Elastic Constants of NdCu$_2$Ge$_2$

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Abstract. The components-separated magnetic transition in NdCu$_2$Ge$_2$ was investigated by measuring elastic constant and specific heat. The specific heat shows clear peak at $T_N = 4.8$ K. The magnetic entropy change reaches $R \ln 2$ at 6 K and $R \ln 8$ at 72 K with increasing temperature. This result indicates that the crystalline electric field ground state of NdCu$_2$Ge$_2$ is a Kramers doublet. In addition, the results of the elastic constant measurements suggest that no degeneracy of quadrupolar degrees of freedom exists below $T_N$. NdCu$_2$Ge$_2$ has a possibility of another mechanism that suppress the magnetic ordering of the $ab$-component unlike other compounds showing component-separated magnetic transition.

1. Introduction
The ternary compounds RT$_2$X$_2$ (R=rare earth, T=transition metal and X=Si, Ge) have attracted considerable interest because of a rich variety of magnetic behaviors or superconductivity. The compounds crystallize in the ThCr$_2$Si$_2$-type structure which has the body-centered tetragonal with space group $I4/mmm$ [1, 2]. Recently, Shigeoka et al. reported the magnetic properties of NdCu$_2$Ge$_2$ [3]. The magnetic susceptibility along the $c$-axis shows a cusp-like anomaly at $T_N = 4.7$ K while those in the $ab$-plane show no clear anomaly around $T_N$ and increase even below $T_N$. The magnetic susceptibility in the $c$-axis is smaller than the one along $ab$-plane in the whole temperature range. Therefore it is unusual that the antiferromagnetic ordering of the $c$-component of the magnetic moments occurs at $T_N$ whereas the $ab$-components are paramagnetic. The paramagnetic behavior along the $ab$-plane implies that the presence of another magnetic transition below $T_N$ associated with the ordering of the $ab$-components. We have considered that the magnetic transition in NdCu$_2$Ge$_2$ is similar to the higher-temperature transition in "Successive components-separated magnetic transitions". CsNiCl$_3$ [4-6], DyB$_4$ [7] and TbCoGa$_5$ [8] are well known examples of compounds that show such successive transitions. More recently, this type of successive transitions is reported in HoRh$_2$Si$_2$ having the same crystal structure of NdCu$_2$Ge$_2$ [9].

In order to examine the magnetic transition in NdCu$_2$Ge$_2$, we grew single crystals and measured their elastic constant and specific heat.

2. Experimental
Single crystals of NdCu$_2$Ge$_2$ were grown by the tetra-arc Czochralski method and the flux method using Sn as flux. The direction of the single crystals were determined by the X-ray back Laue method. The elastic constants were examined by ultrasonic measurement in the temperature range from 1.8 K to 40 K using the single crystalline sample obtained by...
the Czochralski method. Ultrasonic measurement is an effective technique for investigating the quadrupolar effect in an f-electron system with an orbitally degenerate ground state, because the quadrupole moment of the f electron couples to the elastic strain. A relative change in the elastic constant, \( \Delta C/T \), of the sample was obtained using \( \Delta C/T = 2\Delta v/v + (\Delta v/v)^2 \), which is derived from \( C = \rho v^2 \), where \( v \) and \( \rho \) represent the sound velocity and the density of the crystal, respectively. \( \Delta v/v \) was measured with a phase comparator using double-balanced mixers. The specific heat of the single crystal obtained by the flux method was measured by the heat-relaxation method in the temperature range from 1.9 K to 100 K.

3. Experimental results and discussion

![Graph showing the temperature dependence of the relative change in the elastic constants of NdCu\(_2\)Ge\(_2\).](image)

Figure 1. Temperature dependence of the relative change in the elastic constants of NdCu\(_2\)Ge\(_2\).

Figure 1 shows the temperature dependence of the relative change in the elastic constants \( \Delta C_{11}/C_{11} \), \( \Delta C_{33}/C_{33} \), \( \Delta C_{44}/C_{44} \), and \( \Delta C_{66}/C_{66} \) of NdCu\(_2\)Ge\(_2\). The longitudinal mode \( \Delta C_{11}/C_{11} \) and \( \Delta C_{33}/C_{33} \) show the monotonic hardening with decreasing temperature down to 1.8 K and no clear anomaly at approximately \( T_N = 4.7 \) K. The transverse mode \( \Delta C_{44}/C_{44} \) and \( \Delta C_{66}/C_{66} \) exhibit the softening down to approximately 15 K and clear anomalies at \( T_N \). \( C_{11} \) and \( C_{33} \) are included in \( C_u = 1/6(C_{11} + C_{12} - 4C_{13} + 2C_{33}) \) and \( 1/2(C_{11} - C_{12}) \) coupled with \( \Gamma_1 \) and \( \Gamma_3 \) symmetry in the \( D_{4h} \) of the ThCr\(_2\)Si\(_2\)-type structure (see Table 1). \( \Gamma_1 \) and \( \Gamma_3 \) are not coupled with any dipole moments, hence it is possible that \( C_{11} \) and \( C_{33} \) show no anomaly associated with a magnetic transition.

If the degeneracy of quadrupolar degrees of freedom exists in a 4f electron system, the elastic constant shows a Curie-type softening written by the equation \( C(T) = C^0(T - T^0_C)/(T - \Theta) \), which is deduced from the Curie term of the quadrupole-strain susceptibility [10, 11]. \( \Theta \) is proportional to the average quadrupole-quadrupole interaction. \( T^0_C = \Theta + E_{JT} \), where \( E_{JT} \) is the Jahn-Teller (4f electron-lattice) coupling. The measured elastic constants of NdCu\(_2\)Ge\(_2\) do not obey the above equation below \( T_N \). Therefore the quadrupolar degrees of freedom should not be degenerate below \( T_N \). These results indicate that the antiferromagnetic transition at \( T_N \) in NdCu\(_2\)Ge\(_2\) is not affected by the quadrupole moment system.

Figure 2 shows the temperature dependence of the specific heat \( C \), magnetic specific heat \( C_{mag} \) in the form of \( C_{mag}/T \), and magnetic entropy change \( S_{mag} \) of NdCu\(_2\)Ge\(_2\). The specific
Table 1. The symmetry of quadrupole moments, elastic constants and dipole moments in a tetragonal system with $D_{4h}$

| Symmetry | Quadrupole Moments | Elastic constants | Dipole moments |
|----------|-------------------|------------------|----------------|
| $\Gamma_1$ | $O_2^J = \frac{1}{2}(2J_z^2 - J_x^2 - J_y^2)$ | $C_\text{u} = \frac{1}{16}(C_{11} + C_{12} - 4C_{13} + 2C_{33})$ | $J_z$ |
| $\Gamma_2$ | $O_2^Z = \frac{1}{2}(J_x^2 - J_y^2)$ | $\frac{1}{2}(C_{11} - C_{12})$ | $C_{66}$ |
| $\Gamma_3$ | $O_{xy} = \frac{\sqrt{3}}{2}(J_x J_y + J_y J_x)$ | |
| $\Gamma_4$ | $O_{yz} = \sqrt{3}(J_y J_z + J_z J_y)$ | $C_{44}$ | $J_x, J_y$ |
| $\Gamma_5$ | $O_{zx} = \sqrt{3}(J_z J_x + J_x J_z)$ | |

Figure 2. (a) Temperature dependence of the specific heat $C$ of NdCu$_2$Ge$_2$ and LaCu$_2$Ge$_2$. The inset shows the low-temperature data. (b) Temperature dependence of the magnetic specific heat $C_{\text{mag}}$ in the form of $C_{\text{mag}}/T$ (left axis) and magnetic entropy change (right axis) of NdCu$_2$Ge$_2$. The horizontal broken lines indicate the values of magnetic entropy.

The magnetic contribution $C_{\text{mag}}$ to the specific heat of NdCu$_2$Ge$_2$ is deduced by subtracting the specific heat of the isostructural nonmagnetic compound LaCu$_2$Ge$_2$ from the total specific heat of NdCu$_2$Ge$_2$. Then, we obtained the temperature dependence of the magnetic entropy $S_{\text{mag}}$ by numerically integrating the data of $C_{\text{mag}}/T$ over temperature. The magnetic entropy change from 0 K to 1.9 K was estimated assuming that $C_{\text{mag}}/T$ is proportional to the temperature. The specific heat of NdCu$_2$Ge$_2$ shows clear peak at 4.8 K. This anomaly is due to the antiferromagnetic ordering of the $c$-component. The magnetic specific heat shows a Schottky-like anomaly around 20 K. The magnetic entropy change reaches $R \ln 8$ at ~6.0 K and $R \ln 10$ at ~72 K. Thus the crystalline electric field (CEF) ground state of NdCu$_2$Ge$_2$ is a doublet. In addition, we consider that another magnetic phase transition is not likely to exist below $T_N$ in NdCu$_2$Ge$_2$ for the following reason. If CEF ground state is a quartet or pseudo-quartet with an additional Kramers doublet, the magnetic entropy of $R \ln 2$ is added to the magnetic entropy change in Fig. 2. Then, total magnetic entropy in NdCu$_2$Ge$_2$ exceeds $R \ln 10$ expected for the
entire multiplet with $J = 9/2$ of Nd$^{3+}$ ion. However, the paramagnetic behavior of the magnetic susceptibility along [100] and [110] direction below $T_N$ indicate the presence of the degeneracy of the internal degrees of freedom [3]. The reason for this discrepancy is still unclear.

In the triangular lattice antiferromagnet CsNiCl$_3$ and the Shastry-Sutherland lattice antiferromagnet DyB$_4$, geometrical frustration is important to suppress the magnetic ordering of particular components. However, the geometrical frustration is not the only keys to the occurrence of the successive components-separated magnetic transitions, because the transitions appear in TbCoGa$_5$ where the Tb atoms form a simple tetragonal lattice. The degeneracy of quadrupolar degrees of freedom exists in the intermediate phase in DyB$_4$ and TbCoGa$_5$ [7, 8]. This suggested that the presence of the degeneracy of quadrupolar degrees of freedom is also important to occur successive components-separated magnetic transitions. On the other hand, the behavior of the elastic constant of NdCu$_2$Ge$_2$ indicates that the quadrupolar degrees of freedom is not degenerate below $T_N$. Thus we conclude that NdCu$_2$Ge$_2$ has a possibility of another mechanism for the appearance of the components-separated magnetic transition that requires no degeneracy of the quadrupolar degrees of freedom unlike those in DyB$_4$ or TbCoGa$_5$. Moreover, the components-separated magnetic transition in NdCu$_2$Ge$_2$ seems to require no magnetic ordering of the $ab$-components below the transition temperature associated with the ordering of the $c$-component.

The magnetic properties of NdCu$_2$Si$_2$ are quite similar to those of NdCu$_2$Ge$_2$ but the magnetic entropy of NdCu$_2$Si$_2$ reaches $R \ln 4$ at transition temperature with magnetic ordering of the c-component [12-14]. This indicates the possibility that the quadrupole moment system influences the magnetic transition in NdCu$_2$Si$_2$. Investigations of the physical property, especially the elastic property, of NdCu$_2$Si$_2$ is very important to study the behavior of quadrupolar degrees of freedom and clarify the magnetic transition in NdCu$_2$Ge$_2$ in addition to NdCu$_2$Si$_2$.

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