Dynamics of the Relaxation-Time Spectrum in a CuMn Spin-Glass

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SQUID magnetometry measurements on a *Cu*Mn spin-glass reveal that the zero-field–cooled magnetization strongly depends on the *time* the sample is kept at constant temperature *prior* to the field application. This result is evidently at variance with the common belief that an equilibrium spin-glass state is quickly obtained after cooling in zero field. The nonequilibrium behavior, as reflected in the complex time dependence of $\partial m/\partial \ln t$, is interpreted to arise from slow dynamics of the relaxation-time spectrum.

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It has generally been believed that the ac susceptibility in spin-glasses displays a fully reversible behavior[1] as long as the frequency of the ac field is kept constant. However, recently we[2] reported a significant time dependence (at constant temperature and frequency) of the complex ac susceptibility, $\chi = \chi' + i\chi''$, on a Cu–4-at.%-Mn spin-glass, having a spin-glass freezing temperature of $T_g = 26$ K. It was then observed that after a step change (increase or decrease) in temperature, and after the corresponding step change of the susceptibility, both the real (χ') and imaginary (χ'') parts of the susceptibility slowly *decreased* in magnitude with time. This effect was particularly noticeable on χ'' at low frequencies (~1 Hz). For a step change in temperature of 1 K χ'' momentarily attains an absolute value, twice that of the equilibrium value, followed by a slow $t^{-1/2}$ decay with time towards equilibrium. In the phenomenological spin-glass model prescribing a wide distribution of relaxation times[3,4] it has previously been shown[4] that χ'' relates to the density of relaxation times, $g(\tau)$, according to

$$\chi''(\omega) = -(\pi/2)[m_0(\tau_m)/h_0]g(\tau_m); \quad \tau_m \approx 1/\omega, \quad (1)$$

where $m_0(\tau_m)$ is the average equilibrium value of the magnetic moments with relaxation time τ_m, and ω is the angular frequency of the applied field $h = h_0 \sin(\omega t)$. Within this model, the time dependence of χ'' was interpreted to arise from a sudden increase of $g(\tau)$ at short relaxation times followed by a slow recovery of the spectrum towards long relaxation times. Furthermore, it was experimentally observed that the time dependence of the susceptibility was *only* dependent on the time the sample had been kept at constant temperature after the temperature step, and *not* on the particular moment the alternating field was applied. This indicates that $\chi''(\omega)$ merely probes $g(\tau_m)$ and its time dependence at constant temperature in a zero-field situation. The possibility to probe the relaxation-time spectrum through Eq. (1) was in the ac susceptibility measurements limited to relaxation times $\tau_m \leq 10^{-1}$ sec.

In a recent paper,[5] we showed that it is possible to obtain information on the relaxation-time spectrum at considerably longer relaxation times from zero-field–cooled (ZFC) magnetization measurements. In this Letter we report measurements of the ZFC magnetization of a Cu–4-at.%-Mn sample in order to explore the behavior of the spectrum in the range from 10 to 10^3 sec. The measurements were made in a SQUID magnetometer[6,7] on a rod-shaped (diameter 2.5 mm, length 5 mm) sample.

ZFC experiments are in principle performed by cooling the sample in zero field from a temperature well above T_g down to a temperature T_m. A constant external field (h_0) is applied and the change of magnetization (m) with time (t_s) observed. The relaxation rate of the magnetization is related to $g(\tau)$ according to[5]

$$\partial m/\partial \ln t_s = m_0(\tau_m)g(\tau_m); \quad \tau_m \approx t_s, \quad (2)$$

where $t_s = 0$ defines the time when the external field is applied. By observing the change of the magnetization with time at a specific t_s the density of relaxation times $g(\tau_m)$ is found. In order to observe the time dependence of $g(\tau_m)$ at a specific τ_m and constant T_m (in analogy with the ac susceptibility experiments), a set of ZFC magnetization curves are recorded *each of which is obtained after various waiting periods, t_w, at T_m before the external field is applied.* In the actual experiments two different procedures were adopted to approach the target temperature T_m. In the first procedure the sample was *cooled* (20 mK/sec) down to T_m in zero field (≤ 0.2 μT).

In the second procedure the sample was cooled in zero field to a temperature of 1 K below T_m. The sample was kept there for 5 min and afterwards step *heated* to T_m. The sample then attains constant temperature within 10 mK in less than 5 sec, and with a long-time stability in temperature of approximately 0.1 mK. The two procedures were found to give very similar results of the following ZFC curves at T_m. Some of the recorded curves, obtained from the latter procedure, are displayed in Fig. 1, where the different curves refer to various waiting times, t_w, at $T_m = 23$ K before the external field of 0.1 mT is applied (at $t_s = 0$). As can be seen in Fig. 1 there is a truly pronounced difference between the curves. Significant differences in relaxation rates of the magnetization can even be observed for waiting periods at T_m in excess of *one hour*! Figure 1 clearly demonstrates that $\partial m/\partial \ln t_s$, at a specific t_s, depends on the waiting time t_w. This implies through Eq. (2) that the density of

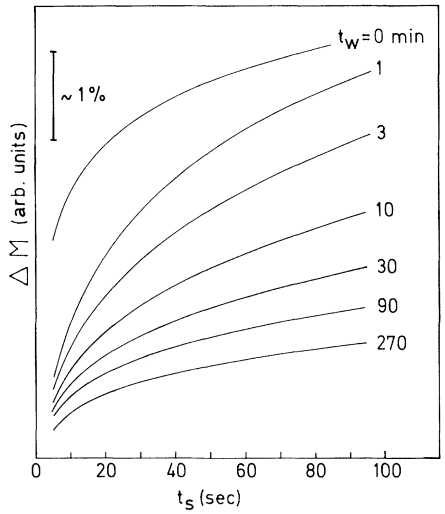

FIG. 1. Zero-field cooled (ZFC) magnetization curves of Cu–4-at.%-Mn at constant temperature $T_m = 23$ K. The various curves refer to different waiting times, t_w, at 23 K before the external field of 0.1 mT is applied (at $t_s = 0$). *Each* curve is recorded after zero-field cooling the sample from a temperature above the spin-glass freezing temperature $T_g = 26$ K. A relative change of the total magnetization of approximately 1% is indicated. The initial ($t_s < 5$ sec) pronounced increase of the magnetization is omitted. The curves are *arbitarily* displaced on the vertical axis. The curves never cross but attain the same asymtotic value as $t_s \to \infty$. Above T_g the time dependence of the ZFC magnetization disappears. At 26.5 K ($T_g + 0.5$ K) the ZFC magnetization changes less than 0.01% in the time interval 10 sec $\leq t_s \leq 10^3$ sec, independent of t_w.

relaxation times $g(\tau_m)$, at a specific τ_m ($= t_s$), strongly depends on the time that the sample has been kept at constant temperature. The common belief that an equilibrium spin-glass state is quickly obtained, at constant temperature, after cooling (or heating) in zero field is evidently gravely untrue.

In Fig. 2 we have plotted $g(\tau_m)$ at various τ_m as a function of the *total elapsed time* t_{tot}, *after which the sample has attained constant temperature* $T_m = 23$ K, i.e., the waiting time t_w at 23 K before the external field is applied plus the time t_s ($= \tau_m$) it takes to monitor $g(\tau_m)$ through Eq. (2). In Fig. 2 we have included $g(\tau_m)$ at $\tau_m = 10^{-1}$ sec found from ac susceptibility data,[2] where $g(\tau_m)$ is derived from Eq. (1). In order to estimate the magnitudes of $g(\tau_m)$ we simply put $m_0(\tau_m)$ equal to the measured magnetic moment at T_g. $g(\tau_m)$ then equals the experimentally observed quantities $[1/M(T_g)](\Delta M/\Delta \ln t_s)$ in ZFC [Eq. (2)] and $-(2/\pi)[1/\chi'(T_g)]\chi''$ in ac susceptibility [Eq. (1)] measurements, respectively. Three distinct features of the curves in Fig. 2 are observed: (1) A sharp rise of $g(\tau_m)$ at time $t_{tot} \approx \tau_m$. (2) A broad maximum of $g(\tau_m)$ at times $t_{tot} > \tau_m$. (3) An exceedingly slow decay of $g(\tau_m)$ at times $t_{tot} \gg \tau_m$.

By analyzing the long-time variation of $g(\tau_m)$ at $\tau_m = 10$ and 10^2 sec we find an algebraic decay $t_{tot}^{-0.4}$ with time (for $\tau_m = 10$ sec at $t_{tot} \geq 1$ min, for $\tau_m = 10^2$ sec at $t_{tot} \geq 10$ min). From this time variation of $g(\tau_m)$ we estimate the equilibrium ($t_{tot} = \infty$) levels to be approximately the same, namely $g(\tau_m) \simeq 0.2 \times 10^{-2}$, i.e., *a factor of 7* smaller than the maximum values of $g(\tau_m)$ for 10

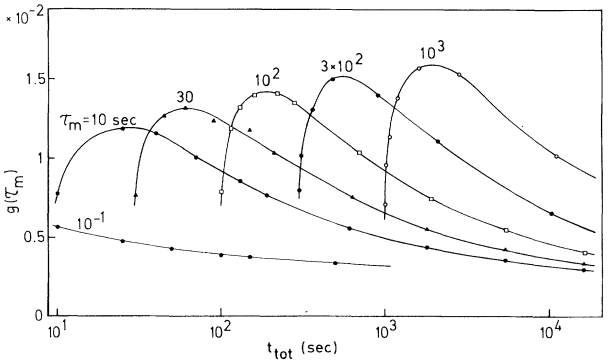

FIG. 2. Density of relaxation times, $g(\tau_m)$, at various τ_m as a function of the time, t_{tot}, the sample has been kept at constant temperature $T_m = 23$ K. The lower left curve ($\tau_m = 10^{-1}$ sec) is obtained from ac susceptibility data (Ref. 2). The spin-glass freezing temperature $T_g = 26$ K. The relaxation-time spectrum is normalized according to $\int g(\tau) d \ln \tau = 1$.

sec $\leq \tau_m \leq 10^3$ sec.

In Fig. 3 we have plotted the evolution of the relaxation time spectrum [$g(\tau)$ vs τ] with the time (t_{tot}) the sample has been kept at constant temperature $T_m = 23$ K. The data points are found from the smoothed curves in Fig. 2 (including some curves not shown in the figure). As can be seen in Fig. 3 the spectrum moves towards longer relaxation times like a wave. The position of the wave edge corresponds to a relaxation time which is equal to the time that the sample has been maintained at constant temperature. This time dependence of the spectrum is at variance with the common picture of a static spectrum, having a flat distribution of relaxation times [i.e., $g(\tau) = \text{const}$]. In the experimental situation such an "equilibrium" spectrum is only observed when the time scale of the experimental probe is some orders of magnitude smaller than the total time, t_{tot}, that the sample has been kept at constant temperature. This implies $t_{tot} \gg 1/\omega$ in ac susceptibility and $t_{tot} \gg t_s$ in ZFC experiments, respectively. However, thermodynamic equilibrium is not obtained until the time that the sample has been kept at constant temperature exceeds the maximum value of the relaxation times (τ_{max}) of the equilibrium spectrum. Since τ_{max} attains astronomic values already some kelvin below T_g, the spin-glass state is a nonequilibrium one, in the thermodynamical sense.

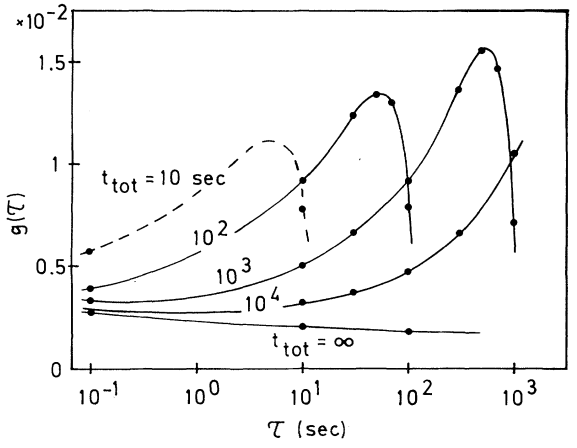

FIG. 3. Evolution of the relaxation-time spectrum [$g(\tau)$ vs τ] with the time (t_{tot}) the sample has been kept at constant temperature $T_m = 23$ K. The data points are found from the smoothed curves in Fig. 2 (including some curves not shown in the figure). The equilibrium level ($t_{tot} = \infty$) is estimated under the assumption of a $t_{tot}^{-0.4}$ decay at long times of $g(\tau)$ at constant τ. The relaxation time spectrum is normalized according to $\int g(\tau) d \ln\tau = 1$.

The remarkable behavior of the spectrum is interpreted as follows: During the heating or cooling processes the correlation between spins is partly broken. Clusters of spins attain excited states with short relaxation times, which momentarily results in a compression of the spectrum towards short times. With time, at constant temperature, these clusters continuously take on new states with gradually increasing relaxation times. However, the passage from one state to another *requires a waiting time equal to the relaxation time of the former state.* This implies a wavelike movement of the spectrum towards long relaxation times, with the position of the wave edge equivalent to the time that the sample has been kept at constant temperature. The height of the wave depends on the amount of disturbance imposed on the system, i.e., the heating or cooling rate and the magnitude of the imposed temperature step. If we assume the field-cooled (FC) magnetization to be the equilibrium value[8] of the ZFC magnetization, we estimate the amount of relaxation times beyond the edge of the wave to be roughly twice the amount contained in the actual wave. Since there exists a wide distribution of equilibrium relaxation times in the material the spectrum will eventually settle down at a finite equilibrium level with a finite maximum value (crudely estimated to be located at 10^{20} sec at $T = 23$ K). It should be valuable to examine the behavior of the wave on its approach towards the equilibrium edge of the spectrum. We may possibly anticipate different behaviors above and below T_g. Such experiments are feasible in the immediate vicinity of T_g, where the equilibrium edge of the spectrum is experimentally accessible.

In this Letter we have shown that a time dependence of the relaxation-time spectrum occurs in spin-glass materials after cooling (or heating) in zero field. This time dependence of the spectrum is revealed from low-field ZFC magnetization experiments. An analogous behavior is expected to be found after cooling in a small constant field, i.e., the decay of the thermoremanent magnetization (TRM) should depend on the time that the sample is kept at constant temperature before the external field is switched off. While the ZFC and TRM experiments mirror the relaxation-time spectrum and its time dependence, the change of the FC magnetization with time, at constant temperature, reflects a time dependence (decrease) of the total magnetization, which part-

ly may arise from the change of relaxation states with time.

When ZFC and TRM measurements are made at "high" fields the application or removal of the field strongly affects the relaxation-time spectrum. This results in an "independence" of the ZFC and TRM on the waiting time at constant temperature. However, the time dependence of the relaxation-time spectrum at high constant fields may be observed by applying a weak probing ac field or a weak probing step (increase or decrease) in the dc field.

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[8]In order to estimate the proportions of relaxation times contained in various parts of the spectrum we have taken the "equilibrium" value of the FC magnetization as the measured FC value after 5 min at 23 K. We then estimate the amount of relaxation times to be 10% beyond the edge of the wave, 5% in the wave, and 85% at shorter relaxation times. However, since the FC magnetization slowly decreases with time [see Refs. 2, 4, 5, and P. Norblad, L. Lundgren, P. Svedlindh, and O. Beckman, in Proceedings of NATO Advanced Study Institute, Geilo, Norway, 1983 (to be published)], at constant temperature, the true equilibrium value of the magnetization is difficult to determine accurately.