Incommensurate magnetic order in Ag$_2$NiO$_2$

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The nature of the magnetic transition of the half-filled triangular antiferromagnet Ag$_2$NiO$_2$ with $T_N$=56K was studied with positive muon-spin-rotation and relaxation ($\mu^+\text{SR}$) spectroscopy. Zero field $\mu^+\text{SR}$ measurements indicate the existence of a static internal magnetic field at temperatures below $T_N$. Two components with slightly different precession frequencies and wide internal-field distributions suggest the formation of an incommensurate antiferromagnetic order below 56 K. This implies that the antiferromagnetic interaction is predominant in the NiO$_2$ plane in contrast to the case of the related compound NaNiO$_2$. An additional transition was found at $\sim$22 K by both $\mu^+\text{SR}$ and susceptibility measurements. It was also clarified that the transition at $\sim$260 K observed in the susceptibility of Ag$_2$NiO$_2$ is induced by a purely structural transition.

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I. INTRODUCTION

Two-dimensional triangular lattice (2DTL) antiferromagnets with a half-filled ($e_g$) state exhibit a variety of magnetically ordered states due to competition between the antiferromagnetic (AF) interaction and geometrical frustration. The discovery of superconductivity in Na$_{0.35}$CoO$_2$1.33H$_2$O leads to an additional interest in the possible relationship between magnetic and superconducting order parameters in the 2DTL near half-filling. The layered nickel dioxides, a series of materials with chemical formula $A^+$Ni$^{3+}$O$_2$, such as rhombohedral LiNiO$_2$, NaNiO$_2$, and AgNiO$_2$, in which Ni ions form the 2DTL by the connection of edge-sharing NiO$_6$ octahedra, has been considered to be good candidates for an ideal half-filled 2DTL. In these materials at low temperature, there is a strong interaction between the Ni$^{3+}$ ions and the crystalline electric field of the Ni$_6$ octahedron. This causes the Ni$^{3+}$ ions to be in the low spin state with a $t^6_2e^1_9$ ($S=1/2$) configuration.

Among the three layered nickel dioxides, NaNiO$_2$ is perhaps the best investigated. It exhibits two transitions at $T_{JT}$ $\sim$480 K and $T_N$=23 K. The former is a cooperative Jahn-Teller (JT) transition from a high-$T$ rhombohedral phase to a low-$T$ monoclinic phase, while the latter is a transition into an A-type AF phase – i.e. ferromagnetic (FM) order in the NiO$_2$ plane but AF between the two adjacent NiO$_2$ planes, as has been reconfirmed very recently by both neutron diffraction and positive muon spin rotation/relaxation ($\mu^+\text{SR}$) experiments.

The magnetic order is associated with the JT induced trigonal distortion which stabilizes a half occupied $d_{z^2}$ orbital.

Although LiNiO$_2$ and NaNiO$_2$ are structurally very similar, LiNiO$_2$ shows dramatically different magnetic properties. LiNiO$_2$ exhibits neither a cooperative JT transition nor long-range magnetic order down to the lowest $T$ investigated. In fact, both heat capacity and NMR measurements suggest a spin-liquid state with short-range FM correlations. However, Chatterji et al. however, found a rapid increase in the muon spin relaxation rates in LiNiO$_2$ below $\sim$10 K using the longitudinal field-$\mu^+\text{SR}$ technique, suggesting a spin-glass-like behavior below 10 K. The discrepancy between the two results is considered to be a sample-dependent phenomenon that arises from the difficulties in preparing stoichiometric LiNiO$_2$. The third compound, AgNiO$_2$, also lacks a cooperative JT transition. A magnetic transition $T_N$ was clearly observed by both susceptibility ($\chi$) and $\mu^+\text{SR}$ measurements but long-range magnetic order was not detected by a neutron diffraction experiment even at 1.4 K.

While the nature of the magnetic ground states of LiNiO$_2$ and AgNiO$_2$ is still not clear, the FM interaction on the 2DTL NiO$_2$ plane has been thought to be common for all the layered Ni dioxides with a half-filled state because of the clear magnetic order observed in NaNiO$_2$. In this paper, we present measurements that demonstrate this supposition is incorrect. This is accomplished by investigating the magnetism in Ag$_2$NiO$_2$, a material that can be represented by the chemical formula (Ag$_2$)$^{3+}$Ni$^{3+}$O$_2$ and hence is expected to have a NiO$_2$ plane that has properties identical to the above three layered nickel dioxides. However, in Ag$_2$NiO$_2$, static AF order, likely the formation of an incommensurate AF struc-
ture in the NiO$_2$ plane, is observed instead.

Disilver nickel oxide Ag$_2$NiO$_2$ is a rhombohedral system with space group $R3m$ ($a_H = 0.29193$ nm and $c_H = 2.4031$ nm for the hexagonal unit-cell) that was found to exhibit two transitions at $T_3=260$ K and $T_N=56$ K by resistivity and $\chi$ measurements, while the symmetry remains rhombohedral down to 5 K. Interestingly, Ag$_2$NiO$_2$ shows metallic conductivity down to 2 K probably due to a quarter-filled Ag 5$s$ band, as in the case of Ag$_2$F. Very recently, Yoshida et al. proposed the significance of the AF interaction in the vicinity of $T_N=56$ K; however, it is difficult to understand the origin of the line-broadening below 20 K using a classical AF model without invoking the presence of an additional magnetic transition. Furthermore, even the spectrum at 30 K, which is the sharpest FFT measured, consists of a main peak at $\sim 14$ MHz and a shoulder around 16 MHz, suggesting a wide distribution of $H_{\text{int}}$ in Ag$_2$NiO$_2$.

We therefore use a combination of three signals to fit the ZF-$\mu$SR time spectrum:

$$A_0 P_{ZF}(t) = A_1 \cos(\omega_{\mu,1} t + \phi) \exp(-\lambda_1 t) + A_2 J_0(\omega_{\mu,2} t) \exp(-\lambda_2 t) + A_{\text{slow}} \exp(-\lambda_{\text{slow}} t),$$

where $A_0$ is the empirical maximum muon decay asymmetry, $A_1$, $A_2$ and $A_{\text{slow}}$ are the asymmetries associated with the three signals, $J_0(\omega_{\mu,2} t)$ is a zeroth-order Bessel function of the first kind that describes the muon polarization evolution in an incommensurate spin density wave (IC-SDW) field distribution, and $\omega_{\mu,1} < \omega_{\mu,2}$.

Although $J_0(\omega t)$ is widely used for fitting the ZF-$\mu$SR spectrum in an IC-SDW state, it should be noted that $J_0(\omega t)$ only provides an approximation of the generic IC magnetic field distribution. This is because the lattice sum calculation of the dipole field at the muon site ($H_{IC}$) due to an IC magnetic structure lies in a plane and traces out an ellipse. The half length of the major axis of the ellipse corresponds to $H_{\text{max}}$, whereas half of the minor axis corresponds to $H_{\text{min}}$. As a result, the IC magnetic



II. EXPERIMENTAL

A powder sample of Ag$_2$NiO$_2$ was prepared at the ISSP of the University of Tokyo by a solid-state reaction technique using reagent grade Ag$_2$O and NiO powders as starting materials. A mixture of Ag$_2$O and NiO was heated at 550°C for 24 h in oxygen under a pressure of 70 MPa. A more detailed description of the preparation and characterization of the powder is presented in Ref. $^1$.

Susceptibility ($\chi$) was measured using a superconducting quantum interference device (SQUID) magnetometer (mpms, Quantum Design) in the temperature range between 400 and 5 K under magnetic field $H \leq 55$ kOe. For the $\mu$SR experiments, the powder was pressed into a disk of about 20 mm diameter and thickness 1 mm, and subsequently placed in a muon-veto sample holder. The $\mu$SR spectra were measured on the M20 surface muon beam line at TRIUMF. The experimental setup and techniques were described elsewhere.$^13$

III. RESULTS AND DISCUSSION

A. Below $T_N$

Figure $^1$ shows zero-field (ZF-) $\mu$SR time spectra in the $T$ range between 1.9 K and 60 K for a powder sample of Ag$_2$NiO$_2$. A clear oscillation due to quasi-static internal fields $H_{\text{int}}$ is observed below 54 K, unambiguously establishing the existence of long-range magnetic order in the sample. Interestingly, as $T$ is decreased from 60 K, the relaxation rate first decreases down to $\sim 20$ K and then increases as $T$ is lowered further. By contrast, the average oscillation frequency increases monotonically down to 1.9 K. This implies that the distribution of $H_{\text{int}}$ at $T \geq 54$ K and $\leq 20$ K is larger than that at 20 K $< T < 54$ K.

This is further established by the $T$ dependence of the Fourier Transform of the ZF-$\mu$SR time spectrum shown in Fig. $^2$. Note that there is clearly line broadening below 20 K as well as above 54 K. The line-broadening above 54 K is reasonably explained by critical phenomena in

![Figure 1: Temperature dependence of the ZF-$\mu$SR time spectra of a powder sample of Ag$_2$NiO$_2$.](image-url)

The spectrum is offset by 0.2 for clarity of the display. The solid lines represent the fitting result using Eq. (1).
The distribution diverges as $H$ approaches either $H_{\text{min}}$ or $H_{\text{max}}$ (see Fig. 3). $J_0(\omega t)$ describes the field distribution very well except in the vicinity of $H_{\text{min}}$, and the value of $\omega$ should be interpreted as an accurate measure of $H_{\text{max}}$. However, $J_0(\omega t)$ provides no information on $H_{\text{min}}$. Hence, the first term $A_1 \cos(\omega_{\mu,1}t + \phi_1) \exp(-\lambda_1 t)$ is added in Eq. 1 to account for the intensity around $H_{\text{min}}$ and to determine the value of $H_{\text{min}} (= \omega_{\mu,1}/\gamma_\mu)$ [10] ($\gamma_\mu$ is the muon gyromagnetic ratio and $\gamma_\mu/2\pi = 13.55342$ kHz/Oe). In other words, only when $H_{\text{min}} = 0$, Eq. [3] is well approximated by $J_0(\omega t)$. Here it should be emphasized that $\mu^+\text{SR}$ spectra are often fitted in a time domain, i.e. not by Eq. [3] but by Eq. [1], since information on all the parameters such as $A$, $\omega$, $\lambda$, and $\phi$ are necessary to discuss the magnetic nature of the sample.

We note that the data can also be well-described using two cosine oscillation signals, $A_1 \cos(\omega_{\mu,1}t + \phi_1) \exp(-\lambda_1 t) + A_2 \cos(\omega_{\mu,2}t + \phi_2) \exp(-\lambda_2 t)$ with $\phi_2 = -54 \pm 10^\circ$ below $T_N$. The delay is physically meaningless, implying that the field distribution fitted by a cosine oscillation, i.e. a commensurate $H_{\text{int}}$ does not exist in Ag$_2$NiO$_2$. [12] Furthermore, as $T$ decreases from 54 K, $A_1$ ($A_2$) decreases (increases) linearly with $T$ from 0.15 (0) at 54 K to 0 (0.15) at 1.9 K. In order to explain the $A_1(T)$ and $A_2(T)$ curves, one would need to invoke the existence of two muon sites, and a situation whereby the population of $\mu^+$ at each site is changing in proportion to $T$. Such behavior is very unlikely to occur at low $T$. Hence, we believe that our data strongly suggests the appearance of an IC-AF order in Ag$_2$NiO$_2$ below $T_N$, as predicted by the calculation using a Mott-Hubbard model (discussed later). Such a conclusion is also consistent with the fact that the paramagnetic Curie temperature is -33 K estimated from the $\chi(T)$ curve below 260 K.

Figures 4(a) - 4(d) show the $T$ dependence of the muon precession frequencies ($\nu_t = \omega_{\mu,i}t/2\pi$), the volume fraction of the paramagnetic phases ($V_{\text{para}}$), $\Delta \nu = \nu_2 - \nu_1$, $\lambda_1$, $\lambda_2$, the asymmetries $A_1 + A_2$, $A_1$, $A_2$, and $\chi$ for the powder sample of Ag$_2$NiO$_2$. Here, $V_{\text{para}}$ is estimated from the weak transverse field (wTF-) $\mu^+\text{SR}$ experiment described later. In agreement with the FFTs shown in Fig. 3 as $T$ is decreased from 60 K, $\nu_2$ appears at 54 K. It then increases monotonically with decreasing $T$ down to around 20 K, and then increases more rapidly upon further cooling. The $\nu_1(T)$ curve exhibits a similar behavior to that observed for $\nu_2(T)$. It is noteworthy that as $T$ is decreased from 80 K, the $V_{\text{para}}(T)$ curve shows a sudden drop down to $\sim 0$ at $T_N$, indicating that the whole sample enters into an IC-AF state.

As $T$ decreases from $T_N$, $\Delta \nu$, which measures the distribution of $H_{\text{int}}$ in the IC-AF phase, rapidly decreases down to $\sim 0.8$ MHz at 40 K, then seems to level off the lowest value down to $\sim 20$ K and then increases with increasing slope ($|d\Delta \nu/dT|$) until it reaches 4 MHz at 1.9 K. The overall $T$ dependence of $\Delta \nu$ is similar to that of $\lambda_t$. This behavior is expected since a large $\Delta \nu$ naturally implies a more inhomogeneous field distribution—i.e., an increased flattening of the ellipse that enhances $\lambda_t$. The asymmetry of the IC magnetic phase, $A_1 + A_2$, also increases monotonically with decreasing $T$, although
the muon precession frequencies \( (\nu_i = \omega_{\mu,i}/2\pi) \) and normalized transverse field asymmetry that roughly corresponds to the volume fraction of the paramagnetic phases in the sample \( V_{\text{para}} \). (b) \( \Delta \nu = \nu_2 - \nu_1 \), \( \lambda_1 \) and \( \lambda_2 \), (c) the asymmetries \( A_1 + A_2 \), \( A_1 \), \( A_2 \) and \( A_{\text{slow}} \) and (d) \( \chi \) for the powder sample of Ag\(_2\)NiO\(_2\). \( \chi \) was measured in zero-field-cooling \( ZFC \) and field-cooling \( FC \) mode with \( H = 100 \) Oe.

![FIG. 4](image)

FIG. 4: (Color online) Temperature dependences of (a) the muon precession frequencies \( (\nu_i = \omega_{\mu,i}/2\pi) \) and normalized transverse field asymmetry that roughly corresponds to the volume fraction of the paramagnetic phases in the sample \( V_{\text{para}} \), (b) \( \Delta \nu = \nu_2 - \nu_1 \), \( \lambda_1 \) and \( \lambda_2 \), (c) the asymmetries \( A_1 + A_2 \), \( A_1 \), \( A_2 \) and \( A_{\text{slow}} \) and (d) \( \chi \) for the powder sample of Ag\(_2\)NiO\(_2\). \( \chi \) was measured in zero-field-cooling \( ZFC \) and field-cooling \( FC \) mode with \( H = 100 \) Oe.

A small jump likely exists around 20 K. The existence of a significant \( A_1 \) underscores the inappropriateness of fitting the ZF-\( \mu^+ \)SR data with only a \( J_0(\omega_{\mu,2} t) \) term. In fact, note that \( A_1 < A_2 \) above 20 K, suggesting that the IC-AF order develops/completes below 20 K. This is consistent with the rapid increases in \( \Delta \nu \) and \( \lambda_i \) below 20 K, as described above.

The behavior of the muon parameters is quite consistent with the \( \chi(T) \) curve, which exhibits a sudden increase in the slope \( (d\chi_{\text{FC}}/dT) \) below \( \sim 22 \) K(=\( T_m \)) with decreasing \( T \). Note the \( \chi(T) \) curve measured under ZFC conditions starts to deviate from that measured in the FC configuration below \( T_N \), suggesting the development of a ferro- or ferrimagnetic component probably due to a canted spin structure. The ferro- or ferrimagnetic behavior is however observed only at low \( H \), although the cusp at \( T_N \) is clearly seen with \( H = 100 - 10 \) kOe (see Figs. 4d and 4d)). Below \( T_m \), \( \chi_{\text{FC}} \) increases with decreasing \( T \), while the slope is suppressed by increasing \( H \) (see Fig. 5).

Keeping in mind that \( \mu^+ \)SR is insensitive to magnetic impurities, we conclude that Ag\(_2\)NiO\(_2\) undergoes a transition from a paramagnetic to an IC-AF state at \( T_N = 56 \) K and then to a slightly different ordered state at \( T_m \sim 22 \) K.

It is worth contrasting the current \( \mu^+ \)SR results on Ag\(_2\)NiO\(_2\) with those in related compounds Na\(_2\)NiO\(_2\) and Ag\(_2\)O\(_2\). The ZF-\( \mu^+ \)SR spectrum on a powder sample of Na\(_2\)NiO\(_2\) consists of two signals below \( T_N \)(\( \sim 20 \) K): an exponentially relaxing cosine oscillating signal (same as the first term in Eq. 1) as the predominant component and a minor signal described by an exponential relaxation. This indicates that the whole Na\(_2\)NiO\(_2\) sample enters into a commensurate AF state below \( T_N \), being consistent with the magnetic structure determined by neutron diffraction experiments, i.e., an A-type AF order. Interestingly, the value of \( \nu_T \) at \( K = 64.2 \) MHz, which corresponds to \( H_{\text{int}} \sim 0.5 \) T, is 2.5 times higher than that for Ag\(_2\)NiO\(_2\). The muon site in Na\(_2\)NiO\(_2\) is assigned to the vicinity of the O ions and is thought to be also reasonable for the other layered nickel dioxides.

The differences between the \( \mu^+ \)SR results on Na\(_2\)NiO\(_2\) and Ag\(_2\)NiO\(_2\) hence suggest that the magnetic structure of Ag\(_2\)NiO\(_2\) is most unlikely to be an A-type AF. Furthermore, there are no indications for additional transitions of Na\(_2\)NiO\(_2\) below \( T_N \) by \( \chi \), \( \mu^+ \)SR and neutron diffraction measurements.

In Ag\(_2\)NiO\(_2\), the primary ZF-\( \mu^+ \)SR signal is one that exponentially relaxes down to the lowest \( T \) (\( \sim 3 \) K). Below \( T_N \)(=\( 28 \) K), three minor oscillating components appear. These have small amplitudes and correspond to internal fields from 0.2 to 0.33 T (27 - 45 MHz). The comparison between Ag\(_2\)NiO\(_2\) and Ag\(_2\)O\(_2\) indicates that the interlayer separation \( d_{\text{NiO}_2} \) enhances the static magnetic order in the NiO\(_2\) plane. It is highly unlikely that the AF

![FIG. 5](image)

FIG. 5: (Color online) Temperature dependence of \( \chi \) measured in both ZFC and FC mode well below \( T_N = 56 \) K with \( H = 10 \) Oe, 20 Oe, 100 Oe and 1 kOe for Ag\(_2\)NiO\(_2\).
interaction through the double Ag\(_2\) layer is stronger than that through the single Ag layer, since \(d_{\text{NiO}_2}=0.801\) nm for Ag\(_2\)NiO\(_2\)\(^{10}\) and 0.612 nm for AgNiO\(_2\)\(^{7}\).

Our results therefore suggest that the AF order exists in the NiO\(_2\) plane, in contrast to the situation in NaNiO\(_2\). Assuming the AF interaction is in the NiO\(_2\) plane, an IC-spiral SDW phase is theoretically predicted to appear in a half-filled 2D TLL\(^{15}\) (calculated using the Hubbard model within a mean field approximation with \(U/t\geq 3.97\), where \(U\) is the Hubbard on-site repulsion and \(t\) is the nearest-neighbor hopping amplitude). In order to further establish the magnetism in Ag\(_2\)NiO\(_2\), it would be interesting to carry out neutron diffraction experiments to determine the magnetic structure below \(T_N\) and below \(T_m\).

We wish here to mention that if the valence state of the Ni ion in the NiO\(_2\) plane can be varied for Ag\(_2\)NiO\(_2\), the resultant phase diagram should serve as an interesting comparison with that of \(A_x\)CoO\(_2\) (\(A=\)alkali elements) with \(x<0.5\). Unlike Li\(_x\)NiO\(_2\), (Ag\(_2\))-deficient samples are currently unavailable, probably because of the metal-like Ag-Ag bond in the disilver layer.\(^{10}\) A partial substitution for Ag\(_2\) by other cations has thus far also been unsuccessful for reasons unknown.

### B. Near \(T_S\)

In order to elucidate the magnetic behavior above \(T_N\), in particular near \(T_S=260\) K, we carried out weak transverse field (wTF-) \(\mu^+\)SR measurements up to 300 K. The wTF-\(\mu^+\)SR spectrum was fitted by a combination of a slowly and a fast relaxing precessing signal; the former is due to the external field and the latter due to the internal AF field (same as the first term in Eq. \(\text{(1)}\)):

\[
A_0 P_{TF}(t) = A_{TF} \cos(\omega_{\mu,TF} t + \phi_{TF}) \exp(-\lambda_{TF} t) + A_{AF} \cos(\omega_{\mu,AF} t + \phi_{AF}) \exp(-\lambda_{AF} t),
\]

where \(\omega_{\mu,TF}\) and \(\omega_{\mu,AF}\) are the muon Larmor frequencies corresponding to the applied weak transverse field and the internal AF field, \(\phi_{TF}\) and \(\phi_{AF}\) are the initial phases of the two precessing signals and \(A_n\) and \(\lambda_n\) (\(n=\) TF and AF) are the asymmetries and exponential relaxation rates of the two signals. Note that we have ignored the \(J_0(\omega t)\) term in Eq. \(\text{(3)}\) since we are primarily interested in the magnetic behavior above \(T_N\).

The results are shown in Fig. \(6\) together with \(\chi^{-1}\). Besides the transition at 56 K, there are no anomalies up to 300 K in the normalized asymmetries, the relaxation rate (\(\lambda_{TF}\)) or the shift of the muon precession frequency (\(\Delta \omega_{\mu,TF}\)). Transverse field (TF-) \(\mu^+\)SR measurements at \(H=2600\) Oe, which should be about 50 times more sensitive to frequency shifts than the wTF measurements, show no obvious changes in \(\Delta \omega_{\mu,TF}\) at \(T_S\) either. On the other hand, the \(\chi^{-1}(T)\) curve exhibits a clear change in slope at \(T_S\). Above 60 K, the normalized wTF-asymmetry (\(A_{TF}\)) levels off to its maximum value — i.e. the sample volume is almost 100% paramagnetic. This therefore suggests that \(T_S\) is induced by a purely structural transition and there is no dramatic change in the spin state of Ni ions; that is, \(T_S\) is unlikely to be a cooperative JT transition. This is consistent with the fact that the crystal structure remains rhombohedral down to 5 K.\(^{11}\)

### IV. Summary

Positive muon spin rotation/relaxation (\(\mu^+\)SR) spectroscopy has been used to investigate the magnetic prop-
erties of a powder sample of Ag$_2$NiO$_2$ in the temperature range between 1.9 and 300 K. Zero field $\mu$SR measurements suggest the existence of an incommensurate anti-ferromagnetic (AF) order below $T_N=56$ K. An additional transition was also found at $T_m=22$ K by both $\mu^+\mathrm{SR}$ and susceptibility measurements.

The current results, when compared to the results in AgNiO$_2$, indicate that magnetism in the half-filled 2DTL of the NiO$_2$ plane is strongly affected by the interlayer distance. In other words, the ground state of the half-filled NiO$_2$ plane is not a ferromagnetic (FM) ordered state or an FM spin-liquid or spin-glass, but is instead an AF frustrated system. The FM behavior in NaNiO$_2$ is therefore thought to be induced by a Jahn-Teller induced trigonal distortion.

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