Successive phase transitions induced by magnetic fields in a cubic system, NdPd$_3$S$_4$

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Abstract. To investigate the role of multipoles in the phase transitions of NdPd$_3$S$_4$, measurements of specific heat, magnetization, and electrical resistivity were performed for single-crystalline samples. We also carried out powder neutron diffraction experiments to identify a magnetically ordered structure. At zero magnetic field, an antiferromagnetic (AFM) transition occurs at $T_N = 1.8$ K. When a magnetic field is applied, the AFM ordered phase, characterized by a propagation vector $k = (1, 0, 0)$, switches into field-induced phases. We propose that the field-induced phases are associated with quadrupolar ordering.

1. Introduction
The interplay between various electronic degrees of freedom results in a complex phase diagram in terms of the magnetic field ($B$) and temperature ($T$) in correlated electron systems. The phase transitions associated with electron multipoles have been reported in several rare-earth compounds, such as CeB$_6$ [1] and TbB$_2$C$_2$ [2].

Recently, complex phase diagrams were also discovered for the RPd$_3$S$_4$ (R: rare-earth ion) family, crystallizing into a NaPt$_3$O$_4$-type cubic structure. Trivalent rare-earth ions form a body-centered cubic sublattice and are subjected to a cubic crystalline electric field (CEF) with a $T_h$ point group. For example, field-induced antiferroquadrupolar (AFQ) ordering in TbPd$_3$S$_4$ [3] and AFQ ordering in DyPd$_3$S$_4$ [4] have been reported previously.

Here, we focus on NdPd$_3$S$_4$. A previous study on a polycrystalline sample revealed that NdPd$_3$S$_4$ shows an antiferromagnetic (AFM) transition at 2.0 K and that the CEF ground state is a quartet [5]. Since the quartet ground state has multipole degrees of freedom, in addition to a magnetic dipole, we expect complex phase diagrams. Multipolar ordering in Nd compounds is rare as far as we know. The purpose of this work is to clarify the contribution of multipole degrees of freedom in the ordered phases. For this purpose, we studied anisotropic behavior under magnetic fields using single-crystalline samples of NdPd$_3$S$_4$.

In this paper, we report phase transitions in NdPd$_3$S$_4$, investigated by measurements of specific heat, magnetization, and electrical resistivity. $B$-$T$ phase diagrams are determined from the results of these measurements. In addition, powder neutron diffraction experiments were performed to identify a magnetically ordered structure in the AFM phase of NdPd$_3$S$_4$. 

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2. Experiments

Single-crystalline samples of NdPd$_3$S$_4$ were synthesized by a chemical transport method with the transport medium KI, as described in Ref. [6].

The specific heat was measured by the relaxation method over the temperature range of 0.5 to 50 K, under applied magnetic fields up to 8 T. Magnetization measurements down to 0.5 K were performed by the capacitive Faraday method in magnetic fields up to 8 T. The electrical resistivity was measured by the DC four-probe method between 0.5 and 300 K and up to 10 T.

Powder neutron diffraction experiments were carried out using the diffractometer HERMES of the Institute of Materials Research, Tohoku University, installed at the cold-neutron guide of JRR-3 at the Japan Atomic Energy Agency, Tokai, Japan. We used neutrons with a wavelength of 1.84772(9) Å provided by the 331 reflection of the single-crystalline Ge monochromator.

3. Results

At first, neutron diffraction data taken at zero magnetic field is shown in order to reveal magnetic ordering. We observed Bragg peaks appearing below 3 K, in addition to the nuclear scattering from the NaPt$_3$O$_4$-type structure. Figure 1 shows the evolution of the 100 Bragg peak intensity as a function of temperature, which is evaluated by integration of a scan profile as shown in the inset. This peak disappears at 3 K, and thus it is clear that the 100 peak indicates the magnetic ordering. We observed other peaks growing at low temperature, corresponding to 111, 300, 311, 410, 621, and so on, which are not shown. These peaks can be characterized by a propagation vector $k = (1, 0, 0)$ for an AFM structure. No magnetic peak indexed by any other propagation vector was observed. This observation means that the direction of the magnetic moments of the corner Nd$^{3+}$ ions is opposite to those of the body-centered sites. The same AFM ordered structure was also observed in TbPd$_3$S$_4$ [7]. The integrated intensity of the 100 peak starts increasing below 3 K and rapidly increases below 2.1 K, which suggests that fluctuation of magnetic dipoles exists below 3 K.

Figure 2 shows the temperature dependence of the specific heat $C(T)$ under various magnetic fields applied along the [110] direction. At $B = 0$ T, $C(T)$ shows a $\lambda$-type peak at $T_N = 1.8$ K. The peak at $T_N$ shifts to the lower temperature side with increasing magnetic field, and it splits into two anomalies at $T_{N'}$ and $T_{Q1}$ above 1 T. The lower temperature anomaly at $T_{N'}$ also shifts with the applied magnetic field. This anomaly vanishes above 2 T, while that at $T_{Q1}$ remains robust. The $T_{Q1}$ anomaly separates into two anomalies at $T_{Q2}$ and $T_{Q3}$ above 2 T. The anomaly at $T_{Q1}$ shifts to the high temperature side when applying magnetic fields up to 8 T, and at $T_{Q2}$, it rapidly shifts to the lower temperature side, vanishing above 3.5 T.

![Figure 1](image1.png)

**Figure 1.** Temperature dependence of the integrated intensity of the 100 peak. The inset shows profiles through the 100 position measured at 1.6 K and 3 K.

![Figure 2](image2.png)

**Figure 2.** Temperature dependence of the specific heat of NdPd$_3$S$_4$ in several magnetic fields applied along the [110] direction.
Figure 3. Magnetization curves (top) with their derivative (bottom) at several temperatures. Magnetic fields were applied along the [110] direction. The magnetization curves $M(B)$ and their derivatives $dM/db$ are shown in the upper and lower parts of Fig. 3, respectively. At 0.5 K, two anomalies in $dM/db$ at $B_1 = 2.2$ T and $B_2 = 3.6$ T were observed. As the temperature increases to $T_N$, $B_1$, and $B_2$ move toward lower fields, vanishing above $T_N$.

At $B = 0$ T, the electrical resistivity $\rho(T)$ shows a sharp drop at 1.9 K near $T_N$ as shown in Fig. 4. As the magnetic field increases, this drop becomes weaker with the shift of the anomaly temperature.

4. Discussion

We measured $C(T, B)$, $M(T, B)$, and $\rho(T, B)$ under magnetic fields along the [100] and [111] directions. Based on the temperatures and magnetic fields of the observed anomalies, we determined the phase diagrams, as summarized in Fig. 5. Para and AFM correspond to the paramagnetic phase and the AFM ordered phase with the propagation vector $\langle 1, 0, 0 \rangle$, respectively. When magnetic fields are applied, the AFM ordered phase switches into field-induced phases $I_{[100]}$, $I_{[110]}$, $I_{[111]}$, $II_{[110]}$, $II_{[111]}$, and $III$.

We will discuss the phase diagrams for NdPd$_3$S$_4$ in comparison with those of the isostructural compound TbPd$_3$S$_4$ [3, 7]. The Tb-based system also undergoes the AFM ordering transition in the lower magnetic field region below 2.55 K. This AFM ordered structure includes collinear alignment of the magnetic moment at the Tb sites, which is the same magnetic ordered structure found for NdPd$_3$S$_4$ in the present study. The AFM phase in TbPd$_3$S$_4$ switches into the canted magnetic structure phases under finite magnetic fields above 0.5 T. The AFQ order is suggested to coexist with the canted magnetic structure in the field-induced phases for TbPd$_3$S$_4$. Because NdPd$_3$S$_4$ exhibits the same AFM ordered structure and because the AFM phase switches into the similar field-induced phases $I_{[100]}$, $I_{[110]}$, and $I_{[111]}$ under finite magnetic fields, we expect that quadrupolar ordering occurs in these field-induced phases.

As shown in the phase diagrams in Fig. 5, the transition temperatures from Para to the field-induced phases $I_{[100]}$, $I_{[111]}$, $II_{[110]}$, $II_{[111]}$ and $III$ slightly increase with the applied magnetic field, similar to the behavior of the transition temperatures from the paramagnetic phase to the field-induced phases with the AFQ order in TbPd$_3$S$_4$. Furthermore, an increase in transition temperatures is commonly observed for quadrupolar ordered phases in other typical quadrupolar ordering systems. We therefore propose that these field-induced phases ($I_{[100]}$, $II_{[110]}$, $I_{[111]}$, $II_{[111]}$, $III$) of NdPd$_3$S$_4$ are due to the AFQ ordered phases with the canted magnetic structure.

Next, we will discuss the order parameter in the field-induced phase $I_{[100]}$, which shows different features from those in the ordered phases discussed above. The anomaly corresponding to the phase transition from $I_{[100]}$ to Para was not clearly observed in the magnetization curves (not shown), and the transition temperature from Para to $I_{[100]}$ does not increase by applying magnetic fields (Fig. 5). These results suggest that the magnetic moment in $I_{[100]}$ is close to a saturated moment. In other words, the
canted angle is considerably smaller than 90°. We consider that $I_{[100]}$ is also associated with the AFQ ordered phase with the canted magnetic structure which is smaller than 90°. We need to carry out further studies in order to elucidate the low-lying CEF states responsible for the successive phase transitions with strongly anisotropic behaviors and the actual order parameter in NdPd$_3$S$_4$, for example, by using the neutron diffraction technique.

![Figure 5](image)

**Figure 5.** $B$-$T$ phase diagrams for fields applied along the [100], [110], and [111] directions.

5. Conclusion
We synthesized single-crystalline samples of NdPd$_3$S$_4$; to the best of our knowledge, this is the first report of such a synthesis. From the results of the specific heat, magnetization, electrical resistivity, and powder neutron diffraction measurements, we constructed the $B$-$T$ phase diagrams. The AFM ordered phase was confirmed by neutron diffraction. The properties of the phase diagrams as well as the behaviors suggested by the measurements indicate that the AFM phase switches into quadrupolar ordered phases under finite magnetic fields.

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References
[1] Effantin J M, Rossat-Mignod J, Burlet P, Bartholin H, Kunii S and Kasuya T 1985 *J. Magn. Magn. Mater.* 47&48 145
[2] Kaneko K, Onodera H, Yamauchi H, Sakon T, Motokawa M and Yamaguchi Y 2003 *Phys. Rev. B* 68 012401
[3] Matsuoka E, Shida H, Matsumura T, Ohoyama K and Onodera H 2011 *J. Phys. Soc. Jpn.* 80 SA085
[4] Matsuoka E, Tayama T, Sakakibara T, Hiroi Z, Shirakawa N, Takeda N and Ishikawa M 2007 *J. Phys. Soc. Jpn.* 76 084717
[5] Abe K, Kitagawa J, Takeda N and Ishikawa M 1999 *Phys. Rev. Lett.* 83 5366
[6] Matsuoka E, Usui D, Tanida H, Nakamura S, Nojima T and Onodera H 2007 *J. Phys. Soc. Jpn.* 76 073707
[7] Matsuoka E, Takahashi F, Kitagawa J, Ohoyama K, Yoshizawa H and Ishikawa M 2001 *J. Magn. Magn. Mater.* 231 L23