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Novel magnetization processes of $NdCu_2Si_2$ single crystal

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Abstract

Magnetic susceptibility, magnetization and specific heat measurements have been performed on a $NdCu_2Si_2$ single crystal and polycrystalline compounds. The susceptibility along the c-axis shows an antiferromagnetic behavior and an anomaly at $T_N = 9.8$ K. Magnetic moments direct to the c-axis, but the magnetic easy direction is nevertheless the [1 0 0] direction in the basal plane. Magnetization along [1 0 0] is only 1.9 μ_B at 7 T. The c-axis magnetization shows a metamagnetic transition at 4.1 T, which comes from a spin-flop. In magnetic specific heat versus T, a λ-type anomaly and a Schottky anomaly appear around T_N and 5 K, respectively. Magnetic entropy of Rln6 is released below 30 K. The existence of three doublet levels having 12 and 39 K intervals can be deduced.

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Keywords: $NdCu_2Si_2$; Antiferromagnetism; Magnetization process; Magnetic susceptibility; Specific heat

1. Introduction

The ternary compounds RM_2X_2 (R = rare earth, M = transition metal and X = Si, Ge) form a large family having the tetragonal $ThCr_2Si_2$-type crystal structure. These compounds have received considerable interest because of a great variety of magnetic behaviors [1,2]. Our attention is now in the RCu_2X_2 series, which show peculiar magnetic behaviors. The compounds $PrCu_2Si_2$ and $PrCu_2Ge_2$ have anomalously high Neel temperatures where effects of a quadrupolar coupling have been suggested [3,4]. In a $PrCu_2Ge_2$ single crystal, very peculiar magnetic behaviors have been reported [3,4]. The magnetic susceptibility is different between the virgin state and one after magnetization saturation process. The virgin susceptibility is enhanced below 3.5 K while one after saturation becomes very small. Moreover, an irreversible magnetization process is observed along the easy c-axis in low temperatures; the magnetization process in the virgin state is different from one in the state after magnetization saturation process. The irreversible process appears only in the virgin state while it becomes reversible after saturation, which has been never seen yet. Recently, in a $NdCu_2Ge_2$ single crystal, very peculiar magnetization process has been also reported [5]. The Nd magnetic moments direct to the c-axis in the antiferromagnetic state, although the magnetic easy direction is nevertheless in the basal plane. The magnetization along the [1 0 0] direction increase initially with a considerable large gradient up to 6.6 T and shows a knee around 6.6 T followed by a gradual increase. It has been proposed that crystalline electric field effects and a quadrupolar coupling play an important role for this magnetization process. The magnetic behaviors of $NdCu_2Si_2$ are very interesting, concerned with these peculiar behaviors. No detailed magnetic study, however, has been reported on $NdCu_2Si_2$ compounds. Magnetic behaviors on a $NdCu_2Si_2$ single crystal have been studied by magnetic susceptibility and magnetization measurements, and specific heat measurements on polycrystalline sample as well.

The single crystal has been grown by the tri-arc Czochralski method. The single-phase nature has been confirmed by X-ray powder diffraction. Magnetization and magnetic susceptibility measurements have been carried out using a superconducting magnet with a sample extracting magnetometer. Specific heat measurement has been performed by a relaxation method. All measurements have been done at the Institute for Solid State Physics, University of Tokyo.

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2. Results and discussion

The temperature dependences of magnetic susceptibilities along the main symmetry axes of the tetragonal cell are shown on a $NdCu_2Si_2$ single crystal for low temperatures in Fig. 1. Along the [0 0 1] direction, the *c*-axis, a cusp is seen at $T_N = 9.8$ K, which is associated with an antiferromagnetic ordering. In the basal plane, the susceptibility increases even below T_N in contrast to one along the *c*-axis, no clear anomaly is detected around T_N. A weak magnetic anisotropy between the *c*-axis and the directions in the basal plane is evidenced; the susceptibility in the basal plane is larger than one along the *c*-axis. On the other hand, those in the basal plane are isotropic; one of [1 0 0] is identical with one of [1 1 0]. The susceptibility behavior along the *c*-axis below T_N is a typical parallel susceptibility one in an antiferromagnetic ordered state with a weak magnetic anisotropy, indicating that the magnetic moments direct to the [0 0 1] direction, the *c*-axis. The behavior in the basal plane is not typical perpendicular one, suggesting the existence of some effects on moments coupling. These behaviors are quite similar to those of $NdCu_2Ge_2$ reported [5].

The reciprocal susceptibility is shown in the inset of Fig. 1. The susceptibilities along all directions obey the Curie–Weiss law above about T_N. The $1/\chi$–T curves along the all directions are almost same though the *c*-axis one and the basal plane ones are slightly different. The effective moments estimated from the slope along the *c*-axis and the directions in the basal plane are 3.61 and 3.56 μ_B, respectively, which are agreement with the Nd^{3+} free ion value (3.62 μ_B) within an experimental accuracy. The paramagnetic Curie temperatures along the *c*-axis and the directions in the basal plane are $\Theta_c = -4.8$ K and $\Theta_a = 2.2$ K, respectively, indicating that the dominant inter-*c*-plane coupling is antiferromagnetic and the intra-plane one is ferromagnetic.

Magnetization curves along the three symmetry axes at 1.8 K are shown in Fig. 2. In the basal plane, a weak magnetic anisotropy is evidenced; the magnetization along the [1 0 0] direction is lager than one along the [1 1 0]. The magnetizations along the [1 0 0] and [1 1 0] directions increase monotonically having a considerably large slope with increasing magnetic field and reach 1.9 and 1.8 μ_B at the maximum field of 7 T, respectively. On the other hand, along the *c*-axis, a metamagnetic transition appears around $B_c = 4.1$ T; magnetization increases rapidly at B_c, followed by a gradual increase. No hysteresis is observed at this transition. The transition may be a spin-flop transition from the [0 0 1] direction to the basal plane. Magnetization value at the maximum field of 7 T is only 1.5 μ_B. The magnetization values along the all directions are much smaller than the full moment for a Nd^{3+} free ion. Further increase in magnetization and/or additional metamagnetic transitions is expected in higher magnetic fields. It should be noted that the easy magnetization direction is the [1 0 0] direction in the basal plane at $B = 7$ T though magnetic moments directs to the *c*-axis at $B = 0$ indicated from the susceptibility behavior (see in Fig. 1). This peculiar behavior has been also reported in $NdCu_2Ge_2$ where the important role of crystal field effects and the quadrupolar coupling has been emphasized [5]. From the similarity of magnetic behaviors between $NdCu_2Ge_2$ and $NdCu_2Si_2$, we should expect that a knee also appear in a high field magnetization curve of the basal plane on the $NdCu_2Si_2$ single crystal, which may be due to the quadrupolar coupling.

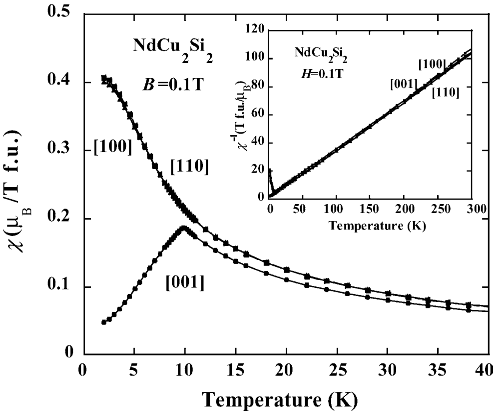

Fig. 1. Temperature dependence of magnetic susceptibility along the main symmetry directions on a $NdCu_2Si_2$ single crystal for low temperatures. The inset shows the temperature dependence of reciprocal susceptibility along the main symmetry directions.

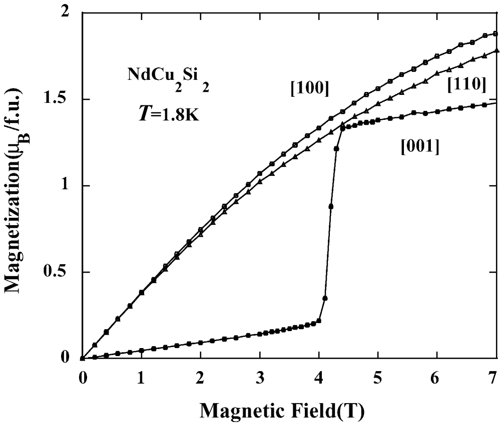

Fig. 2. Magnetization curves along the main symmetry axes at 1.8 K below 7 T on the $NdCu_2Si_2$ single crystal.

The *c*-axis magnetization curves at various temperatures are shown in Fig. 3. The transition is smeared and the transition field becomes smaller with increasing temperature. The magnetization behavior becomes a paramagnetic above T_N. The temperature dependence of the critical field is plotted in the inset of Fig. 3. The spin-flop transition is usually caused by a competition between magnetic anisotropy energy and exchange interaction energy. The dependence suggests the anisotropy energy becomes smaller with increasing temperature.

The magnetic specific heat, which is obtained by subtracting the phonon contribution from the total specific heat, is shown for $NdCu_2Si_2$ in Fig. 4. The phonon contribution is

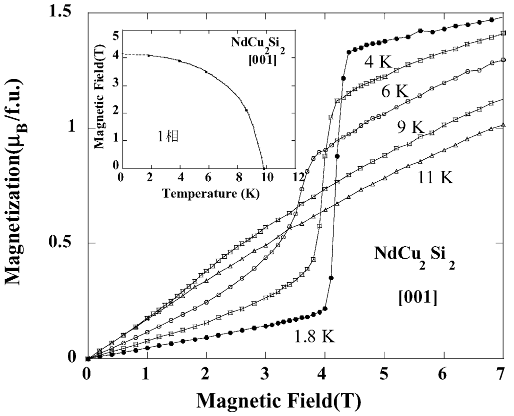

Fig. 3. The *c*-axis magnetization curves at various temperatures on the NdCu$_2$Si$_2$ single crystal. The temperature dependence of critical field B_c is shown in the inset.

estimated from the specific heat of LaCu$_2$Si$_2$ [6]. A λ-type anomaly is observed around T_N. Moreover, a broad peak, which may be a Schottky anomaly coming from the crystalline electric field level splitting, appears around 5 K. From this anomaly, we can deduce the energy splitting between the ground level and first excited level is about 13 K. The magnetic entropy estimated is shown in Fig. 5. It is evidenced from the figure that the entropy of Rln4 and Rln6 is released below about T_N and 30 K, respectively. From above results, the following level scheme is deduced; the first doublet excited level and the second doublet one lie at 13 K and about 30 K above the doublet ground level, respectively. This scheme is consistent with the inelastic neutron result reported by Goremychkin et al. [7]. They have shown that three doublet levels exist having 12 and 39 K interval. They have also deduced the crystal field parameters. Using the parameters, we tried to calculate magnetization curves. We, however, do not reproduce satisfactorily the experimental magnetization curves; the value of magnetization calculated for the basal plane in low fields is about two times as large as the experimental one. And the calculated magnetic easy direction is the [1 1 0] direction that is inconsistent with the experimental fact. We are now investigating the better CEF parameters.

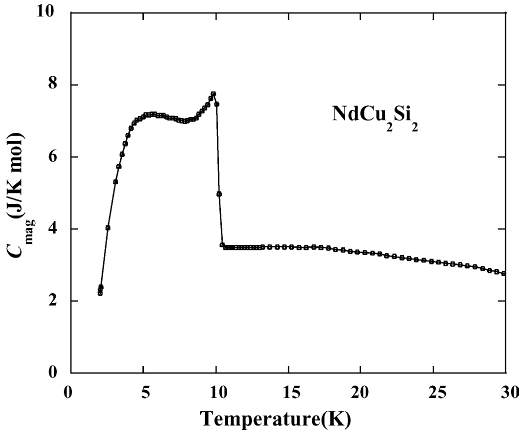

Fig. 4. Temperature dependence of magnetic specific heat on a NdCu$_2$Si$_2$ polycrystalline compound.

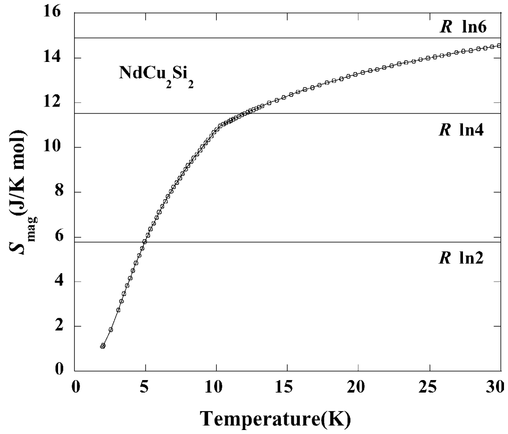

Fig. 5. Magnetic entropy estimated from the results in Fig. 4 is shown on the NdCu$_2$Si$_2$ polycrystalline compound.

A preliminary neutron diffraction study on the NdCu$_2$Si$_2$ single crystal has been performed using a double-axis spectrometer at Kyoto University Reactor, Japan. Antiferromagnetic reflections of ($h\,0\,l$) ($h + l$ = odd) have been observed except for ($0\,0\,l$) (l = odd) below T_N. This result shows that the antiferromagnetic structure is the AF-type I: a simple collinear one with the wave vector $\boldsymbol{Q} = (0, 0, 1)$ and magnetic moments parallel to the *c*-axis, consisting of ferromagnetic *c*-planes coupled antiferromagnetically with the + − + − sequence. This structure is a similar one to PrCu$_2$Ge$_2$ [8,9] and NdCu$_2$Ge$_2$ [5]. It is consistent with the positive sign of Θ_a and the negative sign of Θ_c: indication of an intra-layer ferromagnetic coupling and an inter-layer antiferromagnetic coupling.

In summary, the magnetic behavior has been studied on a NdCu$_2$Si$_2$ single crystal by measurements of magnetic susceptibility and magnetization, and specific heat measurement on a polycrystalline sample as well. The main features obtained are similar to those of NdCu$_2$Ge$_2$ and followings:

1. The compound has an antiferromagnetic order below $T_N = 9.8$ K.
2. Magnetic susceptibility behavior and the preliminary neutron study show that magnetic moments direct to the *c*-axis.
3. Magnetization behavior is peculiar; in spite of the *c*-axis moment direction, the easy magnetization direction is in the basal plane.
4. A metamagnetic transition, a spin-flop transition, appears around 4.1 T along the *c*-axis magnetization process.
5. The magnetization along the easy [1 0 0] direction at the maximum field of 7 T is 1.9 μ_B, which is much smaller than the moment expected for the Nd^{3+} free ion.
6. A λ-type anomaly and a Schottky anomaly appear in the magnetic specific heat versus T curve.
7. From the specific heat and magnetic entropy, the crystal field level scheme is deduced; two excited doublet levels exist 12 and 39 K above the ground doublet state.

Now, we could not understand completely the magnetic behavior of $NdCu_2Si_2$. We failed the reproduce of the magnetization process using crystal field parameters. We believe that the quadrupolar effect plays important roles in $NdCu_2Si_2$. Further study, high field magnetization measurements and the CEF analysis, etc., should be expected.

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