seem possible to account for the details of the observed cusp within "cluster-freezing" or percolation models.[9]

The samples were prepared by sputtering, as described in detail by Cuomo and Gambino.[10] Static-magnetic-susceptibility measurements were made on pieces of a film about 3×10^{-4} cm^3 of the same amorphous $GdAl_2$ sample by two methods in applied fields of various magnitudes, with the results shown in Figs. 1 and 2. A force-balance magnetometer[11] offered adequate sensitivity in fields above 1000 Oe (Fig. 1), while the response to fields below 100 Oe was measured (Fig. 2) with a Superconducting Technology susceptometer.[12] This is a superconducting quantum interference device (SQUID)-type instrument sensitive to field changes of 10^{-8} G.

The measuring technique using the SQUID susceptometer involves moving the sample through a superconducting pickup loop which is located at the center of the superconducting coil which generates the applied magnetic field. As the sample is inserted into the loop, a current is induced

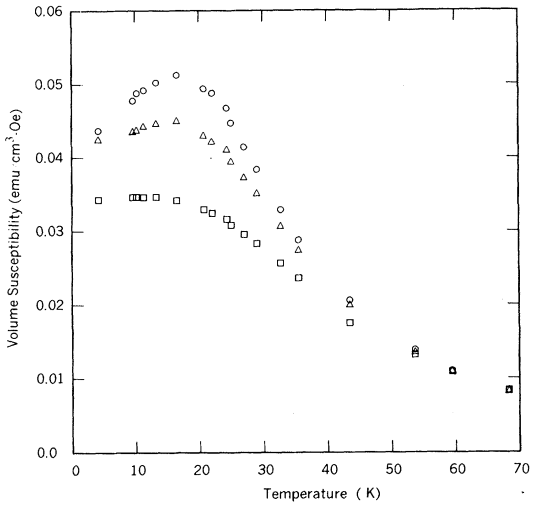

FIG. 1. Magnetic susceptibility of a $Gd_{0.37}Al_{0.63}$ sample at fields of 2 kOe (circles), 3 kOe (triangles), and 6 kOe (squares).

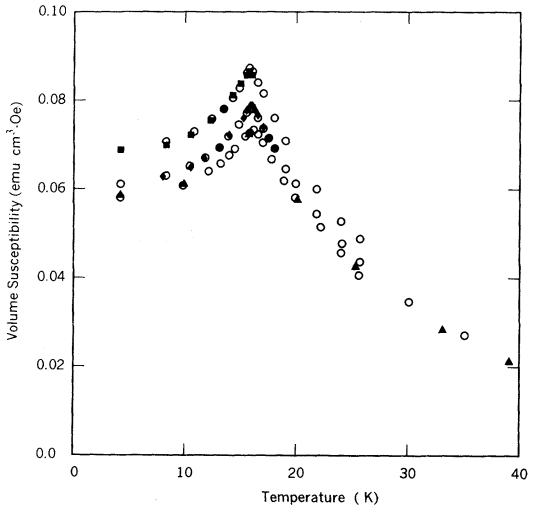

FIG. 2. Static magnetic susceptibility of a $Gd_{0.37}Al_{0.63}$ sample at fields of 9.0 Oe (triangles and circles), 2.5 Oe (diamonds and circles), and 0.12 Oe (squares and circles). In each case the solid data points were taken in decreasing temperatures, and the open points in increasing temperatures. Some of the vertical separation between the three sets of data may be the result of errors in measuring the small applied fields.

proportional to the magnetic flux from the sample linking the loop. Since the loop and its associated circuitry is superconducting, this induced current depends only on sample position and does not decay with time. The current is then measured utilizing the SQUID features of the instrument.

The applied field in the SQUID measurements was provided by flux trapped inside a superconducting shield. It was measured by a Hall probe (at room temperature) in the sample position, and by measuring the diamagnetic susceptibility of a quartz rod. The trapped-flux configuration gave exceptional stability, but made it inconvenient to change the magnitude of the applied field. The temperature is controlled with a silicon diode sensor in the path of the gas-flow heat-exchanger and measured with a platinum resistance thermometer 4 cm above the sample, connected to it by a high-purity Cu rod. Measurements were made at both increasing (open data points) and decreasing (solid data points) temperatures. The data were reproducible to better than $\pm 5\%$.

Only a rounded maximum is seen in the high-field magnetic susceptibility, shown in Fig. 1, and the susceptibility decreases with increasing field. Extrapolating χ^{-1} against T using high-field data taken between 60 K and room temperature gives a paramagnetic Curie temperature of roughly 30 K, indicating that the dominant exchange interactions are ferromagnetic in sign. The Curie constant, C_M, obtained from this high-temperature extrapolation under the assumption that the density of the $Gd_{0.37}Al_{0.63}$ film is the average of the metallic densities of its constituents, is roughly 30% greater than a calculated value using $J=\frac{7}{2}$ and $g=2$ for Gd. The slope of the inverse susceptibility decreases steadily as the temperature is lowered. Both of these observations are consistent with the "superparamagnetic" behavior observed in alloy spin-glasses[1,3-5] and usually attributed to the formation of stable clusters of spins, locked together by the stronger exchange interactions. This causes the average value of the remaining exchange interactions to decrease.

Two new features appear when the measurements are carried out in low fields. First, below the spin-glass transition a thermal hysteresis and relaxation of magnetization to its equilibrium value is observed. This relaxation is quite temperature-dependent and characterized by nonexponential time dependence near 8 K. Thermal hysteresis has also been observed in alloy spin-glasses by Borg and Kitchens.[13] Second, the susceptibility maximum seen in Fig. 1 becomes, in Fig. 2, a sharp, asymmetric cusp at 15.8 K. Cannella and Mydosh,[2] in extrapolating their ac susceptibility data on Cu-Mn alloys to zero field, have argued for a discontinuous derivative in $\chi(T)$, but could not resolve any curvature in χ.

ac measurements on more concentrated crystalline transition-metal alloys[14] do show curvature, but dc measurements on the same alloys are dominated by relaxation effects. The data of Fig. 2 are the first dc measurements, to our knowledge, which clearly resolve an upward curvature around the cusp. We shall argue below that measurements of the shape of $\chi(T)$ about its maximum can be used to discriminate between the predictions of various theories of the spin-glass transition.

Smith[9] has suggested that the susceptibility maximum in a spin-glass should be viewed as a percolation threshold for the freezing of spins into an infinite cluster, and thus a static phenomenon. He argues that any pairs of spins joined by exchange interactions $J > kT$ will be stable against thermal fluctuations. As the temperature is lowered, the fraction of rigid spins increases, until the percolation threshold is crossed and a rigid infinite cluster, which no longer contributes to χ, appears. The prediction, therefore, is that

$$T\chi(T) \propto 1 - P(p(T)), \tag{3}$$

where $P(p)$ is the percolation fraction[15] and $p(T)$ is the fraction of bonds which are rigid at temperature T. This description is not a thermodynamic calculation, but it does account in a natural way for the asymmetry of the transition, seen in Fig. 2, and predicts[16]

$$T\chi(T) \propto C(T_{SG})[1 - A(T_{SG} - T)^{\beta}], \tag{4}$$

where β is known to be 0.39 ± 0.01 for the percolation threshold in three dimensions.[15] We attempted to fit the data of Fig. 2 to the form (4), extrapolating $T\chi(T > T_{SG})$ by eye to obtain $C(T_{SG})$ and using values of T_{SG} from 15.8 to 16.0 K. Values of T_{SG} outside this range were just not plausible, in view of the sharpness of the observed cusp. The result, $\beta \approx 1.0 \pm 0.2$, contradicts the percolation hypothesis.

To see if the results in Fig. 2 are compatible with the Edwards-Anderson hypothesis we first extrapolated $\chi^{-1}(T)$ for the lowest-field data, shown in Fig. 3, to find the intercept $\theta(T_{SG})$ and slope $C(T_{SG})$, then used (2) to obtain

$$q(T) \approx 1 - T\chi(T)[C(T_{SG}) + \theta(T_{SG})\chi(T)]^{-1}. \tag{5}$$

We find that $\theta(T_{SG})$ lies between 0 and 4.1 K (the two lines in Fig. 3). The values of $q(T)$ extracted using (5) with these two choices of $\theta(T_{SG})$ are shown in Fig. 4. The results are seen not to be sensitive to the choice of $\theta(T_{SG})$.

The measured $q(T)$ increases slightly more rapidly than the mean-field theory of Ref. 8 predicts, and is slightly concave downward. Graphical analysis of the data in Fig. 4, using values of T_{SG} from 15.8 to 16.0 K, showed that a power law, $q(T) \propto (T_{SG} - T)^{\beta}$, with $0.8 \leq \beta \leq 0.9$, fits either set of points down to $T \approx 11$ K. Thus $q(T)$, as shown in Fig. 4, has the qualitative appearance predicted by mean-field theory, but its onset is slightly steepened ($\beta < 1$), just as occurs in con-

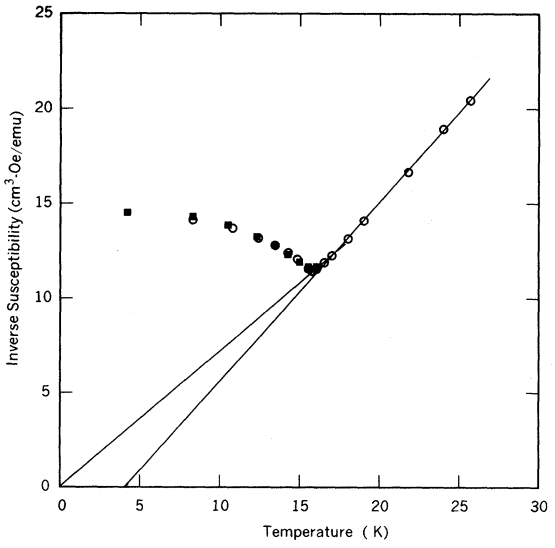

FIG. 3. Inverse susceptibility of $Gd_{0.37}Al_{0.63}$, measured in a field of 0.12 Oe, the lowest field studied.

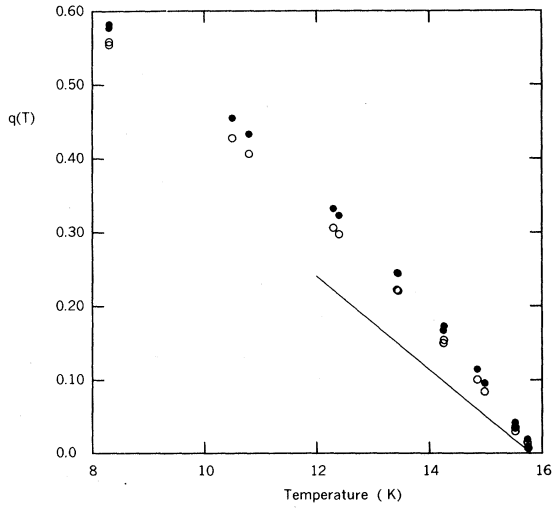

FIG. 4. Spin-glass order parameter, $q(T)$, extracted from the data of Fig. 3 using Eq. (2), as explained in the text. The dots show the result of choosing $\theta(T_{SG}) = 4.1$ K in extrapolating χ_0 from above T_{SG}; the circles the result of assuming $\theta = 0$. The solid line is the mean-field-theory prediction of Ref. 8 for $q(T)$.

ventional magnetic transitions, where β(three-dimensional) $< \beta$(mean-field).

We should note that our results do not agree with the calculation of β by Harris, Lubensky, and Chen.[17] By expanding about six spatial dimensions they obtain

$$\beta(d) \sim 1 + (6 - d)/2 \qquad (6)$$

for dimension d less than 6. The disagreement may mean only that six spatial dimensions is too far from the real world for the analytic continuation to be valid.

Further study of static and transport[18] properties of spin-glasses like the present films will be valuable. When the critical temperature is sufficiently high that no "glassy" phenomena (i.e., slow relaxation and hysteresis) occur in the critical region, the susceptibility cusp can be clearly resolved. The importance of doing such measurements in the lowest possible external fields should be apparent from Figs. 1 and 2.

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^{31}P Chemical-Shift Study of the Ferroelectric Transition in KD_2PO_4

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The ^{31}P chemical-shift tensors $\overleftrightarrow{\sigma}$ have been determined as a function of temperature on going through the ferroelectric phase transition in a single crystal of KD_2PO_4, and an abrupt change in $\overleftrightarrow{\sigma}$ was found at T_c. The results show that the transition is not driven by an electronic instability but is a pure lattice transition of the order-disorder type, and demonstrate the usefulness of chemical-shift studies of structural phase transitions in solids.

In this paper we report what we believe to be the first study of a ferroelectric phase transition via the determination of a chemical shift tensor. With the help of a superconducting magnet and a pulsed NMR spectrometer we have determined the temperature dependence of the ^{31}P chemical-shift tensor in a single crystal of KD_2PO_4 on going through the ferroelectric phase transition at $T_c = 220$°K. The results show that this ferroelectric transition is not driven by an electronic instability[1] but is a pure lattice transition of the order-disorder type, and demonstrate the usefulness of chemical shift studies of structural phase transitions in solids.

Chemical shifts in solids are usually masked by much stronger nuclear magnetic dipolar interactions and until recently this technique could not be used for the study of structural phase transitions. In the usual NMR spin Hamiltonian

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_\sigma + \mathcal{H}_d , \qquad (1)$$

the dipolar term $\mathcal{H}_d$ is smaller than the Zeeman