Anomalous Temperature Evolution of the Internal Magnetic Field Distribution in the Charge-Ordered Triangular Antiferromagnet $AgNiO_2$

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Zero-field muon-spin relaxation measurements of the frustrated triangular quantum magnet $AgNiO_2$ are consistent with a model of charge disproportionation that has been advanced to explain the structural and magnetic properties of this compound. Below an ordering temperature of $T_N = 19.9(2)$ K we observe six distinct muon precession frequencies, due to the magnetic order, which can be accounted for with a model describing the probable muon sites. The precession frequencies show an unusual temperature evolution which is suggestive of the separate evolution of two opposing magnetic sublattices.

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Magnetic frustration of spins in triangular-lattice antiferromagnets has been studied in a variety of experimental systems [1,2]. The series $XNiO_2$, in which planes of Ni^{3+} ($t_{2g}^6 e_g^1$) ions are arranged at the vertices of a triangular lattice, provides the possibility that not only the magnetic but also the charge and orbital degrees of freedom may be frustrated. Although it is expected that the fourfold ground-state degeneracy of an isolated Ni^{3+} ion would be lifted via a cooperative Jahn-Teller (JT) distortion (implying orbital ordering [3]) followed by magnetic ordering at a lower temperature [4], the triangular geometry of the $XNiO_2$ ($X =$ Na, Li, Ag) system may frustrate both of these transitions and the ground state of such a system continues to be a matter of debate [4–6].

Three energy scales determine the physics of these orbitally degenerate systems [7]: the on-site Coulomb energy U, the electronic bandwidth W, and the intra-atomic Hund rule coupling J_H. In insulating systems (such as $NaNiO_2$), for which $U \gg W$, the degeneracy of partially occupied orbital states is usually lifted by a cooperative JT distortion as described above. This contrasts with an itinerant system for which $W \gg U$ (such as $LaNiO_2$) where the kinetic energy term dominates and the JT distortion is suppressed. It has recently been proposed [7] that in an intermediate regime where U and W are comparable, J_H may overcome the on-site repulsion leading to charge ordering (CO). This provides another method for the system to lift its orbital degeneracy, this time by removing degenerate electrons at some sites, leading to double occupation at others.

Such a CO scheme has been advanced [8] to explain the crystal structure and magnetic properties of recently synthesized hexagonal $AgNiO_2$, a polymorph [9,10] of the better known rhombohedral polytype [11]. This material is a moderately delocalized metal [9] whose orbital degeneracy may be lifted [8] by a $\sqrt{3} \times \sqrt{3}$ CO transition, achieved via $3e_g^1 \rightarrow e_g^2 + 2e_g^{0.5}$. This transition is indicated by a structural distortion to a tripled unit cell with expanded and contracted NiO_6 octahedra. The e_g^2 ions, which correspond to $S = 1$, Ni^{2+}, are located at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, and these so-called Ni1 sites form the tripled triangular lattice as shown in Fig. 1(a). The Ni1 spins order magnetically below $T = 20$ K in a collinear structure of spins aligned along the c direction, organized in ferromagnetic rows of stripes running parallel to b and alternating in direction along a [Fig. 1(a)]. The $e_g^{0.5}$ sites [Ni2 located at $(0, 0, \frac{1}{4})$ and Ni3 at $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$] form a honeycomb network around the Ni1 sites and appear to have a much reduced ordered moment ($\leq 0.1\mu_B$) due to hybridization [8]. It should be noted that complete disproportionation is not required in order to foster the complete spin polarization on a particular site that is proposed in the model. The delocalized nature of the system makes it possible for the band of states corresponding to a class of sites to be completely polarized, despite being composed of a mixture of e_g^2 and $e_g^{0.5}$ states [7].

Muon-spin relaxation (μ^+SR) measurements have been employed to explore the properties of the $XNiO_2$ system for $X =$ Na [12] and Li [13] from a local perspective. In this Letter we report μ^+SR measurements made on $AgNiO_2$. Our results may be explained in terms of the CO model described above providing further evidence for the existence of this newly proposed phase. We show that the magnetically ordered phase shows very little disorder, with six muon precession frequencies observed with very little dephasing. However, the temperature evolution of the frequencies is unusual and points to the separate evolution of the Ni1 sublattice (described above) and an additional sublattice that may be formed from small moments on the Ni2 and Ni3 sites.

Powder samples of hexagonal $AgNiO_2$ (with $<1\%$ of the rhombohedral polytype) were prepared as described in Ref. [9]. Zero-field (ZF) μ^+SR measurements were

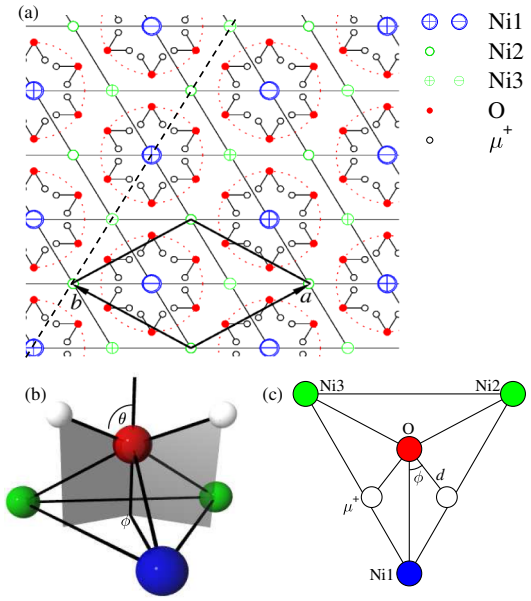

FIG. 1 (color online). (a) Structure of $AgNiO_2$ viewed along the c direction with proposed muon stopping sites shown. The magnetic structure involves ordered Ni1 sites with moments aligned parallel (+ sign) or antiparallel (− sign) to the c direction, surrounded by a honeycomb of Ni2 and Ni3 sites. The + and − signs on the Ni3 sites give the orientation of the Ni1 spins in the neighboring layer directly above and below. The thick lines show the chemical unit cell, while the dashed line indicates the mirror plane for the magnetic structure (see text). (b) Proposed muon stopping sites occur 1 Å from each oxygen ion. Taking the oxygen position as the origin of coordinates, muons are found at $\theta = 65°$ and $\phi = \pm 38°$, separated by 1.4 Å from the Ni planes along c. (c) As (b) but viewed along c.

made on the sample using the DOLLY instrument at the Swiss Muon Source (SμS). The sample was wrapped in 25 μm Ag foil and mounted on a Ag backing plate. In a μ^+SR experiment [14], 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 $A(t)$.

Typical ZF μ^+SR spectra measured above and below T_N are shown in Fig. 2(a). Above the magnetic transition the spectra are well described by an exponential relaxation function as expected for a paramagnet with dynamically fluctuating magnetic moments [15]. Below T_N we observe oscillations in the time dependence of the muon polarization (the "asymmetry" [14]) which are characteristic of a quasistatic local magnetic field at the muon stopping site. This local field causes a coherent precession of the spins of those muons for which a component of their spin polarization lies perpendicular to this local field (expected to be $\frac{2}{3}$ of the total spin polarization). The frequency of the oscillations is given by $\nu_i = \gamma_\mu |B_i|/2\pi$, where γ_μ is the muon

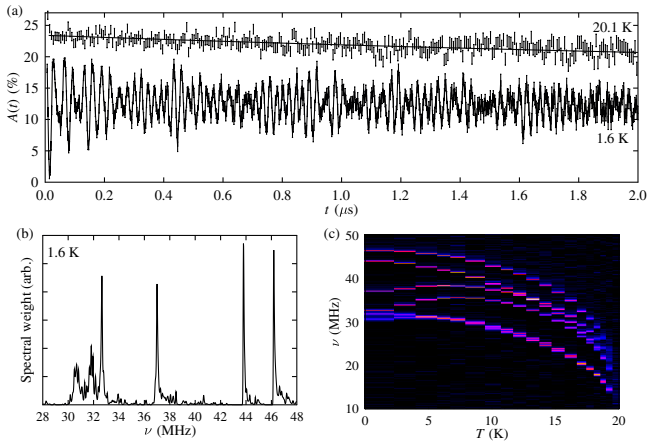

FIG. 2 (color online). (a) Time-domain μ^+SR spectrum measured above and below the antiferromagnetic transition with time-domain fits as described in the main text. (b) Maximum entropy analysis of the spectrum measured at $T = 1.6$ K showing six distinct frequencies. (c) Temperature evolution of the frequency spectrum extracted from maximum entropy analysis.

gyromagnetic ratio ($= 2\pi \times 135.5$ MHz T^{-1}) and B_i is the average magnitude of the local magnetic field at the ith muon site. Any fluctuation in magnitude of these local fields will result in a relaxation of the oscillating signal, described by relaxation rates λ_i [see Eq. (1)].

The measured spectra for $AgNiO_2$ are unusual in that they are composed of oscillations at several frequencies with very low depolarization rates. This suggests the existence of several, well-defined, magnetically inequivalent muon sites in the material. In order to account for all frequencies in the spectra measured below T_N, maximum entropy analysis was used to decompose the signal. The results are shown in Figs. 2(b) and 2(c), where six well-defined frequencies are seen, corresponding to six magnetically inequivalent muon sites in the material. We label these ν_1–ν_6 in order of decreasing magnitude at $T = 1.6$ K. μ^+SR spectra are recorded in the time domain, and a knowledge of the number of frequencies allows us to use time-domain fitting for more detailed analysis. In a magnetically ordered powder with N magnetically inequivalent muon sites, we would expect the spectra to be of the form

$$A(t) = \sum_{i=1}^{N} A_i \left(\frac{1}{3} + \frac{2}{3} e^{-\lambda_i t} \cos(2\pi\nu_i t + \phi_i) \right) + A_{\mathrm{bg}}, \quad (1)$$

where A_{bg} represents a constant background contribution from those muons that stop in the sample holder or cryostat tail and the $\frac{1}{3}$ term accounts for that fraction of muon-spin components that lie parallel to the local magnetic field. The measured spectra were fitted to Eq. (1), with $N = 6$. Constant nonzero phases ϕ_i were also required to fit the data due to the difficulty in determining $t = 0$ in the spectra and the high oscillation frequencies involved. All

components occurred with the same amplitude $A_i = A(0)/6$ across the temperature range $T < T_N$, from which we conclude that each of the muon sites occurs with the same probability and that the material is magnetically ordered throughout its bulk.

The temperature evolution of the fitted frequencies is shown in Fig. 3(a), which is seen to be identical to that extracted from the maximum entropy analysis [Fig. 2(c)]. The magnitude of the frequencies ν_i are expected to act as an order parameter for a magnetic system. The variation of these frequencies is therefore unusual, with some frequencies decreasing and some increasing with increasing T. However, the average frequency ν_{av} behaves as expected, decreasing smoothly as T is increased towards T_N. Fits of the average frequency to the phenomenological form $\nu_{\mathrm{av}}(T) = \nu_{\mathrm{av}}(0)[1 - (T/T_N)^{\alpha}]^{\beta}$ yield $\alpha \approx 2.4$, $\beta \approx 0.3$, and $T_N = 19.9(2)$ K. This estimate for T_N is consistent with the results of previous studies of $AgNiO_2$ [9].

The relaxation rates λ_i are shown in Fig. 3(d). For $T < 17$ K we note that the magnitudes of all relaxation rates λ_i are very low. This implies [15] that the distribution of local fields is exceptionally narrow at all muon sites and that the spin disorder in $AgNiO_2$ is remarkably low. All λ_i have very similar temperature dependence except λ_5 and λ_6, which are larger than λ_{1-4} across the entire temperature regime and show a rough decrease with increasing temperature for $T < 17$ K. As T_N is approached from below, all λ_i increase sharply as would be expected for the onset of critical fluctuations near a magnetic transition.

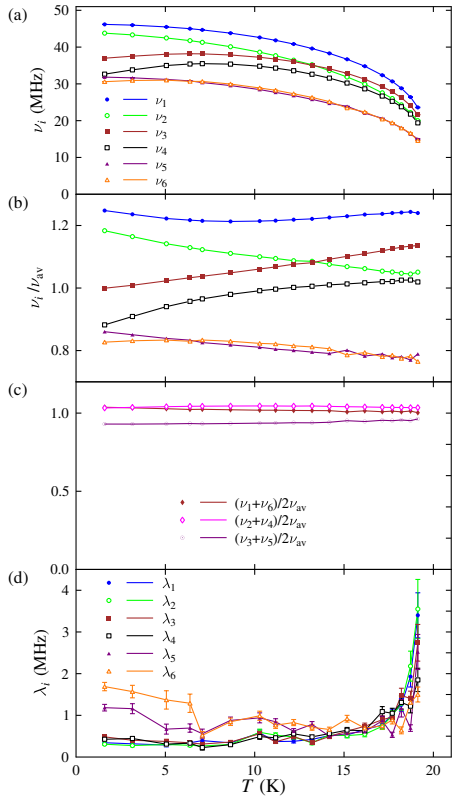

FIG. 3 (color online). (a) Temperature evolution of the frequencies ν_i, extracted from the spectra measured below T_N, fitted to Eq. (1). (b) The normalized frequencies $\nu_i/2\nu_{\mathrm{av}}$ form three pairs with roughly equal and opposite gradients. (c) Adding the pairs of normalized frequencies as indicated results in approximately flat lines. (d) Relaxation rates λ_i showing a steep increase as T_N is approached from below.

A knowledge of $\nu_i(T = 0)$ allows a determination of the muon sites in $AgNiO_2$. Dipole fields were calculated in a sphere containing $\sim 10^5$ Ni ions, using the magnetic structure described above [8]. A positive muon's stopping position is usually 1 Å from the electronegative O^{2-} ion [16] and calculated local magnetic fields corresponding to the observed frequencies are found at several positions around 1 Å from each oxygen ion. In order to narrow the choice of muon sites, the electrostatic potential was also calculated at positions on the 1 Å sphere surrounding an oxygen, assuming the proposed [8] $\sqrt{3} \times \sqrt{3}$ CO on the Ni sites. Two distinct regions of negative electrostatic potential are found, separated from the Ni planes along c by 1.4 Å and occurring closer to the Ni1 ions (which have e_g^2) than the Ni2 and Ni3 ions (with $e_g^{0.5}$). These regions are found to contain the positions where the local magnetic fields give rise to the observed precession frequencies. For each oxygen ion we may therefore identify two muon sites. We take an oxygen as the origin of a polar coordinate system [shown in Fig. 1(b)] with the z direction parallel to the c axis and the x direction defined by the projection onto the a-b plane of the vector joining the O^{2-} and the Ni1 ions. The muon sites are found 1 Å from the origin at $\theta = \pm 65°$ (plus sign for oxygens above the Ni planes, minus for those below) and $\phi = 38°$ and $\phi = -38°$. These proposed muon sites are shown in Fig. 1. For the 12 muon sites surrounding a Ni1 ion [Fig. 1(a)], the proposed magnetic structure involving alternating ferromagnetic rows of ordered moments gives rise to six magnetically distinct sites. This is because the magnetic structure has a mirror plane that runs transverse to the magnetic stripe direction [Fig. 1(a)] and which causes sites linked by this symmetry to be equivalent. This approach accounts successfully for the six observed magnetic frequencies. Unfortunately, however, the large field gradients in these positions, along with the possibility of small moments on the Ni2 and Ni3 sites, make it difficult to assign precise positions for each of the observed frequencies.

We now turn to the unusual temperature dependence of the frequency spectrum. The exceptionally small relaxation rates permit the extraction of the detailed temperature dependence of the local magnetic field at each muon site. Normalizing the frequencies ν_i by the average value $\nu_i/2\nu_{\mathrm{av}}$ [Fig. 3(b)] gives three pairs with approximately equal and opposite gradients. These pairs ($\nu_1 + \nu_6$, $\nu_2 + \nu_4$, and $\nu_3 + \nu_5$) are shown in Fig. 3(c) to yield approximately flat lines when added together, demonstrating that they vary in equal and opposite senses about the average.

This suggests that within a pair, one muon site sees an increase in local magnetic field at the expense of its partner, which sees a decrease, as temperature is increased. In a polycrystalline material the muon-spin polarization depends only on the *magnitude* of the local magnetic field at the muon site. Our picture of the six muon sites in $AgNiO_2$ therefore comprises three pairs of sites, where the pairs see opposing variation with temperature in the magnitude of the local dipole fields. Figure 3(b) shows that this effect is quite small (but clearly detectable) and that the variation in local field at a particular muon site is $\lesssim 15\%$ about the average.

A possible explanation for this anomalous behavior involves a continuous temperature evolution of the direction of the ordered moment, so that the field magnitude increases at one muon site while correspondingly being reduced at another. Such a reorientation would not change the amplitudes associated with each frequency component due to the effects of angular averaging necessary for our polycrystalline sample, so would be consistent with our measurements. However, it is difficult to see how a reorientation would be energetically favored as it would involve the interactions between spin components in the c direction (i.e., along the local threefold easy axis) driving a reorientation to directions in the a-b plane along a further threefold symmetric easy axis. If these components were to order with the same wave vector as the components aligned along c, two of the three in-plane spins could not point along their local easy axis direction. We note further that it is unlikely that this effect is caused by a temperature-dependent reordering of charges. The structural distortion that indicates the CO transition occurs above room temperature and involves the expansion and contraction of NiO_6 octahedra. Any charge reordering should be observable as a change in Ni—O bond lengths, which is not seen in neutron diffraction studies [17].

A more probable scenario involves the separate temperature evolution of two magnetic sublattices. A second magnetic sublattice could arise from Ni2 and Ni3 sites, which band-structure calculations suggest [8] may carry a magnetic moment of $0.1\mu_B$. An ordered moment on this second sublattice may be induced by the large ordered moment on the Ni1 sites and would, therefore, presumably lie along c. Although the temperature dependence of the Ni1 moment will be determined by Ni1 intrasublattice exchange, the T dependence of the Ni2,3 sublattice would most likely depend not only on its intrasublattice exchange but also on its interaction with the large Ni1 moment, possibly causing the two sublattices to evolve differently in temperature. This scenario would require that the pairs of muon sites be arranged such that a decrease at one site would also lead to an increase at another. For example, if the Ni3 sites become spin-polarized by interaction with the Ni1 sites in the planes immediately above and below, the Ni3 sublattice will give rise to a small additional dipolar field which augments that produced by the Ni1 sublattice for half the muon sites, but diminishes the field for the other half. Thus a temperature-dependent interplanar coupling between Ni1 and Ni3 sites could give rise to the anomalous temperature evolution that we have observed.

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