Possible Multipolar Transition in NdB₄

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Abstract. Physical properties of neodymium tetraboride NdB₄ which crystallizes in the ThB₄-type structure belonging to space group D₅₄h - P4/mbm have been studied. The specific heat measurement on single crystal of NdB₄ shows that this material undergoes successive phase transitions at T_Q = 17.2 K (second-order transition), T_N₁ = 7.0 K (second-order transition) and T_N₂ = 4.8 K (first-order transition). The magnetic entropy of approximately R ln 2 and R ln 4 is released below T_N₁ and T_C, respectively. The crystalline electric field (CEF) ground state of NdB₄ is a pseudo-quartet consisting of two Kramers doublets. At around T_Q, no anomalies of the magnetic susceptibility along the c-direction which is easy axis of magnetization are observed. Moreover, the susceptibility within the ab-plane shows only a very small peak. These results seem to indicate that NdB₄ undergoes a quadrupolar (or higher rank multipolar) transition at T_Q followed by two magnetic transitions since the behaviors are quite different from those of conventional magnet.

1. Introduction
The orbital (quadrupole) degrees of freedom for 4f electron systems have been studied extensively. Localized 4f electron systems with a degenerate ground state may undergo a quadrupole order transition. Especially, antiferroquadrupole (AFQ) order without a lattice distortion shows little change in magnetic susceptibilities, hence the quadrupole moment is known as a hidden order parameter. For example, in DyB₂C₂, the magnetic susceptibility does not show any anomaly at T_Q = 27.4 K which corresponds to the AFQ transition temperature, although the specific heat shows a λ-like anomaly at this temperature. In this paper, we reveal a novel quadrupolar (or higher rank multipolar) ordering system NdB₄.

NdB₄ crystallizes in the tetragonal ThB₄-type structure belonging to space group D₅₄h - P4/mbm. [1, 2, 3] The boron atoms form a continuous three-dimensional network. The Nd atoms are located below and above the centers of the seven-membered boron rings in densely packed planes of boron atoms. All Nd atoms occupy the equivalent sites having orthorhombic symmetry C₂ᵥ. The two-dimensional layer of the Nd atoms is formed by fused equilateral triangles and squares. It can be considered that this arrangement of the Nd atoms is the Shastry-Sutherland lattice. Previous studies of the magnetic properties of NdB₄ have shown that it orders antiferromagnetically at 7.0 K. [4, 5, 6] There are very few reports on the physical properties of NdB₄ and studies from the point of view of the role of quadrupolar degrees of freedom are lacking. Here we investigate the details of the magnetic properties of NdB₄ by means of magnetic susceptibility and specific heat measurements.
2. Experimental

Single crystals of NdB$_4$ were prepared by a self-flux method using Nd as a flux. The magnetizations of NdB$_4$ were measured using a SQUID magnetometer (MPMS, Quantum Design Co.) in the temperature range of 1.8-300 K and under magnetic fields up to 5 T. The magnetic susceptibility measurements were performed after zero-field-cooled (ZFC) and after field-cooled (FC) conditions. For the single crystal of NdB$_4$, the magnetization measurements, where the magnetic field $B$ is applied parallel ($B \parallel c$) and perpendicular ($B \perp c$) to the c-axis, were carried out between 1.8 K and 300 K, and at several temperatures under magnetic fields up to 5 T. Specific heat measurements were carried out by a heat-relaxation method down to 1.9 K (using PPMS, Quantum Design Co.).

3. Results and discussion

![Figure 1](image1.png)

**Figure 1.** Magnetic susceptibility $\chi$ of NdB$_4$. The inset shows the inverse susceptibility.

Figure 1 shows the magnetic susceptibility $\chi$ of the single crystal of NdB$_4$. No difference between the FC and ZFC susceptibilities in any direction is observed throughout the whole temperature range; therefore, only ZFC data are shown for clarification. The coincidence of the ZFC and FC data suggests that no spontaneous magnetization is present in NdB$_4$. The susceptibility for $B \parallel c$ shows a maximum at about 7.2 K and a small discontinuous drop at 4.8 K, while no anomalies are found at around 17 K, in which the $\lambda$-like anomalies are observed by the specific heat measurement as described below. On the other hand, susceptibility for $B \perp c$ shows a small cusp at 17.2 K and kinks at 6.9 K and 4.9 K.

The inverse molar susceptibilities $\chi^{-1}$ of NdB$_4$ (the inset of Fig. 1) follows the Curie-Weiss law from 50 K up to room temperature. The effective paramagnetic moments and the Weiss temperatures are estimated at $\mu_{\text{eff}}^{\|c} = 3.72 \mu_B$ and $\theta_p^{\|c} = -16.2$ K for $\chi$ for $B \parallel c$, and $\mu_{\text{eff}}^{\perp c} = 3.62 \mu_B$ and $\theta_p^{\perp c} = -38.1$ K for $\chi$ for $B \perp c$, respectively. The effective magnetic moment is close to the calculated value of 3.62 $\mu_B$ for a free Nd$^{3+}$ ion. The negative Weiss temperature $\theta_p$ indicates an antiferromagnetic interaction between the local magnetic moments.

The specific heat of the single-crystalline sample of NdB$_4$ shows two $\lambda$-like anomalies at $T_Q = 17.2$ K and $T_{N1} = 7.0$ K, and a very sharp peak at $T_{N2} = 4.8$ K as shown in Fig. 2. The transition at $T_{N1}$ was consistent with those reported previously. [6] We newly found two phase transitions at $T_Q = 17.2$ K and $T_{N2} = 4.8$ K. The phase transitions at $T_Q$ and $T_{N1}$ are typical
second-order transitions. On the other hand, since the peak of the specific heat at $T_{N2}$ is very sharp, and moreover, $\chi$ for $B \parallel c$ shows the discontinuity at $T_{N2}$, the phase transition at $T_{N2}$ seems to be a first-order one.

The magnetic contribution $C_{mag}$ to the specific heat of NdB$_4$ is estimated by subtracting the phononic and electronic contributions from the total specific heat of NdB$_4$; the phononic and electronic contributions are obtained from a measurement of the isostructural and nonmagnetic compound LaB$_4$. The temperature dependence of the magnetic entropy per Nd$^{3+}$ ion $S$ was calculated by numerically integrating the data of $C_{mag}/T$ vs $T$. The magnetic entropy reaches $R \ln 2$ and $R \ln 4$ at about 11 K and 41 K, respectively. The crystalline electric field (CEF) ground-state multiplet $J = 9/2$ of Nd$^{3+}$ splits into five $E_1/2$ ($\Gamma_5$) doublets in the CEF potential of the site with $C_{2v}$ symmetry in NdB$_4$. The result indicates that the CEF ground state of NdB$_4$ is a pseudo–quartet consisting of two Kramers doublets with $E_1/2$ ($\Gamma_5$) symmetry.

![Figure 3](image.jpg)

**Figure 3.** Specific heat of NdB$_4$ at various magnetic field strengths for $B \parallel c$. The curves are vertically shifted for clarity by 5 J/mol K for successively higher magnetic field.

![Figure 4](image.jpg)

**Figure 4.** Specific heat of NdB$_4$ at various magnetic field strengths $B \perp c$. The curves are vertically shifted for clarity by 5 J/mol K for successively higher magnetic field.

Figure 3 and 4 show the specific heat of the single crystalline sample of NdB$_4$ under various magnetic fields for $B \parallel c$ and $B \perp c$, respectively. For $B \parallel c$, $T_{N1}$ and $T_{N2}$ peaks broaden and shift to lower temperature as the magnetic field increases between 0 T and 3 T. Above 4 T, these peaks disappear and a Schottky-like anomaly appears. In contrast, the $T_Q$ peak at the highest temperature transition hardly change over the whole magnetic field ranges. On the other hand, for $B \parallel c$, all peaks slightly shift to lower temperature as the magnetic field increases.

Figure 5 shows the magnetic field vs. temperature phase diagram of NdB$_4$ for $B \parallel c$ and $B \perp c$, as determined from the present results of the specific heat and magnetization.
measurements. Phase I is a paramagnetic and paraquadrupolar state. As mentioned above, the phase transitions at $T_{N1}$ and $T_{N2}$ are magnetic phase transitions. On the analogy of similar behaviors of the specific heats and magnetic susceptibility on HoB$_2$C$_2$ [10], ErB$_2$C$_2$ [11] and HoB$_4$ [12], phase III and IV may be incommensurate and commensurate magnetic ordered states, respectively. At around $T_Q$, no anomalies of the magnetic susceptibility along the c-direction which is easy axis of magnetization are observed. Moreover, the susceptibility within the ab-plane shows only a very small peak. These results seem to indicate that NdB$_4$ undergoes a multipolar transition at $T_Q$ followed by two magnetic transitions since the behaviors are quite different from those of conventional magnet.

A similar behavior of the magnetic susceptibility and the entropy change are shown by the quadrupolar ordering compounds DyB$_2$C$_2$ [8] and YbRu$_2$Ge$_2$ [9]. In these compounds of which the CEF ground states are pseudo–quartet, the twofold Kramers degeneracy is conserved since time–reversal symmetry is not broken by the quadrupolar ordering. Moreover, at the quadrupolar transition temperature, the magnetic susceptibility does not show a large anomaly such as that at a magnetic transition, although the specific heat shows a $\lambda$-like anomaly. Therefore, present results of the specific heat and magnetization measurements strongly suggest that phase II of NdB$_4$ is quadrupolar (or higher rank multipolar) ordered state. If the transition at $T_Q$ of NdB$_4$ is purely associated with an antiferroquadrupole (AFQ) order, it will be the first case of AFQ ordering in neodymium compounds. In order to directly confirm that phase II of NdB$_4$ is nonmagnetic state, neutron diffraction and resonant x-ray scattering experiments are now in progress.

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