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Aging in a topological spin glass

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We have examined the nonconventional spin-glass phase of the two-dimensional *kagomé* antiferromagnet $(H_3O)Fe_3(SO_4)_2(OH)_6$ by means of ac and dc magnetic measurements. The frequency dependence of the ac susceptibility peak is characteristic of a critical slowing down at $T_g \simeq 18$ K. At fixed temperature below T_g, aging effects are found which obey the same scaling law as in spin glasses or polymers. However, in clear contrast with conventional spin glasses, aging is remarkably insensitive to temperature changes. This particular type of dynamics is discussed in relation with theoretical predictions for highly frustrated nondisordered systems.

I. INTRODUCTION

Much recent work has been focused on the nature of glassy magnetic states in the absence of quenched disorder.[1] Simple experimental realizations of nondisordered systems in which glassy phases have been found are antiferromagnets (AFM's) with *kagomé*, pyrochlore, and hyper*kagomé* geometries: $(H_3O)Fe_3(SO_4)_2(OH)_6$, $Y_2Mo_2O_7$, $Tb_2Mo_2O_7$, $Y_2Mn_2O_7$, $Yb_2Ti_2O_7$, and $Gd_3Ga_5O_12$.[2–8] In the case of the two-dimensional (2D) *kagomé* AFM, it is believed that an *xy* anisotropy can induce a finite-temperature glass transition.[9] This glassy phase has been termed a *topological* spin glass, in order to distinguish it from conventional site-disordered systems. While the high degeneracy of these lattices is expected to be robust against the addition of small amounts of impurities, and so should not result in a spin-glass state,[10] in some cases conventional behavior can be recovered if this dilution is sufficient. Examples of this are the 3D pyrochlore $Y_2Mn_2O_7$ where the effect of increasing disorder is to progressively restore conventional spin-glass kinetics,[11] and the 2D *kagomé* $(D_3O)Fe_{3-x}Al_y(SO_4)_2(OD)_6$ where reduction of the Fe occupancy to $\simeq 90\%$ has been found to induce long-range magnetic order.[4]

At present, very little is known about the glassy phases found in nondisordered frustrated systems. In this paper, we study the $S=5/2$ 2D *kagomé* AFM $(H_3O)Fe_3(SO_4)_2(OH)_6$. Our ac susceptibility measurements indicate the critical character of the freezing process around $T_g \simeq 18$ K. We find that while aging effects at a fixed temperature below T_g are the same as in site-disordered spin glasses, there is a very weak sensitivity of these aging phenomena to temperature variations that is in sharp contrast with conventional spin glasses. We discuss the transition found in this 2D system, and the slow dynamics observed, in terms of a theoretical picture of a spin-glass state of the ordered *kagomé* AFM, based on topological excitations termed *spin folds*.[9]

Our sample was that used in previous studies of the crystal structure, susceptibility, and μSR responses.[2,12] Neutron-diffraction measurements on the deuterated compound have shown that the glassy phase involves 2D antiferromagnetic correlations that saturate to a maximum at low temperature, with a spin-spin correlation length of $\xi = 19 \pm 2$ Å.[3] Associated with these correlations is a T^2 specific heat, which contrasts with the linear dependence of conventional spin glasses[13] and suggests the presence of 2D antiferromagnetic spin waves.

II. NATURE OF THE FREEZING MECHANISM

We examined the nature of the freezing transition by measuring the frequency dependence of the ac susceptibility at eight frequencies ranging from 0.04 to 80 Hz. The out-of-phase component χ'' was too weak to allow a precise study, but its overall shape compares well with spin glasses.[13] We have found that the temperature of the χ' peak shifts very slowly with frequency [$T_f(80\ \text{Hz}) = 18.5$ K, $T_f(0.04\ \text{Hz}) = 18.0$ K]. Quantitatively, the shift amounts to $\Delta T_f / (T_f \Delta \ln \omega) \simeq 0.008$, which is in the same range as obtained for the critical behavior of conventional 3D spin glasses.[14,13] As a confirmation, a fit of the $T_f(\omega)$ data to an Arrhénius function $\omega = \omega_0 \exp(-U/k_B T_f)$ yields an unphysical value of $\omega_0 \sim 10^{130}$ Hz (in agreement with the previous interpretation of results from the deuterated sample in terms of a Vogel-Fulcher law[3]).

The critical character of the freezing transition can also be confirmed by a dynamic scaling analysis of the same data. The fit to the critical scaling law[13] $\omega = \omega_0 \{[T_f(\omega) - T_f(0)]/T_f(0)\}^{z\nu}$ yields, fixing $z\nu = 7$, the plausible values of $T_f(0) = 17.8$ K and $\omega_0 = 5.9 \times 10^{11}$ Hz. This transition temperature is far below the Curie-Weiss temperature, which is here $\Theta_{CW} = -1200 \pm 200$ K, emphasizing a strong influence of frustration. In Ref. 9, it has been proposed that, in the presence of some *xy* anisotropy, the *kagomé* AFM experiences a Kosterlitz-Thouless-type transition to a glassy state. The prediction of an upper estimate of the transition temperature $T_{KT} \simeq \Theta_{CW}/48$, obtained from the spin-wave stiffness in the *xy* limit, agrees well with the experimental transition temperature, as here $\Theta_{CW}/48 = 25$ K ~ 17.8 K.

Zero-field cooled (ZFC) and field-cooled (FC) dc magnetization measurements show another aspect of the freezing transition (Fig. 1). The ZFC curve peaks at approximately $T_{ZFC} = 17.8$ K [$\simeq T_f(\omega \to 0)$], but slight irreversibilities are still visible as a ZFC-FC separation up to ~ 25 K, indicating that some freezing occurs well above the transition. Also,

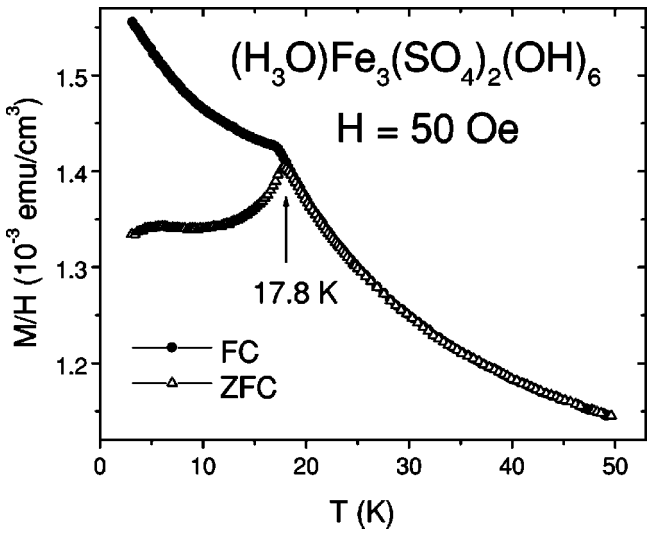

FIG. 1. dc magnetization as a function of temperature.

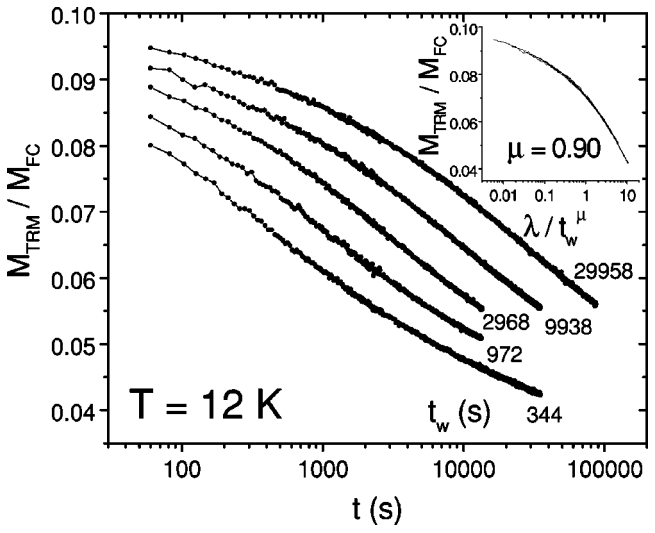

FIG. 2. Decay of the thermoremanent magnetization at 12 K, for various values of the waiting time t_w. The inset shows the scaling of the same data as a function of the time reduced variable (Ref. 22) λ/t_w^{μ}, with $\mu=0.90$.

instead of the low-temperature FC plateau that is usual in conventional spin glasses,[13] there is below T_{ZFC} a rise in the FC magnetization towards low temperature. Both these features point towards a progressive freezing of some superparamagnetic entities over a wide temperature range.[15] These species are presumed to be the cause of the slight influence of the thermal history between 18 and 25 K on the slow dynamics below T_g (see Sec. III B), and their fluctuations are the probable origin of the dynamic component observed in the μSR measurements at low temperature.[12] This progressive freezing is superimposed on the critical behavior at the transition, and does not prevent the transition from taking place.

In a study of other jarosite samples,[16] which show stronger superparamagnetic components, the divergence of the nonlinear susceptibility, normally associated with a spin-glass transition, could not be clearly characterized.

The origin of superparamagnetism at low temperatures in this *kagomé* system is an open question. Although analytic calculations have shown that dilution of the magnetic sites creates superparamagnetic components at high temperatures,[17] it is not clear whether the presence of such superparamagnetic entities in the spin-glass state is intrinsic to the (2D) *kagomé* lattice, or is the result of disorder, despite its small level in our sample [the occupancy of the magnetic sites, determined from neutron diffraction, is 97.3(6)% (Ref. 2)].

III. AGING PHENOMENA

A. Spin-glass-like behavior at constant temperature

In site-disordered spin glasses, the out-of-equilibrium dynamics is characterized by aging effects: the response to a small magnetic excitation depends on the time (''age'') spent after the quench from above the freezing temperature.[18–21] As the ac signal of our present sample is small, we have explored the nonequilibrium dynamics by means of dc magnetization relaxation. In such measurements, aging results in the dependence of the response to a small field variation, applied after waiting a time t_w from the quench, on two time variables: t, the observation time (i.e., the time from the field variation), and $t_a=t_w+t$, the total aging time.[20] In our experiments the sample was first cooled from 25 to 12 K in a field of 50 Oe. Then, after waiting a time t_w at 12 K, the field was removed, and the slow decay of the ''thermoremanent'' magnetization (TRM) was recorded as a function of t.

The observed behavior, shown in Fig. 2, is precisely the same as that of site-disordered spin glasses:[20] the longer the t_w, the slower the decay of the TRM. The system has become ''stiffer'' with time. The curves also present the commonly observed inflection point in the region of $\ln t \sim \ln t_w$.[13,18] The t_w dependence of these responses satisfies the same scaling properties as site-disordered spin glasses[22] and glassy polymers,[23] as shown in the inset of Fig. 2.

B. Weak sensitivity to temperature variations

In site-disordered spin glasses, temperature cycling protocols have been developed in order to characterize the influence on aging of small temperature variations (remaining below T_g). They have shown, in contrast with the expectations for thermally activated processes, that a small *positive* temperature cycle can erase previous aging (''rejuvenation'' or ''chaoslike'' effect) instead of simply speeding up the evolution.[21,19,20]

We have investigated the effect of such temperature variations on the jarosite system. The procedure of *positive* temperature cycling is sketched in the inset of Fig. 3. After aging 9700 s at $T=12$ K, the sample is heated to $T_0+\Delta T$ during a short time ($\sim$100 s). Following this cycle, aging at 12 K is continued during 300 s, and the field is cut off (at $t=0$). Figure 3 shows the comparison of the resulting decay curves with the reference TRM curves obtained after an *isothermal* aging of $\sim$300 s or 10 000 s at 12 K.

All curves obtained after the positive cycling are *lower* than the $t_w\sim 10\,000$ s isothermal reference: cycling to $T_0+\Delta T$ has *not* increased the age of the system. This result also differs *strongly* from the site-disordered spin-glass case, in which (in an equivalent experiment) $\Delta T=2.5$ K has been found to completely erase previous aging.[21,20] Here, erasure

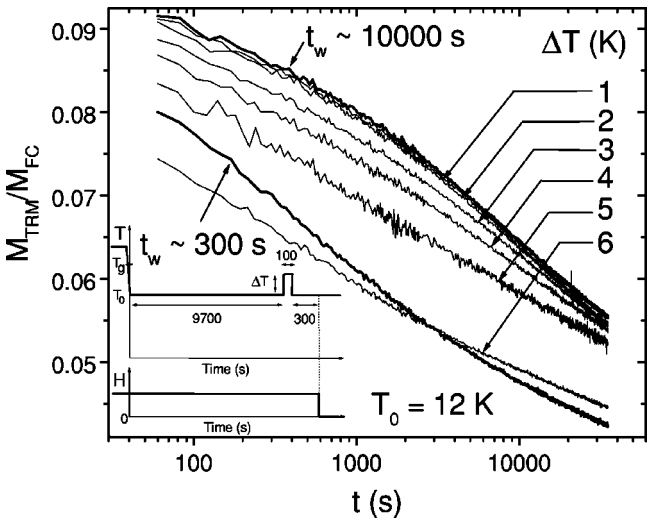

FIG. 3. Effect on the TRM decay at $T_0=12$ K of a *positive* temperature cycling of amplitude ΔT (thin lines). $T_g=17.8$ K corresponds to $\Delta T=5.8$ K. Reference curves (isothermal aging during $t_w\sim 300$ and 10 000 s at T_0) are also shown as thick lines.

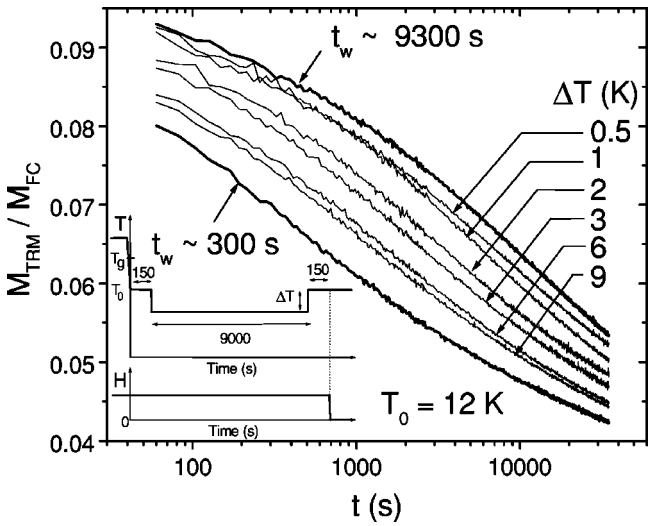

FIG. 4. Effect on the TRM decay at $T_0=12$ K of a negative temperature cycling of amplitude ΔT (thin lines). Reference curves (isothermal aging during t_w at T_0) are also shown as thick lines.

only occurs when $T_0+\Delta T$ crosses T_g (for $\Delta T=6$ K), and even then results in a curve with a weaker slope than that of the isothermal $t_w\sim 300$ s reference. We note that aging at temperatures $T\geqslant T_g$ still results in some slowing down of the dynamics, as heating up to ~ 25 K is needed to fully reinitialize aging (at this time scale).

For intermediate ΔT values (2–5 K), Fig. 3 shows a partial erasure of previous aging (but the influence is again much weaker than in conventional spin glasses). The effect on the curves is the same as in site-disordered spin glasses,[21,20] partial erasure corresponds to a stronger effect on the short-time part of the curves (which approaches the ''younger'' $t_w\sim 300$ s reference), while the long-time part is less affected (and remains close to the ''older'' $t_w\sim 10\,000$ s reference).

Negative temperature cycling experiments in site-disordered spin glasses have shown that the stage of aging before the temperature cycle can be *memorized* during the lower-temperature aging, in such a way that aging can restart from the same point when the system returns to temperature T. That is to say, a long aging at $T_0-\Delta T$ can be of no influence on the effective age at T_0, even for *small* ΔT's $(1-2$ K) for which little thermal slowing down is expected. This *memory* effect is equivalent to a growth of free energy barriers as the temperature is lowered.[19–21]

When applied the negative cycling protocol does not yield these simple memory effects and confirms the surprisingly weak influence of temperature changes on aging, already observed in the positive cyclings of Fig. 3. These data are shown in Fig. 4. Since the resulting curves have approximately the same shape as those obtained after *isothermal* aging, they can be ascribed an *effective waiting time*, by application of the scaling procedure evoked above[22] (this is not the case for the ''mixed age'' curves obtained after *positive* cyclings). Similar (but slightly lower) values of the effective age can be directly estimated from the position of the inflection point. Qualitatively we find that larger values of ΔT lead to a younger effective age (less influence of aging at T_0 $-\Delta T$). However, *quantitatively*, the freezing effect is much weaker than expected from thermal slowing down, and hence is minuscule when compared with the freezing processes of site-disordered spin glasses.[19–21]

For $\Delta T=9$ K, aging at $T_0-\Delta T=3$ K is still seen to add a contribution to aging at $T=12$ K (the curve is clearly ''older'' than the $t_w\sim 300$ s reference). Simple arguments of thermal slowing down with fixed energy barriers for such a temperature change, would lead to the expectation of even astronomic waiting times having no effect. In other words, in terms of thermal activation, the observed influence at 12 K of aging at 3 K corresponds to that of a much higher effective temperature (of the order of 11 K).

IV. DISCUSSION

Thus, we have found that the slow dynamics and aging effects in this *kagomé* antiferromagnet are, *at constant temperature*, similar to those of site-disordered spin glasses, but the role played by temperature changes is markedly different. Positive and negative cycling experiments have shown that aging is neither reinitialized nor drastically frozen by temperature changes: it is mostly unaffected, as long as T_g is not crossed. This behavior is in marked contrast with conventional site-disordered spin glasses.[24]

In a ground-state configuration of the *kagomé* AFM, the nearest-neighbor moments are related by 120°, and the local chirality of the triangular motifs is either uniform or staggered. The domain walls that separate regions of uniform and staggered chirality correspond to topological defects which cost zero internal energy. In Ref. 9, the transition of the *kagomé* AFM to a glassy state is described in terms of a Kosterlitz-Thouless-type mechanism involving the binding of these defects. It has been argued[9] that the processes of defect propagation are ''non-Abelian,'' i.e., their formation does not commute. This creates a further hindrance to the evolution towards a given spin configuration and means that defect propagation is not simply a matter of thermally activated barrier crossing.

While at a given instant the *kagomé* system can be thought of as a mosaic of chiral domains, the equilibrium state itself is believed to involve fluctuating short-range chiral correlations.[25] The existence of aging effects is in agreement with Monte Carlo studies[25] and indicates that this state is approached by slow relaxation and a gradual evolution of the system. The equilibrium state may correspond to a temperature-dependent distribution of domains. They will have different Boltzmann weights because those with uniform chirality develop extended defects, whereas those within domains of staggered chirality are localized.[25,9] The weak effect of temperature changes can be interpreted in this context as an indication that this distribution of chiral ordering varies only slowly with temperature.

In conclusion, we believe that $(H_3O)Fe_3(SO_4)_2(OH)_6$ is representative of an additional class of ''topological'' spin glasses. There is good evidence from ac measurements that a critical transition to a glassy state occurs at $T_g \neq 0$. While its aging dynamics at a given temperature follows that of conventional spin-glass systems, there is a remarkable insensitivity to temperature changes that demonstrates clearly the different natures of site-disordered and such topological spin glasses.

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