Magnetization Process of Geometrically Frustrated Spinel Oxide up to an Ultra-high Magnetic Field

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Abstract. We conducted precise magneto-optical Faraday rotation measurements in CdCr$_2$O$_4$ and ZnCr$_2$O$_4$ up to ultra-high magnetic fields using methods of the single turn coil (up to 190 T) and also the electro-magnetic flux compression (up to 360 T). In CdCr$_2$O$_4$, we have succeeded in observation of the full magnetization process. In ZnCr$_2$O$_4$, we observed magnetization process up to 2.7 $\mu_B$ (the full moment is 3.0 $\mu_B$). The magnetization processes of both materials were well described by a 4 sub-lattice Heisenberg-spin model including spin-lattice interactions.

1. Introduction
A real geometrically frustrated magnet possessing a macroscopically degenerated ground state (a spin liquid) has been explored over the last several decades. Although many frustrated spin systems have been found, most of them at a low temperature do not show a spin liquid state but an ordered state. This is because the macroscopically degenerated state is metastable and the perturbations (lattice distortions, quantum fluctuations, etc) lift the degeneracy in order to reduce the frustration. A frustrated state is very sensitive to any type of perturbations. It is expected that such a frustrated system will show a variety of phases depending on the temperature and the magnetic field[1].

To understand the essence of the physics of geometrically frustrated spin systems, it is very important to investigate the magnetic phases in magnetic fields up to the full saturation of magnetic moments in a simple real system and compare the observed magnetic properties with those of theoretical models. Chromium spinel oxides (CdCr$_2$O$_4$, ZnCr$_2$O$_4$) in which Cr$^{3+}$ ions form a pyrochlore lattice are prototypes of geometrically frustrated antiferromagnets. Those systems are ideal for studying geometrical frustration in that they have the following characteristics: 1) A strong geometrical frustration. $T_N \ll \Theta_{CW}$ where $\Theta_{CW}$ and $T_N$ show the Curie-Weiss temperature (-70 K in CdCr$_2$O$_4$ and -390 K in ZnCr$_2$O$_4$) and the Neel temperature (7.8 K in CdCr$_2$O$_4$ and 12 K in ZnCr$_2$O$_4$), respectively[2]. 2) A lack of an orbital degree of freedom (a feature for the Cr$^{3+}$ ion in cubic symmetry). Therefore, the systems behave like a typical Heisenberg spin system and the Jahn-Teller effect is elucidated. 3) Their exchange energy $J$ estimated from $\Theta_{CW}$ is relatively large (0.8 meV in CdCr$_2$O$_4$ and 4.5 meV in ZnCr$_2$O$_4$). Due to 2) and 3) described above, the systems are described by simplified model Hamiltonians with a small number of terms.
It is known that lattice distortions occur synchronously with antiferromagnetic (AF) ordering in those systems [3]. It is thought that spin-lattice interactions reduce strong geometrical frustration and lift the macroscopic degeneracy.

Ueda et al. reported magnetization measurements of CdCr_2O_4 in magnetic fields up to 50 T generated by a long pulse magnet [2]. They found a first-order phase transition at 28 T followed by a wide magnetization plateau with a half-of-full moment (1/2 plateau). They considered that spins form a 3-up 1-down collinear configuration (3:1) in the 1/2 plateau state. Their magnetostriction data showed that lattice distortion takes place in association with the first-order phase transition. Recently, Mitamura et al. performed the magnetization measurement in magnetic fields up to 80 T at 6 K by the induction method [4]. They have reported a second order phase transition at 61 T and a first order phase transition at 77 T. HgCr_2O_4 is also one of chromium spinel oxides. Total magnetization process of HgCr_2O_4 up to 50 T has already been observed by an induction method [5]. Ueda et al. also reported magnetization measurements of ZnCr_2O_4 in magnetic fields up to 50 T [2]. No phase transition is observed in the magnetic field up to 50 T.

Penc et al. calculated the magnetization process of a pyrochlore spin system under a high magnetic field based on a theoretical model that included spin-lattice interaction [6]. They simplified the model Hamiltonian and derived an effective Hamiltonian with biquadratic-bilinear terms $H = \sum_{i<j} J [\mathbf{S}_i \cdot \mathbf{S}_j - b (\mathbf{S}_i \cdot \mathbf{S}_j)^2] - \mathbf{h} \cdot \sum_i \mathbf{S}_i$ ($b$ is a biquadratic term coefficient which reflects the strength of the spin-lattice coupling.). By solving the model Hamiltonian, they calculated magnetization processes and reproduced the 1/2 magnetization plateau with the 3-up 1-down collinear spin configuration. A classical Monte-Carlo simulation has been extended to a finite temperature by Motome et al., and a detailed phase diagram and high-field magnetization process were predicted for the same system [7].

On the other hand, recent theoretical reports (D.L. Bergman et al. [8] or J. Schulenburg et al. [9]) suggested that new phenomena related to Bose-Einstein condensations of magnons (a quantum jump) could occur in geometrically frustrated antiferromagnets in the vicinity of the full moment saturation. In order to justify these theories, an experimental study of magnetization process up to a full moment saturation in CdCr_2O_4 and ZnCr_2O_4 has been strongly desired.

A fairly large antiferromagnetically coupled exchange $J$ in those systems requires an ultrahigh magnetic field over 100 T for achieving a full moment saturation in the total magnetization process. However, direct magnetization measurements using the induction method are extremely difficult in such extreme conditions like a 100 Tesla region accompanied with noisy environments. The method has been successful only to the materials with sufficiently large absolute value of magnetization [10-11]. Therefore, we adopted a magneto-optical Faraday rotation method as a magnetization probe. This method has been employed for studies of the magnetic properties of materials under ultra-high magnetic fields [12].

In this work, we measured the magnetization processes of geometrically frustrated chromium spinel oxides CdCr_2O_4 and ZnCr_2O_4 using a Faraday rotation method up to ultra-high magnetic fields and systematically compared the magnetic properties of them with the theoretical model.

2. Experimental methods
In the Faraday rotation measurements under the ultrahigh-magnetic fields of up to 190 T, a single-turn coil method was used to generate fields. As higher fields were required to observe the full magnetization process of ZnCr_2O_4, an electro-magnetic flux compression (EMFC) method was used to generate magnetic fields of up to 360 T. The magnetic field was measured by means of a calibrated pick-up coil wound near the sample. The field measurement error was ±3 %. A semiconductor laser (a Coherent “Cube”) having a central wavelength of 635 nm and a He-Ne laser (632.8 nm) were used as light sources. A Faraday rotation measurement was performed using a similar method shown in [12].

The detection limit of $\frac{d\theta_f}{dB}$ ($\theta_f$ shows a Faraday rotation angle) was 0.1 deg/T. The samples were
single crystals of CdCr$_2$O$_4$ and ZnCr$_2$O$_4$ grown using the flux method. The sample was cut parallel to the (111) crystal surface. In order to ensure an adequate light intensity, the sample thickness was adjusted to an optical density of about 1 because of the limited exposure time (~μs) for the optical detection in the short pulse fields. The adjusted sample thicknesses were about 40 μm in CdCr$_2$O$_4$ and about 50 μm in ZnCr$_2$O$_4$, respectively. The magnetic field was applied to the [111] direction. The samples were cooled in a handmade plastic cryostat of a liquid He flow type. The sample temperature was monitored using an Au-Fe/Chromel thermocouple with an accuracy of +1 and -2 K.

3. Results and Discussion

3.1. CdCr$_2$O$_4$

$\theta_F$'s of CdCr$_2$O$_4$ at various temperatures are plotted by the solid lines in figure 1(a). A diamagnetic component which is often observed in the high field region[13] is subtracted from the raw data. The $\theta_F$ are well proportional to $M$ up to 50 T[14]. We converted the $\theta_F$ (the right axis in figure 1(a)) to magnetization $M$ (the left axis in figure 1(b)) using the proportionality between $\theta_F$ and $M$. A dotted line in figure 1(a) shows a calculated magnetization curve by Penc et al.[6] when the biquadratic term coefficient “$b$” is chosen as 0.08. Symbols (circles, diamonds, and triangles) show the points of phase transitions.

![Figure 1](image_url)

**Figure 1.** (a) Solid lines: Magnetization processes of CdCr$_2$O$_4$ at various temperatures measured by Faraday rotation methods. Lines at 9 K and 11 K are vertically shifted for clarity. Dotted line: A calculated magnetization curve by Penc et al. (taken from [6]). Symbols show points of phase transitions. (b) A phase diagram of CdCr$_2$O$_4$. Open squares are taken from [2].

The general features of magnetization processes and the critical fields in figure 1(a) are in close agreement with those calculated by Penc et al. and also by Motome et al.[7]. Their calculations predict that a coplanar canted 3:1 phase(Cant 3:1) and a moment-saturated phase(Ferro) should appear in higher fields than 3:1 phase.

The $\theta_F$ at 5 K between 62 T and 95 T behaves similarly to Cant 3:1 phase. The region above 95 T should be Ferro phase since the moment is fully saturated. The $\theta_F$ at 9 K show almost the same
behavior as that at 5 K. However, the position of the triangle shifts to a lower magnetic field by about 10 T, while that of the diamond remains almost the same. That of circle shows a very weak low field shift. There observed a drastic change in $\theta_e$ between 9 K and 11 K. At 11 K, $\theta_e$ at critical fields is smeared out due to thermal effects. These behaviors of the magnetization process shown in figure 1(a) are similar to those of $M$ calculated by Motome et al.[7].

A $dM/dB$ measured up to 80 T recently conducted by the induction method[4] showed a very similar behavior to ours except the region of the highest magnetic field, where the induction method loses its sensitivity.

Figure 1(b) shows a phase diagram of CdCr$_2$O$_4$. The magnetization measurements by Ueda et al. using a long pulse magnet up to 50 T [2] showed the AF-3:1 phase boundary that exhibited a very weak but a finite low field shift on increasing temperature, which is well reproduced. The temperature dependence of the 3:1-Cant 3:1 phase boundary is also weak, and 3:1 phase stably exists between 28 T and 62 T below 9 K. On the other hand, the Cant 3:1-Ferro phase boundary shows a clear low field shift on increasing temperature. These are resulted from the fact that collinear spin configurations (like 3:1 phase) is more robust against thermal fluctuations than non-collinear spin configurations (like Cant 3:1) as predicted by Motome et al.[7]. The Para-3:1 phase boundary as well as the Para-Cant 3:1 phase boundary is hardly identified due to the limitation of our measurement.

3.2. ZnCr$_2$O$_4$

$\theta_e$ s of ZnCr$_2$O$_4$ at various temperatures are plotted by the solid lines in figure 2(a). The left axis shows $M$ converted from $\theta_e$ in the right axis. The $\theta_e$ s at 9 K and 14 K are measured in the single turn coil system and the $\theta_e$ at 17 K is measured in the EMFC system. Symbols show the points of phase transitions. At 9 K, we observed a discontinuous jump of $\theta_e$ at 120 T, a linear increase between 120 T and 135 T, a plateau between 135 T and 158 T, and an increase above 158 T. The phase of linear increase of $M$ between 120 T and 135 T is peculiar to ZnCr$_2$O$_4$, and there observed no corresponding phase in CdCr$_2$O$_4$.

A dotted line in figure 2(a) show a calculated magnetization curve by Penc et al.[6] when the biquadratic term coefficient “$b$” is chosen as 0.03. The calculated magnetization process well reproduces the measured one at 9 K. According to the model calculation, the system makes a first order phase transition into state with a coplanar 2:1:1 canted state(Cant 2:1:1) when $b < 0.05$. The region between 120 T and 135 T is considered to be Cant 2:1:1 phase. The observed plateau region between 135 T and 158 T with a half of full magnetization moment is considered to be 3:1 phase which is also observed in CdCr$_2$O$_4$. The region above 158 T is considered to be Cant 3:1 phase. The magnetization curve at 14 K is quite different from 9 K. The curve at 14 K is smooth due to thermal effects. However, some singularities which show phase transitions are still observable at 108 T and at 158 T.

We successfully observed the magnetization process up to 360 T at 17 K using an EMFC system. The magnetization reaches 2.7 $\mu_B$ at 360 T, which is very near the full moment (3.0 $\mu_B$). The phase transitions at 108 T and at 160 T are observed. In the region above 160 T, any phase transitions are not observed.

The phase between 108 T and 160 T at 17 K exists in the wider field range than the Cant 2:1:1 phase at 9 K. The state with a non-collinear spin configuration(Cant 2:1:1) is less robust against the thermal fluctuations than that with a collinear spin configuration(3:1 phase), and the region of the phase with a non-collinear spin state becomes narrow with increasing temperature as discussed in the section 3.1. Therefore, we think that the region between 108 T and 160 T is 3:1 phase not Cant 2:1:1 phase. 3:1 phase at 17 K exists in a wider field range than that at 9 K, which shows 3:1 phase is more stabilized by “the order-from-disorder effect” due to thermal fluctuations[15-16]. As Cant 3:1 phase is non-collinear magnetic phase, it is much less stable at high temperatures than 3:1 phase according to the theory[7]. It is not clear at present that the region above 160 T at 17 K belongs to Cant 3:1 phase or Para phase. The phase diagram of ZnCr$_2$O$_4$ based on the discussion above is summarized in figure 2(b).
Figure 2. (a) Solid lines: Magnetization processes of ZnCr$_2$O$_4$ at various temperatures measured by Faraday rotation methods. The $\theta_s$ at 9 K and 14 K are measured in the single turn coil system and the $\theta_s$ at 17 K is measured in the EMFC system. These are vertically shifted for comparison. Dotted line: A calculated magnetization curve by Penc et al. (taken from [6]). Symbols show points of phase transitions. (b) A phase diagram of ZnCr$_2$O$_4$. An open square is taken from [2].

3.3. Comparison among chromium spinel oxides (CdCr$_2$O$_4$, ZnCr$_2$O$_4$, HgCr$_2$O$_4$)

Our observed experimental results in CdCr$_2$O$_4$ and ZnCr$_2$O$_4$ are well explained by the theoretical model of Penc et al. [6] when we assume that the coefficient “$b$” of the bi-quadratic term “$b (S_i \cdot S_j)^2$” in each material holds the relation $b_{ZnCr_2O_4} < b_{CdCr_2O_4}$. In our previous publication, we reported that the “$b$” in CdCr$_2$O$_4$ and that in HgCr$_2$O$_4$ hold the relation $b_{CdCr_2O_4} < b_{HgCr_2O_4}$ [14]. Therefore, we obtained the relation of “$b$” among the chromium spinel oxides $b_{ZnCr_2O_4} << b_{CdCr_2O_4} < b_{HgCr_2O_4}$, which show the differences of the spin-lattice interaction among those materials.

The magnetization process and the phase diagram of CdCr$_2$O$_4$ in figure 1(b) are similar to those of HgCr$_2$O$_4$ in [5]. However, those of ZnCr$_2$O$_4$ are obviously different from those of two other materials. There are two major differences. One is that the cant 2:1:1 phase is observed in ZnCr$_2$O$_4$ but not in CdCr$_2$O$_4$ or in HgCr$_2$O$_4$. The other is that the existence field range of 3:1 phase in ZnCr$_2$O$_4$ becomes noticeably wider on increasing temperature. Neither of two other materials shows the same tendency. This fact means that ZnCr$_2$O$_4$ shows much stronger “order-from-disorder effect” than others. This is probably because the macroscopic degeneracy in ZnCr$_2$O$_4$ due to the geometrical frustration is not completely lifted by lattice distortions and it partially remains and the thermal fluctuations lift the remaining degeneracy.

4. Summary

In summary, we investigated the magnetic properties of geometrically frustrated CdCr$_2$O$_4$ and ZnCr$_2$O$_4$ under an ultrahigh magnetic field through the use of a high-resolution Faraday rotation measurement. In CdCr$_2$O$_4$, we observed the two phases, Cant 3:1 phase and Ferro phase in the high-field region above 60 T. In ZnCr$_2$O$_4$, we observed Cant 2:1:1 phase between the antiferromagnetic phase and 3:1 phase. The general features of $\theta_s$ and the phase diagrams of both materials are well explained by the theoretical model incorporating a bi-quadratic term. It was found that the relation
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