Magnetic Properties of NdCr₂Si₂C Single Crystal

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Abstract. We have prepared a NdCr₂Si₂C single crystal by Czochralski technique and investigated it by heat capacity and magnetization measurements in the temperature range 2-300 K and magnetic fields up to 6 T applied parallel to the principal crystallographic axes. A strongly anisotropic ferromagnetism has been observed with the \( T_C = 24 \) K and the ordered magnetic moment oriented entirely along the c-axis of the tetragonal structure whereas the basal plane response is weak paramagnetic. We also studied the electronic structure of the compound by first-principles DFT calculations, which predict existence of a stable Cr magnetic moment. Results of our present experiments do not allow resolving the question on the existence of the ordered Cr moments unambiguously.

1. Introduction
NdCr₂Si₂C belongs to the recently described group of RCr₂Si₂C compounds \((R = \text{rare-earth element})\) crystallizing in the tetragonal CeMg₂Si₂-type structure with the space group \(P4/mmm\) [1-3]. In this structure, the atoms occupy the following crystallographic sites: 1R in 1a: 0, 0, 0; 2Cr in 2e: 0, \(\frac{1}{2}, \frac{1}{2}\); 2Si in 2h: \(\frac{1}{2}, \frac{1}{2}, z\); 1C in 1b: 0, 0, \(\frac{1}{2}\). According to Ref. [3], the R ions \((R = \text{Pr, Nd, Gd-Dy})\) order ferromagnetically at low temperatures \((T_C \leq 30 \, \text{K})\), and the Cr sublattice probably does not exhibit any magnetic ordering. To the contrary, in the closely related ThCr₂Si₂-structure \((\text{space group } I4/mmm)\), in the compounds RCr₂Si₂ \((R = \text{Tb, Ho, Er})\), the Cr ions bear stable magnetic moments which order antiferromagnetically at temperatures lower than 700 K [4].

To get intrinsic experimental information on magnetism in NdCr₂Si₂C, we have grown a single crystal of this compound, and investigated it by specific heat and magnetization measurements. We also studied electronic structure of this material by the first principles methods based on the density functional theory (DFT) with a special emphasis on the existence of the Cr magnetic moment.

2. Experimental and computational
The single crystal of NdCr₂Si₂C has been grown in a triarc furnace by the Czochralski pulling technique from about 6 g of melt. Prior to the crystal growth, the constituent rare-earth element had been refined by the solid-state electrotransport (SSE) [5]. The grown ingot was sealed in an evacuated quartz tube and annealed at 800°C for two weeks. Part of the crystal was pulverized and characterized by X-ray powder diffraction (XRPD). The XRPD data were analyzed by the Rietveld technique [6] using the program FULLPROF [7]. Both, the single-crystal quality and orientation of the grown ingot...
were determined by the standard Laue method. The heat capacity and magnetization measurements were performed with a PPMS 14T (Quantum Design) facility, using the standard heat capacity and VSM options, respectively, in the temperature range 2-300 K and magnetic fields up to 6 T applied parallel to the principal crystallographic axes.

The ground state electronic structure was calculated within the local spin density approximation (LSDA) and generalized gradient approximation (GGA) [8]. For this purpose, we used the full-potential WIEN2k code [9]. The Nd 4f-electron states are localized and were treated in the open-core approximation with the stable 4f3 atomic configuration.

3. Results and discussion

The XRPD analysis confirmed the single-phase composition of the ingot. The lattice parameters and the z parameter of the Si atom were determined as \( a = 4.023 \) Å, \( c = 5.341 \) Å and \( z_{Si} = 0.227 \).

Figure 1 shows the temperature dependence of the specific heat measured in various magnetic fields applied along the \( c \)-axis (\( B \parallel c \)). The zero-field curve shows a considerable anomaly at about 24 K, which is caused by a magnetic phase transition. This anomaly is suppressed and shifted to higher temperatures with the increasing magnetic field applied along the \( c \)-axis as expected for a ferromagnet. This evolution with the magnetic field in conjunction with the magnetization data discussed below allows us to conclude that NdCr2Si2C becomes ferromagnetic at the Curie temperature \( T_C = 24 \) K. The additional minor anomaly on the \( C \) vs. \( T \) curve, which is present at ~ 3 K, is shifted to 4 K in a magnetic field of 5 T. The origin of this effect is not clear at the moment and requires further investigation.

The temperature dependence of the estimated magnetic entropy \( S_{mag} \) is represented in Figure 1b. Slightly above \( T_C \), \( S_{mag} \) reaches a value of about \( R \ln 2 \) and, above 200 K, it approaches to \( R \ln 10 \), which is the value expected for the Nd\(^{3+} \) ion (\( gJ = 9/2 \)).

![Figure 1](image.png)

**Figure 1.** (a) Temperature dependence of the specific heat measured in different magnetic fields up to 5 T for \( B \parallel c \). Inset shows a detail of \( C \) vs. \( T \) curve in magnetic fields 0 and 5 T. (b) Temperature dependence of the estimated magnetic entropy.

The magnetization curves measured at selected temperatures are displayed in Figure 2. The \( c \)-axis magnetization measured at 3 and 10 K saturates already at 0.4 T yielding the saturated value of 3 \( \mu_B/\text{f.u.} \) at 3 K, whilst the \( a \)-axis magnetization is linear with the increasing magnetic field reaching the value of 0.08 \( \mu_B/\text{f.u.} \) only at 6 T. The magnetization curves clearly manifest the strong uniaxial magnetocrystalline anisotropy with the easy magnetization along the \( c \)-axis. The 3-K saturated magnetic moment of (3 \( \mu_B/\text{f.u.} \)) is somewhat lower value than the ordered moment of a Nd\(^{3+} \) free ion (\( gJ = 3.2 \ \mu_B \)).
Figure 2. Magnetization isotherms of the NdCr$_2$Si$_2$C single crystal measured along the principal crystallographic axes.

Figure 3 shows the temperature dependencies of the $a$- and $c$-axis magnetization, respectively. The sharp increase of small-field magnetization along the $c$-axis below $T_C$ is consistent with the scenario of the transition from paramagnetic to ferromagnetic state. The $a$-axis magnetization exhibits a broad anomaly around 100 K which is tentatively attributed to crystal-field effect. The sharp decrease of the magnetization below $T_C$ and the further low-temperature features is fairly resistant to the magnetic field $B || a$. A possible reason for $a$-axis magnetization drop just below $T_C$ may be speculated in connection with the expected sudden enhancement of the magnetocrystalline anisotropy below $T_C$. Further investigation can help to resolve this problem.

Figure 3. Temperature dependence of the $a$-axis (a) and $c$ axis (b) magnetization measured in selected magnetic fields. The FC and ZFC curves are identical for $B = 2$ and 4 T ($B || c$), respectively.

The $c$-axis magnetization data resemble the corresponding magnetization behavior of the PrCr$_2$Si$_2$C single crystal [10], which is ferromagnet below $T_C = 30$ K with the same easy magnetization axis as
for NdCr$_2$Si$_2$C. However, the low temperature anomalies were not observed in the measurement along the hard magnetization axis.

The first-principles calculations provided ordered magnetic moment both on the Nd and Cr sites. The calculated Cr moment amounts about 0.89 $\mu_B$ using GGA [7]. The value depends on the method used (GGA or LSDA). The Cr moment is stabilized by the 5$d$ states of Nd which are polarized by the localized Nd spin moment of about 3 $\mu_B$ and strongly hybridized with the Cr 3$d$ states. When considering the expected parallel coupling of the Nd and Cr magnetic moments along the c-axis a value of the saturated magnetic moment should be $\sim 4.8 \mu_B$/f.u., which is a dramatically larger value of the experimental value measured at 2 K (3 $\mu_B$/f.u.).

4. Conclusions
A single crystal of NdCr$_2$Si$_2$C has been grown and studied by heat capacity and magnetization measurements. The compound is characterized by strong uniaxial magnetocrystalline anisotropy with the c-axis as the easy direction of magnetization and ferromagnetic ordering ($T_C = 24$ K). The first-principles calculations also suggest ordered magnetic moment on Cr atoms. The experimental observation seems to be that the compound undergoes magnetic ordering from Nd, and not from Cr, which is in contradiction to DFT calculations. We are aware that bulk magnetization data do not provide unambiguous information allowing to resolving the question concerning existence of the ordered Cr moments. Therefore, polarized neutron-diffraction and XMCD experiments with our single crystal are envisaged as the inevitable next steps of our research, which may resolve the question of Cr magnetism in NdCr$_2$Si$_2$C on microscopic scale.

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