Magnetism and Magnetic Structure of NdCr$_2$Si$_2$C

Marcela Janatová$^1$, Jana Poltierová Vejpravová$^1$, Jan Prokleška$^1$, Vladimír Sechovský$^1$,
Martin Diviš$^1$, Olivier Isnard$^2$

$^1$Charles University, Faculty of Mathematics and Physics, DCMP, 121 16 Prague 2, Czech Republic
$^2$Institut Laue Langevin, and University J. Fourier Grenoble, 38042 Grenoble Cedex 9, France

Email: janatova@mag.mff.cuni.cz

Abstract. A NdCr$_2$Si$_2$C polycrystal has been prepared and characterized by heat-capacity and magnetization, X-ray and neutron powder diffraction measurements. Ferromagnetism below $T_C = 21$ K with Nd magnetic moments aligned parallel to the c-axis has been confirmed. We also studied the electronic structure of NdCr$_2$Si$_2$C by first-principles calculations, which predict the ordered magnetic moment both on the Nd and Cr sites. The magnetization and neutron diffraction data, however, do not allow resolving the question of existence of the Cr moment unambiguously.

1. Introduction
NdCr$_2$Si$_2$C is a member of the recently described family of the RCr$_2$Si$_2$C compounds (R = a rare-earth element) crystallizing in the tetragonal CeMg$_2$Si$_2$-type structure with the space group $P4/mmm$ [1-3]. In this structure, the atoms occupy the 1R in 1a: 0, 0, 0; 2Cr in 2e: 0, 0, 1/2; 2Si in 2h: 0, 0, 1/2; 1C in 1b: 0, 0, 1/2 crystallographic sites. According to Ref. [3], the R ions (R = Pr, Nd, Gd-Dy) order ferromagnetically at low temperatures ($T_C \leq 30$ K), and the Cr sublattice probably exhibits no magnetic ordering. Contrary, Moze et al. [4] reported that in the related RCr$_2$Si$_2$ compounds ($I4/mmm$), the Cr stable magnetic moments exist and order antiferromagnetically below 700 K.

In this paper, we report on magnetism in NdCr$_2$Si$_2$C investigated by heat-capacity and magnetization measurements and by neutron powder diffraction (NPD). First-principles calculations based on the density functional theory (DFT) have been performed to investigate the Cr magnetism.

2. Experimental and computational
We have prepared a polycrystalline sample of NdCr$_2$Si$_2$C by arc melting in a protective argon atmosphere. The sample was several times re-melted to improve the homogeneity. Prior to the sample preparation, the Nd metal had been refined by the solid-state electrotransport (SSE) [5]. The sample was characterized by X-ray powder diffraction (XRPD) and field-emission scanning electron microscopy (SEM). The heat capacity and magnetization measurements were performed with a PPMS 9T (Quantum Design) facility, using the standard Heat Capacity, ACMS and VSM Oven option, respectively, in the temperature range 2-900 K and magnetic fields up to 9 T. Neutron powder diffraction (NPD) measurements were performed in the temperature range 2-27 K and at the room
temperature on the multidetector powder diffractometer D1B ($\lambda = 2.52$ Å) at ILL, Grenoble. The XRPD and NPD data were analyzed by the Rietveld method [6] using the program FULLPROF [7].

To obtain direct information about the ground-state electronic structure and magnetic properties, we performed first-principles theoretical calculations. The ground state electronic structure was calculated within the local spin density approximation (LSDA) and generalized gradient approximation (GGA) [8] using the full-potential WIEN2k code [9]. The localized Nd 4f-electron states were treated in the open-core approximation with the stable 4f$^3$ atomic configuration.

3. Results and discussion

The XRPD and microprobe analyses confirmed the sample containing only the desired tetragonal NdCr$_2$Si$_2$C phase with the lattice parameters $a = 4.018$ Å, $c = 5.333$ Å and $\varepsilon_{\text{Si}} = 0.232$.

The temperature dependence of the specific heat is presented in Figure 1a. A sharp $C(T)$ anomaly is observed at about 21 K, which is attributed to the magnetic phase transition from paramagnetic to ferromagnetic state at the Curie temperature $T_C$. The derived magnetic entropy $S_{\text{mag}}$, which was calculated on the basis of the difference between the total specific heat measured for NdCr$_2$Si$_2$C and corresponding non-magnetic analogue LaCr$_2$Si$_2$C, is presented in Figure 1b. Slightly above $T_C$, $S_{\text{mag}}$ reaches a value of $R\ln2$ expected for a doublet and, above 200 K, $S_{\text{mag}}$ approaches the value of $R\ln10$, which is expected for the Nd$^{3+}$ ion ($J = 9/2$).

![Figure 1](image)

**Figure 1.** Temperature dependence of the specific heat as the $C/T$ vs. $T$ curve (a) and magnetic entropy (b).

Figure 2a shows the temperature dependence of the magnetization measured at various magnetic fields. The low-field ZFC and FC curves bifurcate approximately at $T_C$. The higher-field $M(T)$ curves coincide below 10 K suggesting rapid saturation of the magnetic moment at magnetic fields larger than 2 T. The plot of the inverse magnetic susceptibility is shown in Figure 2b. One can clearly see, that there are no high-temperature anomalies connected with the antiferromagnetic ordering of the Cr sublattice, which has been reported for the related RCr$_2$Si$_2$ compounds [4]. The high-temperature curve can be fitted using the modified Curie-Weiss law:

$$\chi = \chi_0 + \frac{C}{T - \theta_p}, \quad C = \frac{N_a\mu_{\text{eff}}^2}{3k_B}.$$

We have obtained an effective magnetic moment value of $3.4(7) \mu_B$/f.u., a paramagnetic Curie temperature $\theta_p = (20 \pm 3)$ K and $\chi_0 = 1.46 \cdot 10^8$ m$^3$/mol. The value of $\mu_{\text{eff}}$ is close to the theoretical effective moment of $3.62 \mu_B$/f.u. for Nd$^{3+}$ ion.
Figure 2. Temperature dependence of the magnetization (a) and inverse magnetic susceptibility (b).

The magnetization curves measured at selected temperatures are displayed in Figure 3. At 2 K, the compound exhibits a strong ferromagnetic component and rapid saturation already at 1 T with the saturation magnetic moment of about 1.86 $\mu_B$/f.u. The hysteresis loop shows a coercivity of about 0.2 T and a remanence, $M_r$, of about 1.55 $\mu_B$/f.u.. The value of $M_t$ decreases with increasing temperature and vanishes at about 20 K ($\sim T_C$).

Figure 3. Magnetization isotherms of the NdCr$_2$Si$_2$C measured at various temperatures.

The first-principles calculations suggest an ordered magnetic moment both on the Nd and Cr sites. The calculated value of the Cr moment depends on the method used (GGA or LSDA); it amounts about 0.89 $\mu_B$ using GGA [8]. 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.

The NPD experiment was performed also in order to investigate the possibility of magnetic ordering of the Cr sublattice. The ferromagnetic ordering in the compound was confirmed by the temperature evolution of the NPD patterns (Figure 4a). Below $T_C$, we observed considerable additional intensities on top of nuclear reflections except for the (00l), which indicates the ferromagnetic alignment of magnetic moments along the c-axis. Two different models were applied for the analysis of the magnetic diffraction data: 1) when assuming only the Nd moments, which are ordering ferromagnetically we obtain $\mu_{Nd} = (3.32 \pm 0.08) \mu_B$, 2) assuming the Nd moments ordering ferromagnetically and also the Cr moments ordered antiparallel to the Nd moments. Then the refined
value of the magnetic moments are $\mu_{\text{Nd}} = (3.31 \pm 0.08) \mu_B$ and $\mu_{\text{Cr}} = (0.46 \pm 0.05) \mu_B$. The refined values of the Nd magnetic moment for both the models are in good agreement with the theoretical value of the ordered moment of $3.27 \mu_B/\text{f.u}$ for the free Nd$^{3+}$ ion. Taking into account the results of our experiments and first-principles calculations, the second model corresponds to our calculated values. However, the two presented models have nearly the same R factor, i.e. the NPD data are not sufficient to resolve the question of existence of Cr magnetic moment unambiguously.

![Graph](https://via.placeholder.com/150)

**Figure 4.** (a) The temperature evolution of the NPD patterns collected for NdCr$_2$Si$_2$C between 5 and 27 K. (b) The NPD pattern at 2 and 27 K.

4. Conclusions
In conclusion, NdCr$_2$Si$_2$C was studied experimentally by XRD, SEM, heat capacity, magnetization and NPD measurements on a polycrystal, and also by first-principles calculations. The magnetization data provide no indication of any antiferromagnetic ordering of the Cr sublattice at high temperatures. The first-principles calculations predict the ground-state ordered Cr moment. The low temperature magnetization and NPD data give no unambiguous answer to the question of the Cr moment. XMCD experiment on a single crystal is planned to investigate the existence of the Cr magnetic moment. Therefore, the polarized neutron diffraction and XMCD experiment on a single crystal are envisaged.

5. Acknowledgements
This work is a part of the research plan MSM0021620834 financed by the Ministry of Education of Czech Republic. The work of M.J. has been supported also by the Grant Agency of the Charles University no. 134309 and the Grant Agency of the Czech Republic no. 202/09/H041.

References
[1] Ch. Tang, S. Fan, M. Zhu, *J. Alloys Compd.* **299**, 1-4 (2000).
[2] M. Janatova, J. Vejpravova, M. Divis, V. Sechovsky, *Physica B* **403**, 2338-2343 (2008).
[3] V. Klosek, A. Vernière, B. Malaman, J. Tobola, S. Kaprzyk, *Phys. Rev. B* **78**, 104419 (2008).
[4] O. Moze, M. Hofmann, J.M. Cadogan, K.H.J. Buschow and D.H. Ryan, *Eur. Phys. J. B* **36**, 511 (2003).
[5] R. G. Jordan, *Contemp. Phys.* **15**, 375-400 (1974).
[6] H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
[7] J. Rodriguez-Cavajal, *Physica B* **192**, 5 (1993).
[8] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
[9] P. Blaha et al, *WIEN2k*, TU Wien, Austria, 2001, ISBN:3-9501031-1-2.
[10] M. Janatova, J. P. Vejpravova, M. Divis, *J. Appl. Phys.* **105**, 07E105 (2009).