Magnetic Phases of a Highly Frustrated Magnet, $ZnCr_2O_4$, up to an Ultrahigh Magnetic Field of 600 T

Atsuhiko Miyata, Hiroaki Ueda,[*] Yutaka Ueda, Hironobu Sawabe, and Shojiro Takeyama[†]

Institute for Solid State Physics, University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba, 277-8581, Japan
(Received 11 August 2011; published 9 November 2011)

The Faraday rotation and magneto-optical absorption spectral measurements were conducted to reveal the full-magnetization process and map out a magnetic phase diagram of a typical geometrical frustrated magnet, $ZnCr_2O_4$, by using the electro-magnetic flux compression method in ultrahigh magnetic fields up to 600 T. A fully polarized ferromagnetic phase is observed in which the absorption spectra associated with an exciton-magnon-phonon transition disappears. Furthermore, prior to the fully polarized ferromagnetic phase above 410 T, we found a novel magnetic phase above 350 T at 4.6 K followed by a canted 3:1 phase.

Geometrically frustrated magnet systems have been a fascinating subject for decades because they have macroscopically degenerated ground states vulnerable to tiny perturbations (spin-lattice interaction, quantum and thermal fluctuation, etc.), which lead to the emergence of exotic magnetic states [1,2]. Interestingly, magnetic fields also cause the appearance of peculiar magnetic phenomena such as the magnetization plateau [3,4], magnetic supersolid [5] and crystalline magnon state [6] due to competition between a magnetic field and frustrated spin exchange interaction. In order to understand the essence of the geometrical frustration, it is indispensable to conduct magnetization measurements up to full magnetization. Most geometrically frustrated magnets show $T_N/|\theta_{CW}| \ll 1$, where T_N and θ_{CW} are the Néel temperature and the Curie-Weiss temperature, respectively, because geometrical frustration suppresses the occurrence of a magnetic order. This inequality is the main reason that investigating the full-magnetization processes of geometrically frustrated magnets has required multiple extreme conditions, such as a high magnetic field and extremely low temperature [3,4]. Here, we developed magnetization measurements by the Faraday rotation method and magneto-optical absorption spectral measurements in photo-wavelengths in the visible light range in magnetic fields up to 600 T and at temperatures down to 5 K by the electro-magnetic flux compression (EMFC) method [7]. Geometrically frustrated magnets mainly consist of transition metal ions, and d-d transitions and the transitions associated with them, such as exciton-magnon transitions, are sensitive to the transformation of crystal and magnetic structures. In addition, most of these transitions can be observed in wavelengths in the visible light range. We applied the magneto-optical methods to a typical three-dimensional geometrically frustrated magnet with a pyrochlore lattice, $ZnCr_2O_4$ ($T_N = 12.5$ K and $\theta_{CW} = -390$ K) [8,9], and revealed the full-magnetization processes at different temperatures.

Cr^{3+} ions in chromium spinel oxides, ACr_2O_4 ($A =$ Zn, Cd, Hg), reside on a pyrochlore lattice, and therefore these compounds are regarded as a candidate for the three-dimensional frustrated magnet. Magnetization measurements in these compounds have revealed various magnetic phases, including a robust $1/2$ plateau phase [5,10–12]. Penc *et al.* suggested that a spin-lattice interaction plays a key role in determining the magnetic phases under magnetic fields in these compounds [13]. The observed magnetization data of $HgCr_2O_4$ and $CdCr_2O_4$ [11,12] showed a fairly good agreement with those of the theory with taking account of a large spin-lattice coupling parameter, i.e., $b \approx 0.1$, which was defined in Ref. [13,14]. Whereas, when b is small which is the case for $ZnCr_2O_4$ ($b \approx 0.02$), the theory predicted the realization of new phase, the canted 2:1:1 phase [13]. This is what we have actually found at a lower magnetic field side of the $1/2$ plateau phase [5]. $ZnCr_2O_4$ approaches an ideal frustrated magnet with only a nearest neighbor exchange interaction, compared with other sister compounds. The magnetization processes of an ideal frustrated pyrochlore antiferromagnet ($b = 0$) have been unclear both experimentally and theoretically. In addition, Kimura *et al.* recently reported that another phase might exist between a canted 3:1 phase and the ferromagnetic phase in $HgCr_2O_4$, and the magnetic phases would be more complicated than those by the theory with a spin-lattice coupling [13,15]. Therefore, full-magnetization measurements of $ZnCr_2O_4$ are needed.

Recently, we developed a copper-lined coil for the EMFC method, which enabled us to generate a magnetic field of over 700 T [7]. We applied this system to measurements of solid-state physics combined with a low-temperature apparatus. We employed a handmade liquid-He flow-type miniature cryostat made completely of "stycast" resin, and achieved a temperature down to 5 K [5]. The sample temperature was monitored by an Au-Fe/Chromel thermocouple attached adjacent to the sample, but the value could be lower than the actual sample

temperature by about 1–2 K due to the temperature gradient between the sample and the thermocouple. The values of magnetic fields were measured by a calibrated pickup coil wound at the vicinity of the sample. The estimated error of the magnetic field was about 3%. A single crystal of $ZnCr_2O_4$ was grown by a vapor transport technique. The sample was cut parallel to the (111) crystal surface, attached on a quartz substrate and polished to a thickness of about 100 μm for the Faraday rotation measurement or 50 μm for optical transmission measurements, and the diameter of the sample was about 1.5 mm.

The Faraday rotation measurement was performed in a manner similar to the measurement described in Ref. [5]. A semiconductor laser (a Coherent "Cube") of 635 nm wavelength was used as a light source. The incident light was linearly polarized to the horizontal axis. The transmitted light was separated into vertical (I_s) and horizontal (I_p) components by a Wollaston prism. The Faraday rotation angle of the sample (θ_M) was determined by subtraction of the diamagnetic contribution from the sample and a quartz substrate from the raw data of $\theta_F = \frac{1}{2} \arccos(\frac{I_p - I_s}{I_p + I_s})$. The magneto-optical absorption spectra measurements were performed using a streak camera system coupled with a CCD detector and a polychromator. A Xe arc-flash lamp was used as a light source and light was guided into and out of the sample by optical fibers as shown in Ref. [16].

In Fig. 1, we obtained the Faraday rotation angle of the sample, which showed good agreement with that by the single-turn coil (STC) method up to 190 T. We could obtain the magneto-optical absorption derived from the intensity of the monochromatic transmitted light in our experimental setup while measuring the Faraday rotation. In a magnetization curve, we clearly observed the transition into a ferromagnetic phase with a saturated magnetization moment of $3\mu_B/Cr^{3+}$ at 410 T, and no clear anomaly was observed between 410 T and 160 T above the transition field from a 1/2 plateau phase to a canted 3:1 phase [5]. The slope of magnetization in the antiferromagnetic phase between 0 T and 120 T was larger than that in the canted 3:1 phase above 160 T. This is a point of difference from that in the theory taking into account the spin-lattice coupling by Penc *et al.* and Bergman *et al.* [13,17]. This discrepancy implies that the exchange interactions should change due to lattice distortion associated with a magnetic phase transition, which agrees with the idea that the 1/2 plateau phase exists widely even above the Néel temperature ($T_N = 12.5$ K), as described in Ref. [5].

On the other hand, we observed a rapid decrease of absorption at 120 T and also in magnetic fields between 350 and 410 T as seen in Fig. 1(b). The absorption peak corresponding to a laser wavelength of 635 nm arises from both a *d-d* transition ($^4A_2 \rightarrow {}^4T_2$) and an exciton-magnon-phonon (EMP) transition in Cr^{3+} [18]. The energy and
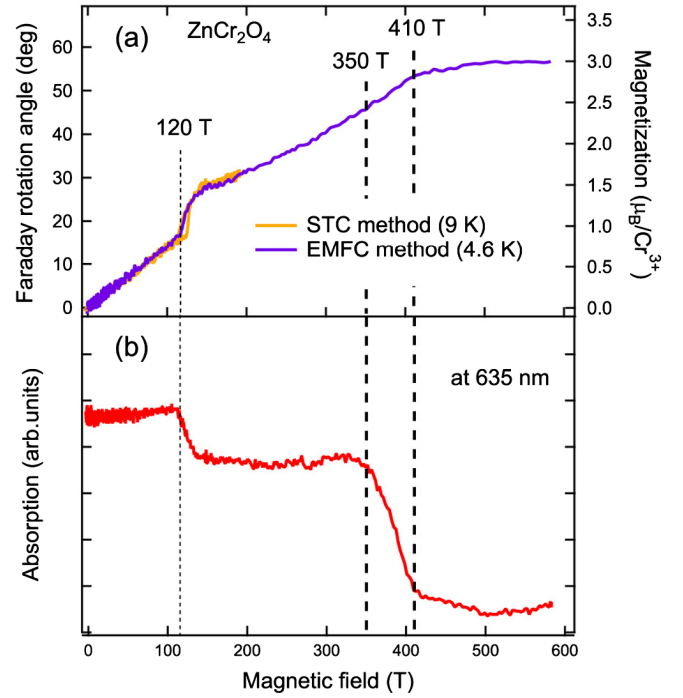

FIG. 1 (color online). (a) Magnetization obtained by the Faraday rotation method in magnetic fields of up to 600 T generated by the EMFC method at 4.6 K and up to 190 T by the STC method at 9 K as described in Ref. [5]. (b) Absorption intensity change at a wavelength of 635 nm at 4.6 K as a function of the magnetic field. The broken lines at 120, 350, and 410 T indicate anomalies observed in the absorption intensity.

spectral shape of these transitions are sensitive to the crystal and magnetic structures. We have shown the magnetization anomaly observed at 120 T as a first-order phase transition from the antiferromagnetic phase to the canted 2:1:1 phase accompanied by a change in the crystal structure [5]. Likewise, the rapid decrease of absorption between 350 T and 410 T implicates a definite change in the crystal and/or the magnetic structure. According to our recent work, there exists a canted 3:1 phase above 160 T [5], and the theories of Penc *et al.* and Bergman *et al.* allow no magnetic phases other than the ferromagnetic phase to exist in magnetic fields higher than the canted 3:1 phase [13,17]. Therefore, the present data are indicative of the certain existence of a novel phase which has not yet been predicted by the conventional theories. To clarify this behavior, we investigated the temperature dependence of the magnetization and magneto-optical absorption measurements.

Figure 2 shows the magnetization curve and magneto-optical absorption change in 635 nm at 4.6, 8.0, and 9.3 K, respectively. In the magnetization curve, we observed the transition to the ferromagnetic phase at 330 T at 8.0 K, and no clear anomaly was observed at 9.3 K. This transition point shifted toward a lower magnetic field with increasing temperature. In addition, a decrease of the absorption at
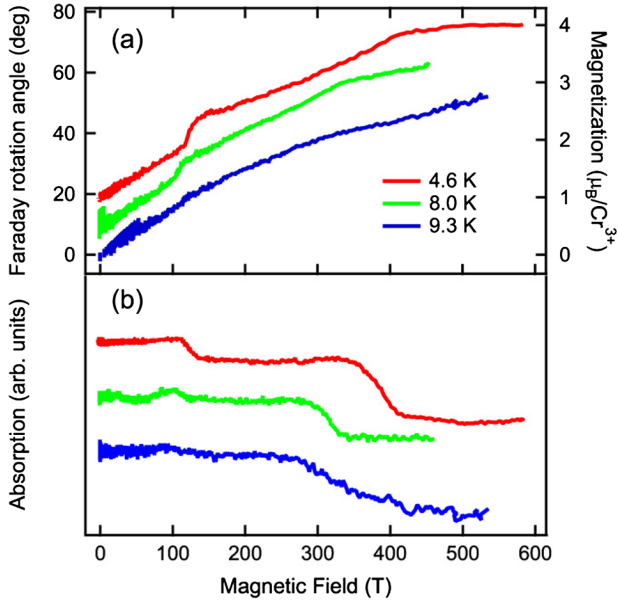
FIG. 2 (color online).   (a) Magnetization processes obtained from the Faraday rotation by the EMFC method measured at several temperatures. (b) Absorption intensity change in the wavelength of 635 nm at several temperatures as a function of magnetic field.

295 T at 8.0 K and at 270 T at 9.3 K were observed, and the field at which the absorption decreased shifted lower as the temperature increased.

Figure 3(a) shows the absorption spectra arising from a d-d transition ($^4A_2 \rightarrow {}^4T_2$) and an EMP transition in Cr^{3+} in several magnetic fields obtained from streak spectroscopy at 12 K. The inset in Fig. 3(a) presents absorption spectra taken at 0 T with a wider wavelength region covering three absorption peaks ($^4A_2 \rightarrow {}^4T_2$ transition, $^4A_2 \rightarrow {}^4T_1$ transition and an EMP transition in Cr^{3+}). Figure 3(b) presents the absorption intensity change in magnetic fields at several chosen wavelengths taken from Fig. 3(a) and also from the absorption obtained in the Faraday rotation measurement. The absorption obtained by the streak spectroscopy at a wavelength of 635 nm and that obtained in the Faraday rotation method [$\lambda =$ 635 nm, dotted arrow shown in Fig. 3(a)] show good agreement. We observed almost complete suppression of the absorption peak arising from an EMP transition when the magnetic field increased up to a region of the fully polarized ferromagnetic phase. A d-d transition with $\Delta S^z = -1$ (exciton, $^4A_2 \rightarrow {}^2E, {}^2T_1$), and magnon excitation with $\Delta S^z = +1$ were simultaneously excited to conserve the spin momentum in the process of EMP transition. However, the magnon with $\Delta S^z = +1$ could not be excited in the fully polarized ferromagnetic phase, and therefore the EMP transition disappeared, which explains the rapid decrease of absorption observed in Fig. 2(b).

Moreover, we observed an anomalous increase of the intensity in the magneto-optical absorption measured at
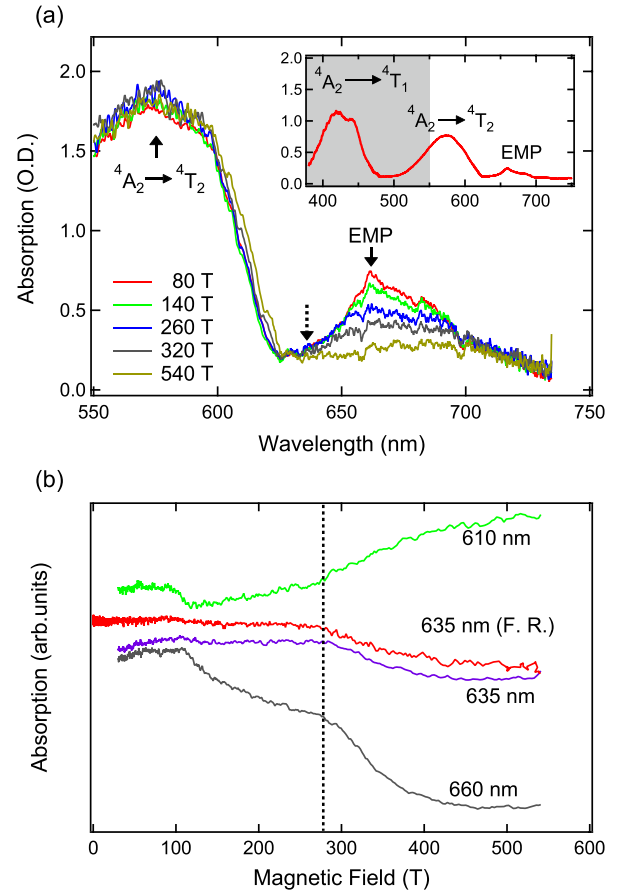

FIG. 3 (color online).   (a) Magneto-optical spectra obtained by streak spectroscopy at 12 K and in several magnetic fields. (b) Absorption intensity changes in several wavelengths at 12 K as a function of magnetic field derived from Fig. 3(a). The dotted arrow is the point of a wavelength (635 nm) used for the Faraday rotation.

the tail of the $^4A_2 \rightarrow {}^4T_2$ transition synchronized with a decrease of the intensity of the EMP transition at 270 T [the dotted line shown in Fig. 3(b)]. This suggests some changes in the crystal structure at 270 T, since the former transition is sensitive to the effect of a crystal field. Previous theoretical [17] and experimental [19,20] works reported that the space group symmetry of the 1/2 plateau state in chromium spinel oxides is universally $P4_332$ symmetry, and that the canted 3:1 phase should be at least as low as the $P4_332$ symmetry. $P4_332$ symmetry could be restored to $Fd\bar{3}m$ symmetry before or at saturation field, since a fully polarized ferromagnetic state has an ideal pyrochlore symmetry $Fd\bar{3}m$ [17]. Our results at 270 T shown in Fig. 3(b) present the possibility of a transition into a partially polarized ferromagnetic state with higher space group symmetry than $P4_332$ symmetry. Kimura *et al.* have pointed out by high magnetic field ESR study the possibility of a novel phase between the canted 3:1 phase and the ferromagnetic phase in $HgCr_2O_4$, where symmetry was higher than $P4_332$ symmetry [15]. Furthermore,
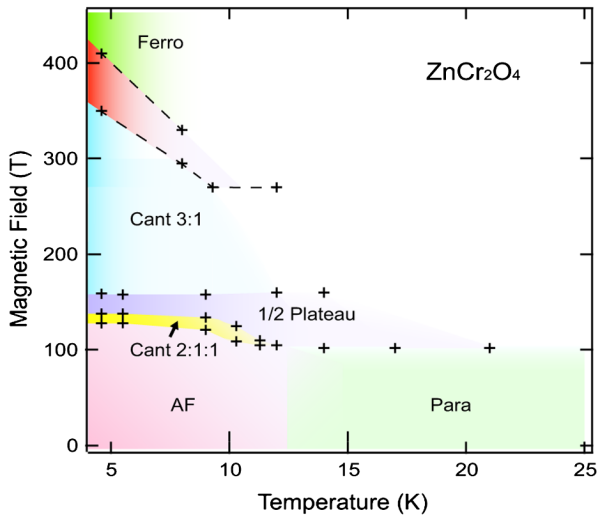
FIG. 4 (color online). Magnetic phase diagram constructed from data in Fig. 2(a) and Ref. [5]. Cross symbols indicate transition points observed by the Faraday rotation method. Broken lines show anomalies appeared in the magneto-optical absorption.

Tsurkan *et al.* reported ultrasound studies on a similar compound $ZnCr_2S_4$ in high magnetic fields, and insisted that this material should show subsequent lattice transformations as a bond frustrated magnet, despite the absence of any anomalies observed in the magnetization curves [21]. In their results, reflecting the importance of the spin-lattice coupling, the structural phase transition from the tetragonal to cubic phase with a partially polarized ferromagnetic phase took place at the vicinity of the saturation field, and then the magnetic transition to the fully polarized ferromagnetic phase occurred at the saturation field. Their results are similar to ours at the vicinity of the saturation field. These findings imply that a transition from a canted 3:1 state to a partially polarized ferromagnetic state with higher crystal symmetry than $P4_332$ occurs at a magnetic field of 350 T, and then at 410 T a magnetic phase transition results in the fully polarized ferromagnetic phase as shown in Fig. 1. This novel magnetic phase has never been predicted by existing theories. Higher-order exchange interactions among the distant sublattices, and/or more complex spin-lattice interactions could be responsible for the appearance of the novel phase.

We have discussed a physical analogy of the magnetic phase diagram of $ZnCr_2O_4$ to that in ^{4}He proposed by Matsuda and Tsuneto [22] and Liu and Fisher [23] in Ref. [5]. The canted 3:1 phase observed in the case of $ZnCr_2O_4$ corresponds to a supersolid state and the ferromagnetic (or paramagnetic) phase to a liquid state. The supersolid (intermediate) state could only exist between the solid and the superfluid state in the phase diagram [22,23]. Thus, the partially polarized ferromagnetic phase between 350 and 410 T is naturally inferred as a superfluid state from the analogy described above. A direct transition

from a ferromagnetic (i.e., liquid) phase to a canted 3:1 (i.e., supersolid) phase requires a simultaneous breaking of the translational and the spin rotational symmetry, which could take place with less probability.

Figure 4 shows a field-temperature phase diagram constructed from the data in Figs. 2 and 3(b) and the data obtained by the STC method in our previous paper [5]. The cross symbols and the broken lines indicate transition points observed by magneto-optical measurements. Between the broken lines, there should exist a novel magnetic phase. As the temperature increases, a rapid decrease is observed in the magnetic field at which the phase transition to the ferromagnetic phase takes place. A similar behavior is observed in other sister materials, $CdCr_2O_4$ and $HgCr_2O_4$, but the decrease is most pronounced in $ZnCr_2O_4$. Thermal fluctuation favors the collinear magnetic structure in the 1/2 plateau phase, or the so-called entropy-driven ''order-by-disorder'' effect [24,25]. This effect becomes pronounced in the small limit of the spin-lattice coupling, and is discussed in Ref. [5]. The same discussion applies equally to the present case for the ferromagnetic phase.

The Faraday rotation and magneto-optical absorption spectra measurements conducted in an ultrahigh magnetic field up to 600 T revealed the full-magnetization processes of $ZnCr_2O_4$, and a magnetic phase diagram was obtained. We found anomalies in the absorption spectra as a function of the magnetic field, which implied the certain existence of a novel phase between a canted 3:1 phase and the ferromagnetic phase, corresponding to the superfluid state in the analogy of ^{4}He. This phase should have higher symmetry than the $P4_332$ one with a partially polarized ferromagnetic structure, and will require a more sophisticated model to interpret. Magneto-optical absorption was found to be a good tool to detect magnetic phase transitions which are insensitive to the magnetization data.

*Present address: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan.
†takeyama@issp.u-tokyo.ac.jp

[1] O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. Lett. **88**, 067203 (2002).
[2] A. V. Chubukov and D. I. Golosov, J. Phys. Condens. Matter **3**, 69 (1991).
[3] H. Kageyama *et al.*, Phys. Rev. Lett. **82**, 3168 (1999).
[4] Y. Okamoto *et al.*, Phys. Rev. B **83**, 180407(R) (2011).
[5] A. Miyata *et al.*, J. Phys. Soc. Jpn. **80**, 074709 (2011).
[6] M. E. Zhitomirsky and H. Tsunetsugu, Phys. Rev. B **70**, 100403(R) (2004).
[7] S. Takeyama and E. Kojima, J. Phys. D **44**, 425003 (2011).
[8] S.-H. Lee *et al.*, Phys. Rev. Lett. **84**, 3718 (2000).
[9] S.-H. Lee *et al.*, Nature (London) **418**, 856 (2002).
[10] H. Ueda *et al.*, Phys. Rev. Lett. **94**, 047202 (2005).
[11] H. Ueda *et al.*, Phys. Rev. B **73**, 094415 (2006).

[12] E. Kojima *et al.*, Phys. Rev. B **77**, 212408 (2008).

[13] K. Penc, N. Shannon, and H. Shiba, Phys. Rev. Lett. **93**, 197203 (2004).

[14] Y. Motome, K. Penc, and N. Shannon , J. Magn. Magn. Mater. **300**, 57 (2006).

[15] S. Kimura *et al.*, Phys. Rev. B **83**, 214401 (2011).

[16] N. Miura *et al.*, Physica (Amsterdam) **256–258B**, 308 (1998).

[17] D. L. Bergman *et al.*, Phys. Rev. B **74**, 134409 (2006).

[18] H. Szymczak, W. Wardzyński, and A. Pajączkowska, J. Magn. Magn. Mater. **15–18**, 841 (1980).

[19] M. Matsuda *et al.*, Nature Phys. **3**, 397 (2007).

[20] M. Matsuda *et al.*, Phys. Rev. Lett. **104**, 047201 (2010).

[21] V. Tsurkan *et al.*, Phys. Rev. Lett. **106**, 247202 (2011).

[22] H. Matsuda and T. Tsuneto, Prog. Theor. Phys. Suppl. **46**, 411 (1970).

[23] K. S. Liu and M. E. Fisher, J. Low Temp. Phys. **10**, 655 (1973).

[24] H. Kawamura and S. Miyashita, J. Phys. Soc. Jpn. **54**, 4530 (1985).

[25] M. E. Zhitomirsky, Phys. Rev. Lett. **88**, 057204 (2002).