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Neutron Diffraction Studies of Magnetic Structures on Mn Formate Di-Urea Single Crystal

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We have performed neutron diffraction experiments of magnetic structures on a partially deutrated manganese formate di-urea single crystal, $Mn(HCOO)_2{\cdot}2(ND_2)_2CO$. In the ($hhl$) type reflections, the magnetic reflections appear for h = odd, while in the ($h0l$) type reflections, no magnetic reflection is observed. The model of the magnetic structure is discussed on the basis of structure factors from Mn atoms and the magnetic scattering vector is determined to be $\boldsymbol{Q}$ =(110).

KEYWORDS: Mn formate di-urea, spin structure, neutron diffraction

§1. Introduction

Manganese formate di-urea, $Mn(HCOO)_2{\cdot}2(NH_2)_2CO$, is a compound derived from Mn formate di-hydrate $Mn(HCOO)_2{\cdot}2H_2O$ by replacing water molecules with urea, $2(NH_2)_2CO$.[1)] This compound belongs to tetragonal $P4_12_12$. The magnetic Mn ions form a two dimensional layer along the c-axis and are essentially arranged in the K_2NiF_4 type structure.[2)]

Magnetization measurements of this material exhibit an antiferromagnetic order below a Néel temperature of $T_N = 3.8$ K.[3)] Though a spin configuration in the K_2NiF_4 type structure is usually considered to be a simple antiferromagnetic order, the a- and c-axes are neither an easy axis nor a hard axis. The magnetization process of this compound along the c-axis shows three magnetic transitions at low temperatures.[4)] These curious results suggest that the spin arrangement of this compound is not a simple antiferromagnet but a complicated one.

Recently, Kubo *et al.*[5)] performed proton NMR measurements and showed that the antiferromagnetic moments of Mn ions point to the direction which is rotated by 15 degrees around the c-axis from the middle direction between the [001] and [$\bar{1}$00] directions. The details of the spin structure are not clear yet because it is difficult to realize the stability of this curious spin arrangement described above from the standpoint of the crystal structure. To determine the magnetic structures of Mn ions directly and compare with the results of proton NMR by Kubo *et al.*, we have carried out neutron diffraction measurements on the manganese formate di-urea single crystal.

§2. Experimental

In this experiment, the partially deutrated specimen, in which the hydrogen atoms of the urea, $(NH_2)_2CO$ were replaced by deuterium atoms, was used. Neutron diffraction measurements were carried out in a double-axis mode with the triple axis spectrometer, HQR installed at the JRR-3M of Japan Atmic Energy Research Institute (JAERI), and also the KUR-TAS at the Kyoto University Reactor, using incident neutrons of 2.458 and of 1.006 Å, respectively. The data were collected in the temperature range form 1.5 K to 7.0 K for the ($h0l$) and (hhl) type reflections.

§3. Results and Discussion

Neutron diffraction patterns scanning along the l direction around the ($h0l$) type reflections with h = 0, 1 and 2 at 1.5 K and 7.0 K, give no magnetic reflections. This indicates that the magnetic scattering vector $\boldsymbol{Q}$ does not exist in the ($h0l$) plane. The spin arrangement estimated from proton NMR measurements[5)] suggests that no magnetic scattering vector in the ($h0l$) plane could be observed, and is consistent with these results.

The magnetic reflections are observed for scanning along the l direction around the ($11l$) type reflections at the position where l is an integer, as shown in Fig. 1. However, no magnetic reflection is observed for h = 2. Similarly, there exist no magnetic reflections for h = 0, but exist magnetic reflections for h = 3. That is, magnetic reflections appear only where h is an odd number in the (hhl) plane. The observed nuclear and magentic reflections in the (hhl) reciprocal plane are schematically represented in Fig. 2.

Figure 3 shows the temperature dependence of the ($11l$) reflections, where l = 0, 1, 2 and 3. The Néel temperature T_N is about 4.2 K and agrees with the magnetization measurements obtained by Takeda *et al.*[3)] Around the transition temperature of T_N, the magnetic peak intensities of the (110) and (102) reflections convexly decrease with rising temperature. On the contrary, the magnetic peak intensities on the (111) and (113) reflections decrease almost linearly with rising temperature. The different temperature variation between l=odd and

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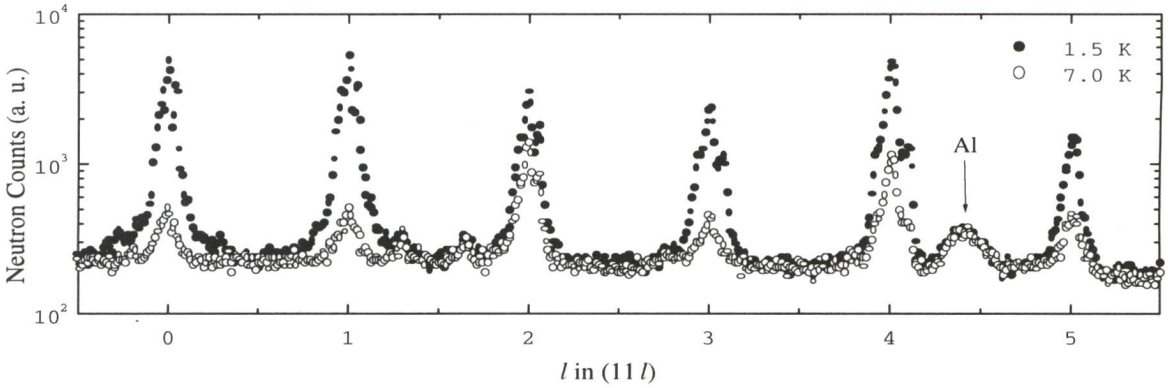

Fig. 1. Neutron diffraction patterns scanning along the c^*-direction for the (11l) type reflections at 1.5 and 7.0 K. Solid and open circles show the magnetic reflections at 1.5 K and the nuclear ones at 7.0 K, respectively.

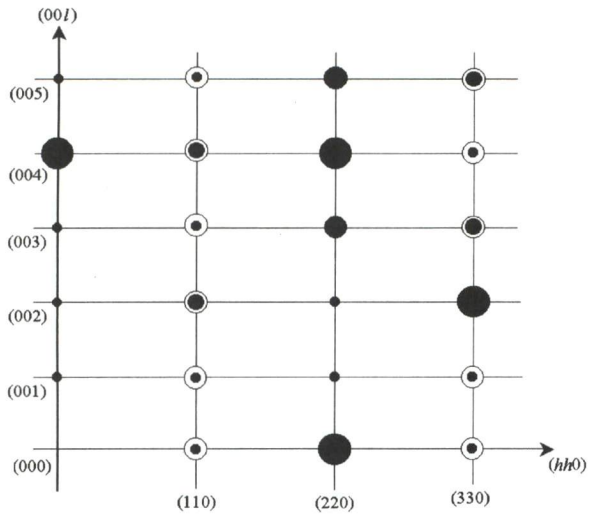

Fig. 2. The observed nuclear and magentic reflections in the (hhl) reciprocal phane. Solid and open circles show the nuclear reflections at 7.0 K and the magnetic ones at 1.5 K, respectively. The magnitudes of the intensities are roughly indicated by the radius in a logarithmic scale. The observed nuclear intensities contain scattering from Mn and all other atoms.

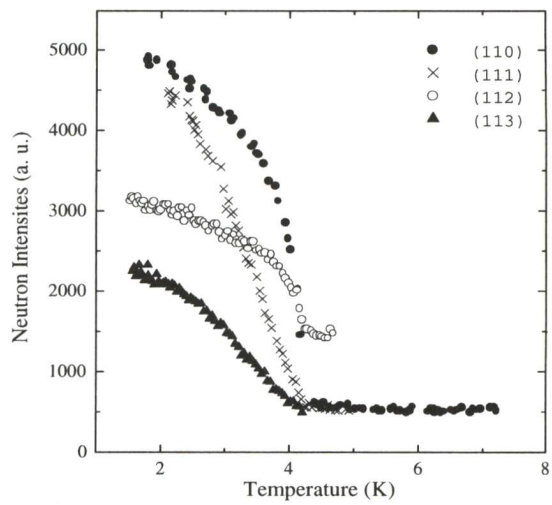

Fig. 3. Temperature dependence of the (11l) reflections of l = 0, 1, 2 and 3.

l=even suggests an effect of the two dimensional arrangement of Mn atoms, and/or a rotation of magnetic moments with temperature.

Since the magnetic reflections stem from the structure factors of Mn atoms, the calculated nuclear structure factors of Mn atoms in the (hhl) type reflections are illustrated in Fig. 4. The strong nuclear reflections from Mn atoms are located only where h is even in the (hhl) plane. This fact shows that the strong magnetic reflections for (11l) appear from (00l) and (22l) reflections. The distribution of the obtained magnetic intensities can be easily presumed from the intensities of Mn structure factors. For example, the weak (112) magnetic reflection arises from no (002) and the very weak (222) Mn structure factors. On the other hand, the strong (114) magnetic reflection comes from the strong (004) and (224) Mn structure factors. The reason why no magnetic reflection in the (332) plane is apparently observed is due to the extremely weak (222) and (442) Mn structure factors. Thus, the magnetic scattering vector of Mn ions obtained in this experiment is $\boldsymbol{Q}$ = (110).

From the spin arrangement by Kubo *et al*, the antiferromagnetic moments of Mn ions within the layer point to the direction which is rotated by 15 degrees around the c-axis from the middle direction between the [001] and [$\bar{1}$00] directions. These moments form a quasi-two-dimensional antiferromagnetic order within the layer and piled up following to the stacking along the four-fold screw axis.

To determine the rotation angle of the spin arrange-

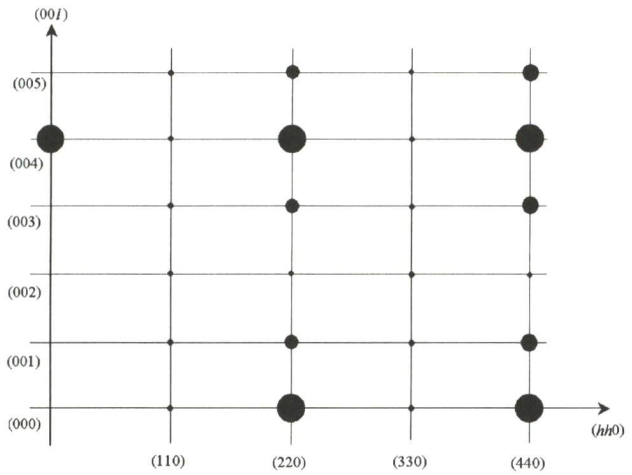

Fig. 4. The calculated nuclear structure factors of Mn atoms only in the (hhl) type reflections. The strcuture factors are roughly indicated by the radius in a logarithmic scale. The structure factors for h=odd are extremely weak.

ment of Mn ions by neutron diffraction experiments, the accurate evaluation of the magnetic intensities is required. More detailed studies are needed to clarify the spin structure on the manganese formate di-urea single crystal, and are now in progress.

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