

Thermal relaxation in a frustrated ferromagnet

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A relaxation-calorimetry study of α -Fe₉₂Zr₈ and α -Fe₉₀Zr₁₀ shows no evidence of nonergodic behavior below 25 K. The positive results of an earlier study are reexamined and the reliability limits of this technique are discussed.

Morgenstern¹ predicted that the heat capacity of spin glasses should exhibit time dependent effects below the spin freezing temperature, and while an investigation of heat capacity in CuMn (Ref. 2) found no time dependent effects, a more recent study of heat capacity in the magnetically frustrated system amorphous Fe_xZr_{100-x} ($x = 90, 92$) showed strong evidence for a time dependent specific heat (C_p) below 20 K which was interpreted as being due to a failure of ergodicity on a 100-ms time-scale in this spin-glass-like material.³ The relaxation was found to follow the stretched-exponential (Kohlrausch-law) form:

$$T(t) = T_0 + \Delta T \exp[-(t/\tau)^\beta]$$

widely reported in disordered systems.⁴⁻⁷ Many relaxation processes have been shown to yield stretched-exponential behavior including defect diffusion,⁸ whereby the relaxation is mediated by defects which perform a random walk through the system, and hierarchical models,^{9,10} where relaxation is constrained to proceed in order through a sequence of levels. Klafter and Shlesinger¹¹ have shown that both of these descriptions are related and that the stretched exponential form arises through scale-invariant relaxation rates generated by the models. A variation on the defect diffusion model due to Campbell *et al.*¹² considers the exploration of available configurations by a system as being a random walk on a hypercube. Reducing temperature makes some configurations inaccessible, the path through phase space becomes sparse and nonexponential relaxation sets in. The underlying feature of all of these descriptions is the absence of a single characteristic length scale or time scale. It is the form of the length- or time-scale distribution that ultimately yields the stretched exponential relaxation form.

The earlier calorimetry results³ are remarkable for several reasons: Firstly, the time scale for the heat capacity relaxation in α -Fe-Zr was found to be about 4 orders of magnitude shorter than for the decay of remanent magnetization in the same system.¹³ Secondly, theoretical models¹² predict the onset of nonergodicity on approaching the spin-glass transition from above, whereas stretched exponential relaxation was only observed below ~ 20 K, well below T_{xy} , the transverse spin freezing transition, (76 and 50 K for $x = 92$ and 90, respectively)

where spin-glass order develops perpendicularly to the ferromagnetic order established at $T_c \sim 200$ K.¹⁴ Finally, α -Fe-Hf, which is magnetically similar to α -Fe-Zr¹⁵, showed no evidence of unusual relaxation behavior.

In order to explain these anomalies and obtain a more detailed understanding of the phenomenon we have repeated the measurements of α -Fe-Zr over a wider range of temperature and time scales. We report here a more extensive analysis of both the new results and the original data.

Metallic glass samples were prepared by conventional melt spinning in an inert atmosphere.¹³ Relaxation calorimetry was carried out using an instrument similar to that in the earlier study³ and described by Bachman *et al.*¹⁶ except that the substrate used here was sapphire. Sample masses ranged from 2 to 35 mg. At each temperature T_0 , the system (calorimeter, addenda, and sample) is allowed to come to equilibrium, then the sample and addenda are raised above ambient by an amount ΔT ($\Delta T/T_0 \sim 1\%$) by passing a current through a heater evaporated on to the addenda. Once the system has re-equilibrated, the power is cut off and the addenda-sample combination relaxes to ambient through a weak thermal link to the calorimeter. Usually $T(t) = T_0 + \Delta T \exp(-t/\tau)$ is observed and the heat capacity of the sample may be deduced from the time constant of the decay (τ) and the conductance of the thermal link, after the contribution of the addenda is subtracted.

Our results for Fe₉₀Zr₁₀ shown in Fig. 1 are in agreement with those of Mizutani *et al.*¹⁷ who used a different technique to measure the heat capacity. At no temperature or time scale did we observe any departure from simple exponential decay.

A clue to the origin of the earlier nonexponential behavior was found when we mounted a long sample so that two thirds of its length hung over the edges of the substrate and were not in direct thermal contact with addenda. This sample gave strongly nonexponential results however the stretched exponential form did not fit our data. We considered two modifications to simple exponential decay in order to model our distorted relaxation curves. Figure 2(a) shows the standard configuration (addenda plus sample, C_{A+S} , connected to the bath by a weak link of conductance K_1) which leads to the simple exponential form with $\tau = C_{A+S}/K_1$. If the sample C_S is poorly connected to the addenda C_A by an extra link K_2

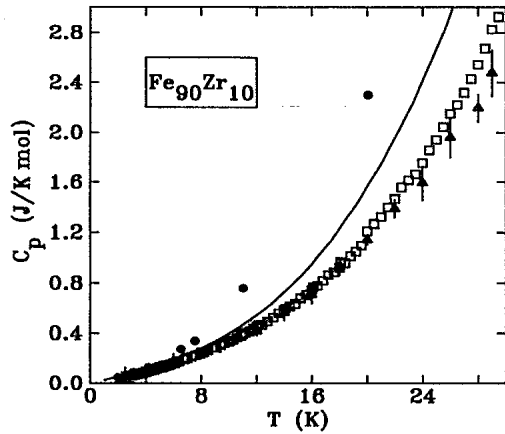


FIG. 1. Specific heat of $a\text{-Fe}_{90}\text{Zr}_{10}$: (\square) data from a 35.27-mg sample fitted with a simple exponential decay, (\triangle) data from a 9.22-mg sample allowed to hang over the edge of the mounting and fitted with a form described in the text. (\bullet) results of two-time-constant fits to data from the previous work [3] obtained on a 1.33-mg sample (this data includes the heat capacity of the glue used to mount this sample). The solid line is taken from the work of Mizutani *et al.*¹⁷

[Fig. 2(b)] then a two-time-constant relaxation is observed:

$$T = T_0 + \frac{\Delta T}{\alpha_+ - \alpha_-} \left[(\alpha_+ + 1) \exp\left(\frac{\alpha_+ - t}{\tau_0}\right) - (\alpha_- + 1) \exp\left(\frac{\alpha_- + t}{\tau_0}\right) \right] \quad (1)$$

where

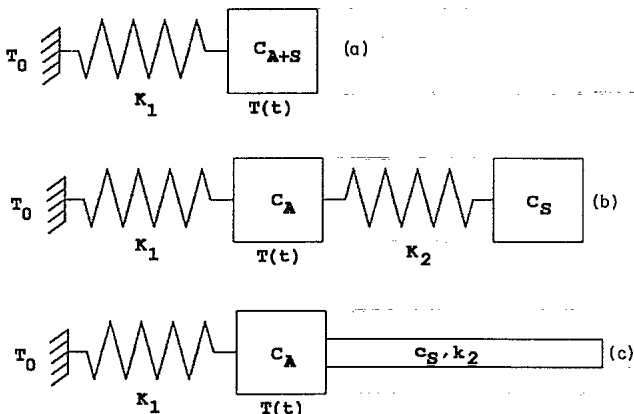


FIG. 2. Various relaxation calorimeter configurations: (a) standard configurations with sample and addenda C_{S+A} in good contact and connected through conductance K_1 to a reservoir at T_0 ; (b) sample C_S connected weakly through conductance K_2 to the addenda C_A leading to a two-time-constant decay [Eq. (1)]; (c) overhanging sample with heat capacity c_S per unit length and thermal conductivity k_2 leading to the complex decay of Eq. (2). In each case $T(t)$ indicates the point where the temperature is recorded during the decay.

$$\alpha_{\pm} = \frac{-(\lambda + h + 1) \pm \sqrt{(\lambda + h + 1)^2 - 4h\lambda}}{2h},$$

$$\tau_0 = C_A / K_1,$$

$$h = K_1 / K_2 \quad (\text{conductance ratio}),$$

$$\lambda = C_A / C_S \quad (\text{specific-heat ratio}).$$

A more realistic treatment of an overhanging sample, length l and cross-sectional area a , is to describe it as a distributed heat capacity c_s per unit volume with a conductivity k_s [Fig. 2(c)]. This leads to relaxation of the form

$$T = T_0 + 2 \Delta T_0 h \sum_n \frac{\exp(-\alpha_n^2 l^2 \lambda t / h \tau_0)}{(h - \lambda \alpha_n^2 l^2)^2 + \alpha_n^2 l^2 (1 + \lambda) + h}, \quad (2)$$

where

$$\alpha_n l \tan(\alpha_n l) = h - \alpha_n^2 l^2 \lambda,$$

$$\tau_0 = C_A / K_1,$$

$$h = K_1 l / k_s a \quad (\text{conductance ratio}),$$

$$\lambda = C_A / c_s a l \quad (\text{specific-heat ratio}).$$

Figure 3(a) shows the residuals after fitting the four relaxation forms at three different temperatures for the overhanging $\text{Fe}_{90}\text{Zr}_{10}$ sample. It is immediately clear that while the stretched exponential fit is a marked im-

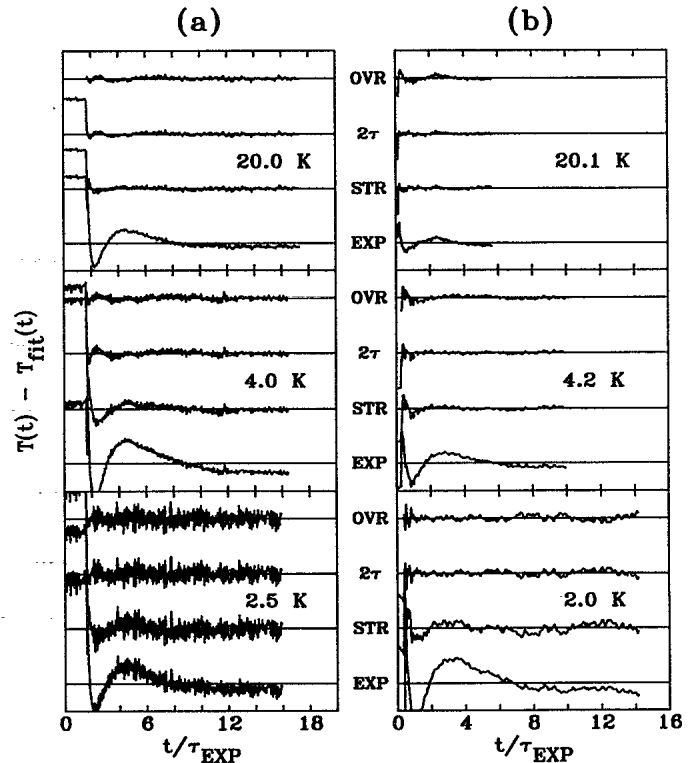


FIG. 3. Residuals of exponential (EXP), stretched exponential (STR), two-time-constant (2τ), and overhang solution (OVR) fits to the data of (a) the present work and (b) the previous work³. Offsets used to separate the residuals are equal to 10% of the signal amplitude and the x axis is scaled in units of the exponential time constant.

provement over the exponential fit, neither form gives a satisfactory fit to the data. Examination of χ^2 shows that the overhang solution [Eq. (2)] gives the best fit at all temperatures with up to a factor of 2 improvement over the other forms. The fit yields specific heats in good agreement with previous results (Fig. 1) and shows that about 70% of the sample is not in direct contact with the addenda. This is consistent with the visual estimate of $\frac{2}{3}$. Finally, the thermal conductivity deduced from the overhang fit shows a linear temperature dependence consistent with the resistivity in this temperature range.

A similar analysis of the earlier data [Fig. 3(b)] shows that both the two-time-constant and stretched exponential fits are close representations of the data with the former yielding systematically lower χ^2 . The overhang solution is a poor fit as expected since this sample did not extend beyond the edge of the substrate and so the experimental conditions do not match the assumptions used to derive this solutions. Examination of the two-time-constant fit suggests that as much as 80% of the sample was in poor contact with the addenda, however, the heat capacity determined from the fit (shown in Fig. 1) is in reasonable agreement with the results both of this work and those of Mizutani *et al.*¹⁷ Indeed, despite their poor match to the data, simple exponential fits also yield reasonable heat capacities.

We draw two conclusions from the results of this study. Firstly, the conclusions of the earlier study³ are in error. Reanalysis of the original data suggests that poor sample-addenda contact is a more likely explanation of the results. That poor contact was only experienced in the case of *a*-Fe-Zr (3 samples out of a series of 8 similar form and mass) remains as a puzzle. Hydrogenated samples, which were difficult to mount as they were distorted

and brittle and therefore expected to give problems, showed no evidence of nonexponential relaxation.

Secondly, relaxation calorimetry is an inappropriate technique for detecting the possible presence of time-dependent heat-capacity effects. To first order, the expected signature of nonergodic behavior (nonexponential relaxation) may be considered to arise from poor internal mounting: either between the lattice and the spin system or between different spin configurations. Unambiguously identifying the observed effects as being due to an intrinsic property of the material demands that the departure from exponentiality be very accurately characterized. However, the differences between real effects and those due to a poorly mounted sample are too small for the two cases to be reliably distinguished, especially when strong addenda-bath links are used to probe short time scales.

Finally, given the variety of models that can yield stretched exponential relaxation it is clear that the form of the decay is not particularly sensitive to the details of the internal dynamics. It is therefore necessary to rule out a large number of alternative forms to a high degree of reliability before the presence of stretched exponential behavior can be established. This is extremely difficult for the time-domain measurements presented here (even for $\beta \sim 0.5$, data over about five decades of time would be needed), and frequency response measurements offer the best sensitivity to the relaxation form.¹⁸

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