Neutron scattering studies of a frustrated spinel antiferromagnet in zero and high magnetic field

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Abstract. A review is given of the neutron scattering studies on a frustrated spinel antiferromagnet CdCr$_2$O$_4$. As observed in ZnCr$_2$O$_4$, which has been most extensively studied in the Cr-based spinel oxides, CdCr$_2$O$_4$ also shows an antiferromagnetic phase transition and a structural phase transition simultaneously, indicating a strong spin-lattice coupling. The magnetic structure of CdCr$_2$O$_4$ was determined by neutron scattering studies. The neutron scattering study in magnetic field up to 10 T indicates an orientation of magnetic domains.

1. Introduction
The ground states of the Cr-based spinel oxides ACr$_2$O$_4$ (A=Mg, Zn, Cd and Hg) are attracting much attention because of its strong magnetic frustration between the Cr$^{3+}$ moments with $S=\frac{3}{2}$ forming a network of corner-sharing tetrahedra [1, 2, 3, 4, 5], as shown in Fig. 3. The system is well described by an almost isotropic (Heisenberg) spin Hamiltonian with dominant antiferromagnetic nearest-neighbor interaction. Since all of the three $t_{2g}$ states are occupied by three electrons of the Cr$^{3+}$ ion, there is no freedom of orbitals. Therefore, Jahn-Teller distortion is not expected in this compound, which makes a magnetic frustration significant down to low temperatures. It has been shown theoretically that the spins on such a pyrochlore lattice cannot order even at zero temperature [6, 7, 8, 9]. Consequently ACr$_2$O$_4$ remains paramagnetic to temperatures far below the Curie-Weiss temperature -390 K, -88 K and -32 K for A=Zn [10], Cd [5, 11, 12] and Hg [13], respectively. The real system, however, undergoes a first order spin Peierls-like phase transition from a cubic paramagnetic phase to a tetragonal Néel state upon further cooling. This strong spin-lattice coupling is most characteristic in this system.

Another interesting feature in ACr$_2$O$_4$ is the magnetic properties in magnetic field. It was reported that CdCr$_2$O$_4$ and HgCr$_2$O$_4$ show a half magnetization plateau state in a wide magnetic field [12, 13]. Theoretical studies predict that stabilization of the plateau state originates from the strong spin-lattice coupling [14, 15, 16].

2. Experimental Details
Single crystals, which have a shape of thin plate and weigh ~100 mg, were used. Since natural Cd has a large neutron absorption cross section, single crystals enriched with $^{114}$Cd were used.

The neutron elastic scattering experiments were carried out on the thermal neutron three-axis spectrometers TAS-2 installed at JRR-3 at Japan Atomic Energy Agency (JAEA) and on the cold neutron three-axis spectrometers SPINS installed at National Institute of Standards.
Figure 1. (Color online) (a) Crystal structure of spinels $\text{ACr}_2\text{O}_4$ ($\text{A}=\text{Mg}, \text{Zn}, \text{Cd}$ and $\text{Hg}$). (b) The $\text{Cr}^{3+}$ moments with $S=3/2$ form a three-dimensional network of corner-sharing tetrahedra.

Figure 2. (Color online) (a) The observed pattern of the magnetic Bragg reflections in the scattering plane in $\text{CdCr}_2\text{O}_4$. (b) The observed reflections are decomposed into three groups depending on the direction of the $c$ axis. The central peaks of the triplets are tails of the doublets that are present above and below the scattering plane. Therefore, the quadruplets are always in the $ab$ plane.

and Technology (NIST). Contamination from higher-order beams is effectively eliminated using PG filter at TAS-2 and Be filter at SPINS. The neutron scattering experiments in magnetic field were performed on TAS-2, using a split-pair superconducting magnet, which is cooled by cryocoolers and can reach fields up to 10 T.

3. Magnetic Structure in Zero Magnetic Field

$\text{ZnCr}_2\text{O}_4$ has been investigated most intensively in the spinels $\text{ACr}_2\text{O}_4$ [1, 3, 4]. There occurs a cubic-to-tetragonal transition at $T_N=12.5$ K with the $c$ axis contracted. Although characteristic spin fluctuations above $T_N$ is well understood [3, 4], it is difficult to clarify the ground state in these compounds uniquely since the magnetic structure shows a multiple $Q$ structure with characteristic wave vectors, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, 1)$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(0, 0, 1)$ and the relative neutron
Figure 3. (Color online) Possible spin structures of CdCr$_2$O$_4$ proposed in Ref. [18]. The magnetic structures are spiral in the $ac$ plane with a modulation vector along the $b$ axis. (a) and (b) represent orthogonal and collinear stacks along the $c$ axis, respectively. After Chung et al. [18].

scattering intensities of these wave vectors are sample dependent [17].

A neutron diffraction study was performed in CdCr$_2$O$_4$ [18]. It was found that the lattice elongates along the $c$ axis and an incommensurate Néel order appears at $T_N=T_{st}=7.8$ K. The high $Q$ resolution data indicate that the incommensurate magnetic structure has a single characteristic wave vector of $Q_M=(0, \delta, 1)$ with the incommensurability $\delta \sim 0.09$ perpendicular to the unique $c$ axis. Thus, the magnetic structure in ACr$_2$O$_4$ depends on the nonmagnetic elements at A site, which change lattice constants and also oxygen sites. This probably indicates that although the dominant interaction in ACr$_2$O$_4$ is the nearest-neighbor antiferromagnetic interaction through the direct overlap, further neighbor interactions, which are much smaller than the nearest-neighbor interaction, play an important role to select the magnetic ground state.

Below $T_N=7.8$ K, the crystal structure becomes tetragonal. In the tetragonal phase, there are three crystallographic domains so that $(hk0)$, $(h0l)$, and $(0kl)$ zones can be observed in the same scattering plane. Figure 2 indicates schematically the incommensurate magnetic peak positions observed in CdCr$_2$O$_4$ [18]. Since there exist three crystallographic and two magnetic $k$-domains, in which incommensurate vectors are different, there are six magnetic domains in total. The magnetic Bragg peaks with $Q_M=(0, \delta, 1)$, $(\delta, 0, 1)$, $(0, 1, \delta)$, $(1, 0, \delta)$, $(1, \delta, 0)$, and $(\delta, 1, 0)$ with $\delta \sim 0.09$ from the six magnetic domains are observed in one scattering plane as show in Fig. 2(a). The observed reflections are decomposed into three groups depending on the direction of the $c$ axis as shown in Fig. 2(b). There are two kinds of incommensurate peak structures, triplet and quadruplet. The quadruplet originates from the scattering in the $(hk0)$ plane. Since $h$ and $k$ are equivalent in the tetragonal phase, the modulation vector can go along both the $a$ and $b$ axes. On the other hand, the triplet originates from the scattering in the $(h0l)$ and $(0kl)$ plane with the $c$ axis in the scattering plane and also perpendicular to the direction along which the three peaks form a line. The central peak does not come from the scattering intensity at the commensurate position in the scattering plane but that at incommensurate positions above and below the scattering plane. The scattering intensity is not so small because the poor $Q$ resolution perpendicular to the scattering plane integrates the two peaks.
In order to understand the magnetic properties in more details, we performed neutron diffraction technique. The present experiments were performed in order to check what goes on the plateau state is extremely important, the magnetic field is difficult to reach with neutron diffraction technique \[18\]. The results show two magnetic excitation modes. Model calculations based on the two magnetic structure models indicate that two and three excitation modes are expected for the models with orthogonal and collinear stacks, respectively. Therefore, a spiral spin order with the orthogonal stack along the \(c\) axis is more likely. As reported in Ref. \[18\], nearest-neighbor direct interactions are dominant in \(\text{CdCr}_2\text{O}_4\). The interactions are estimated to be \(J_{ab} \sim 1.2\) meV and \(J_c \sim 1\) meV. However, the simple model assuming only \(J_{ab}\) and \(J_c\) can give incommensurability along (110) not (010). This suggests that further-neighbor interactions should be taken into consideration.

4. Orientation of Magnetic Domains in Magnetic Field

In order to understand the magnetic properties in more details, we performed neutron diffraction measurements under magnetic field \[19\]. It is reported that \(\text{CdCr}_2\text{O}_4\) shows a half-magnetization plateau above \(\sim 28\) T \[12\]. Although to clarify the magnetic structure and crystal distortion in the plateau state is extremely important, the magnetic field is difficult to reach with neutron diffraction technique. The present experiments were performed in order to check what goes on below the transition field. Figure 4 shows the incommensurate magnetic Bragg peak profiles as a function of magnetic field at 5.5 K. In Fig. 4(a) magnetic field is applied along the \(a\) or \(b\) axis. The intensity at the central peak of the triplet grows with increasing magnetic field while that at the incommensurate peaks disappears. On the other hand, in Fig. 4(b), magnetic field is applied along the \(c\) axis. The intensity at the quadruplet decreases with increasing magnetic field. The other two peaks at the quadruplet also show the same behavior.

The magnetic field dependence of the magnetic peak intensity at 5.5 K is shown in Fig.
almost constant up to 5. With increasing magnetic field, the intensity of the incommensurate peaks at the triplet is increasing by a factor of 3. On the other hand, with decreasing field, the intensity stays to zero down to 0 T, indicating a large hysteresis behavior.

The intensity at the central peak increases by a factor of ~4 and also shows a large hysteresis. The increase in intensity of the central peak of the triplet can originate from the two things as follows. One is increase in incommensurate peaks above and below the scattering plane, indicating an orientation of the magnetic domains. Other is increase in the commensurate peak in the scattering plane, indicating an incommensurate-to-commensurate transition. In order to check whether the central peak originates from the commensurate peak or incommensurate peaks above and below the scattering plane, we performed measurements changing vertical $Q$-resolution. The vertical $Q$-resolution was adjusted by changing slit sizes before and after the sample. The slit sizes are 30 mm and 6.5 mm in Figs. 4(a) and 6, respectively. One recognizes that the relative intensity of the central peak compared to the side peaks is much weaker at 0 T and quickly disappears around 2.5 T. On the other hand, with increasing field, the intensity stays to zero down to 0 T, indicating a large hysteresis behavior. The intensity at the central peak increases by a factor of ~4 and also shows a large hysteresis.

5. With increasing magnetic field, the intensity of the incommensurate peaks at the triplet is almost constant up to ~1.5 T and quickly disappears around 2.5 T. On the other hand, with decreasing field, the intensity stays to zero down to 0 T, indicating a large hysteresis behavior. The intensity at the central peak increases by a factor of ~4 and also shows a large hysteresis.

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Figure 5. Magnetic field dependence of the peak intensity at (0, 1.91, 1), (0, 2, 0), and (1.09, 1, 0) magnetic Bragg reflections at 5.5 K. Filled and open circles represent that the data measured when the field is increasing and decreasing, respectively. After Matsuda et al. [19].

Figure 6. Incommensurate magnetic Bragg peaks around (0, 2, 1) at 5.5 K. The effective $Q$ resolution perpendicular to the scattering plane is better in these scans than in those shown in Fig. 4.
magnetic fields. Therefore, applying magnetic field along the \( a \) axis, intensity at \((0, 2\pm\delta, 1)\) disappears and intensity at \((2\pm\delta, 0, 1)\) develops. This behavior suggests an orientation of the magnetic domains with applying magnetic field along the \( a \) axis. The magnetic domains with spins perpendicular to the magnetic field grow and others disappear. This orientation of the magnetic domains can be considered as a kind of spin-flop transition since the spin direction in one magnetic domain changes by 90° perpendicular to the magnetic field without changing relative spin structure. The magnetic field to orientate the magnetic domain is \( \sim 2 \) T (\( \sim 0.4 \) meV), which corresponds to a spin-flop field. This energy scale is reasonable because the anisotropy gap of spin wave excitations at the zone center, which was observed in inelastic neutron scattering study \[18\], is \( \sim 0.5 \) meV.

The intensity at the quadruplet decreases monotonically with increasing magnetic field and disappears around 7 T as shown in Fig. 5(c). With decreasing field, the magnetic intensity recovers up to \( \sim 70\% \) of the initial value. This behavior is quite different from that in triplets with magnetic field along \( a \) or \( b \) axis. However, this is also considered to correspond to the orientation of the magnetic domains as follows. When the magnetic field is applied along the \( c \) axis, which is in the spin easy plane, it is unlikely that the the magnetic domains orientate. Only when the magnetic field changes the crystal structure, that is, the magnetic field along the \( c \) axis switches the \( c \) axis to the \( a \) or \( b \) axis, the magnetic domains can orientate. In this case all the peaks at quadruplet disappear in magnetic field. Since the magnetic field to eliminate the quadruplet magnetic peaks is \( \sim 5 \) T (\( \sim 0.9 \) meV) larger than that to eliminate the triplet peaks, it probably corresponds to a characteristic energy to cause a structural change. Our preliminary neutron diffraction study with high-\( Q \) resolution suggests that magnetic field along the \( c \) axis switches the \( c \) axis to the \( a \) or \( b \) axes. It is noted that recent x-ray measurements in magnetic field showed an orientation of the magnetic domains at 2-4 T, which is consistent with our results, and also showed a structural change above 28 T in the half-magnetization plateau state \[20\].

In summary, neutron scattering study under magnetic field below the half-magnetization plateau state in \( \text{CdCr}_2\text{O}_4 \) shows that the magnetic domains reorientate. Interestingly, an orientation of structural domains may be driven in a fairly small magnetic field of \( \sim 5 \) T when the magnetic field is applied along the \( c \) axis, indicative of a strong spin-lattice coupling. Magnetic field does not affect incommensurability of the spiral structure at all up to 10 T.

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