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Dynamical behavior of the susceptibility around the freezing temperature in (Eu,Sr)S

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New measurements of the ac susceptibility in zero field for a $(\mathrm{Eu}_{0.2}\mathrm{Sr}_{0.8})\mathrm{S}$ single crystal are reported. For the first time in a spin-glass we can resolve the frequency dependence of the in-phase component χ' (dispersion) *as well as* the out-of-phase component χ'' (absorption). From these studies a clear change in the dynamic behavior of the system around the freezing temperature is found, which can be related to large ferromagnetic clusters. The susceptibility behavior is described in terms of a wide distribution of relaxation times characterizing the intercluster interactions.

The unusual magnetic behavior of the mixed EuS-SrS system has led many investigators to classify this system as a spin-glass.[1] In this system there is supposedly a competition between ferromagnetic and antiferromagnetic interactions and a random distribution of Eu with Sr atoms on a fcc sublattice. These properties are basic ingredients for spin-glasses, even though with many so-called spin-glasses they are not fully satisfied. In $(\mathrm{Eu}_x\mathrm{Sr}_{1-x})\mathrm{S}$ the interactions are mixed, but of short range, and until now there has been no experimental proof for a random distribution of magnetic Eu atoms. On the contrary, at the large-x values ($\gtrsim 0.13$) needed to observe spin-glass-like effects one might expect large deviations from randomness. A further question also arises as to the exact nature of the spin-glass state and how to characterize its freezing behavior, e.g., as an equilibrium phase transition or as a metastable, dynamical one.

Over the past few years much interest has been devoted to the temperature and frequency dependences of random spin systems.[2] Typically the results of the ac susceptibility are limited to the in-phase susceptibility χ' (dispersion) with the subsequent interpretation restricted to characterizing time dependences in terms of an Arrhenius behavior or a Vogel-Fulcher law[3] and a determination of blocking temperatures (Wohlfahrt model).[4] Experimental results of the out-of-phase susceptibility χ'' (absorption) are sometimes presented but rarely analyzed in any detail owing to the smallness of this signal. However, a study of the frequency dependence of this part of the susceptibility can give further information about the dynamical behavior of the spin-glass freezing.[5]

Our measurements on a $(\mathrm{Eu}_{0.2}\mathrm{Sr}_{0.8})\mathrm{S}$ single-crystal sample show χ'' signals which are much greater than those observed in most metallic spin-glasses. Consequently, we are now able to analyze our data via Argand diagrams, i.e., plots of χ'' vs χ' at different frequencies. From such plots one can determine an average relaxation time in the internal field produced by the correlated spins.[6] Based upon these analyses our interpretation is that ferromagnetic clusters are formed at high temperatures and these clusters continuously relax at slower and slower time constants as the temperature is lowered through T_f. Thus the freezing behavior in $(\mathrm{Eu}_{0.2}\mathrm{Sr}_{0.8})\mathrm{S}$ is more of a dynamical type than a sharp, equilibrium phase transition.

The complex susceptibility $\chi = \chi' - i\chi''$ was measured by a standard mutual inductance technique in the frequency range from 5.4 Hz to 2.8 kHz. Both the dispersive (χ') and absorptive (χ'') signals were measured simultaneously by means of a two-phase lock-in amplifier. Temperatures between 40 mK and 1.50 K were generated by a specially constructed $^3\mathrm{He}$-$^4\mathrm{He}$ dilution refrigerator[7] with the sample, coil system, and thermometer inside an epoxy mixing chamber to ensure good thermal contact. Data were taken at discrete, well-stabilized temperatures ($\Delta T < 1$ mK). The coil system was carefully calibrated against cerium magnesium nitrate and no detectable change in the phase angle of the system was observed in the temperature range investigated.

A $\mathrm{Eu}_{0.2}\mathrm{Sr}_{0.8}\mathrm{S}$ single crystal (~ 6 mm diam and ~ 15 mm in length) was grown in a sealed tungsten crucible by the Bridgeman technique at a 10-mm/h growth rate.[8] In order to minimize possible concentration gradient effects, only a portion (~ 270 mg) from the center of this crystal was used in this investigation.

The results of the complex susceptibility as a function of temperature for several frequencies are shown in Fig. 1. At the highest temperatures ($T > 1$ K), one sees no difference in the dispersion for the various measuring frequencies within the experimental error. This feature plus the absence of any absorption indicates the measured χ' is the isothermal susceptibility χ_T, i.e., the system is in thermodynamic equilibrium. Decreasing the temperature, one observes a nonzero absorption signal starting at the

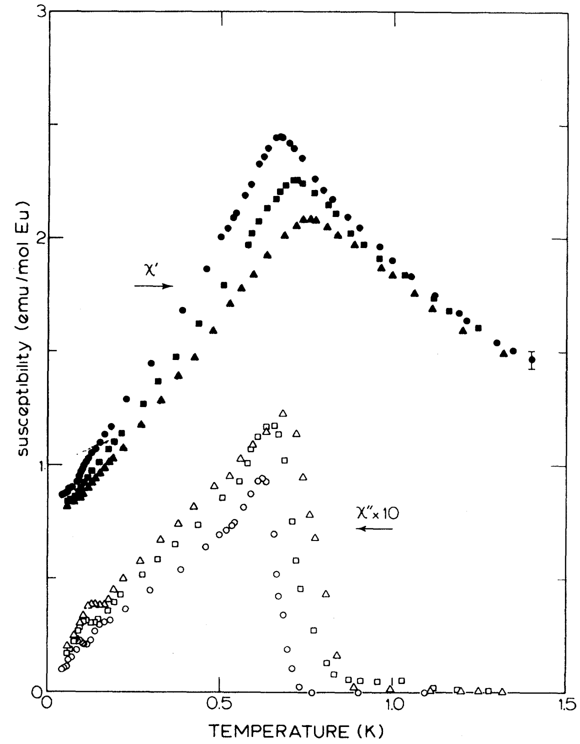

FIG. 1. Temperature dependence of the dispersion χ' (solid symbols) and absorption χ'' (open symbols) for $Eu_{0.2}Sr_{0.8}S$. ● ○, 10.9 Hz; ■ □, 261 Hz; ▲ △, 1969 Hz (applied ac field $h \simeq 0.1$ Oe).

higher frequencies. Similarly, deviations in the dispersion signal from the isothermal susceptibility are evidenced. We also note that the temperature of the inflection point of the absorption corresponds to the temperature T_f of the dispersion maximum for each measuring frequency. For temperatures below the susceptibility maximum, the various dispersion curves remain separated, but they converge to a nonzero frequency-independent value in the limit of T approaching absolute zero similar to metallic spin-glasses. However, the absorption χ'' shows a remarkable difference. For *Cu*Mn, *Au*Mn, and *Ag*Mn the absorption χ'' extrapolates at low temperatures to about 60% of their maximum value,[9] whereas in $Eu_{0.2}Sr_{0.8}S$ it extrapolates to a nearly zero value. In the temperature range 40–150 mK, a slight upturn is barely observable in χ' while a frequency-dependent "plateau" in χ'' is clearly detectable. This low-temperature feature may be ascribed to the blocking of isolated spin pairs and triplets similar to that reported earlier for very dilute samples.[10]

Qualitatively, the dispersion maxima broaden and shift to higher temperatures with increasing frequency similar to previous investigations on insulating spin-glasses. Accordingly, one can compare these shifts in T_f with frequency to an Arrhenius or Fulcher-type behavior. The characteristic values are listed in Table I. As is usually observed the activation relaxation of the Arrhenius type gives unphysical values of τ_0 and E_a/k_B ($\gg J_{NN}$ or T_f). The Fulcher description has therefore been employed in order to describe the frequency effects with reasonable physical values as is now the case. In comparing these characteristic parameters of the single-crystal results to the earlier work on a powder sample,[1] reasonable agreement is obtained. Nevertheless, the 28% difference in E_a/k_B is a direct result of the lower T_f's in the single-crystal sample than that of the powder one at each measuring frequency. This suggests that different kinds of preparations strongly affect the dynamic behavior near T_f and consequently the freezing temperature. (This effect has been previously seen in more concentrated samples—see Ref. 11.)

TABLE I. Characteristic parameters of Arrhenius and Fulcher laws.

$x=0.20$	Single crystal		Powder (Ref. 1)
	Arrhenius[a]	Fulcher[b]	Arrhenius[a]
τ_0 (sec)	10^{-21}	10^{-10}	10^{-21}
E_a/k_B (K)	28	4.4	36
T_0 (K)		0.43	

[a] $\ln\omega\tau_0 = -E_a/k_BT_f$.

[b] $\ln\omega\tau_0 = -E_a/k_B(T_f - T_0)$.

The frequency dependences of the dispersion χ' and absorption χ'' of the complex susceptibility are given in the case of magnetic relaxation by the Casimir and du Pré equations[12]:

$$\chi' = \chi_S + \frac{\chi_T - \chi_S}{1+\omega^2\tau^2} , \tag{1}$$

$$\chi'' = \omega\tau \frac{\chi_T - \chi_S}{1+\omega^2\tau^2} , \tag{2}$$

where χ_T is the isothermal susceptibility in the limit $\omega \rightarrow 0$ and χ_S the adiabatic one in the limit $\omega \rightarrow \infty$. At $\omega = 1/\tau$ the dispersion will have an inflection point, whereas the absorption will show a maximum. This maximum thus provides a method for determining a relaxation-time constant τ_{av} for each temperature. Also, the absorption should follow a $\text{sech}(\ln\omega\tau)$ functional dependence for a single relaxation time according to Eq. (2) and can be considerably broadened if a distribution of relaxation times is introduced. Therefore, the absorption usually provides more information about the dynamics of the freezing process around T_f than the dispersion. In Fig. 2, the absorption χ'' is shown over the frequency

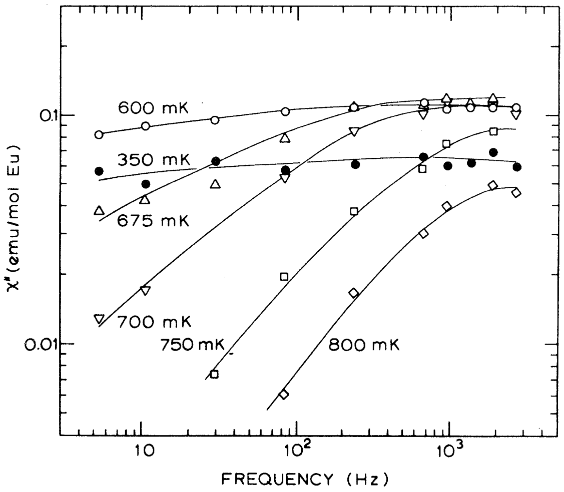

FIG. 2. Absorption χ'' as a function of frequency for different temperatures. The solid lines are a visual guide.

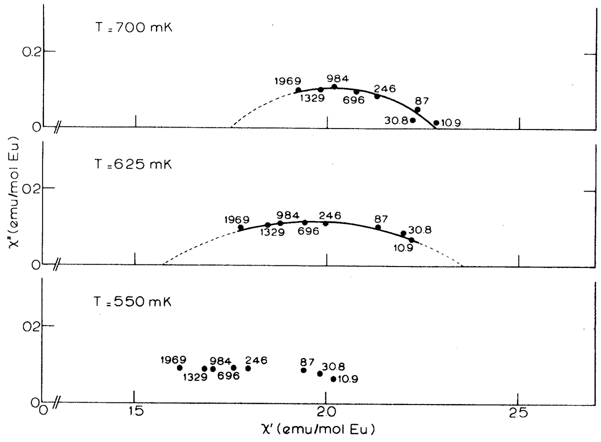

FIG. 3. Argand diagrams for three different temperatures. The numbers indicate the frequency of the ac driving field *h*. The lines are computer fits to the data points assuming a symmetric diagram (see text).

range of 5.4 Hz to 2.8 kHz for several temperatures around T_f (10.9 Hz) = 640 mK. One should note that for all temperatures the absorption does not show a clear maximum over the frequency range investigated. The width of the measured χ'' curves exceeds that which can be attributed to a single relaxation time from Eq. (2). Thus a distribution of relaxation times is necessary to describe the curves even for $T = 800$ mK $= 1.25T_f$. Furthermore, the absorption width (as determined from the frequency range measured) increases gradually as the temperature decreases from 800 to 700 mK, and then dramatically increases in the temperature interval from 700 to 600 mK. For temperatures below 600 mK, the absorption is essentially flat with all curves remaining parallel to one another. In addition, no apparent maximum in χ'' is observable in the measured frequency range for temperatures down to 200 mK. The above behavior signifies that the dramatic change in the distribution of relaxation times occurs in the temperature range of 600 to 700 mK. This change can be attributed to a sudden appearance of relaxation times greater than 30 msec ($\sim 1/2\pi\nu_{\mathrm{lowest}}$) and not solely to a sudden shift in the average relaxation time.

To illustrate the broadness of the distribution of relaxation-time constants in more detail, we have plotted the susceptibility data in the complex plane. These so-called Argand diagrams are shown in Fig. 3 for three different temperatures around T_f. For $\omega \rightarrow 0$ one measures the isothermal susceptibility χ_T, and for $\omega \rightarrow \infty$, the adiabatic susceptibility χ_S, Eqs. (1) and (2). In Fig. 3 it is seen that all three curves cannot be described as semicircles which indicates that the relaxation process is not characterized by a single relaxation time. The ratio $\chi''_{\mathrm{max}}/(\chi_T - \chi_S)$ is a measure for the flattening in the Argand diagrams and thus for the width of the distribution of relaxation times. One usually defines a deviation parameter d as follows[13]:

$$d = 1 - \frac{2\chi''_{\mathrm{max}}}{\chi_T - \chi_S} \quad . \tag{3}$$

d is zero for a single relaxation time and 1 for an infinite broad distribution. If we assume the curve of 700 mK to be symmetric as indicated by the dashed line, these data lead to a $d = 0.6$. Under the approximation that a distribution function of relaxation times is a rectangular block with width τ_2 to τ_1 on a logarithmic time scale, this d value corresponds to a ratio $\tau_2/\tau_1 = 2.5 \times 10^3$. The reciprocal value of the angular frequency at the maximum of the curve in the Argand diagram gives the average relaxation time constant, $\tau_{\mathrm{av}} \approx 1.5 \times 10^{-4}$ sec. A similar analysis for the curve at 625 mK, which by estimating both the low- and high-frequency limits gives $d = 0.7$, leads to a distribution width with ratio $\tau_2/\tau_1 = 4 \times 10^4$ and a $\tau_{\mathrm{av}} \approx 2.5 \times 10^{-4}$ sec. It is clear that analyzing the curve at 550 mK is highly speculative as no experimental data, from which one can determine χ_T and χ_S, are available. Our experimental data definitely indicate that an extremely broad distribution of relaxation-time constants is present at all temperatures.

The preceding results clearly show dramatic increases in both the absorption part χ'' and the distribution of the relaxation-time constants near the freezing temperature. It is well known that the nearest-neighbor interaction in (Eu,Sr)S is ferromagnetic ($J_{\mathrm{NN}} = 0.2$ K) which leads in the spin-glass concentration regime to ferromagnetic cluster formation at low temperatures.[14] The probability of large ferromagnetic clusters is further enhanced when chemical short-range order (SRO) is taken into account. These large ferromagnetic clusters are evidenced by the magnitude of the susceptibility per impurity spin near the freezing temperature. In the metallic spin-glasses, the maximum value of the susceptibility is much less ($\lesssim 10^{-3}$) than that determined by the demagnetizing factor for a ferromagnetic sample. But in $(\mathrm{Eu}_x\mathrm{Sr}_{1-x})\mathrm{S}$, the susceptibility maximum decreases only gradually with concentration in the range from $x = 0.51$ (long-range ferromagnetic limit) to 0.13 (superparamagnetic limit). For example, the present sample with $x = 0.2$ has a maximum value of 25% of the demagnetizing limit. These large χ values must be due to a strong ferromagnetic character of this system. With decreasing concentration, the range of magnetic ordering or size of the ferromagnetic cluster is slowly diminished. As T approaches T_f, these ferromagnetically ordered clusters cause an increase of the absorption signal. If these clusters were isolated, one would have superparamagnetism and the dynamic behavior would be equivalent to paramagnetic relaxation in a magnetic field. However, the sudden change in the absorption χ'' and in the distribution of relaxation-time constants around T_f suggest that intercluster interactions must play a role. This leads to a formation of some larger clusters which are further restricted in their rotational freedom, i.e., their relaxation times increase dramatically. Of course there still remains a distribution of smaller cluster sizes (pairs, triplets, etc.) which could relax with shorter time constants. The longest relaxation times are therefore related to these largest clusters which probably grow with decreasing temperature into semi-infinite ones. The nature of the intercluster interaction is such that the semi-infinite clusters still maintain their ferromagneticlike character. Also the fact that the absorption signal is nearly zero at very low temperatures indicates that nearly all spins are linked to clusters, in contrast to metallic spin-glasses. These measurements clearly demonstrate SRO relaxation processes. Thus the freezing behavior in this sample is more of a dynamical type than a sharp equilibrium phase transition. Further measurements are in progress to elucidate the relaxation-time spectrum at higher frequencies.

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