Magnetism in the $S = 1$ frustrated antiferromagnet GeNi$_2$O$_4$ studied using implanted muons

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(Dated: January 4, 2022)

We present the results of a muon-spin relaxation study of GeNi$_2$O$_4$. We provide further clarification of the two transitions to the antiferromagnetic state and measure the magnetic field dependence of the heat capacity up to 14 T. Both oscillatory and relaxing signals are observed below the lower transition (at temperature $T_{N2}$) in the muon-decay positron asymmetry spectra, arising from two distinct types of magnetic environment. A possible explanation is suggested in terms of the separate ordering of two magnetic subsystems, one of which does not order fully down to the lowest measured temperature.

PACS numbers: 75.50.Ee, 76.75.+i, 75.40.-s, 75.50.-y

I. INTRODUCTION

Materials experiencing geometric frustration have been the topic of much recent interest. Their rich behavior is due to a large ground-state degeneracy, which renders them highly unstable to perturbations. In the case of a frustrated model system comprising Heisenberg-type antiferromagnetic nearest-neighbor interactions, cooperative paramagnetic behavior (i.e. fluctuations at all temperatures down to absolute zero) is expected. This state of affairs is altered, however, by perturbations due to other interactions (including next-nearest neighbor, dipole, crystal field etc.) which cause a variety of low temperature states to be realized, including spin-liquid and spin-ices in some rare-earth pyrochlores and structural phase transitions for some spinels with transition metal ions on the frustrated B sublattice.

Many geometrically frustrated systems with half-integer spins relieve the frustration by undergoing a structural phase transition at low temperatures to a magnetically ordered state; this is the case for the spinels ZnCr$_2$O$_4$ ($S = 3/2$), GeCo$_2$O$_4$ ($S = 3/2$) and powder samples of ZnFe$_2$O$_4$ ($S = 5/2$) which cause a variety of low temperature states to be realized, including spin-liquid and spin-ices in some rare-earth pyrochlores and structural phase transitions for some spinels with transition metal ions on the frustrated B sublattice.

The integer spin ($S = 1$) frustrated antiferromagnet GeNi$_2$O$_4$ has therefore been of recent interest, since it undergoes a transition to an antiferromagnetically ordered state below $\sim 12$ K (observed in both powder and single crystal samples) with no accompanying structural transition. GeNi$_2$O$_4$ has the normal spinel structure, having Ni$^{2+}$ ions (3d$^8$) at the vertices of corner sharing tetrahedra (the spinel B site), coordinated by a nearly regular octahedron of oxygen ions, resulting in a $^{3}A_2g$ triplet ground state. The crystal field lowers the degeneracy of this triplet, further splitting it into a close lying spin-singlet and doublet expected to be separated by only a few cm$^{-1}$. Recent experimental studies of this system by Crawford et al. show that the ordered state is reached by two separate transitions at $T_{N1} = 12.13$ K and $T_{N2} = 11.46$ K. It was found from heat capacity measurements that the magnetic entropy $S_{mag}$ of GeNi$_2$O$_4$ is only half of the expected $2R\ln 3$ per mole, with the same measurements suggesting the existence of both gapped and gapless excitations within the Néel state.

In recent years, muon-spin relaxation ($\mu^+\text{SR}$) measurements have been highly successful in observing frustration-related behavior in several frustrated systems, including the observation of spin-ice behavior and cooperative paramagnetism (see e.g. Ref. [11]). In this

FIG. 1: Heat capacity measured in (a) zero field and in an applied magnetic field of (b) 7 T and (c) 14 T. (d) Magnetic phase diagram deduced from (a)-(c) (circles) and from spin flogs observed in high field magnetization measurements (squares) (phases I and II are antiferromagnetic phases, phase III is paramagnetic).
In this paper we report on the first muon-spin relaxation measurements on GeNi$_2$O$_4$. We have probed the magnetically ordered region from a local viewpoint and provide evidence for muons stopping in separate magnetic environments in the ordered state. It is suggested that the double transition may be due to the separate ordering of these two subsystems.

II. EXPERIMENTAL

Polycrystalline GeNi$_2$O$_4$ was prepared in a solid-state reaction using high purity (> 99.99 %) GeO$_2$ and NiO. The stoichiometric mixed powder was calcined in an O$_2$ flow atmosphere at 1200°C for 48 hours. The sample was characterized using X-ray diffraction analysis (which revealed no contribution from impurity phases) and heat capacity measurements. The latter were carried out on a sintered pellet sample on warming using a 14 T Quantum Design PPMS system. Heat capacity data taken in zero field (ZF) and in an applied field of 7 T and 14 T are shown in Fig. 1(a-c). The ZF results show two sharp maxima at $T_{N1}$ and $T_{N2}$, in agreement with previous studies.\(^9\) In addition, we find a small shoulder below $T_{N1}$, also observed by Hara et al.\(^9\) who speculated about a possible third transition. The temperature of the two main peaks decreases markedly with applied field (as expected for an antiferromagnet, see e.g. Ref.\(^14\)), as shown in the phase diagram in Fig. 1(d). Both main peaks broaden and decrease in intensity with increasing field, the effect being more pronounced for the lower temperature peak. Also included in Fig. 1(d) are the two spin-flop transitions measured at 4.2 K in a recent high field magnetization study,\(^15\) and our phase diagram associates these with our heat capacity peaks.

Zero-field muon-spin relaxation measurements have been made on polycrystalline GeNi$_2$O$_4$ using the DOLLY instrument at the Swiss Muon Source, Paul Scherrer Institute (PSI), Villigen, Switzerland.\(^16\) The sample was wrapped in 25 μm Ag foil and mounted on a Ag backing plate. In a $\mu^+$SR experiment, 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 $B$ at the muon site, and which is proportional to the positron asymmetry function\(^17\) $A(t)$.

III. RESULTS

Our $\mu^+$SR data allow us to identify three distinct regions of temperature as follows: (a) phase I ($T < T_{N2}$), (b) phase II ($T_{N2} \leq T \leq T_{N1}$) and (c) phase III ($T > T_{N1}$). We now discuss each of these regimes in turn.

A. Phase I ($T < T_{N2}$)

For phase I (Fig. 2(a)), oscillations in the asymmetry are clearly discernible, though with a rather small amplitude, and a fast initial relaxation of the muon polarization is visible at early times. The oscillations are characteristic of a quasistatic local magnetic field at the muon site, which causes a coherent precession of the spins of those muons with a component of their spin polarization perpendicular to this local field; their presence provides strong evidence for the existence of long range magnetic order (LRO) in phase I, in agreement with previous neutron diffraction measurements.\(^18\) The frequency of the oscillations is given by $\nu_i = \gamma \mu_i B_i / 2\pi$, where $\gamma$ is the muon gyromagnetic ratio ($\approx 2\pi \times 135.5$ MHz T$^{-1}$), and $B_i$ is the local field at the $i$th muon site. The existence of oscillations in the asymmetry in a polycrystalline sample is a signature of a narrow distribution of the magnitudes of the static local magnetic fields, at symmetry-related muon sites in the crystal, associated with LRO. A

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{ZF spectra measured (a) at 5.14 K, in phase I ($T < T_{N2}$), (b) at 11.55 K and 12.00 K, in phase II ($T_{N2} \leq T \leq T_{N1}$) and (c) at 12.32 K, in phase III ($T > T_{N1}$). The oscillations seen in (a) are observed to vanish above $T_{N2}$ (b), with the Gaussian component vanishing above $T_{N1}$ (c).}
\end{figure}
broader distribution of these fields leads to the occurrence of the Kubo-Toyabe (KT) function, which is well approximated by a Gaussian function at early times with relaxation rate \( \sigma^2 = \frac{\gamma}{2} \Delta B^2 / 2 \), where \( \Delta B^2 = \langle (B - \langle B \rangle)^2 \rangle \) is the second moment of the local field distribution. The recovery of asymmetry at late times, characteristic of the KT function, is often lost due to the presence of slow dynamics in the local field distribution. Because of the additional fast relaxation signal in the data, a full description also requires an additional component. This is well described over the measured temperature regime by a Gaussian functional form \( A_2 \exp(-\sigma^2 t^2) \) with a large relaxation rate (see below). The large magnitude of the relaxation at very low temperatures makes it impossible to unambiguously assign it a Gaussian lineshape over the entire temperature range. However, the continuous temperature evolution of \( \sigma \) and the line-shape seen at temperatures \( T > 10 \) K makes this a reasonable assumption.

The spectra are found to be best fitted in the range \( T < T_{N1} \) with the resulting functional form

\[
A(t) = A_1 \{a_1 + a_2 \exp(-\lambda_1 t) \cos(2\pi \nu_1 t)\} + A_2 \exp(-\sigma^2 t^2) + A_{bg},
\]

where \( A_{bg} \) represents a constant background contribution from those muons that stop in the sample holder or cryostat tail. The factor multiplied by \( A_1 \) accounts for the component of the spectra associated with LRO (normalized to 1), expected to be made up from contributions from those muons with spin components parallel to the local magnetic field \( a_1 \) and those with perpendicular components \( a_2 \). The value of \( a_1 \) consistent with the measured spectra is much higher than expected \( (a_1 = 0.59 \) compared to the expected value of 1/3). This may be due to muons stopping at similar sites of LRO but whose transverse spin contributions are rapidly dephased (although we note that this should lead to a missing fraction of asymmetry, which we do not observe); an unambiguous assignment of the amplitudes for the lowest measured temperatures is hindered by the large value of the relaxation rate \( \sigma \) so the situation may be more complex than considered here.

The amplitude \( A_1 \) is found to be approximately constant up to \( T \approx 9 \) K (Fig. 4a), where it is seen to decrease as the transition at \( T_{N2} \) is approached from below. This is accompanied by a corresponding rise in the amplitude of the Gaussian component \( A_2 \). The existence of two distinct components in the measured spectra (i.e. Gaussian and oscillatory) provides evidence for two sets of muon sites (or subsystem) in the material, such that a localised muon experiences one of two distinct magnetic environments. The first of these subsystems, with occupancy proportional to the amplitude \( A_1 \), has a sufficiently narrow distribution of quasistatic magnetic fields that oscillations are observable. The other subsystem, with occupancy proportional to \( A_2 \), is associated with a wider distribution of fields (preventing oscillations being observable) and slow dynamics preventing any recovery of the asymmetry at later times. The \( \mu^+ \)SR data show that the fraction of the sample associated with the Gaussian component gives rise to a very different local magnetic environment to that causing the fraction associated with amplitude \( A_1 \). Since the muon is a local probe, it is not possible to conclude whether the two magnetic environments suggested by the data are spatially separated or spatially coexisting. If these two subsystems were spatially separated, then the exchange of amplitudes seen as \( T_{N2} \) is approached from below would probably be due to those regions associated with Gaussian relaxation growing at the expense of those sites related to the oscillations. If, in contrast, the two environments are coexisting, then the changes in amplitude may be due to a reordering of the magnetic moments as the temperature is increased.

The frequency of the oscillations (Fig. 3b) varies little below the transition temperature \( T_{N2} \), at which point \( A_1 \rightarrow 0 \), indicating first-order behavior, in agreement with the heat capacity measurements. This could suggest that the subsystem associated with the oscillating component undergoes an ordering transition at \( T_{N2} \). The stability of the oscillation frequency across the temperature range means that we see no effect due to depopulation of the upper level of the split \( ^3A_{2g} \) triplet state at low temperatures.

**B. Phase II (\( T_{N2} \leq T \leq T_{N1} \))**

In phase II (Fig. 2b) the oscillations vanish and the spectra are described by relaxing components only. The Gaussian component persists into this regime, with no discernible discontinuity in \( \sigma \) at \( T_{N2} \). This suggests that this component arises from the same mechanism responsible for the corresponding component in Eq. 1. Also evident in the spectra measured in phase II is an exponential component \( A_3 \exp(-\lambda_3 t) \). An exponential function is often the result of fast, dynamic fluctuations in the local field, in which case the relaxation rate \( \lambda_3 \propto \gamma \Delta B^2 / \delta \), where \( \delta \) is the fluctuation rate. This behavior points to dynamic fluctuations of a paramagnetic subsystem, coexisting with the subsystem associated with the Gaussian component seen in phase I. The data are therefore described by the resulting relaxation function

\[
A(t) = A_2 \exp(-\sigma^2 t^2) + A_3 \exp(-\lambda_3 t) + A_{bg}.
\]

With increasing temperature, we see (Fig. 4a) the increase in the amplitude of the fluctuating component \( A_3 \) increases along with a decreasing fraction of the Gaussian component \( A_2 \) decreases). The relaxation rate \( \sigma \) decreases smoothly across the entire temperature range (Fig. 4c), showing no features corresponding to the transition at \( T_{N2} \) but vanishing at \( T_{N1} \). The smooth decrease of \( \sigma \) with increasing temperature suggests that this parameter is dominated by the magnitude of the local field distribution, as seen in other muon studies of magnetically ordered systems. This may suggest that the sub-
IV. DISCUSSION

The fact that only half of the expected magnetic entropy $S_{\text{mag}} = 2R \ln 3$ is accounted for in heat capacity measurements made below 75 K points to unconventional magnetic behavior in GeNi$_2$O$_4$. The double transition is seen in neutron diffraction measurements through discontinuities in the intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ magnetic Bragg peak, the intensity of which is proportional to the ordered volume-fraction multiplied by the magnetic moment. These results suggest that LRO exists throughout the material with the same wavevector at all temperatures below $T_{N1}$.

The muon provides us with a local perspective. Of the two magnetic subsystems identified in the data, the one giving rise to oscillations may unambiguously be attributed to the presence of LRO. In phase I the magnetic moment (proportional to the frequency $\nu_1$) shows little temperature dependence, in contrast to the volume fraction, which decreases as $T$ tends to $T_{N2}$. This component cannot be resolved in phase II, and the disappearance of magnetic order in this subsystem may cause the discontinuity in the Bragg peak intensity seen in the neutron data.

Since the neutron diffraction results strongly suggest that LRO exists throughout the sample in phase II, it may be that the Gaussian component associated with the other magnetic subsystem seen in phases I and II could also be an artifact of LRO. An incomplete ordering of the magnetic moments, for example, may provide sufficient spin disorder in this subsystem to wash out an oscillatory signal. The magnitude of the local magnetic field in this subsystem may still be probed from the behavior of the relaxation rate $\sigma$ (provided that any dynamics are slow and only weakly temperature dependent), which decreases smoothly. The amplitude of this component decreases with increasing temperature, before vanishing at $T_{N1}$, perhaps accounting for the other discontinuity in the Bragg peak intensity.

The observed behavior in GeNi$_2$O$_4$ may, therefore, be analogous to Gd$_2$Ti$_2$O$_7$, in which there are two magnetic subsystems with different ordering temperatures. In that system ordering takes place at the higher transition in one subsystem. At the lower transition temperature the other subsystem weakly orders. If a similar mechanism were to be the cause of the observed behavior in GeNi$_2$O$_4$, we note that the higher transition at $T_{N1}$ would probably be associated with a weakly ordering subsystem (with sufficient spin disorder to prevent the observation of coherent oscillations) followed by the ordering of the second subsystem below $T_{N2}$.

Such behavior in GeNi$_2$O$_4$ could also explain the missing contribution to the magnetic entropy. In their heat capacity study Crawford et al. assume that $\lim_{T \to 0} S_{\text{mag}} = 0$ and detect only 56.5 % of the expected $S_{\text{mag}} = 2R \ln 3$ up to $T = 75$ K. If a subsystem does indeed exist which does not undergo full magnetic ordering then the magnetic entropy would take a nonzero

C. Phase III ($T > T_{N1}$)

In Phase III (Fig. 3(c)) the Gaussian component is absent and the data are best described by a two exponential form $A(t) = A_3 \exp(-\lambda_3 t) + A_4 \exp(-\lambda_4 t) + A_{bg}$, typical of relaxation due to dynamic fluctuations, as would be expected in a purely paramagnetic material.
value below the transitions. Assuming that all of $S_{\text{mag}}$ is accounted for by $T = 75$ K, then the amount of magnetic entropy associated with the partially ordered subsystem would be 43.5% of $2R\ln 3$. Such a value is possible given that the amplitude $A_2$ associated with the Gaussian component approximately twice $A_1$ at low temperatures (Fig.2(a)) suggesting that around two thirds of the spins are associated with the partially ordered subsystem.

Finally, it has been suggested that the unusual ordering behavior and smaller than expected magnetic entropy may stem from the integer spin, which may also be the case for the recently reported pyrochlore Y$_2$Ru$_2$O$_{22}$.

V. CONCLUSION

In conclusion we have investigated magnetic transitions in GeNi$_2$O$_4$ using implanted muons. We observe two separate contributions to the measured spectra below the upper magnetic transition at $T_{N1}$ suggestive of two different magnetic environments coexisting in the material. Our data may be interpreted in terms of two distinct magnetic subsystems that undergo separate ordering transitions. The first subsystem, which accounts for the larger portion of the sample, partially orders at the higher transition temperature $T_{N1}$ leaving significant spin disorder that persists to the lowest measured temperature. This subsystem coexists with a second subsystem that is fluctuating dynamically down to the lower transition temperature $T_{N2}$, where this second subsystem undergoes full magnetic ordering. The exchange in amplitudes of the signals corresponding to each subsystem suggests that the number of Ni$^{2+}$ spins associated with each subsystem is not constant but varies above $T \approx 9$ K. Further magnetic neutron diffraction measurements would be required to elucidate the precise nature of the proposed subsystems.

Part of this work was carried out at the Swiss Muon Source, Paul Scherrer Institute, Villigen, Switzerland. We thank Hubertus Luetkens and Robert Scheurmann for technical assistance and Paul Goddard and Michael Brooks for useful discussion. This work is supported by the EPSRC. T.L. acknowledges support from the European Commission under the 6th Framework Programme through the Key Action: Strengthening the European Research Area, Research Infrastructures. Contract no: RII3-CT-2003-505925

Acknowledgments

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12. We note that the peaks observed in our ZF measurements appear slightly broader than those observed previously, but this is the effect of a lower sampling frequency rather than an intrinsic property of our sample.
13. In all of the fits, the initial asymmetry $A(t=0)$ and the background $A_{bg}$ was held constant for all temperatures. The relaxation rate $\lambda_1$ was found also approximately constant in phase I, and was fixed at 11.7 MHz. This resulted in three degrees of freedom that were found to vary with $T$ across the measured temperature range.
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