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Spin freezing and dynamics in $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 0.95$) investigated with implanted muons: Disorder in the anisotropic next-nearest-neighbor Ising model

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We present a muon-spin relaxation investigation of the Ising chain magnet $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 0.95$). We find dynamic spin fluctuations persisting down to the lowest measured temperature of 1.6 K. The previously observed transition at around 18 K is interpreted as a subtle change in dynamics for a minority of the spins coupling to the muon that we interpret as spins locking into clusters. The dynamics of this spin fraction freeze below a temperature $T_{SF} \approx 8$ K, while a majority of spins continue to fluctuate. An explanation of the low-temperature behavior is suggested in terms of the predictions of the anisotropic next-nearest-neighbor Ising model.

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The magnetic chain multiferroic $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 1$) has been the subject of considerable recent investigation.[1–4] This material is based on the Ising spin chain magnet $Ca_3Co_2O_6$, with (close to) half of the cobalt ions replaced with manganese.[5–7] The observation of up-up-down-down ($\uparrow\uparrow\downarrow\downarrow$) order in this system has led to the proposal that, at low temperatures, $Ca_3Co_{2-x}Mn_xO_6$ may be described by the anisotropic next-nearest-neighbor Ising (ANNNI) model.[1] This model[8–11] describes Ising spins on a three-dimensional lattice in which, along one direction, there is nearest-neighbor ferromagnetic exchange (J_{FM}) and next-nearest-neighbor antiferromagnetic (AFM) exchange (J_{AFM}). For $|J_{AFM}/J_{FM}| > 1/2$ the ground-state magnetic order is of the $\uparrow\uparrow\downarrow\downarrow$ type. As temperature is increased from $T=0$ the magnetic behavior is determined by the existence of domain wall solitons, which separate regions with different commensurate AFM spin arrangements.[9,10] Although a continuum description of the ANNNI model predicts an infinity of high order commensurate AFM phases (known as the devil's staircase) a description in terms of a discrete Hamiltonian shows the possibility of metastable states of randomly pinned solitons. In magnetic systems, these so-called "chaotic states" are expected to lead to frozen-in disorder or spin-glasslike behavior.[8] Here we present an investigation of the low-temperature static and dynamic magnetism in $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 1$) that we have observed at a local level using muon-spin relaxation (μ^+SR). We find that the low-temperature magnetic state of $Ca_3Co_{2-x}Mn_xO_6$ is reached through a complex freezing out of dynamic processes, and we conjecture that the existence of chaotic states provides an explanation for the disordered magnetism and persistent dynamics that we observe at low temperature.

$Ca_3Co_{2-x}Mn_xO_6$ is formed from chains of magnetic ions arranged along the c axis in alternating oxygen cages of face-shared trigonal prisms and octahedra. Mn^{4+} ions preferentially occupy the octahedral sites while the trigonal prisms are occupied by Co^{2+} ions. The magnetic chains form a triangular lattice in the ab plane separated by Ca^{2+} ions. While it is agreed that $3d^3Mn^{4+}$ is in the $S=3/2$ high-spin configuration, the spin state of $3d^7Co^{2+}$ has been questioned. Although fits to magnetic neutron diffraction data[1] suggest a low spin $S=1/2$ state, electronic structure calculations[3,4] and x-ray absorption spectroscopy[3] favor the high-spin $S=3/2$ state. The neutron diffraction and magnetic susceptibility measurements[1] indicate that below $T_B \approx 18$ K spins align along the c axis, adopting the $\uparrow\uparrow\downarrow\downarrow$ configuration with Mn and Co ordered moments of $0.66\mu_B$ and $1.93\mu_B$, respectively. The considerable width of the magnetic Bragg peaks suggests that this is not a state of true long-range order (LRO) but rather represents the locking in of spins into finite sized domains. Taken with the Ising-like character of the magnetic ions, the observation of $\uparrow\uparrow\downarrow\downarrow$ order is suggestive that this material can be described as a realization of the ANNNI model or its extension[12] to the case of chains of unequal Ising spins. It is also notable that the inversion symmetry breaking of $\uparrow\uparrow\downarrow\downarrow$ order, along with the alternating charge order, results in magnetism driven ferroelectricity in this material.[1]

μ^+SR has proven useful in elucidating the static and dynamic properties of Ising systems[13] including the parent compound $Ca_3Co_2O_6$.[14,15] In a μ^+SR experiment,[16] spin-polarized positive muons are stopped in a target sample, where the muon usually occupies an interstitial position in the crystal. The observed property in the experiment is the time evolution of the muon-spin polarization, the behavior of which depends on the local magnetic field at the muon site, and which is proportional to the positron asymmetry function $A(t)$. Measurements were made at the Swiss Muon Source (SμS) using the GPS instrument. A polycrystalline sample of $Ca_3Co_{2-x}Mn_xO_6$ with $x=0.95$ was packed in a Ag foil packet and mounted on a Ag plate in a helium cryostat.

Spectra measured for $Ca_3Co_{1.05}Mn_{0.95}O_6$ are shown in Fig. 1. For temperatures $T > 10$ K [Figs. 1(a) and 1(b)] we observe purely relaxing asymmetry spectra. We do not observe oscillations in the asymmetry, which usually signal the presence of long-range magnetic order. For $T < 8$ K the form

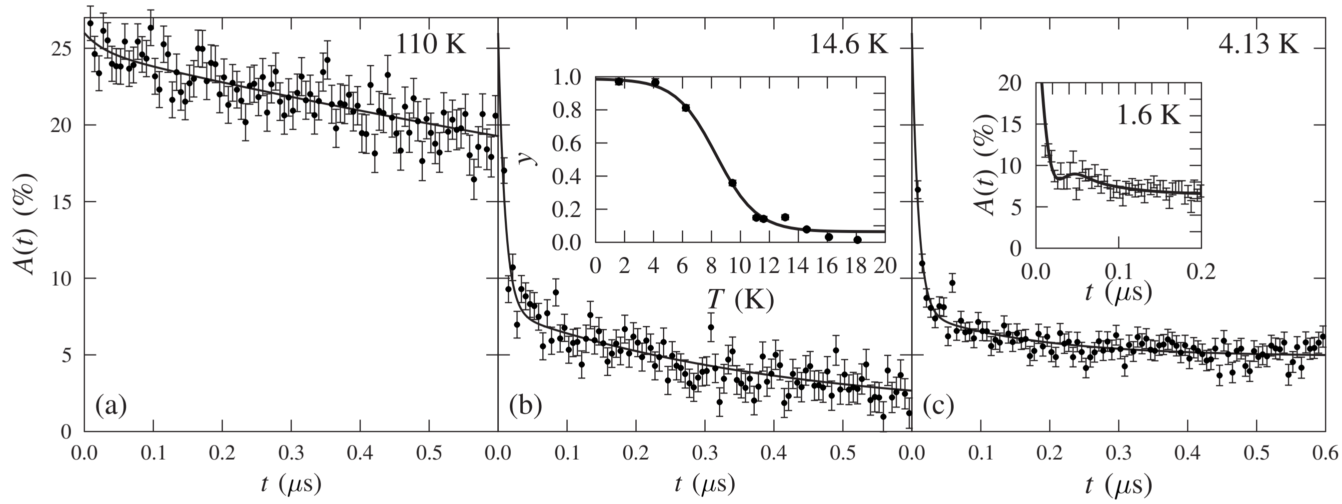

FIG. 1. ZF μ^+SR spectra measured at (a) $T=110$, (b) 14.6, and (c) 4.13 K. Solid lines are fits to Eq. (1). Inset to (b): the parameter y from Eq. (1) shows evidence of static freezing around $T\approx 8$ K. Inset to (c): spectra measured at 1.6 K, showing a small heavily damped oscillation. The solid line is a guide to the eye.

of the spectra alters, most notably with an increase in the nonrelaxing baseline of the asymmetry. There is also a small undulation in the asymmetry that emerges at early times in high statistics spectra measured at the lowest temperatures [inset of Fig. 1(c)]. This feature, which may represent a low amplitude heavily damped oscillation displayed little temperature dependence and was too indistinct to be fitted systematically. Instead, the spectra are best modeled over the entire temperature range by a sum of asymmetry functions, one with a large relaxation rate λ_1 and the other with a smaller rate λ_2,

$$A(t) = A_{\mathrm{bg}} + A_0\left(pe^{-\lambda_1 t} + (1-p)\left[\frac{y}{3} + \left(1-\frac{y}{3}\right)e^{-\lambda_2 t}\right]\right), \tag{1}$$

where A_0 represents the amplitude of the signal arising from the sample and the term A_{bg} represents a temperature-independent nonrelaxing background from those muons that stop in the sample holder or cryostat tails. The parameter $y=0$ above ≈ 10 K but takes nonzero values at low temperatures (see below). The amplitude p was found to be $p=0.75$ across the entire measured temperature regime. Exponential relaxation is often expected in cases where dynamic fluctuations in the local magnetic field at the muon site represent the dominant relaxation process,[17] and it is likely that this mechanism is at work in $Ca_3Co_{2-x}Mn_xO_6$. Fast field fluctuations lead to relaxation rates that vary as $\lambda_i \propto \gamma_\mu^2 \langle B_i^2 \rangle \tau$, where γ_μ is the muon gyromagnetic ratio, B_i is the local magnetic field at the ith muon site, and τ is a fluctuation rate. In the present case, the interpretation of dynamic fluctuations is supported by the observation that applied longitudinal magnetic fields of up to 0.6 T do not decouple the relaxation, as would be expected for relaxation from static field inhomogeneities.[18]

The coexistence of two relaxation rates, λ_1 and λ_2, implies the existence of two classes of spatially separate muon sites in $Ca_3Co_{2-x}Mn_xO_6$. In general, these sites might differ in the width of the field distribution $\langle B^2 \rangle$, or the fluctuation time at each site may be different. (It is not possible to have a single class of site with two correlation times giving rise to two different relaxation rates; the shorter time will always dominate, giving the smaller relaxation rate.[19]) The first class of muon site (with amplitude p and relaxation rate λ_1) accounts for $\approx 75\%$ of the muon sites, with the second, with amplitude $(1-p)$, accounting for the remaining $\approx 25\%$ of muon sites. As there is no evidence (from our measurements or previous work[1]) for phase separation in this system, it is probable that both classes arise from the intrinsic behavior of the bulk of the material. Possibilities for this include the coupling of each class of site preferentially to one or other of the magnetic cations (i.e., one class sensitive to fields arising from Co^{2+} and the other sensitive to Mn^{4+}), as is the case in of $X_3V_2O_8$ (X=Ni, Co),[20] or that the classes of muon site are sensitive to different components of the same spin distribution as in $GeNi_2O_4$.[21] In the latter case, a system with local site anisotropy might, for example, give rise to relaxation time scales for longitudinal and transverse fluctuations that could be quite different. If different muons sites were selectively sensitive to longitudinal or transverse components, dynamics with two time scales may arise from the same spin site.

The temperature dependence of λ_1 and λ_2 resulting from fits of the data to Eq. (1) are shown in Fig. 2. Both relaxation rates show the same trend of behavior, with their magnitude increasing as the temperature is reduced, followed by saturation of the relaxation rate at a constant value below ≈ 30 K. This trend is sometimes seen in the μ^+SR of complex systems with low-temperature dynamics,[22,23] and its origin is not completely understood. It can arise due to the existence of two relaxation channels, one of which is strongly T dependent with a correlation time τ_{s} while the other shows little variation with T and has a correlation time τ_{w}. As noted above, in the presence of two competing relaxation processes, that with the shorter correlation time wins out, giving the smaller relaxation rate. At high temperature, therefore,

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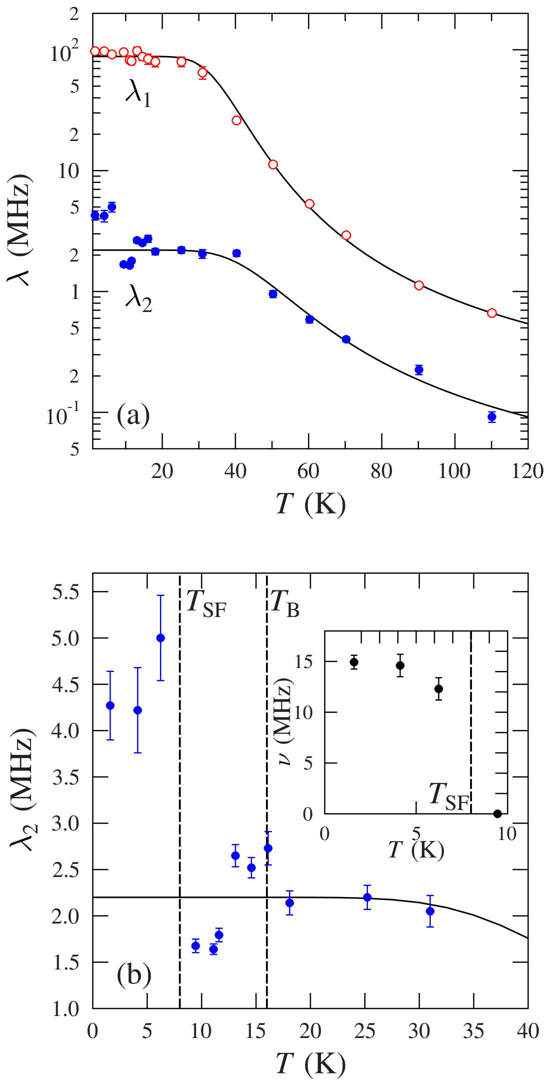

FIG. 2. (Color online) (a) Evolution of the relaxation rates λ_1 (open circles) and λ_2 (closed circles) as a function of temperature in ZF. (b) Detail from (a) showing departure of λ_2 from the trend around the transition at T_B and the spin freezing transition T_{SF}. Inset: temperature evolution of the frequency of the small oscillatory feature seen below 8 K at early times.

we have $\tau_s(T) \ll \tau_w$ which results in a strongly T-dependent relaxation, which we can fit phenomenologically by $\lambda_i = C_i \exp(U_i/T)$. At low temperatures, where $\tau_w \ll \tau_s(T)$, we have $\lambda_i \sim \lambda_i^{sat}$, resulting in a phenomenological fitting function $1/\lambda_i(T) = 1/\lambda_i^{sat} + 1/[C_i \exp(U_i/T)]$. Fitting this function to our data allows us to parametrize the relaxation rates with $\lambda_1^{sat} = 88(3)$ MHz, $U_1 \approx 275(5)$ K for the fast relaxation and $\lambda_2^{sat} = 2.2(2)$ MHz, $U_2 \approx 270(20)$ K for the slowly relaxing component. Given the similarity between U_1 and U_2, it is likely that similar relaxation processes are at work at both sites, sharing similar correlation times. This would imply that the widths of the magnetic field distributions differ for the two classes of site and are in the ratio $(\langle B_1^2 \rangle / \langle B_2^2 \rangle)^{1/2} \approx (\lambda_1^{sat}/\lambda_2^{sat})^{1/2} \approx 6$. We note further that, with the large activation energies involved, it is unlikely that the temperature-dependent behavior is related to dynamics predicted by the ANNNI model. This is not surprising since models of this sort provide a low-energy description of real magnetic systems. Rather, it is likely that the observed behavior arises due to the single ion anisotropies of the magnetic ions. For free Co^{2+}, for example, the spin-orbit coupling constant[24] is −270 K, which resembles our energy scale U. This is suggestive that the energy scale for the temperature-dependent contribution to the relaxation rates is set by fluctuations between spin-orbit split components of the low-lying electronic states of the magnetic Co^{2+} ions. It should be expected that Mn^{4+} will affect the magnetic field distribution at the muon sites making the true situation more complex.

In addition to this general trend reflecting the dynamics of the system, the smaller relaxing component, with relaxation rate λ_2, shows additional features at low temperature (although it is not obvious why these features are not seen in λ_1). For the material in this regime, where the ANNNI model provides a good effective description of the magnetic behavior, the spin fluctuations will include excitations involving the domain wall solitons described by the ANNNI model,[8] along with diffusive modes resulting from coupling of the Ising spins to nonmagnetic degrees of freedom. At around $T_B \approx 18$ K we see a small peak in the relaxation rate λ_2, which occurs near the temperature below which (broadened) magnetic Bragg peaks appear in neutron diffraction.[1] The absence of a change at T_B in the form of the signal or its amplitudes indicates that this is not a transition to LRO or to a static magnetic state. Rather, it is more likely to represent the freezing out of one or more relaxation processes, likely to involve the free motion of domain walls and leading to the formation of poorly correlated clusters of ordered spins. This is consistent with the observation of broadened peaks in the neutron diffraction[1] signaling that the order that gives rise to the magnetic Bragg peaks is not truly long range.

The more significant change in the slowly relaxing component of the muon asymmetry occurs below 8 K. Here the parameter y in Eq. (1) increases upon cooling from $y=0$ to $y=1$ at the lowest measured temperatures, as shown in Fig. 1, indicating a transition to a static local field distribution at low T. Such a distribution, whether ordered or disordered, will only dephase those muon-spin components that lie perpendicular to the initial muon-spin polarization direction, expected to be 2/3 of the total polarization for a powder sample, leaving the other 1/3 polarized. Although the magnetic field distribution experienced by these muons below $T \approx 8$ K is static on the muon time scale, it is unlikely that the system locks into true LRO. Instead of the oscillations that would usually be observed in the presence of LRO, we see only a very small minimum in the asymmetry at early times [inset of Fig. 1(c)] in the minority component of our spectra measured below 8 K. This may originate from Kubo-Toyabe-like relaxation[17] typical of a static ensemble of disordered moments or may be a highly damped oscillation due to static order occurring over only a short length scale. Assuming the latter interpretation, the inset to Fig. 2(b) shows the frequency $\nu(=\gamma_\mu B_i/2\pi)$ of this feature.[25] The static disordered magnetism observed in our experiments, taken together with the peak measured in the χ'' susceptibility and broad maximum in the heat capacity observed around 8 K,[1] points to a freezing of domain walls to form spin clusters, resulting in a static disordered or glassy magnetic system.[26]

There are also, of course, still significant slow dynamic fluctuations in the system, measured by the majority asymmetry component with amplitude p.

The observed disorder may be explained in terms of the predictions of the ANNNI model.[8] Although the devil's staircase of commensurate spin structures is predicted from a continuum treatment of the model, a treatment based on a discrete Hamiltonian predicts the existence of an array of "chaotic" states at a higher energy than the devil's staircase, comprising a random array of domain wall solitons and antisolitons. Such states are metastable but are separated from the true Devil's staircase of stable states by relatively high energy barriers, making it impossible for a system to relax into the devil's staircase states in a finite amount of time.[8] Instead of LRO, the chaotic state possesses an intrinsic randomness, which means it may be described as spin glasslike. This picture therefore provides an explanation within the framework of the ANNNI model for the disordered magnetic state that we observe in $CaCo_{1.05}Mn_{0.95}O_6$. We note, however, that additional factors not considered in this simple model may contribute to the glassy character, including the possibility of clustering of the Mn^{4+} and Co^{2+} ions and the effect of complex interchain exchange interactions.[27]

Finally we note that it is possible that the behavior observed in $CaCo_{1.05}Mn_{0.95}O_6$ reflects the existence of both series spin relaxation processes (where the freezing of one relaxation process allows another to freeze at a lower temperature) and also coexistent parallel relaxation processes, which persist independently. Both of these types of process have been advanced to explain dynamics in glassy systems[28] and it is likely that they are important in a complex dynamic system such as $Ca_3Co_{1.05}Mn_{0.95}O_6$.

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