High-field optical spectroscopy of the chromium spinel CdCr$_2$O$_4$

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Abstract. We have performed high-field optical spectroscopy measurements of the geometrically frustrated chromium spinel oxide CdCr$_2$O$_4$ in the visible light region. We succeeded in observing the pure exciton excitation peak, and identified some other absorption peaks as exciton-magnon excitation peaks from the theoretical calculations of density of states of the spin wave. Furthermore, from the high-field experiment, large variations of absorption peaks were observed at around 4 T. This result indicates that some magnetic phase transition occurs around this field.

1. Introduction

The chromium spinel oxides $A$Cr$_2$O$_4$ ($A$ = Zn, Mg, Cd, Hg), in which Cr$^{3+}$ ions interact antiferromagnetically between nearest-neighbour sites and form a pyrochlore lattice, are typical examples of a three-dimensional geometrically frustrated magnet. Due to the strong geometrical frustration, these materials do not show magnetic ordering and remain a paramagnetic state down to low temperature. In such materials, it is known that a novel magnetic ground state or a peculiar phenomenon sometimes appears, and therefore, their physical properties have attracted much interest and have been studied extensively.

In this work we focus on CdCr$_2$O$_4$. This material remains a paramagnetic state far below its Weiss temperature $|\Theta_W| = 70$ K. Eventually, it undergoes the magnetic phase transition from the paramagnetic state with a cubic symmetry to the antiferromagnetic ordered phase with a tetragonal symmetry at $T_N = 7.8$ K [1]. In this magnetic ordering accompanied by the lattice distortion, the spin-lattice coupling plays an important role to relieve the geometrical frustration. From the neutron scattering experiment [2], helical spin ordering, represented by an incommensurate wave vector $Q = (0, \delta, 1)$ with $\delta \sim 0.09$, has been suggested. Furthermore, by applying a magnetic field at low temperature, it is known that the transition to the 1/2 magnetization plateau phase accompanied by a large magnetostriction appears at 28 T [3]. A small anomaly of the magnetization was also observed around 4 T [4]. From the recent optical spectroscopy measurements of CdCr$_2$O$_4$, complicated absorption peaks including a spin-forbidden d-d transition of $^4A_{2g} \rightarrow ^2E_g$ were reported [5]. These absorption peaks were found in the lowest energy side of the absorption peaks in the visible light region and were considered to come from the various types of multiple excitations including excition, magnon, and phonon excitation. In this work, we report high-field optical spectroscopy measurements of CdCr$_2$O$_4$ in the magnetically ordered phase. We observed an exciton absorption peak in the visible light region and large variation of absorption spectra at 4 T. In addition, from the theoretical calculation, we
identified that absorption peaks located at higher energy side of an exciton line come from the simultaneous excitation of the exciton and magnon.

2. Experimental procedures
High-field optical spectroscopy measurements of CdCr$_2$O$_4$ were carried out by utilizing a conventional superconducting magnet. In the high-field optical spectroscopy system that was developed in the High-field Laboratory for Superconducting Materials, a deuterium and a halogen-tungsten lamp as light sources that cover from the near-infrared to the ultraviolet region, a single grating spectrometer (HORIBA iHR550) with the focal length 550 mm, and a multichannel CCD camera (ANDOR iDus DV401A) were used. Three types of grating (150, 600, and 1800 g/mm) were employed. The details of the measurement system can be found in Ref. [6]. The thickness of a polished sample is approximately 100 µm, and is mounted on a quartz substrate. The direction of the applied magnetic field is parallel to the [100] direction. The measurements were performed in the Voigt configuration. A CdCr$_2$O$_4$ single crystal was prepared according to the method described in Ref. [7].

3. Results and discussions

3.1 Absorption spectrum at zero magnetic field
Figure 1 shows the absorption spectrum of CdCr$_2$O$_4$ in the visible light region measured at 4.2 K using a 150 g/mm grating. Three broad absorption peaks with strong absorbance, indicated by solid arrows, and several sharp absorption peaks, indicated by a dotted arrow, are observed. The observed spectrum is compatible with that reported by the previous work [5]. The observed absorption peaks are assigned to be the d-d transitions according to the Tanabe-sugano diagram [8]. The strong absorption peaks are assigned to be the spin-allowed d-d transitions as follows: $^4A_{2g} \rightarrow ^4T_{1g}(1)$ around 29000 cm$^{-1}$, $^4A_{2g} \rightarrow ^4T_{1g}(2)$ around 22500 cm$^{-1}$, and $^4A_{2g} \rightarrow ^4T_{2g}$ around 17000 cm$^{-1}$. The absorption peaks around 14500 cm$^{-1}$ correspond to the spin-forbidden d-d transition. A number of sharp absorption peaks observed around this energy were considered to come from simultaneous excitations of exciton, magnon, or phonon [5].

Figure 2 shows the absorption spectrum at around 14500 cm$^{-1}$ obtained by using a 600 g/mm grating. In this region, the spectrum shows complex structures. The inset shows the enlarged absorption spectrum from 14100 to 14150 cm$^{-1}$ which corresponds to the hatched region in figure 2. This enlarged spectrum is obtained by using an 1800 g/mm grating. A weak absorption peak at 14115 cm$^{-1}$.

Figure 1. Absorption spectrum of CdC$_2$O$_4$ in the visible light region. The solid and dotted arrows indicate the spin-allowed and spin-forbidden d-d transition, respectively.

Figure 2. Absorption spectrum at around 14500 cm$^{-1}$. The inset shows the enlarged spectrum in the low energy region. The exciton peak was observed at 14115 cm$^{-1}$. 
cm$^{-1}$ was found. Because this peak is located at the lowest energy side of the complex absorption spectrum, we conclude that the absorption peak at 14115 cm$^{-1}$ is due to a pure exciton excitation.

Next, we move on to the discussion about other absorption peaks observed around the exciton peak. From the previous study, Schmidt et al. indicated that the peaks at 14130 and 14149 cm$^{-1}$ come from the simultaneous excitation of the exciton and magnon [5]. To confirm this indication, we calculate the magnon energy of CdCr$_2$O$_4$. The recent theories demonstrated that the spin structure of CdCr$_2$O$_4$ suggested by neutron scattering measurements [2] is compatible with a staggered lattice distortion with the symmetry lowering of the crystal structure to $E_u$ symmetry, which leads to the $I4_122$ space group with lacking inversion symmetry [9]. This lattice distortion changes the direct exchange interaction between the nearest-neighbour sites. As a result, magnetic frustration is relieved and the 8 sub-lattice collinear Neel ordering with wave vector $Q = (0, 0, 1)$ depicted in figure 3 is stabilized.

Then, it was indicated that the Dzyaloshinskii-Moriya (DM) interaction inherent in the pyrochlore lattice modulates the collinear structure to the helical one, and the experimentally observed $Q = (0, \delta, 1)$ structure is stabilized by the third neighbour antiferromagnetic interaction $J_3$. It was also suggested that the magnon spectrum, which is numerically calculated by assuming the 8 sub-lattice collinear ordering model without DM interaction, can reproduce overall features of the experimentally observed magnon dispersion [9].

Thus, we analytically calculate the magnon excitation of the Neel ordered state with the 8 sub-lattice collinear spin structure, shown in figure 3, in terms of a classical spin wave theory, and derive the density of states (DOS) of the magnon. In the spin wave calculation, we assume that the value of the nearest neighbour exchange interaction $J_1$ between the spins, aligning antiparallel to each other, is different from that of $J_2$ with a parallel spin alignment because of the lattice distortion. The third-neighbour interaction $J_3$ is also taken into account. We evaluated the exchange interaction parameters as $J_1 = 9.04$ K, $J_2 = 5.8$ K and $J_3 = 1.05$ K. These parameters are determined so as to reproduce the experimentally observed magnon dispersion. The details of the spin wave calculation will be published elsewhere.

The DOS of the magnon is shown in figure 4 together with the observed absorption spectrum. The wavenumber of the spectrum is shifted by 14115 cm$^{-1}$, which corresponds to the energy of the pure exciton. The calculated DOS shows two peaks at around 17 and 30 cm$^{-1}$. This result is in good agreement with the observed absorption peaks at 14130 and 14149 cm$^{-1}$ that are 15 and 34 cm$^{-1}$ higher

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**Figure 3.** Collinear 8 sub-lattice magnetic structure. $J_1$ and $J_2$ indicate the nearest-neighbour interactions, and $J_3$ indicates the third-neighbour interaction, respectively.

**Figure 4.** Density of states (DOS) of the magnon excitation and the absorption spectrum around the exciton excitation peak. The vertical arrows indicate the absorption peaks at 14130 and 14149 cm$^{-1}$.
energy than that of the exciton peak, respectively. Thus, we conclude that these two absorption peaks are exciton-magnon excitation peaks. The sharp absorption peak at 14190 cm\(^{-1}\) is likely to come from the excitation of the exciton and multiple magnons, as suggested by Schmidt et al. \[5\]

3.2 High-field experiment

Figure 5 shows the magnetic field dependence of exciton-magnon peaks measured in magnetic fields from 0 to 10 T at 2.0 K. Large variations of the absorption peaks were observed at around 4 T. Drastic decrease of the absorbance of exciton-magnon peaks above 4 T suggests the change of the spin wave dispersions due to the change of the magnetic structure. Furthermore, the number of the exciton peaks increases above 4T. At least four peaks are found above 4 T. The positions of the exciton peaks shift toward lower wavenumber as the field is increased above 4 T, as indicated by arrows in figure 5. These behaviour of the exciton peaks above 4 T is probably ascribed to the Davydov splitting \[10\]. The Davydov splitting occurs when the exciton migrates through the system. Such migration can take place only if the nearest neighbour spins are aligned parallel each other. Therefore, our results suggest the abrupt increase of the ferromagnetic component in the ground state above 4T. We consider that this behaviour relates to the magnetic transition from the incommensurate helical spin structure to the commensurate spin structure, suggested from the previous high-field ESR measurement \[4\]. For further detailed analysis, the calculations of the exciton dispersion in magnetic fields are necessary.

4. Conclusions

From the optical spectroscopy measurements of CdCr\(_2\)O\(_4\), we found the exciton excitation peak in the visible light region, and succeeded in identifying the exciton-magnon peaks by the theoretical calculations. In the high-field experiment, we observed large variations of absorption peaks at 4 T, where the anomaly of the magnetization was found. This result indicates that the magnetic phase transition occurs at this field.

5. References

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![Figure 5. Magnetic field dependence of the absorption peaks measured at 2.0 K. Large variations of exciton-magnon peaks and the splitting of the exciton peak were observed.](image-url)
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