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Neutron diffraction study of layered Ni dioxides: Ag_2NiO_2

Hiroshi Nozaki[1], Jun Sugiyama[1], Marc Janoschek[2], Bertrand Roessli[3], Vladimir Pomjakushin[3], Lukas Keller[3], Hiroyuki Yoshida[4] and Zenji Hiroi[4]

[1] Toyota Central R & D Laboratories Inc., 41-1 Yokomichi, Nagakute Aichi 480-1192, Japan
[2] Physik Department E21, TU München, 85748 Garching, Germany
[3] Laboratory for Neutron Scattering, ETH Zürich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
[4] Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

E-mail: h-nozaki@mosk.tytlabs.co.jp

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Abstract

In order to elucidate the antiferromagnetic (AF) nature of hexagonal Ag_2NiO_2 with $T_N = 56$ K and to know the mechanism of the structural phase transition of $T_S \sim 270$ K, neutron powder diffraction patterns have been measured in the temperature range between 1.5 and 330 K. One magnetic Bragg peak indexed as $\frac{1}{3}\ \frac{1}{3}\ 0$ is clearly observed below T_N, confirming the formation of long-range AF order, reported by a muon-spin spectroscopy measurement. The weak intensity of the magnetic peak also suggests the two-dimensional nature of the AF order, but the spin structure is still unknown. In addition, the precise structural analysis of the data between 160 and 330 K shows that only the c_H-axis length changes drastically at T_S, which suggests the appearance of local Jahn–Teller distortion below T_S.

1. Introduction

Depending on the ground state of their two-dimensional triangular lattices (2DTL), a variety of interesting magnetic ordering states appear on 2DTL materials as a function of spin concentration, particularly for a half-filled state, in which geometrical frustration plays a significant role in determining the magnetic nature of the 2DTL, when the nearest neighbor interaction is antiferromagnetic (AF). The layered nickel dioxides, a series of materials with chemical formula $A^+Ni^{3+}O_2$, such as hexagonal $LiNiO_2$ [1, 2], $NaNiO_2$ [3–5], $AgNiO_2$ [6, 7], and Ag_2NiO_2 ($Ag_2^+Ni^{3+}O_2$) [8, 9], in which Ni ions form the 2DTL by the connection of edge-sharing NiO_6 octahedra, have been considered to be good candidates for an ideal half-filled 2DTL. This is because the Ni^{3+} ions are in the $S = 1/2$ low spin state, with a $t_{2g}^6e_g^1$ configuration, due to a strong crystalline electric field splitting of the d orbitals in the NiO_6 octahedron.

Nevertheless, for $ANiO_2$ with A = Li, Na, and Ag, a long-range AF order on the 2DTL has so far not been found, whereas the A-type AF phase, i.e. ferromagnetic (FM) order in the NiO_2 plane but AF between the two adjacent NiO_2 planes, was found in $NaNiO_2$ below 23 K [3–5]. This could simply imply that the interaction between the Ni spins is not AF but FM for the layered nickel dioxides. However, according to magnetic susceptibility, electrical resistivity and heat capacity measurements [9], it was found that Ag_2NiO_2 exhibits two transitions: one is a small structural phase transition at $T_S = 270$ K and the other is an AF transition at $T_N = 56$ K. Furthermore, our recent positive muon-spin rotation and relaxation (μ^+SR) experiment has clearly confirmed static incommensurate (IC) AF order below T_N [10]. Since NiO_2 planes are separated by Ag_2 layers, the inter-plane coupling is thought to be negligibly small for Ag_2NiO_2. The IC-AF order is thus most unlikely to be helical order along the c_H-axis, where H stands for the hexagonal setting, but likely to locate only in the NiO_2 plane. The μ^+SR result has therefore revealed the existence of the IC-AF order on the 2DTL in the layered nickel dioxides.

In order to further elucidate the nature of the AF phase of Ag_2NiO_2, it is necessary to perform a neutron diffraction experiment because of its unique power to determine the spin structure of long-range AF order. Furthermore, since the details of the structural transition at 270 K are still unknown,

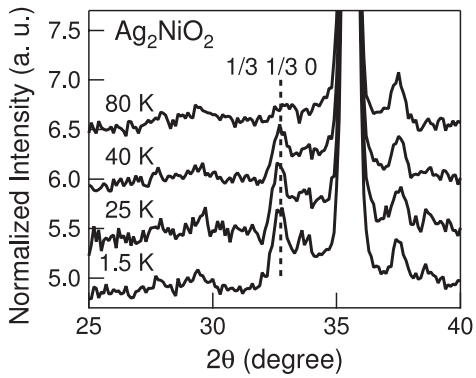

Figure 1. Neutron diffraction pattern taken at DMC. Each pattern is shifted for clarity.

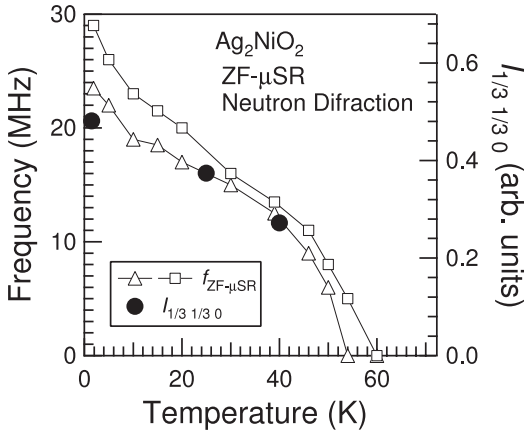

Figure 2. Temperature dependences of the intensity of the magnetic Bragg peak of $\frac{1}{3}\ \frac{1}{3}\ 0$ reflection (●) and the two muon-spin precession frequencies obtained by ZF-μSR measurements (△ and □) [10].

we need to know the variation of the crystal structural parameters with T in the vicinity of T_S. Here, we report the results of neutron powder diffraction (NPD) experiments on Ag_2NiO_2 in the T range between 1.5 and 330 K.

2. Experimental details

A powder sample was prepared at ISSP of University of Tokyo by a conventional solid state reaction technique, using Ag_2O and NiO powders under high oxygen pressure [8, 9]. A powder x-ray diffraction (XRD) analysis showed that the sample was single phase Ag_2NiO_2. The neutron diffraction experiments were performed on the cold neutron powder diffractometer (DMC) [11] to detect magnetic diffraction peaks at low T, and the high resolution powder diffractometer for thermal neutrons (HRPT) [12] to study the change in crystal structural parameters around 270 K, at the Paul Scherrer Institut (PSI) at Villigen, Switzerland. The wavelength of the neutron beam was 0.2453 nm for DMC and 0.1494 nm for HRPT. The NPD data were analyzed using Fullprof [13].

3. Result and discussion

3.1. Magnetic diffraction below $T_N = 56$ K

Figure 1 shows the T dependence of the NPD pattern for Ag_2NiO_2. One magnetic Bragg peak is clearly observed around $2\theta = 32.5°$ below T_N (= 56 K) plus several weak peaks. The main peak is reasonably well indexed as $\frac{1}{3}\ \frac{1}{3}\ 0$—i.e., the magnetic unit cell is three times larger than the chemical one. The fact that there are only weak magnetic Bragg peaks even at 1.5 K suggests a weak intensity of magnetic diffraction for Ag_2NiO_2, in contrast to the clear μ^+-spin oscillation below T_N. This suggests that the value of the magnetic moment at saturation is small. Indeed, comparing the μ^+SR result on Ag_2NiO_2 [10] with that of $NaNiO_2$ [5], the internal magnetic field (H_{int}) of Ag_2NiO_2 is about 1/2.5 of that of $NaNiO_2$, for which the ordered moment $\vec{m}$ is estimated as (0.17, 0, 0.96) μ_B ($|\vec{m}| = 0.97\mu_B$) by NPD measurements. If we ignore the difference of the AF structure between Ag_2NiO_2 and $NaNiO_2$, the ordered moment of Ag_2NiO_2 would then be below 0.39 μ_B. Furthermore, the T dependence of the intensity of the magnetic Bragg peak is very consistent with that of the two muon-spin precession frequencies [10], which are proportional to the internal magnetic field (see figure 2). The present NPD result is therefore very consistent with the μ^+SR result. It is, however, impossible to determine the spin structure based only on one magnetic diffraction peak. For such a purpose, particularly for increasing the magnetic signal to noise ratio, we need a large high quality single crystal sample, which is not currently available.

Table 1. Crystallographic parameters of Ag_2NiO_2 with a space group of $R\bar{3}m$ (hexagonal axes).

Atom	Site	x	y	z
Ag	6c	0	0	z
Ni	3a	0	0	0
O	6c	0	0	z

Table 2. Atomic positions of Ag_2NiO_2 at various temperatures.

T (K)	Ag (z)	O (z)
160	0.213 82	0.624 05
190	0.213 89	0.624 13
210	0.213 98	0.624 11
230	0.213 96	0.624 02
250	0.214 01	0.624 07
270	0.214 03	0.624 02
290	0.214 04	0.624 03
310	0.214 10	0.624 09
330	0.214 13	0.624 02

3.2. Structural phase transition at $T_S = 270$ K

High resolution NPD patterns were measured in the T range between 160 and 330 K. The structural parameters were determined by analyzing the diffraction pattern using FullProf. Crystallographic parameters are shown in table 1 and the refined parameters of the atomic positions in table 2.

Figure 3 shows the T dependences of the length of the a_H- and c_H-axes, the unit cell volume (V_H), the distance between the Ni and O ions (d_{Ni-O}), and the distance between the Ag_2

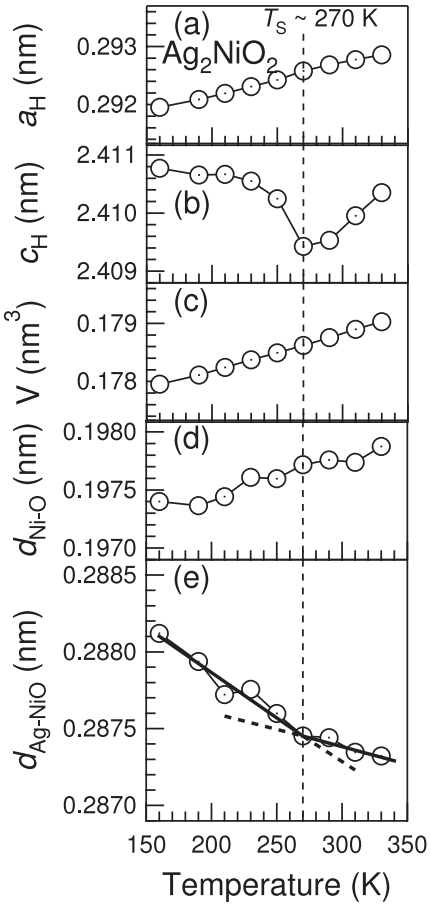

Figure 3. Temperature dependences of (a) *a*-axis length, (b) *c*-axis length, (c) unit cell volume, (d) distance between Ni ion and O ion, and (e) distance between the double Ag plane and the NiO_2 plane.

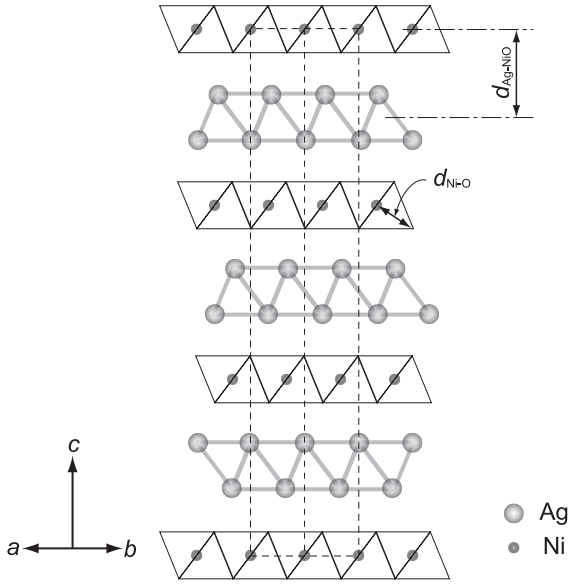

Figure 4. Crystal structure of Ag_2NiO_2. The crystallographic unit cell is indicated by the dashed line.

layer and NiO_2 plane (d_{Ag-NiO}). The definitions of d_{Ni-O} and d_{Ag-NiO} are shown in figure 4. As T decreases from 330 K, the a_H-axis length decreases almost in proportion to T, but the slope changes slightly at T_S. On the other hand, the c_H-axis length decreases monotonically with decreasing T above T_S, and then suddenly increases by about 0.01 nm between 270 and 250 K and finally levels off to about 2.4108 nm below 230 K. Interestingly, V_H decreases linearly with T without changes at T_S, suggesting a lack of drastic change in the electronic state. This means that T_S is most unlikely to be caused by a spin state transition of Ni^{3+} ions, because a spin state transition would change d_{Ni-O} due to a rearrangement of the electron configuration of Ni^{3+} ions.

Indeed, d_{Ni-O} also decreases monotonically with decreasing T in the whole T range measured. However, the slope of the d_{Ag-NiO} (T) curve changes at T_S, accompanying the abrupt change in the c_H (T) curve. The essential change at T_S is thus found to be the sudden increase in the c_H axis at T_S with decreasing T. In order to explain the present result, it is reasonable to assume that a local Jahn–Teller (JT) distortion appears at T_S. That is, due to the electron configuration of $t_{2g}^6 e_g^1$ of the Ni^{3+} ions, two of the six Ni–O bond lengths in the NiO_6 octahedron increase while the other four decrease at T_S, in order to keep the average d_{Ni-O} constant. Since there is currently no report on the change in crystal symmetry at T_S [8, 9], in contrast to $NaNiO_2$ [3–5], the JT distortion is thought to be not cooperative but local/short range in nature. The distorted NiO_6 octahedra are considered to increase the effective thickness of the NiO_2 plane, resulting in the increase of the c_H-axis length. In order to confirm this assumption, it is necessary to measure the XRD pattern preferably using synchrotron radiation as a function of T, and such work is in progress.

4. Summary

According to a neutron powder diffraction experiment, the formation of long-range antiferromagnetic (AF) order is confirmed for Ag_2NiO_2 below $T_N = 56$ K. Although the spin structure is still unknown, the result looks consistent with muon-spin spectroscopy measurement; that is, the appearance of the static incommensurate AF order below T_N in the NiO_2 plane. This suggests that the half-filled two-dimensional triangular lattice of the NiO_2 plane is the AF coupled frustrated system.

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