Quest for the high-field phase of CdCr$_2$O$_4$ using an X-ray diffraction technique

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Abstract. Single-crystal x-ray diffraction experiments on the geometrically frustrated magnet CdCr$_2$O$_4$ have been carried out under pulsed magnetic fields up to 31 T. By applying magnetic fields, CdCr$_2$O$_4$ exhibits a magnetization plateau which is one-half of the saturated magnetization above 28 T, and it is expected that a structural transition from a tetragonal to a rhombohedral or cubic structure occurs simultaneously through a so-called “spin Jahn-Teller” mechanism. Our diffraction experiments confirmed that a sharp structural transition occurs at 28 T and that the 440 reflection is a single peak, suggesting that the crystal structure of the high-field plateau phase is cubic.

1. Introduction
Geometrically frustrated magnets, such as spins on a kagomé or pyrochlore lattice connected by a Heisenberg antiferromagnetic interaction, have been the subject of recent theoretical and experimental research in condensed matter physics, because they remain disordered far below the Curie-Weiss temperature $\Theta_{CW}$ and persist in strongly interacting paramagnetic states, in which novel behavior is anticipated[1]. In real magnets, however, small perturbations (for instance, further-neighbor interactions, single-ion anisotropy, or quantum or thermal fluctuations) lift the large degeneracy of ground states and lead to a Néel ordered state.

A magnetoelastic coupling can also be such a perturbation and suppress frustration. For a pyrochlore lattice, which is a network of corner-sharing tetrahedra, a uniform or staggered lattice distortion changes equivalent exchange interactions in a tetrahedron into inequivalent ones. In this distorted lattice, collinear or coplanar Néel ordered states are selected and the total system energy is lowered[2, 3]. By analogy with the Jahn-Teller effect, in which orbital degeneracy is lifted by lowering symmetry, this mechanism driven by spin degeneracy is called a “spin Jahn-Teller” mechanism. What happens to this class of magnets if magnetic fields are applied? Magnetic fields may favor another ground state, thus a different lattice distortion must be realized in order to stabilize the newly selected ground state.
The cubic spinel CdCr$_2$O$_4$ is one of geometrically frustrated antiferromagnets and the Cr$^{3+}$ ions reside on a pyrochlore lattice. Antiferromagnetic order sets in at $T_N = 8$ K well below $\Theta_{CW} = 70$ K$^4$. The antiferromagnetic transition is accompanied by a cubic-to-tetragonal structural transition with the elongated c-axis owing to the above-mentioned spin Jahn-Teller mechanism. The ordered state is not a simple collinear antiferromagnet, but incommensurate helical spin order along the b-axis$^5$. Magnetization well below $T_N$ increases linearly with increasing magnetic fields and shows a sudden jump at 28 T. Above 28 T, magnetization is constant as a function of magnetic fields, and thus a broad plateau is seen in the magnetization curve as shown in figure 1$^4$. The magnetization at the plateau phase is just one-half of the saturated magnetization and therefore a tetrahedron consists of three up-spins and one down-spin. Under this restriction, two spin arrangements, rhombohedral and cubic, are possible, depending on the sign of the next nearest neighbor interaction$^4$. Accordingly, a structural change from tetragonal to rhombohedral ($R3m$) or cubic ($P4_132$) symmetry through the magnetoelastic coupling is expected at 28 T. In fact, a sharp lattice contraction is observed by magnetostriction measurements, and thus the occurrence of a structural change at 28 T is confirmed. However, through magnetostriction measurements the lattice symmetry is not determined unambiguously, hence diffraction experiments under high magnetic fields are highly desired.

Recently, we have developed an x-ray diffraction technique under pulsed magnetic fields$^6, 7, 8$. Utilizing a small pulsed magnet and intense synchrotron x-rays, we performed single-crystal x-ray diffraction experiments above 30 T. In this paper, we report on a useful development of a technique using a two-dimensional detector and its application to the plateau phase of CdCr$_2$O$_4$.

2. Experimental details
Single crystals of CdCr$_2$O$_4$ were grown by a flux method. X-ray diffraction experiments were carried out at undulator beamline BL22XU at SPring-8. Magnetic fields up to 31 T were generated using a small pulsed magnet (20 mm in outer diameter and 24 mm in length) wound by a CuAg wire$^7, 8$. The pulse duration is about 0.6 msec. The magnet is a split-pair, and two 30-degree windows are prepared for incoming and outgoing x-rays. The magnet was attached to a sample rod and was inserted into an ILL-type orange cryostat.

The x-ray energy was 12.4 keV. X-rays were monochromatized using a Si(111) double-crystal monochromator and were focused by a pair of bent and cylindrical mirrors. The sample was mounted so as to measure the $hk0$ zone and magnetic fields were applied along the c-axis. We used two different detectors. One is an avalanche photodiode (APD: Hamamatsu SPL1518). The APD is a high-counting-rate point detector and is used for measurements of time-domain spectra with a typical time resolution of 20 μsec. A detailed magnetic-field dependence of Bragg peaks was obtained using the APD. The other is an area detector, which is powerful to search for

![Figure 1](image-url). Schematic illustration of the magnetization curve of CdCr$_2$O$_4$. The initial linear increase in the magnetization is followed by a sudden jump at 28 T. Above 28 T, the magnetization is almost constant over a wide field range and is just one-half of the saturated magnetization. The expected magnetic structures at the plateau phase are also shown.
a tiny Bragg peak in the vast reciprocal space. We employed a flat panel sensor (Hamamatsu C7942), which consists of a two-dimensional array of photodiodes placed at 50 μm intervals. Since the detector does not possess the required time resolution, we combined an x-ray chopper and a shutter and created an x-ray pulse of 150 μsec. Magnetic fields were synchronized with an x-ray pulse as depicted in figure 2 and we observed a diffraction pattern in a selected field range.

3. Results and discussion
A major difficulty in high-field diffraction experiments is how to find a Bragg peak that newly appears somewhere in the reciprocal space. Below $T_N$, CdCr$_2$O$_4$ is composed of a number of tetragonal domains, and thus the rocking curve of the 404 and 044 reflections showed many peaks which were distributed over about one degree. Magnetic fields orient these domains so that the $b$-axes of the domains become parallel to the field direction, because the helical plane of the spins is perpendicular to the $b$-axis. This domain reorientation occurs at 2 to 4 T[9]. Accordingly, all Bragg peaks at 0 T are wiped out above 4 T and we have to find a Bragg peak of the reoriented domain. To accomplish this task, an area detector is very useful. First we applied pulsed magnetic fields up to 4 T, synchronized an x-ray pulse to the top of the magnetic fields, and took a two-dimensional image using the area detector. Next we rotated the sample by 0.02 degrees and took another image at 4 T. The same procedure was repeated 36 times. Finally a three-dimensional intensity map of the reciprocal space was obtained. The result was rather striking. A single sharp peak was observed. The rocking-curve width is as sharp as that in the high-temperature phase. This finding indicates that widely distributed tetragonal domains are almost completely oriented by magnetic fields.

The same procedure was also applied to the plateau phase and in fact we successfully found a Bragg peak above 28 T. The results are summarized in figure 3. Without magnetic fields, two Bragg peaks were observed; one is the 440 reflection and the other is the 404 and 044 reflections. The scattering angle ($2\theta$) of the 440 reflection is higher than that of the others, because $c > a, b$. Above 4 T, the 440 reflection disappeared because of the domain reorientation and only the 404 reflection was observed. Above 28 T, the Bragg peak moved to a higher scattering angle, which is very close to that of the high-temperature cubic phase. Detailed field dependences of these Bragg peaks were measured using the APD. The results showed that the 404 peak in the low-field phase disappears suddenly and that the 440 peak in the plateau phase emerges sharply at 28 T.

The crucial outcome is that the 440 reflection above 28 T is a single peak. This fact indicates

![Figure 2. Timing diagram of x-ray pulses and magnetic fields. (a) Incident x-rays are first cut by an x-ray shutter, and (b) the created x-ray pulse is further sliced by a chopper (a rotating disk with slits). (c,d) A diffraction pattern at high (low) fields is obtained by tuning an x-ray pulse to the top (tail) of the pulsed magnetic fields.](image-url)
Figure 3. Field dependence of the 440 reflection at 5 K. (a) At $H=0$ T, two peaks (peak A: 440, peak B: 404 and 044) due to the tetragonal deformation ($c>a$) were observed. (b) $13.4 \, T < H < 27.9 \, T$. Above 4 T, the $b$-axis points to the field direction. As a result, only the 404 reflection was observed. (c) $27.7 \, T < H < 29.5 \, T$. Above 28 T, a new peak marked C appeared. Since the field range includes the transition field, the low-field phase was also seen. The scattering angle of the peak C is close to that of the 440 reflection in the high-temperature cubic phase shown in (d).

that the plateau phase is cubic. If the plateau phase was rhombohedral, the 440 reflection would split into two peaks. It is possible that the rhombohedral deformation might be very small and that the split can not be detected. However, the tetragonal deformation below $T_N$ due to the spin Jahn-Teller mechanism is fairly large ($c/a - 1 = 4 \times 10^{-3}$), thus the rhombohedral deformation is also expected to be large. It is likely that two widely separated peaks would be easily observed. Hence, although careful determination of the space group requires observation of a superlattice reflection, our results strongly suggest that the space group of the plateau phase is cubic $P4_{1}32$.

4. Summary
We investigated the field-induced structural phase transition of CdCr$_2$O$_4$ at 28 T by means of single-crystal x-ray diffraction. Utilizing a large area detector and a fast APD detector, the structural transition at 28 T was successfully observed. The detected Bragg peak in the plateau phase was a single peak, indicating that the high-field plateau phase has cubic symmetry.

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