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Critical Dynamics and Spin Relaxation in a Cu-Mn Spin-Glass

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A dramatic increase in the width of the exchange-narrowed paramagnetic resonance line in $Cu_{75}Mn_{25}$ is reported and shown to result from the critical dynamics of the spin-glass transition. The divergence of the linewidth as $(T_f - T)^{-1}$ is the first observation of power-law behavior at the spin-freezing temperature.

Spin-glass phases of magnetic alloys are generally recognized to result from the freezing of spin motion at a temperature T_f, without an accompanying appearance of long-range magnetic order.[1] While there is experimental evidence[2] for the slowing down of spin motion in spin-glasses, no singular behavior has yet been reported. In this Letter we present the results of electron paramagnetic resonance (EPR) measurements on a concentrated Cu-Mn alloy which show clearly, for the first time, power-law behavior of the critical dynamics associated with the spin-glass transition. Moreover, the behavior of this alloy is shown to be surprisingly close to that predicted by a time-dependent Ginzburg-Landau (TDGL) model proposed recently by Ma and Rudnick.[3]

As is well known, the linewidth of EPR signals in magnetic materials is dominated by exchange-narrowed dipolar broadening.[4] Korringa processes, dominant in dilute alloys, are estimated to contribute $\lesssim 10\%$ of the observed width, because of the strong "bottleneck" effect.[5] The relaxation rate T_2^{-1} is given approximately by

$$T_2^{-1} \sim \chi^{-1}\omega_d^2\tau_s, \tag{1}$$

where χ is the static susceptibility; ω_d, the dipolar frequency $g^2\mu_B^2/\hbar v_s$; v_s, the volume per spin; and τ_s, the characteristic spin-spin relaxation time. Critical slowing down or speeding up[6] of τ_s increases or decreases χ/T_2, respectively. The critical behavior of χ tends to mask the effect of critical dynamics for ferromagnets, but the same is not true of antiferromagnets nor spin-glasses which have nonsingular susceptibilities. As we show below, the unique dynamics of the spin-glass transition, in which the relaxation time diverges while spatial correlations remain finite, leads to especially strong changes in the EPR linewidth.

Shown in Fig. 1 is the relaxation rate T_2^{-1} for a sphere of $Cu_{75}Mn_{25}$. The sample was quenched from high temperatures and subsequently maintained at 77 K except for experimental runs. The ac susceptibility[7] of an identical sample, also shown in Fig. 1, exhibits quite clearly the cusp associated with spin freezing at $T_f \simeq 115$ K. The initial dc susceptibility above T_f has Curie-Weiss-like behavior with a Weiss temperature $\Theta \simeq 97$ K.[8] EPR data, taken by conventional methods at 9.4

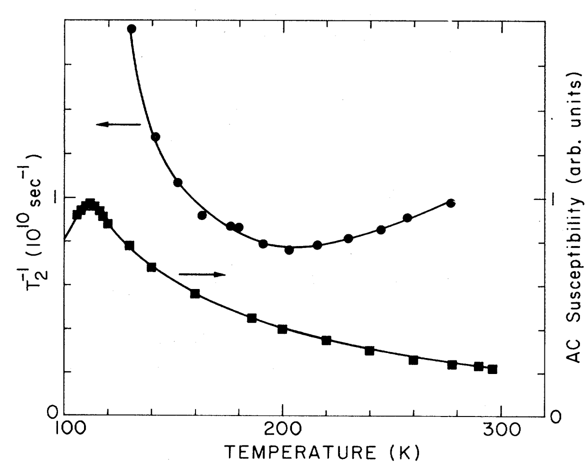

FIG. 1. Relaxation rate T_2^{-1} and ac susceptibility (Ref. 6) of quenched $Cu_{75}Mn_{25}$.

GHz, were computer fitted to Lorentian lines appropriate for a metallic sample, with T_2 and the g value as adjustable parameters. Accompanying the sharp increase in T_2^{-1} evident in Fig. 1 is a noticeable increase in g value from $g=1.985$ at room temperature to $g=2.125$ at T_f+11 K, the broadest line which could be measured. There is also some decrease in integrated intensity. We shall not attempt to treat these latter effects here. Similar anomalies in the EPR properties of spin-glass alloys are abundantly reported in the literature,[5] but none has been carried out with sufficient detail to permit the comparison with the spin-glass dynamics reported here. These results have been reviewed by Beck.[9]

In order to proceed with the analysis it is convenient to introduce a kinetic coefficient

$$L=T\chi/T_2C, \tag{2}$$

where the Curie constant $C=Ng^2\mu_B{}^2s^2/3k_B$ and s is the magnitude of the spin. Kawasaki[5] and Huber[10] have calculated L for exchange narrowing of the dipolar linewidth near critical points. The general expression is

$$L=(3/Ns^2)\int_0^\infty dt\langle\dot{S}_0(t)\dot{S}_0(0)\rangle, \tag{3}$$

where $S_0(t)$ is the time-dependent, $k=0$ Fourier component of the spin density,

$$\mathring{S}_0(t)=(ih)^{-1}[S_0(t),\mathcal{H}_d],$$

and the dipolar Hamiltonian[11] is written

$$\mathcal{H}_d=\sum_{ij}\sum_{\alpha\beta}g_{ij}{}^{\alpha\beta}S_i{}^\alpha S_j{}^\beta.$$

One obtains, following expansion of the resulting four-spin correlation functions in the random-phase approximation,

$$L=(s^2\omega_d{}^2/6\pi N)\int_0^\infty d\omega\sum_{\vec{k}}\{|f_{\vec{k}}{}^{+0}|^2+2|f_{\vec{k}}{}^{++}|^2+4|f_{\vec{k}}{}^{-+}|^2+|f_{\vec{k}}{}^{-0}|^2\}C^2(\vec{k},\omega); \tag{4}$$

the factors $f_{\vec{k}}{}^{\alpha\beta}$ are the Fourier transforms of $v_s g_{ij}{}^{\alpha\beta}/g^2\mu_B{}^2$. The two-spin correlation function $C(\vec{k},\omega)$ will be discussed below. The dipolar factors strongly influence the effectiveness of critical dynamics in modifying L. For cubic crystals, the sum in brackets in (4) vanishes at $k=0$ and at points in the Brillouin zone having cubic symmetry.[10,12] Strictly speaking, this suppresses any low-k singularity in $C(\vec{k},\omega)$. However, the region of strong k dependence is small, permitting anomalies such as those observed in cubic ferromagnets.[13] In the spin-glass case, no low-k singularity is expected—the susceptibility is finite at the freezing temperature—but a vanishing relaxation rate is expected in the frequency dependence.[3] Because the dipolar factors play no important role in the behavior of the linewidth, we simply replace the bracketed terms, which must be calculated for a distribution of Mn atoms, by an averaged function $F(k)$. We expect $F(k)$ to be zero over a narrow range near $k=0$, and to be constant over the remainder of the Brillouin zone.

In a recent Letter, Ma and Rudnick[3] presented a TDGL model of the spin-glass based on a random-ferromagnetic, Ginzburg-Landau Hamiltonian. In the ladder approximation, they calculate the response function to be

$$[G(k,\omega)]^{-1}=r+\xi_0{}^2k^2+\nu(k,\omega). \tag{5}$$

Here r decreases with decreasing T and would vanish at $T=\Theta$, but acquires a term proportional to the spin-glass order parameter at $T=T_f>\Theta$, producing a cusp in the static susceptibility $G(0,0)$. Above T_f, we approximate the behavior of $[G(0,0)]^{-1}$ by $r\simeq T/\Theta-1$. In the same calculation,[3] the frequency dependence of $[G(k,\omega)]^{-1}$ is found to satisfy

$$\nu=-i\omega\tau_0+\Pi\Delta\nu+O(\nu^2). \tag{6}$$

The quantity $\Pi\Delta$ is a decreasing function of temperature which achieves its maximum value $\Pi\Delta=1$ at T_f. Thus, (6) indicates that $\nu(k,\omega)=-i\omega\tau_s$, for $T>T_f$, with

$$\tau_s\simeq\tau_0(1-T_f/T)^{-1}. \tag{7}$$

As noted above, only the characteristic relaxation time τ_s diverges at the freezing temperature—there is no corresponding singularity in the static correlation length $\sim r^{-1/2}$. The two-spin correlation function may now be obtained from the fluctuation-dissipation theorem, $C(k,\omega)=(2/\omega)\,\mathrm{Im}G(k,\omega)$, and substituted into (4). The resulting transport coefficient is

$$L=\frac{s^2\omega_d{}^2\tau_0}{6(1-T_f/T)}\frac{v_s}{(2\pi)^3}\int dk\,k^2F(k^4)(r+\xi_0{}^2k^2)^{-3}. \tag{8}$$

In (8) we have assumed a non-conserved-spin model for the relaxation, which shows slowing down of spin fluctuations of all wave vectors in a way similar to the replica calculations.[1] Discussion of the appropriateness of such a model to the present problem will be taken up following a presentation of the experimental results. With the use of Eqs. (2) and (8) we can write our result in the form

$$\Theta L/T \equiv [(T/\Theta - 1)T_2]^{-1} = (L_0\Theta/T_f)(T/T_f - 1)^{-1}. \tag{9}$$

In Fig. 2 we have plotted our experimental values for the left-hand side of (9) versus $(T/T_f - 1)$ on a logarithmic scale. A background contribution[13] and the freezing temperature $T_f = 120$ K have been adjusted to produce the best fit. The data clearly lie on a straight line given by

$$\Theta L/T = 2\times 10^9 \text{ sec}^{-1} + (4.2\times 10^9 \text{ sec}^{-1})(T/T_f - 1)^{-1.00\pm 0.07}, \tag{10}$$

in excellent agreement with (9). We are limited in our approach to T_f by the extreme broadness of the lines, and may not have reached the true critical region. This could explain the close agreement of our results with a mean-field theory, despite the fact that renormalization-group methods show these to be invalid for dimensionality $d < 6$.[14] The spin dynamics associated with the spin-glass transition evidently dominates the magnetic behavior over a very wide temperature range, extending beyond $2T_f$ in this case.

The freezing temperature obtained from the fit of Fig. 2 is somewhat higher than the cusp temperature shown in Fig. 1. This may be due to the fact that the measurement is performed at finite field, however, the peak temperature tends to decrease as the magnetic field increases.[9] A similar effect has been noted[2] in neutron scattering where the peak in the quasielastic cross section occurs 5–10 K higher than the corresponding cusp in the ac susceptibility χ_{ac}. Murani[2] has attributed this difference to the time scale of the measurement: $\sim 10^{-11}$ sec for neutrons, but $\sim 10^{-2}$ sec for χ_{ac}. For exchange narrowing, the scale is set by the dipolar frequency, so that we are sensitive to times $\sim 10^{-9}$ sec, still far shorter than the ac susceptibility time scale.

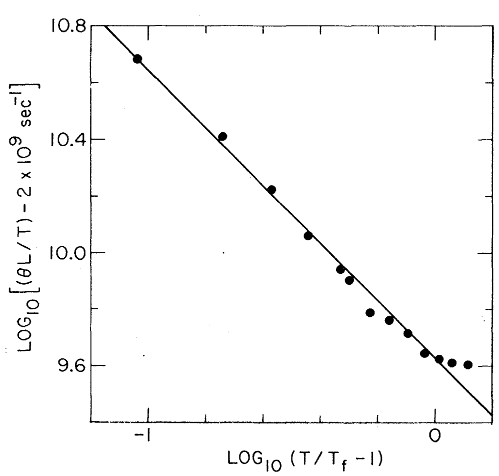

FIG. 2. Kinetic coefficient $\Theta L/T$ vs $T/T_f - 1$. The straight line is Eq. (10), a least-squares fit to the data.

Some evidence for dynamical freezing in spin-glass alloys has been noted previously. The width of the neutron quasielastic peak[2] narrows as the temperature is lowered, but then has a rather broad minimum around the freezing temperature. The overall narrowing is by less than a factor of 2. It may be that neutron results are masked by the effects of inhomogeneities which nucleate clusters near the freezing temperature.[9] Such clusters would be inhomogeneously broadened and thus unobservable in the EPR data. In fact, the loss of signal intensity near T_f may reflect the growth of such regions. The NMR spin-spin relaxation rate has also been reported to increase strongly near T_f.[2]

Quite recently Hertz and Klemm[15] extended the TDGL model to include both mode coupling and conserved spin. Somewhat surprisingly, no slowing down of the relaxation rate, as in the non–spin-conserving Ma-Rudnick model, occurs. Rather, mode coupling causes a speeding up of the relaxation rate, which in three dimensions is given by

$$\Delta(\tau_s^{-1})/\tau_s^{-1} \sim (T - T_f)^{-1/3}. \tag{11}$$

In the usual treatment of dynamical narrowing presented above, the dipolar interaction is treated as a perturbation, with the correlation functions which arise derived from an exchange-only, and therefore spin-conserving, Hamiltonian. Our results, however, are consistent with the non–spin-conserving model. This may be a shortcoming of the Hertz-Klemm model, which fails, after all, to predict spin freezing for any but the $k = 0$ mode. Equation (8) shows that, in fact, dipolar terms relax the $k = 0$ mode so that the inclusion of dipolar terms always leads to spin nonconservation. We require, clearly, a calculation of the spin dynamics of a spin-glass, which includes explicitly the effect of dipolar coupling on the transverse relaxation rate, with which to compare our empirical results.

We have shown, in summary, that the TDGL model describes surprisingly well the static and dynamical behavior of this concentrated *Cu*Mn spin-glass. EPR measurements are, in this case, especially useful in investigating the critical dynamics of the spin-glass transition. Anomalies in the EPR spectra have been noted over the years in a variety of alloys,[5] but were not pursued. It is quite clear that careful remeasurement of the linewidth and g-value anomalies on other well-characterized spin-glass alloys will lead to further clarification of the dynamical nature of the freezing transition.

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Direct Measurement of Quasiparticle-Lifetime Broadening in a Strong-Coupled Superconductor

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We have measured the quasiparticle recombination time in the strong-coupled superconductor $Pb_{0.9}Bi_{0.1}$ directly by measuring the lifetime-broadened energy gap edge. This is done by measuring the I-V characteristics of a superconducting tunnel junction of the type $Pb_{0.9}Bi_{0.1}$-insulator-$Pb_{0.9}Bi_{0.1}$. Agreement with the calculated value is excellent.

Nonequilibrium properties in superconductors have been the subject of substantial interest recently.[1] The response of a superconductor when driven away from equilibrium is very much dependent upon the various electron and phonon relaxation times. Central to the relaxation phenomenon is the recombination time τ_R which is the time taken for two quasiparticles at or near the energy gap edge Δ to recombine into the superfluid condensate. In this Letter we demonstrate that τ_R can be measured in a strong-coupled superconductor directly by measuring the lifetime-broadened energy gap width in a tunneling experiment. Measurements for the alloy $Pb_{0.9}Bi_{0.1}$ are presented and good agreement with calculations is achieved.

Previous measurements of the intrinsic quasiparticle recombination time in a superconductor have been plagued by thin-film phonon bottlenecking problems or have been rather complicated, requiring model analysis of data.[1,2] Very recently, a determination of τ_R in single-crystal Pb was made by measuring the thermal diffusivity and extracting a quasiparticle scattering rate which could be related to the recombination time.[2] In thermal equilibrium well away from the superconducting critical temperature T_c the recombination rate is given by[1]

$$\frac{1}{\tau_R}=\left(\frac{T}{\Delta}\right)^{1/2}\frac{1}{\tau_0}e^{-\Delta/kT}, \tag{1}$$

where τ_0 is related to the electron-phonon coup-

