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LETTER TO THE EDITOR

A muon-spin relaxation (μSR) study of the geometrically frustrated magnets $Gd_3Ga_5O_{12}$ and $ZnCr_2O_4$

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Abstract

We present the results of muon-spin-relaxation experiments for two materials which show geometric frustration. $ZnCr_2O_4$ has a spinel structure with $S = \frac{3}{2}$ spins on a lattice of corner-sharing tetrahedra. Our experiments show that a local magnetic field which is quasi-static on the muon timescale develops below $T_c = 12.5$ K, a transition which has been associated with a three-dimensional analogue of the spin–Peierls transition. In contrast, $Gd_3Ga_5O_{12}$ has a garnet structure with $S = \frac{7}{2}$ spins arranged on interpenetrating triangular sublattices. In this material the muon data exhibit a temperature-dependent spin-relaxation rate indicative of slow spin fluctuations. We discuss these differing behaviours and relate them to the underlying physics in the two materials.

In a number of materials, long-range magnetic order of an arrangement of strongly interacting spins is not possible because of their geometric arrangement in the crystal lattice. This phenomenon is called *geometric frustration* [1]. Systems which exhibit geometric frustration cannot achieve a state that entirely satisfies the microscopic constraints, but nevertheless these systems possess a multiplicity of equally unsatisfied states. As a result these frustrated systems show metastability, hysteresis effects and time-dependent relaxation towards equilibrium. Geometric frustration is often realized in lattices which either (i) consist of stacks of two-dimensional nets which are in turn composed of corner-sharing triangles (such as Kagomé systems and garnets) or (ii) are three-dimensional arrangements of corner-sharing tetrahedra (such as pyrochlore systems). In each case, the lattices contain transition metal or rare-earth ions with antiferromagnetic exchange interactions between them. Frustrated systems also

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possess unusual spin dynamics because of the complex distribution of metastable low-energy states. This feature can be effectively probed by using implanted muons, since the muon spin is particularly sensitive to fluctuations on a rather long timescale. Muon-spin relaxation (μSR) has been used widely in the last thirty years as a sensitive probe of magnetism [2, 3]. It has been found to be ideally suited to studying small-moment magnetism [4], spin glasses [5, 6], organic magnets [7], spin-freezing effects [8] and frustrated systems [9, 10].

In this letter we demonstrate the sensitivity of the muon to slow spin dynamics in two such frustrated systems, $ZnCr_2O_4$ [11] and $Gd_3Ga_5O_{12}$ [12]. $ZnCr_2O_4$ is a spinel antiferromagnet composed of interpenetrating tetrahedra. Cr^{3+} ($S = \frac{3}{2}$) is an orbital singlet so spin–orbit effects are small and the Heisenberg exchange dominates. $ZnCr_2O_4$ is believed to show magnetic ordering at $T_c = 12.5$ K. Inelastic magnetic neutron scattering reveals a localized spin resonance at 4.5 meV in the ordered phase, and it has been argued that the transition is a three-dimensional analogue of the spin–Peierls transition because it is associated with a lattice distortion [13]. $Gd_3Ga_5O_{12}$ is a realization of a geometrically frustrated magnet in which the magnetic Gd ions sit on two interpenetrating corner-sharing triangular sublattices. The exchange interactions are almost purely antiferromagnetic and the system has a Curie–Weiss temperature of about -2.3 K [14]. The Gd spins ($S = 7/2$) are nearly isotropic with only a very small single-ion anisotropy of less than 0.04 K. The appearance of short-range order, deduced from bulk measurements such as heat capacity and dc and ac susceptibility ones, sets in around 1 K; an applied magnetic field suppresses the onset temperature [15, 16]. At lower temperatures, at around 130 mK, signatures of a spin glass appear; the ac susceptibility becomes frequency dependent and the dc magnetization differs for zero- and finite-field cooling. This spin-glass phase can be suppressed by a magnetic field and long-range order appears at around 1 T. Neutron scattering (with the non-absorbing isotope ^{160}Gd replacing the strongly neutron absorbing ^{157}Gd present in natural Gd) shows that the low-temperature phase is not an ordinary spin glass as inferred from the bulk measurements but rather a mixture of a spin-liquid state with a set of rigid magnetic pieces nucleated around impurity centres [12].

$ZnCr_2O_4$ was prepared by solid-state reaction between stoichiometric amounts of Cr_2O_3 and ZnO [13]. Our sample of $Gd_3Ga_5O_{12}$ was obtained commercially and was ground into a powder for these experiments to ensure good thermal conductivity with the cold finger on the dilution refrigerator. Magnetic susceptibility measurements were made using a SQUID magnetometer. The μSR measurements were performed on the EMU and μSR beamlines at the Rutherford Appleton Laboratory (using both a closed-cycle refrigerator and a ^{3}He cryostat) and on the πM3 beamline at the Paul Scherrer Institute (using the ^{4}He cryostat on the GPS spectrometer and the dilution refrigerator on the LTF spectrometer). In these experiments, an almost 100% spin-polarized beam of positive muons (μ^+, energy 4 meV) is implanted in polycrystalline samples of $ZnCr_2O_4$ and ground up crystals of $Gd_3Ga_5O_{12}$. The samples are contained in silver foil packets which are mounted on a silver backing plate for the higher-temperature measurements. With the lower-temperature measurements in the dilution refrigerator on $Gd_3Ga_5O_{12}$, the sample was mounted directly onto a silver backing plate and glued in place and covered by a 10 μm thick silver foil. The implanted muons thermalize in the sample rapidly and come to a complete rest (in a time $<10^{-10}$ s). They subsequently decay (lifetime 2.2 μs) into positrons. The positrons are emitted preferentially along the instantaneous spin direction of the muon at the time of the decay. The angle dependence of the time-dependent positron emission is used to infer the muon-spin polarization as a function of time after implantation.

Raw muon data in zero applied field, taken at ISIS and plotted for the first 2.5 μs, are shown for each sample in figure 1. The two samples show strongly contrasting behaviour. The muon polarization in $ZnCr_2O_4$ (figure 1(a)) relaxes rather slowly, while the relaxation

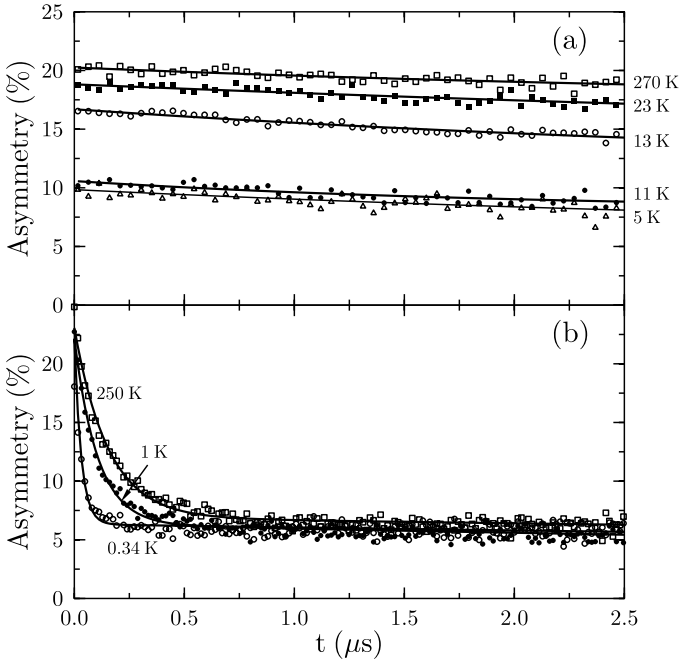

Figure 1. Raw μSR data taken at ISIS for (a) $ZnCr_2O_4$ and (b) $Gd_3Ga_5O_{12}$ at various temperatures. The fits are to an exponential relaxation form. The drop in initial asymmetry in (a) is due to the development of a precession signal, unobservable in the ISIS time window.

in $Gd_3Ga_5O_{12}$ (figure 1(b)) is much larger and strongly temperature dependent. However, in $Gd_3Ga_5O_{12}$ the initial asymmetry (proportional to the muon polarization measured at $t = 0$) does not vary with temperature, but in $ZnCr_2O_4$ the initial asymmetry falls rather dramatically at temperatures below 23 K.

We consider first the data for $ZnCr_2O_4$. The raw data were fitted to an exponential form and the results of the fits are shown in figure 2, together with the measured magnetization (using the SQUID magnetometer). A sharp transition can be seen very clearly in the magnetization data (figure 2(a)) and correlates well with a dramatic drop in the initial asymmetry at 12.5 K (figure 2(b)) which is consistent with the presence of a magnetic transition. The drop in initial asymmetry is connected with magnetic ordering, resulting in a precession signal unobservable at a pulsed source of muons such as ISIS. To check this hypothesis, we performed an experiment at PSI (a continuous muon source with a better time resolution for fast precession signals) which revealed a precession signal which developed below 12.5 K (see figure 3). This provides unambiguous evidence of the development of magnetic order and demonstrates that the local magnetic field at the muon site (which tends to 0.2 T at absolute zero) is static on a microsecond timescale. The temperature dependence of the frequency of the spin-precession oscillations can be used to infer the internal field at the muon site and hence the temperature dependence of the order parameter. This is shown in the inset of figure 3. The temperature dependence of the relaxation rate is shown in figure 2(c). This rises slowly with decreasing temperature, with a small cusp appearing close to the transition. The cusp can be associated with the appearance, on cooling just below the transition, of highly damped oscillations which then disappear out of the ISIS time window on further cooling. Below the transition, the relaxation rate continues to increase on cooling, in contrast to the expected behaviour for antiferromagnets. This behaviour

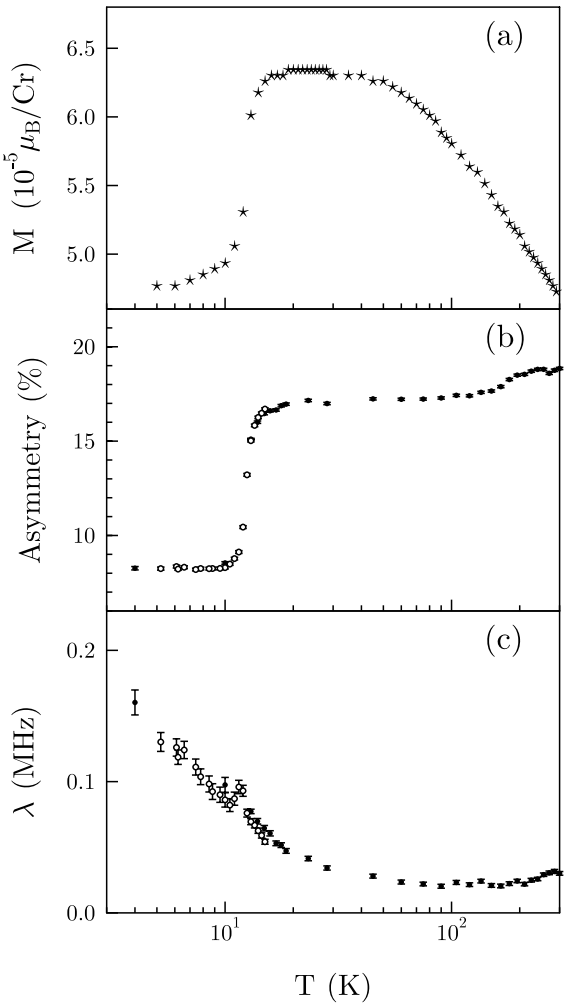

Figure 2. The temperature dependence of (a) the magnetization measured in an applied field of 10 mT, (b) the initial positron asymmetry and (c) the muon-spin relaxation rate for $ZnCr_2O_4$.

might be associated with slow spin dynamics, perhaps related to the inherent frustration in this system. These dynamics slow down with cooling and hence lead to faster muon-spin relaxation.

Very different behaviour is found for $Gd_3Ga_5O_{12}$. In contrast to another μSR study on this material [17] (which was performed over a more limited temperature range), our study found that a simple exponential, rather than a root exponential (which is difficult to justify on theoretical grounds for a non-dilute spin system), gave the best fit to our data over the entire temperature range. The temperature dependence of the relaxation rate is shown in figure 4(a). We identify three temperature regions as follows: in the high-temperature region (2–300 K), the relaxation rate is approximately constant; in the intermediate-temperature region (0.2–2 K), the relaxation rate follows a T^{-1}-law as a function of temperature T; at low temperatures <0.2 K, the relaxation rate begins to saturate. The high- and intermediate-temperature data agree with the results of [17]. Following this work, we identify the high-temperature relaxation

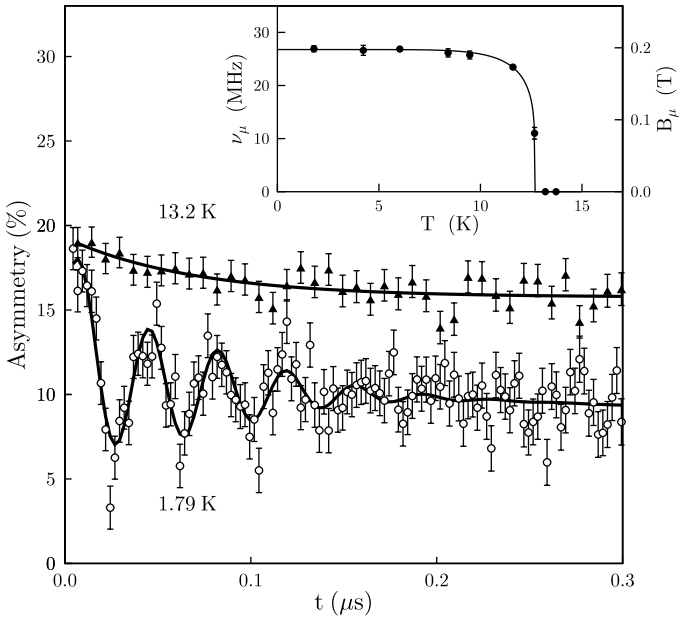

Figure 3. Raw data for $ZnCr_2O_4$ for $T = 1.79$ K (base temperature) and $T = 13.2$ K (just above the transition) measured at PSI. The inset shows the temperature dependence of the muon-spin-precession frequency ν_μ and the deduced internal field at the muon site (B_μ). The fit is to the phenomenological function $\nu_\mu(T) = \nu_\mu(0)(1 - (T/T_N)^\alpha)^\beta$ which yields $\alpha = 8 \pm 1$ and $\beta = 0.20 \pm 0.01$.

rate with Gd spin fluctuations at a rate ν_∞ given by $h\nu_\infty = \sqrt{2J^2zS(S+1)/3}$ [18] where z is the number of nearest neighbours and J is the exchange constant ($J/k_B = 0.107$ K) obtained from specific heat measurements [19]. This allows us to extract a fluctuation rate $\nu(T)$ over the whole temperature range using the equation $\lambda \approx 2\Delta^2\nu(T)^{-1}$ which is valid when $\nu(T) \gg \Delta$ (i.e. in the fast-fluctuation limit). Using the high-temperature value of λ and the predicted value of $\nu_\infty = 14.5$ GHz, we obtain $\Delta = 0.19$ GHz. We will assume that Δ is temperature independent, since it reflects only the width of the distribution of possible local fields irrespective of dynamical effects. With this assumption, the Gd spin-fluctuation rate $\nu(T)$ can then be extracted and this is plotted in figure 4(b).

In the intermediate-temperature region, when $\lambda \propto T^{-1}$, the Gd spin-fluctuation rate must therefore be proportional to temperature. A linear temperature dependence of the spin-fluctuation rate is predicted by Moessner and Chalker [20] for a system of classical spins on a class of frustrated lattices which includes the Kagomé and pyrochlore lattices. Their calculation yields $\nu = \alpha k_B T/\hbar$ where α is a numerical prefactor of order unity which depends on the details of the lattice. This prediction describes our data well at temperatures between about 0.2 and 2 K, and gives a value of $\alpha = 0.06$. At the lowest temperatures, we find that λ begins to saturate. This corresponds to ν saturating to a value $\nu_0 = 1.5$ GHz which is still much larger than Δ, demonstrating that the fast-fluctuation limit is still valid, as assumed earlier. It appears that some new mechanism of temperature-independent relaxation appears at these low temperatures, which causes a departure from the Moessner and Chalker linear temperature dependence. We cannot definitively identify the origin of this relaxation mechanism, but it could be associated with the small magnetic anisotropy or the presence of disorder. In this context we note that frustrated antiferromagnetic lattices are believed to have a cooperative paramagnetic ground state with

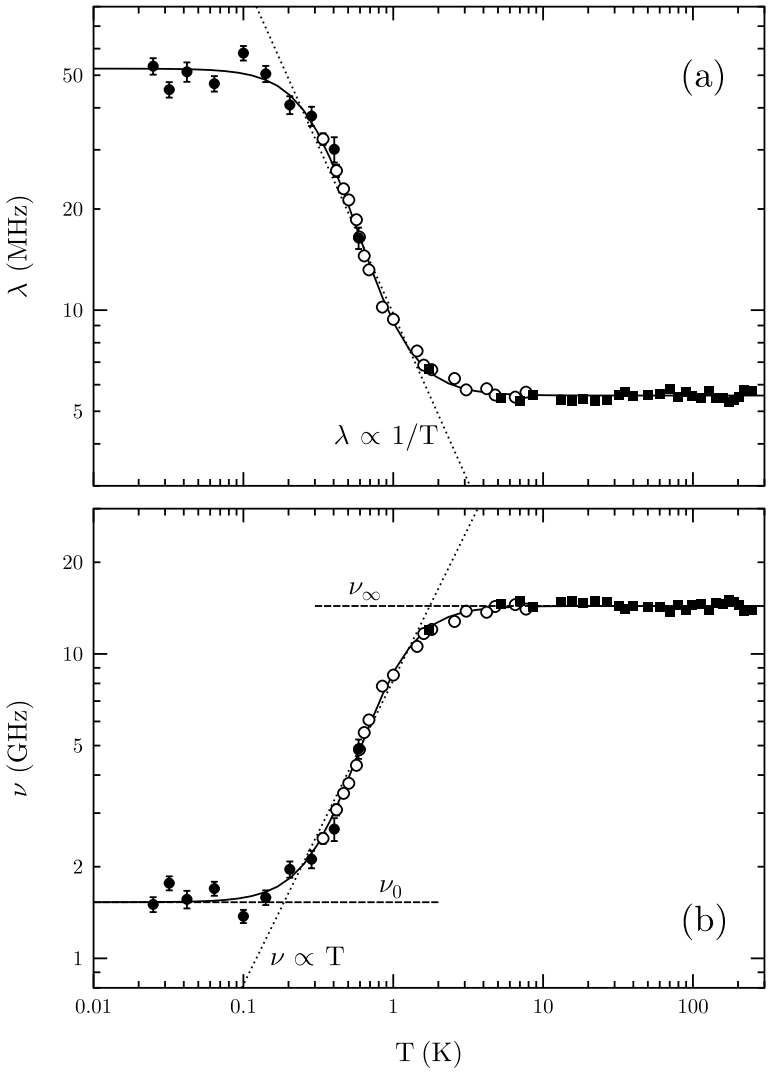

Figure 4. (a) muon-spin relaxation rate λ and (b) inferred fluctuation rate ν as a function of temperature. In (a) and (b), the data plotted with filled squares were taken using a closed-cycle refrigerator at ISIS, the data plotted with open circles were taken using a sorption cryostat at ISIS and the data plotted with filled circles were taken using a dilution refrigerator at PSI. In (a) and (b) the solid curves are guides to the eye and the dotted lines show the regime in which $\lambda \propto 1/T$ and $\nu \propto T$. In (b) the horizontal dashed lines show the low- and high-temperature fluctuation rates, showing the saturation behaviour.

only short-range spin–spin correlations for all $T > 0$ [21] unless this ground state is avoided by, for example, magnetic anisotropy [22]. We also speculate that the temperature-independent relaxation is related to the occurrence of the spin-liquid state which develops below 0.14 K according to neutron scattering measurements [12] and which appears to be related to minor chemical disorder. In this picture, spin-ordered regions of relatively large magnetic correlation length nucleate around impurities which consist of Gd ions occupying Ga sites [12]. If this state develops below ∼0.2 K, it could explain the departure from the Moessner and Chalker behaviour.

The two samples presented in this study are both geometrically frustrated but show contrasting behaviour at low temperatures. In $ZnCr_2O_4$, although magnetic order cannot develop, a lattice distortion drives the system into a spin-ordered phase (in contrast with a spin–Peierls transition in which a lattice distortion drives the system into a spin-singlet phase). μSR measurements measure the presence of magnetic order, but also show significant relaxation which increases on cooling. In $Gd_3Ga_5O_{12}$, there is no such avoidance of a frustrated ground state by a lattice distortion. In this material we find a progressive slowing down of the Gd spin fluctuations with cooling which is consistent with the predictions of Moessner and Chalker. However, at temperatures below 0.2 K, we observe instead a temperature-independent relaxation which may be a signature of a spin-liquid state.

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