Long-time cooling-rate dependence of spin-glass freezing

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Superconducting-quantum-interference-device magnetometry is used to study the long-time cooling-rate dependence of the susceptibility cusp of the spin-glasses, *Cu*Mn 4.6 at.% and *Al*Gd 37 at.%. Over a range of time delay $\Delta T = 6$ to 2400 min per temperature change $\Delta T = 0.2$ K, no change is observed in the position of the cusp. These long-time results do not fit an extrapolation from Tholence's earlier ac susceptibility data as a function of frequency ($\nu = 10$ to 30 000 Hz). Thus, they appear to be inconsistent with current nonequilibrium models for spin-glass freezing and rather suggest a phase-transition phenomenon.

The freezing temperature T_f of many spin-glasses has been found to depend on measuring frequency[1–6] in a way suggestive to the Arrhenius law used to describe nonequilibrium effects in ordinary glasses. The susceptibility cusp is rounded and hysteresis persists above it.[7] These observations have been used as evidence against a phase transition. Furthermore, computer calculations of Ising and Heisenberg exchange Hamiltonians,[8–11] particularly the recent work of Morgenstern and Binder,[10] have shown that while Monte Carlo simulations exhibit susceptibility peaks, thermodynamic calculations using the full partition function show that no phase transition occurs until $T = 0$ and suggest that the susceptibility χ of the true equilibrium state of the system should continue to climb with decreasing temperature T. For example, in Heisenberg systems with exchange distributions symmetric around zero, the dc susceptibility χ is given by[12]

$$\chi = (\mu^2/3kT)(1 - Q) \quad , \tag{1}$$

where μ is the local moment and Q a spin-glass order parameter. In the nonequilibrium picture, Q should relax slowly to 0, leading to a monotonic smooth $\chi(T)$.

In this paper we report long-time superconducting-quantum-interference-device (SQUID) magnetometer measurements of two characteristic spin-glasses,[5,13,14] 4.6 at.% *Cu*Mu and 37 at.% *Al*Gd (amorphous). These new results, taken in conjunction with the recent results of Ferré *et al.*[15] on another much studied spin-glass $Eu_{0.4}Sr_{0.6}S$, and of Guyot *et al.*[16] on PrP_y, show T_f becoming constant at low frequency and indicate an interpretation of spin-glass freezing as a phase transition rather than as a nonequilibrium phenomenon.

Although many SQUID measurements of spin-glasses have been reported,[7,14,17,18] including measurements of *Cu*Mn and *Al*Gd from which Q has been extracted according to Eq. (1), none of these studies has yet addressed long-time behavior around the susceptibility peak to confirm if a phase-transition model is really applicable. And yet, if spin-glass freezing is truly a nonequilibrium phenomenon with a smooth distribution of activation energies, the system will ultimately relax to its true equilibrium state showing no peak or cusp whatsoever, and the time constants for this process should be rather short near and above T_f, decreasing continuously with increasing temperature.[8–11]

These considerations suggest the following experiment: to monitor the dc susceptibility in the immediate vicinity of the freezing temperature with the slowest cooling rate possible. The important point is to focus on the cooling rate, because this is what determines the freezing in a kinetic nonequilibrium experiment. By slow cooling rate we also mean long waiting time at each temperature after cooling through a small temperature interval.

The experiment was performed with a SHE SQUID susceptometer, model VTS-50, whose stability over several days in a quiet environment is ±0.05% in signal and ±20 mK in the 15–30-K temperature range. The field, produced by a superconducting coil,[19] was 4.5 Oe, which is sufficiently small to permit achieving a maximally sharp susceptibility peak in the samples of interest. The first sample was a 0.37-g roughly rod-shaped chunk of 4.6 at.% Mn in Cu, hung from a light thread whose susceptibility could be completely ignored. The second sample was a (1.4×10^{-4})-cm^3 piece of 37 at.% Gd in Al ~ 3.7 μm thick, on a glass substrate, shaped like a sliver, hung from a balsam rod. The diamagnetic susceptibility of the glass and balsam have not been subtracted from the data but are essentially constant in the temperature range of interest. The long axis of the samples was parallel to the field; in any case the magnetization was so small that shape demagnetizing effects could be neglected. The samples travel up and down with a full cycle time[20] of 37 sec through two counterwound superconducting coils whose output is monitored by an rf SQUID, and the peak-to-peak values of the out-

put of each half cycle give the magnetization of the sample in the fixed field at a given temperature.

Because of Guy's report[7] of hysteresis up to 2 K above the transition temperature in both *Cu*Mn and *Al* Gd, each run was started at a temperature three or more degrees above the peak (at 30 K in *Cu*Mn and 20 K in *Gd*Al). Then temperature was reduced in steps of about 1 K to within 1 K of the peak, and in steps of 0.2 or 0.4 K thereafter. At each step the temperature controller responded by first reducing the temperature to roughly 1.5 K below the target temperature of interest and then approaching the target temperature from below in an overdamped way. The 1.5-K drop in temperature should not affect the results because at lower temperatures the time constants of relaxation are larger according to a nonequilibrium picture. The time for the temperature to adjust to within 10 mK of the target value was about 6 min and determined the fastest rate at which a run could be done. The moment as a function of temperature during such runs is shown by the × 's in Figs. 1 and 2 for the *Cu*Mn and *Gd*Al samples, respectively (many runs superimposed). Then the longer-time runs were done by changing the temperature in steps of 0.2 or 0.4 K. At each temperature, the moment was first recorded and then the system was allowed to sit for either 60 ± 10 or 600 ± 200 min, and at the end of the time the moment was recorded again. The results are shown as circles and triangles on Figs. 1 and 2. One ultralong point of 40 h (2400 min) was taken on *Cu*Mn at 26.8 K just below the peak, giving the squares on Fig. 1.

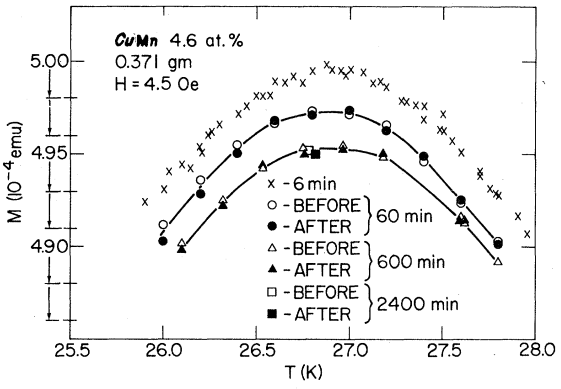

FIG. 1. Moment vs temperature of the *Cu*Mn sample in a constant field of 4.5 Oe. × 's show superposition of many runs in which temperature was stepped down in approximately 0.2-K intervals, with 6 min between points. Circles (displaced down by 0.02 units) show one run in which temperature was stepped down in 0.2-K intervals, with data taken immediately after the temperature step (i.e., *before* a waiting period of 1h) and *after* the waiting period. Triangles (displaced down by 0.04 units) show similar data with a waiting period of 10 h. The squares (also displaced down by 0.04 units) show one such temperature point with a waiting period of 40 h. Each run began after a data point at 30 K.

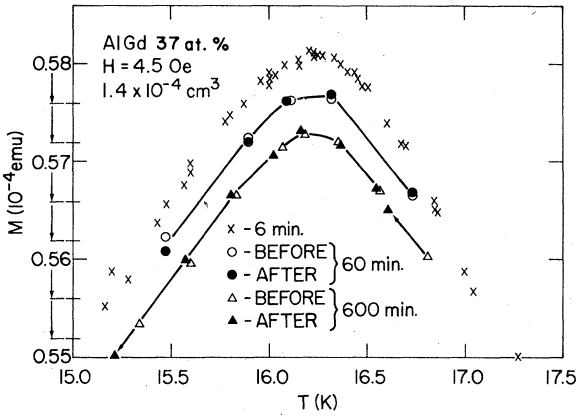

FIG. 2. Moment-vs-temperature of the *Gd*Al sample in a constant field of 4.5 Oe. The procedure is as in Fig. 1, except for the 10-h run, in which the sample was brought to 30 K between each waiting period to check on temperature drift; the drift is indicated by arrows between the before-and-after data points.

Figures 1 and 2 show essentially no change as a function of cooling rate over more than two decades (6 to 2400 min). There is no evidence for the upward relaxation in moment expected from nonequilibrium models [i.e., Q in Eq. (1) relaxing to zero].

Next we compare our results to the ac frequency-dependent susceptibility data of Tholence[5] on the identical *Cu*Mn sample and a closely related 25 at.% *Al* Gd sample. We define our effective frequency as the inverse of *twice* the waiting time between temperature steps, for that waiting time corresponds to roughly half a cycle of the ac experiments, which is the time during which the system relaxes to a new equilibrium state. The exact coefficient of the conversion is not so important because the SQUID results are cooling-rate independent anyway. In this way we can plot our data on the same Arrhenius plots ($\ln\nu$ vs $1/T_f$) as Tholence's data.

The results are shown in Figs. 3 and 4. One must allow for a shift of all the SQUID points together along the temperature axis, because of composition discrepancy between Tholence's and our *Gd*Al samples, and also because of possible absolute-temperature calibration error. Even with such shifts, however, the experimental results are clearly inconsistent with an Arrhenius relation, that is, a straight-line fit on Figs. 3 and 4. They are also inconsistent with the Fulcher law (solid line in Figs. 3 and 4) which Tholence has used to fit his data:

$$\nu = \nu_0 \exp[-E_a/k(T_f - T_0)] \ , \qquad (2)$$

where ν_0 is the attempt frequency, E_a the activation energy, k Boltzmann's constant, and T_0 a constant. The best fit achieved by varying ν, E_a, T_0, and an assumed temperature calibration error ΔT in the *Cu*Mn data is shown by the dashed line in Fig. 3. It requires

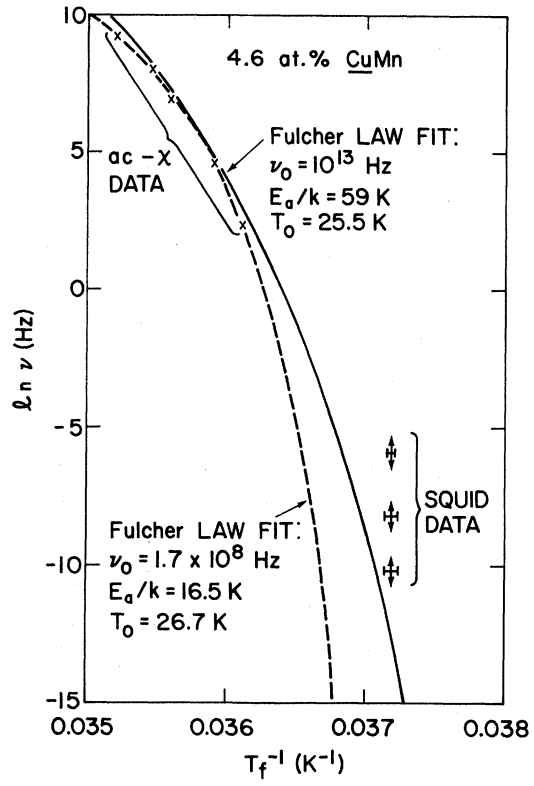

FIG. 3. Arrhenius plot (natural logarithm of frequency vs inverse freezing temperature) for the *Cu*Mn sample. ×'s are ac susceptibility data of Tholence (Ref. 5) and the data with error bars are present SQUID data assuming $\nu = (2\Delta T)^{-1}$ where ΔT is the waiting time between temperature changes. Solid and dashed lines are two Fulcher law fits.

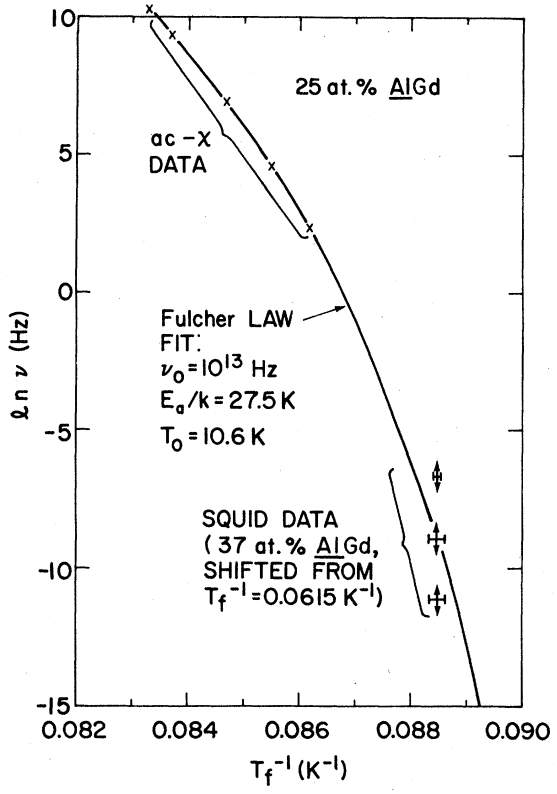

FIG. 4. Arrhenius plot for the *Gd*Al sample, as in Fig. 3. The ac data are on a 25 at.% sample, SQUID data on a 37 at.% sample; so SQUID data have been arbitrarily shifted along the temperature axis to give the best fit to Fulcher law.

the implausibly low value of $\nu_0 = 1.7 \times 10^8$, as well as $E_a/k = 16.5$ K, $T_0 = 26.7$, and $\Delta T + 0.4$ K.

The susceptibility peak can be interpreted in the nonequilibrium picture as occurring at the temperature at which the equilibration time, which increases with decreasing temperature, becomes comparable with the characteristic time of the experiment; hence the downward shift of the peak with decreasing frequency. The absence of such "frequency" shifts in our measurements suggest that either the peak is a true equilibrium phenomenon, or that the equilibration time increases suddenly by several orders of magnitude within a small fraction of a degree. The above results suggest quantitatively that such a sudden increase of the relaxation time is not consistent with previous descriptions of its temperature dependence, not even with the Fulcher law of Eq. (2) which may already be understood as implying something like a phase transition at the critical temperature T_0. Such a sudden increase of relaxation time would thus entail a phenomenon not less remarkable than the spin-glass transition itself.

Could it be that thermally induced relaxation such as occurs in the SQUID experiment has a different and much larger activation energy than the field-induced relaxation of the ac measurement? There is no obvious reason why this should be so. Indeed ac results are known to be not strongly dependent on the size of the applied ac field, and the presence of moderate (< 100 Oe) dc fields is also known not to affect the ac results.[6] Further, Ferré *et al.*[15] in their ac measurements of $Eu_{0.4}Sr_{0.6}S$, and Guyot *et al.*[16] in PrP_y found a rollover in T_f vs $\ln\nu$, similar to the effect shown in Figs. 3 and 4, but in their case, they used one and the same measuring technique *throughout* the frequency range from 10^5 to 10^{-2} Hz. We have also done one measurement changing the *field* at the cusp of the *Gd*Al sample (16.2 K) and found that from 6 to 600 min after the field change, the magnetization relaxed by less than 0.1%. This indicates that the response to a field change behaves with similar alacrity as the response to a temperature change.

These results raise strong questions about the interpretation of spin-glass freezing as a nonequilibrium phenomenon. If we turn to the alternative picture of

a phase transition, we must consider why the peak is rounded and why there is hysteresis above the peak.[7] We estimate the rounding in Figs. 1 and 2 by extrapolating straight lines from the linear regions on either side of the peak and measuring the length of the horizontal line through the peak between these extrapolations. The result is 0.6 K for *Cu*Mn and 0.4 K for *Gd*Al.

We now demonstrate that the roundings can be qualitatively understood in terms of sample inhomogeneities. In fact, microprobe analysis shows relative spatial variations of 6 and 2% in the magnetic ion concentrations, Mn and Gd, respectively. Coupled with dT_f/dc of 400 ± 100 and 50 ± 10 K/atom fraction,[5] these figures give T_f smearings of 1.2 and 0.4 K, respectively, in rough agreement with observation. The experimentally observed smearing ΔT_f implies a maximum correlation length, $\xi_m \sim \xi_0(\Delta T_f/T_f)^{-\nu}$ where ν is roughly 0.6–0.7 and ξ_0 is a microscopic length (several angstroms). ξ_m is larger by no more than an order of magnitude than ξ_0, and is therefore much less than the inhomogeneity scale of $\sim 10^{-4}$ cm for the microprobe analysis. This justifies the above estimates which assume parts of the system on the latter scale to go through their transitions independently. Note also that the statistical fluctuations in the magnetic ion density[21] for the 10^{-4}-cm scale would be on the order of 10^{-3}%, i.e., negligible compared with the observed large-scale inhomogeneity. These arguments, of course, only show that our observations are *consistent* with a phase transition rounded with inhomogeneities; the possibility of an intrinsic broadening of the transition[22] still exists. Samples of much better homogeneity will be needed to establish the phase transition with the same (finite, better by about two orders of magnitude—but never "infinite") sharpness as in the best ferromagnetic or antiferromagnetic samples.

In summary, our experimental results on a classic polycrystalline spin-glass *Cu*Mn and on an amorphous spin-glass *Gd*Al, coupled with the result of Ferré *et al.*[15] on an insulating spin-glass EuSrS, and of Guyot *et al.*[16] on PrP_y, are inconsistent with standard nonequilibrium models and suggest that spin-glasses in general show phase transitions. But computer simulations including exchange and Zeeman energies have failed to show phase transitions.[10] Thus a successful theory of spin-glass behavior should consider other terms such as anisotropy, dipolar energies, or various local symmetry breakings.[23]

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[19]From the shape of the SQUID output as a direct function of time during the cycle of sample motion through the two pickup coils, a field inhomogeneity of roughly 10% between the two coils can be detected. It was checked that this inhomogeneity had no significant effect on the results by comparing two 6-min runs (see text), one in which the peak-to-peak signal was monitored and the other in which the sample was held at a constant position in one of the coils. The latter procedure is not favorable for longer-time measurements because it is more susceptible to drift.
[20]The possibility that the cycle time affects the measurement was excluded by a 10-min run using a cycle time 10 times as long as for a 6-min run. The results were unchanged.
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