Kohlrausch Thermal Relaxation in a Random Magnet

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Specific-heat measurements on amorphous Fe_xZr_{100-x} ($x=90$ and 92) by a thermal relaxation method reveal a temperature decay of the form $T(t)=T_0+\Delta T\exp[-(t/\tau)^{\beta}]$ below 20 K, where the alloys are asperomagnetically ordered. $\beta\simeq 0.5$ when $T_0\rightarrow 0$. The stretched exponential is a manifestation of nonergodic behavior, due to the inability of the spin system to explore the available random magnetic configurations on the 100-ms time scale of the experiment.

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Magnetic glasses with competing exchange interactions are useful materials for exploring the influence of disorder on familiar physical properties.[1] We show here that their specific heat can become ill-defined at low temperatures, where the times needed to establish thermal equilibrium are much longer than those for normal magnets.

The system we have studied is amorphous Fe_xZr_{100-x}. Notable changes in magnetism occur over a narrow range of concentration, $88\leq x\leq 93$, where these binary alloys can be prepared by melt spinning.[2] Figure 1 summarizes their magnetic properties. The figure resembles part of the mean-field-theory diagram of Gabay and Toulouse[3] for Heisenberg spin-glasses, provided x is identified with the ratio of the width of the exchange distribution to its positive mean value. Somewhat similar magnetic phase diagrams, with the x axis reversed, have been established for crystalline Fe_xAu_{100-x} spin-glasses with $x\sim 20$,[4] and for amorphous systems[5] including Fe_xB_{100-x}, Fe_xSn_{100-x}, and $(Fe_xM_{100-x})_{80}G_{20}$ glasses with $M=$Cr, Mn, or Ni near the critical concentration for the appearance of ferromagnetism.[6] For our purposes, a-Fe_xZr_{100-x} possesses some advantages over these other systems. The low-temperature specific heat is largely magnetic in origin,[7] and complications associated with the appearance of magnetism on the iron are absent. The alloys can be regarded as amorphous iron, stabilized by relatively small amounts of nonmagnetic zirconium impurities, with an average magnetic moment per iron atom of $(1.70\pm 0.05)\mu_B$ throughout the range of interest.[2]

By focusing on thermal relaxation in zero field, rather than decay of the remanence or the response to an ac magnetic field, as in previous studies of spin-glass dynamics, it is possible to follow the evolution of the system in states of no net magnetization. Problems of magnetic aging are avoided. These nonmagnetic states are more stable and overwhelmingly more probable than the magnetic states favored by an applied field, which in any case couples only indirectly to the order parameter. Time-dependent effects in the specific heat of spin-glasses were predicted by Morgenstern,[8] but an earlier attempt to observe them in a dilute Cu:Mn spin-glass was unsuccessful.[9]

Before describing the specific-heat measurements, we elaborate on the nature of the magnetic order. Essential-

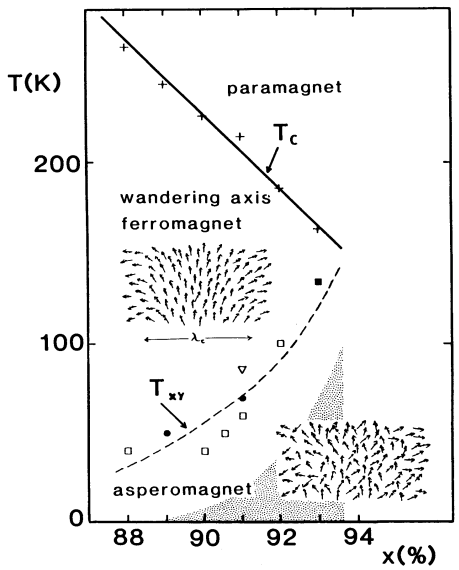

FIG. 1. Magnetic phase diagram of iron-rich a-Fe_xZr_{100-x}. Schematic magnetic structures of the wandering-axis ferromagnetic and asperomagnetic states are shown in the insets. The shaded region is where hysteresis can be observed. (After Ref. 2: Different symbols refer to different types of measurement.)

ly, two magnetic transitions are seen in Fig. 1, at T_c and T_{xy}. Below T_c, the alloys order as "wandering-axis ferromagnets," with a finite magnetic correlation length λ_c of order 25 Å.[10] The spin structure in a wandering-axis ferromagnet is locally ferromagnetic with no large variations in spin direction on neighboring sites, but the local ferromagnetic axis changes direction over distances of order λ_c. Although the susceptibility[11] behaves quite like that of a soft ferromagnet, the value of the magnetization at any given reduced temperature is much less than expected for a collinear ferromagnet with a zero-temperature moment of $1.7\mu_B$. There is a large high-field slope on the magnetization curves, but the only component of the iron moment stable in time when $T_{xy} < T < T_c$ is that along the applied field direction.

T_{xy} is the temperature where the transverse spin components begin to freeze at random, transforming the wandering-axis ferromagnet into an asperomagnet[1] (ferromagnetic spin-glass) with little change in λ_c.[10] The passage at T_{xy} is marked in the following ways: (i) appearance of a difference between field-cooled and zero-field-cooled magnetization, in small fields[12]; (ii) divergence between the average iron moment deduced from the hyperfine field distribution, and its z component deduced from magnetization measurements[2]; (iii) appearance of $\Delta m = 0$ transitions in Mössbauer spectra obtained[2] in an applied field of 2 T; (iv) onset of a Lorenztian-squared term in the neutron small-angle scattering intensity[10] $I(q)$; and (v) broad maximum in the transverse[2] or longitudinal[13] ac susceptibility measured in a longitudinal dc field.

Although there are some discrepancies between the values of T_{xy} obtained by different methods, we are certain that the transition is *not* directly related to the onset of hysteresis and coercivity, which takes place at lower temperatures. Taking a-$Fe_{93}Zr_7$ for example, the onset of the divergence of field-cooled and zero-field-cooled magnetization is at $T_{xy} = 85$ K in a field of 10 mT, whereas the coercivity only reaches 10 mT at 33 K. The boundary of the region of strong irreversibility where hysteresis is observed is somewhat arbitrary, since the coercivity declines exponentially with temperature. In Fig. 1 the shaded region is where the coercivity exceeds 3 mT; it is also here that the specific heat is clearly anomalous.

Measurements were made on milligram samples of alloys with $x = 90$ and 92, by a thermal relaxation method.[14] A small current i is passed to heat the diamond substrate on which the sample is mounted, increasing the temperature by ΔT above the temperature T_0 of the surroundings ($\Delta T/T_0 \sim 10^{-3}$). The current is then cut off, and the thermal decay from $T_0+\Delta T$ to T_0 is observed. Usually $T(t) = T_0 + \Delta T e^{-t/\tau}$, and the specific heat of sample plus addenda can be deduced from the decay time τ and the conductivity of the weak thermal link between the substrate and its surroundings. We find *nonexponential* decays for both alloys in the liquid-helium temperature range; typical data are shown in Fig. 2. Such behavior is normally associated with poorly mounted samples where, effectively, there is a second weak thermal link between sample and substrate. Yet the following observations establish that the nonexponential decay is *not* an experimental artifact.

(i) No change is found when the samples are remounted. (ii) The decay approaches a normal exponential as the temperature is raised. (iii) When the sample is hydrogenated and mounted as before, all trace of nonexponential behavior disappears. (Hydrogenation turns the asperomagnetic a-Fe-Zr alloys into good ferromagnets, with $T_c \gtrsim 400$ K[15]).

A fit of the 255 data points of Fig. 2 by a single exponential gives a bad fit, with a reduced χ^2 of approximately 5. A fit with two exponentials is still unsatisfactory. However, a stretched exponential,

$$T(t) = T_0 + \Delta T e^{-(t/\tau)^\beta}, \quad (1)$$

fits the data perfectly, with $\chi^2 \simeq 10^{-3}$. Following Palmer *et al.*,[16] we refer to Eq. (1) as the Kohlrausch relaxation law, since a similar equation was first used by Kohlrausch to describe viscoelastic relaxation. The variation of β as a function of temperature is shown in Fig. 3. Extrapolating the curve to $T \sim 0$, where the magnetic contribution to the specific heat will be several times

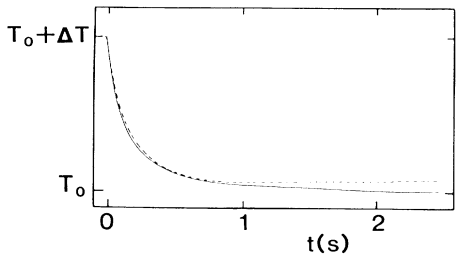

FIG. 2. Thermal decay in a-$Fe_{92}Zr_8$ at 2.03 K. The dashed line is the best exponential fit. The solid line, which is indistinguishable from the 255 data points on this scale, is a fit by Eq. (1) with exponent $\beta = 0.56$.

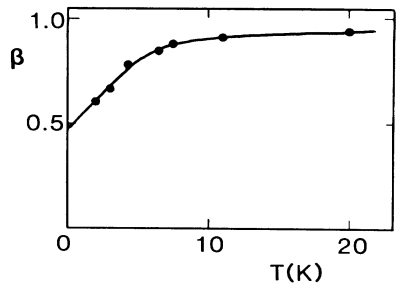

FIG. 3. Temperature variation of the exponent β for a-$Fe_{90}Zr_{10}$.

greater than the electronic and lattice terms,[7] gives $\beta \simeq 0.5$.

Our interpretation of the data is as follows: On displacement of the sample from thermal equilibrium by the cutting off of *i, the specific heat appears to increase with time on a time scale of 100 ms.* At first, only a small subset of all possible magnetic configurations is readily accessible, and more time is needed to explore a significant fraction of the configurations in phase space, and thereby approach thermal equilibrium. Unlike normal ferromagnets, where exploration takes place at spin-wave frequencies ($\sim 10^{14}$ s^{-1}), the dynamics of spin-glasses is sluggish. The system is not ergodic for measurements on a time scale of 100 ms, and indeed there may be no accessible time scale at low temperatures on which the ergodic hypothesis is valid.[17]

The stretched exponential law, Eq. (1), has been derived from several models of relaxation in disordered materials, based on different physical assumptions, which nonetheless possess a common mathematical structure.[18] The model of serial dynamics of Palmer *et al.*[16] supposes that relaxation occurs by stages so that the spins at level $n+1$ are only free to respond when some number μ_n of the N_n spins at the preceding level in the hierarchy have adopted a particular configuration. By assuming $N_n = N_0/\lambda^n$ and $\mu_n = \mu_0/n$, Palmer *et al.* derive Eq. (1). In our case, $\beta = \frac{1}{2}$ gives $\mu_0 = 1/\ln 2$, and hence $\mu_n \ll 1$, which means that the hierarchical constraint is weak; it is actually absent at most stages in the relaxation. The Förster model[18,19] of many parallel relaxation channels supposes that the probability of a site remaining excited after time t is $\phi_i(t) = e^{-W(R_i)t}$, where energy is transferrred to a site i at a distance R_i. If we assume $W(R) \propto R^{-s}$, Eq. (1) is recovered with $\beta = D/s$, in D dimensions. $\beta = \frac{1}{2}$ implies $s = 6$ in three dimensions. A picture of dipoles relaxing via a continuum of low-energy excitations whose density of states is proportional to energy also yields a stretched exponential.[20] Defect-diffusion models in either one[18] or two[21] dimensions can give Eq. (1) with $\beta = \frac{1}{2}$. The data do not indicate which of these models best represents the physical reality in a-Fe_xZr_{100-x} but, in our view, the most appealing picture of relaxation is diffusion of magnetic defects (a configuration of a group of spins) in the two-dimensional space of the transverse frozen spin components.

Finally, we comment on the relation between thermal relaxation and the time decay of the remanence, which is the other property of spin-glasses that was reported to follow a Kohlrausch law,[21,22] although it has since been shown that the stretched exponential there is related to sample aging in the applied field.[23,24] In our measurements, the aging time is at least three orders of magnitude greater than the relaxation time, and in these circumstances the remanence is expected to exhibit a power law, rather than a Kohlrausch decay.[24] Nevertheless, irrespective of the exact form of the decay, there is a great disparity in the time scales involved; the time taken for similar Fe-Zr samples to decay "half way" is 0.1 s for thermal relaxation, and 1000 s for relaxation of the remanence. The former involves exploring some $2^{N/2}$ of the $\sim 2^N$ nearly degenerate states with no net magnetization (for N Ising spins), whereas the latter relaxation is highly constrained—the system must pick a tortuous path through a sequence of sparse states with ever decreasing net magnetization, sampling an appreciable fraction of all 2^N states in the process. If we assume that the relaxation time is proportional to the number of sites explored, the ratio of these times implies that the magnitude of N is only of order 100, which suggests that the dynamics of spin-glasses are controlled by interconfigurational fluctuations of very small groups of spins.

In summary, we have demonstrated directly, without using a magnetic field, the failure of ergodicity at low tempertures in a type of spin-glass via the stretched exponential form of the thermal relaxation.

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