Field-induced incommensurate-to-commensurate transition in the triangular lattice antiferromagnet GdPd$_2$Al$_3$

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Abstract. The stacked triangular lattice antiferromagnet GdPd$_2$Al$_3$ has a helical magnetic structure of extremely long incommensurate modulation below $T_{N2}$ ($= 13.3$ K). In order to observe the dependence of the magnetic structure on magnetic field applied in the spin plane, we performed resonant magnetic x-ray diffraction experiments in magnetic fields up to 0.15 T at 4 K and observed a first-order incommensurate-to-commensurate transition around 0.04 T. This result indicates that the free energy has a double-well structure around the K-point.

1. Introduction
A helically modulated magnetic structure was first postulated theoretically by Yoshimori for the magnetic structure of $\beta$-MnO$_2$[1]. He suggested that competition between the nearest- and next-nearest-neighbor interactions gives rise to such screw-type magnetic structures, and neutron diffraction experiments have actually confirmed these helical structures in several heavy rare-earth elements and transition metal compounds[2, 3, 4, 5]. The response of helical structures to magnetic fields has also been well investigated. Nagamiya et al. theoretically predicted that a helical structure undergoes a first-order phase transition to a fan structure followed by a second-order transition to a forced ferromagnetic state when a magnetic field is applied in the plane of the helix[6]. Such a helical-to-fan transition was experimentally observed in MnP[4].

The rare-earth intermetallic compound GdPd$_2$Al$_3$ crystallizes to a hexagonal structure ($P6/mmm; a=5.39$ Å and $c=4.19$ Å). The fractional coordinates of the Gd, Pd and Al ions are (0,0,0), (1/3,2/3,0) and (1/2,0,1/2), respectively. The Gd ion has a large, spin-only magnetic moment $S=7/2$, which is approximated by a Heisenberg spin, and forms a stacked triangular lattice. Magnetic susceptibility, magnetization and specific heat were measured to investigate three characteristic features of GdPd$_2$Al$_3$[7]; (i) Successive phase transitions at $T_{N1}=16.8$ K and $T_{N2}=13.3$ K. (ii) Small ferromagnetic moments at 0 T. Magnetizations extrapolated to 0 T both parallel and normal to the hexagonal $c$-axis have net moments of 0.22 $\mu_B$/Gd and 0.16 $\mu_B$/Gd, respectively. (iii) A one-third magnetization plateau between 6.2 T and 11.8 T under magnetic field parallel to the $c$-axis. These features are perfectly consistent with the expected behaviors of a Heisenberg triangular lattice antiferromagnet (TAF) with weak Ising anisotropy[8, 9]. For ideal Heisenberg TAFs with weak Ising anisotropy, the magnetic structure
Figure 1. Magnetic structures of a Heisenberg TAF with weak Ising anisotropy: (a) below $T_{N2}$, (b) between $T_{N1}$ and $T_{N2}$, and (d) under magnetic fields in the basal $ab$-plane (along the [110] direction in this figure). (c) An example of incommensurate magnetic structures, where the moments rotate by approximately 120° in numerical order.

in the low-temperature (LT) phase (below $T_{N2}$) is a slightly distorted 120° structure, as shown in Fig. 1(a). Since the canting angle $\alpha$ is smaller than 60° due to the weak Ising anisotropy, the sum of the moments in the distorted 120° structure does not amount to zero. Hence, a small ferromagnetic moment parallel to the $c$-axis is generated. This small net moment can be detected in magnetization measurements when the two-dimensional triangular lattices couple ferromagnetically to each other, as in the case of GdPd$_2$Al$_3$. In the intermediate phase (between $T_{N1}$ and $T_{N2}$), only the $c$-axis component of the magnetic structure in the LT phase shows long-range ordering [Fig. 1(b)].

In GdPd$_2$Al$_3$, recent resonant magnetic x-ray diffraction experiments revealed that the magnetic moments parallel and normal to the $c$-axis successively become ordered at $T_{N1}$ and $T_{N2}$[10], in accordance with theoretical calculations[8]. However, in contrast to the expected 120° structure, the magnetic structure below $T_{N2}$ was found to be a helically-modulated incommensurate (IC) structure [Fig. 1(c)]. The wave vector $q_M$ was described as $(1/3-\delta, 1/3-\delta, 0)$. The incommensurability $\delta$ developed below $T_{N2}$ concomitantly with the evolution of the $ab$-plane components of the magnetic moments and reached 0.0013 at 5 K. Since the commensurate intermediate phase cannot be derived from a set of isotropic interactions that may produce the IC ground state, this very long-period IC magnetic structure is most likely the result of the competition between the nearest-neighbor exchange interaction and anisotropic dipole-dipole interactions. The Fourier transform of the nearest-neighbor exchange interaction has a maximum at the K-point $(1/3,1/3,0)$ in the hexagonal reciprocal lattice, whereas two branches ($x$ and $y$ components in the $ab$-plane) of the dipole-dipole interactions intersect at the K-point, producing a conical point anomaly at the K-point[11]. As a result, stable points appear at IC positions very close to the K-point.

Since the helically modulated IC structure does not carry ferromagnetic moments, the application of magnetic fields parallel to the $c$-axis stabilizes the commensurate structure depicted in Fig. 1(a). Thus, it is expected that the IC structure eventually evolves into the commensurate structure as the magnetic field ($\parallel c$) is increased. An interesting feature of TAFs is that a distorted 120° structure that has a small ferromagnetic moment normal to the $c$-axis shown in Fig. 1(d) is stabilized by the application of magnetic fields normal to the $c$-axis. For an ordinary helix, a cone structure whose spin plane is perpendicular to the magnetic field is stabilized in the presence of a magnetic field when anisotropy can be ignored, since the transverse susceptibility is larger than the longitudinal susceptibility. However, the distorted 120° structure, which has a spin plane parallel to the magnetic field, is preferred in TAFs. Therefore, it is also expected that the IC helix develops into the commensurate 120° structure in GdPd$_2$Al$_3$ when a
2. Experimental
Resonant x-ray diffraction experiments were carried out at beamline BL22XU in SPring-8. The photon energy was tuned near the $L_2$ absorption edge of Gd (7.930 keV). A single crystal of GdPd$_2$Al$_3$ was grown by using the Czochralsky pulling method in a tetra-arc furnace. The sample was cut into a parallelepiped of $4 \times 4 \times 2$ mm$^3$ in volume, and a (110) surface was polished. The sample was placed inside a continuous-flow cryostat inserted into a horizontal-field superconducting magnet. The magnet was mounted on a diffractometer with a horizontal scattering plane. We set the c-axis of the sample perpendicular to the scattering plane, and the magnetic field was applied parallel to the [110] direction up to 0.15 T. The polarization of incident x-rays was parallel to the scattering plane, and the polarization of diffracted x-rays was not analyzed. The mosaic width of the 110 reflection of the sample was about 0.015° full width at half maximum, indicating the high quality of the crystal.

3. Results and Discussion
The photon-energy and temperature dependences of the magnetic reflections were reported in a separate paper[10]. The (nominal) $4\overline{4}0$ magnetic reflection exhibited an enormous enhancement in intensity at the absorption edge with scanning the photon energy. The temperature dependence of the magnetic reflections distinctly demonstrated successive phase transitions of the c-axis and $ab$-plane components at $T_{N1}$ and $T_{N2}$, respectively, and the development of the incommensurability $\delta$ below $T_{N2}$.

Intensity maps in the $(H, K, 0)$ reciprocal plane around the $\overline{4}4\overline{0}$ magnetic reflection at several magnetic fields are shown on a logarithmic scale in Fig. 2. In the virgin state at 0 T shown

![Intensity maps example](image_url)

**Figure 2.** Field dependence of magnetic diffraction intensity in the $(H, K, 0)$ reciprocal plane around the $\overline{4}4\overline{0}$ Bragg reflection at 4 K. The intensity is plotted on a logarithmic scale, and the units are counts per second. Magnetic fields were first increased and then decreased in the following order. (a) 0 T (virgin state) → (b) 0.04 T → (c) 0.1 T → (d) 0.03 T → (e) 0 T.
in Fig. 2(a), a magnetic peak was observed at the IC position \(Q_{IC} = (1.332, 1.332, 0)\). With increasing magnetic field parallel to the [110] direction, the intensity of the IC peak decreased suddenly around 0.04 T, and a peak emerged at the commensurate position \(Q_C = (4/3, 4/3, 0)\) [Fig. 2(b)]. At 0.1 T, only the sharp commensurate peak remained [Fig. 2(c)]. The resulting commensurate spin arrangement was stable. Reduction of the magnetic field did not alter the commensurate structure into the IC structure. The peak continued to stay at the commensurate position when the magnetic field was decreased [Figs. 2(d) and 2(e)]. Although weak magnetic intensity grew up on the left side of the peak with decreasing magnetic field, we believe that this intensity arises from imperfections in the crystal, since a similar asymmetric distribution of the intensity is also observed on the right side of the IC peak in Fig. 2(a). It is considered that magnetic structures with various modulation wave vectors between \(Q_{IC}\) and \(Q_C\) are stabilized by dislocations, impurity sites, and residual strains. Heating the sample above \(T_{N1}\) initialized the system, and the IC state was obtained again by reduction of the temperature below \(T_{N2}\).

According to Nagamiya’s theory, it is likely that an IC fan structure intervene between the IC helix and the commensurate structure in the phase diagram. However, a first-order, direct transition from the IC helix to the commensurate structure was experimentally observed. Since the transition between the IC fan and the commensurate 120° structures is considered to be of second order, the observed significant hysteresis disagrees with the existence of the IC fan phase. The metastable commensurate 120° structure illustrates that a local minimum of the free energy exists at the K-point at 0 T in addition to the IC stable points. It is thus concluded that the free energy has a double-well structure in contrast to a single-well structure derived from the conical point anomaly. Therefore, interactions which are not incorporated in the calculation in Ref. [11], such as dipole-dipole interactions between the c-axis components of the magnetic moments, may play a crucial role in the magnetization process of GdPd\(_2\)Al\(_3\).

4. Conclusions
The low-field magnetization process of the Heisenberg TAF GdPd\(_2\)Al\(_3\) was investigated by means of resonant magnetic x-ray diffraction under magnetic fields parallel to the [110] direction. The experimental results clearly demonstrated that the first-order incommensurate-to-commensurate transition occurs around 0.04 T when the magnetic field is increased. The hysteresis is substantially large for the field-induced commensurate 120° structure to be stable down to 0 T when the magnetic field is decreased. These findings indicate that the free energy has an additional minimum at the K-point at 0 T in addition to the main incommensurate minimum.

Acknowledgment
This work was partly supported by Grant-in-Aid for Scientific Research on priority Areas “High Field Spin Science in 100 T” (No. 451) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

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