Low-temperature specific heat and magnetic properties of the filled skutterudite ferromagnet NdRu$_4$As$_{12}$

A. Rudenko, Z. Henkie, T. Cichorek *

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

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ABSTRACT

We present the low-temperature specific heat and magnetic properties of the filled skutterudite compound NdRu$_4$As$_{12}$ that exhibits a ferromagnetic transition at $T_C \simeq 2.3$ K. Magnetic entropy considerations point at a quartet ground state of the Nd^{3+} ions. Deep in the ferromagnetic state, the heat capacity shows a Schottky anomaly that we ascribe to the Zeeman splitting in the presence of a molecular field. Comparison of the specific heats of NdRu$_4$As$_{12}$ and its Os-based homologue near their Curie temperatures supports our earlier observation suggesting an unusual lowering of the T_h cubic point symmetry in the latter filled skutterudite.

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1. Introduction

Binary skutterudites TPn_3 (structure type CoAs$_3$) are a well-known example of so-called cage-forming materials [1]. A complete filling of nanocages formed by twelve pnictogen Pn atoms can be artificially realized for T being a transition metal of the 8-th group. As a result, the filled skutterudite compounds MT_4Pn_{12} are composed of rigid covalently bonded cage-forming frameworks T_4Pn_{12} enclosing differently bonded guest atoms M such as alkali, alkaline earth, lanthanide or light actinide [2]. For the M atom with partially filled 4f shell, the MT_4Pn_{12} compounds exhibit a wealth of emergent quantum phenomena such as, e.g., metal-insulator transition, BCS-type and unconventional superconductivity, magnetic and quadrupole order, and heavy-fermion behavior [3].

All the Nd-filled pnictide skutterudites show ferromagnetic (FM) phase transition. While NdFe$_4$As$_{12}$ [4] and NdFe$_4$Sb$_{12}$ [5] order ferromagnetically at around 15 K, one order of magnitude lower critical temperature displays a sister compound NdFe$_4$P$_{12}$ [3]. Furthermore, a Curie temperature T_C varying between 0.9 K and 2.3 K is characteristic for other members of the NdT_4Pn_{12} family. Among them, NdOs$_4$Sb$_{12}$ with $T_C = 0.9$ K has attracted considerable attention due to a possible heavy-fermion behavior in the low-T paramagnetic state [6]. However, if composed quasiparticles are indeed formed in NdOs$_4$Sb$_{12}$, their origin must be very different from that induced through the screening of magnetic degrees of freedom, as usually observed in many cerium- and uranium-based intermetallic compounds. According to extended

x-ray absorption fine structure (EXAFS) analysis, neodymium ions in NdOs$_4$Sb$_{12}$ are on-center inside the pnictogen cage, but the Nd–Os distances are disordered [7]. Most likely, this is because the Os cubes distort with some of the Os atoms moving either towards or away from the Nd ions. Quite similar EXAFS results were obtained for PrOs$_4$Sb$_{12}$ [7].

Very recently, thermodynamic evidence for a lowering of the T_h cubic point symmetry of the Nd^{3+} ions was found in NdOs$_4$As$_{12}$ with $T_C \simeq 1.1$ K [8]. In zero external field, the heat capacity displays a Schottky-like anomaly with the maximum on the border of localized ferromagnetism, i.e., at $\simeq 0.85T_C$. Upon small external fields $B \leq 0.25$ T, a Schottky-like peak shifts above T_C, which value is essentially unaffected in this field range. Since these results cannot be ascribed to the Zeeman splitting in the presence of a molecular field, low-energy excitations of a quartet ground state of the Nd^{3+} ions could be caused by a distortion of the Os cubes surrounding the Nd^{3+} ions in the skutterudite structure. In contrast, NdFe$_4$As$_{12}$ with $T_C = 14.6$ K shows a Schottky-like anomaly deep inside the ferromagnetic state, whose origin was convincingly explained by the Zeeman splitting of a quasi-degenerate sextet ground state of the Nd^{3+} multiplet due to an internal field [4].

A lowering of the T_h cubic point symmetry of M guest atoms may be a key ingredient to figure out exotic properties of certain filled skutterudites such as, e.g., PrOs$_4$Sb$_{12}$ (unconventional superconductivity [9], quadrupole order [10]) and SmOs$_4$Sb$_{12}$ (nonmagnetic heavy-fermion behavior [11]). Therefore, to gain more insight into unusual features of the Nd-filled Os-based ferromagnets, we have synthesized the closely related compound NdRu$_4$As$_{12}$ with $T_C = 2.3(1)$ K, whose physical properties have not yet been investigated. Alike NdOs$_4$As$_{12}$, magnetic entropy considerations reveal a fourfold-degenerate ground state of the Nd^{3+}

* Corresponding author.
E-mail address: T.Cichorek@int.pan.wroc.pl (T. Cichorek).

ions. However, in striking contrast to the Os-based counterpart, a Schottky-like anomaly in $NdRu_4As_{12}$ appears far below the FM order and hence, it is likely caused by the Zeeman effect in an internal field.

2. Methods

Dendrite crystals of $NdRu_4As_{12}$ with dimensions up to 0.3 mm were grown by a self-flux method. Elemental components in the atomic ratio Nd:Ru:As=1.2:4:60 and with purities better than 99.9% were used. Details of the synthesis in an arsenic flux and a characterization of $NdRu_4As_{12}$ crystals will be given in our forthcoming publication [12]. Nevertheless, main technical aspects of the self-flux method are virtually the same as those already described for the molten Cd:As flux method [13]. Typical crystal of $NdRu_4As_{12}$ is depicted in Fig. 1.

Powder x-ray diffraction measurements were made using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Specific heat for a collection of a few (6) crystals with a total mass $m = 1.44(2)$ mg was determined with the aid of the thermal-relaxation method utilizing a commercial ^{3}He microcalorimeter (PPMS). Magnetization, both as a function of temperature and magnetic field, was measured for a randomly oriented collection of $NdRu_4As_{12}$ single crystals with a total mass $m = 50.1(2)$ mg using a SQUID magnetometer (MPMS). The temperature-dependent ac susceptibility was determined for four single crystals in the drive field $B_{ac} = 10$ μT.

3. Results and discussion

$NdRu_4As_{12}$ has the $LaFe_4P_{12}$–type structure with two formula units per unit cell. The lattice parameter $a = 8.494(1)$ Å determined from powder x-ray diffraction measurements is in good agreement with $a = 8.495$ Å inferred from Ref. [14].

Fig. 2 shows magnetic properties of $NdRu_4As_{12}$. The inverse susceptibility $\chi_{dc}^{-1}(T)$, measured in $B = 1$ T, is depicted in Fig. 2(a). At high temperatures $T \gtrsim 55$ K, the linear slope of $\chi_{dc}^{-1}(T)$ yields a Curie constant 1.61(1) cm^3 K/mol, a Weiss temperature $\Theta_W = -37.4(5)$ K, and an effective moment $\mu_{eff}^{HT} = 3.58(2)$ μ_B. The

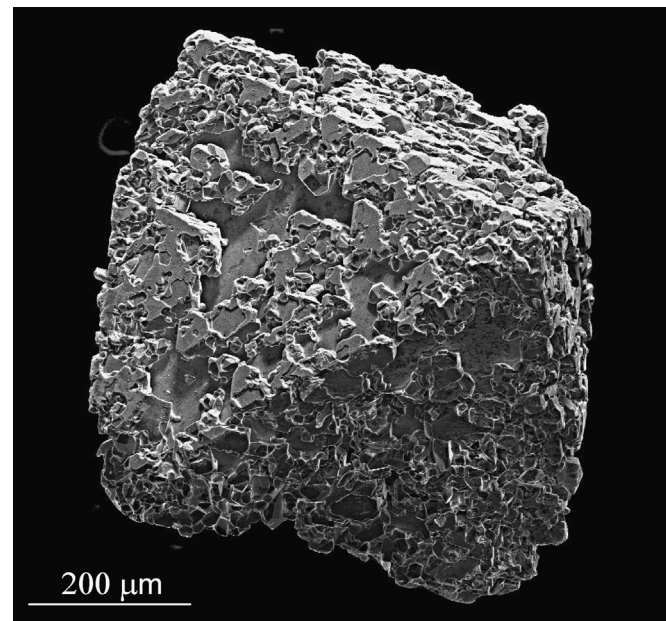**Fig. 1.** Dendrite crystal of $NdRu_4As_{12}$ with dimensions up to 0.3 mm grown by mineralization in an As flux.

latter parameter is very close to the Nd^{3+} free-ion value of $\mu_{eff} = 3.62$ μ_B and hence, points at a complete filling of the skutterudite structure with the guest Nd atoms. Upon lowering temperature, an influence of the crystalline electric field (CEF) becomes evident. At low temperatures $T \leq 10$ K, the Curie-Weiss fit to $\chi_{dc}^{-1}(T)$ gives $\mu_{eff}^{LT} = 2.21(2)$ μ_B. More importantly, however, a horizontal intercept of the low-T Curie–Weiss behavior is positive, thus indicative of a ferromagnetic order below about 2.3(1) K [cf. Fig. 2(b)].

Solid evidence for ferromagnetism in $NdRu_4As_{12}$ comes from the temperature and magnetic field dependences of the magnetization M. In Fig. 2(c), we show $M(T)$ measured in $B = 0.01$ T at $T \leq 6$ K. Below 4 K, the $M(T)$ data increase by almost two orders of magnitude and show a tendency to saturation at the lowest temperatures. A Curie temperature $T_C = 2.3(1)$ K determined from an inflection point in the $M(T)$ curve coincides very well with a peak in real part of the ac susceptibility [cf. the inset of Fig. 2(c)].

In Fig. 2(d) are depicted the magnetization data obtained at various temperatures ranging from 1.8 K to 10 K. At 1.8 K, the magnetization is strongly nonlinear and increases rapidly with field up to about 0.1 T. (In $B = 0.1$ T, the magnetization approaches a half of the $B = 5$ T value.) In higher fields $B > 1.5$ T, the $M(B)$ data display a much weaker increase, but no saturation is reached up to 5 T. At $B = 5$ T, the observed magnetic moment amounts for 1.47 μ_B/f.u. Above $T = 8$ K, the magnetization isotherms basically exhibit a linear-in-B dependence.

The low-temperature dependence of the specific heat $C(T)$ of $NdRu_4As_{12}$ is shown in Fig. 3. The $C(T)$ data display a sharp peak at $\simeq 2.2$ K that signals the ferromagnetic phase transition. As for other filled skutterudites, the lattice heat capacity C_{lat} of $NdRu_4As_{12}$ can be modeled by a combination of an Einstein mode C_E due to the filler Nd atom and the usual Debye term C_D due to the remaining 16 atoms of the polyanion [Ru_4As_{12}]. Then, the $C(T)$ results above 6 K ($\simeq 2.5T_C$) can be expressed as $C(T) = \gamma T + C_E + C_D$ with $\gamma \simeq 240$ mJ/molK^2, the Einstein temperature $\Theta_E = 67$ K, and the Debye temperature $\Theta_D = 370$ K, as shown by the dashed line in Fig. 3. (We have assumed a complete filling of the $2a$ lattice position by the Nd atoms, in accordance with the magnetic susceptibility results.) Comparison with the nonmagnetic homologue $LaRu_4As_{12}$ ($\Theta_E = 98$ K and $\Theta_D = 388$ K) [15] emphasizes a good agreement of the above estimate with the general trend for the lattice specific heat of filled skutterudites: While the Debye temperature depends on the species [T_4Pn_{12}] forming the cage, the Einstein temperature decreases with the guest free distance in the Pn_{12} icosahedron [16]. Finally, we note that a sum of $\gamma T + C_E + \beta T^3$ shows small deviations from the measured specific heat above 12 K, which can be removed by including the Debye δT^5 term with $\delta = 0.84$ μJ/molK^6 (cf. the solid line in Fig. 3).

The temperature dependence of the magnetic entropy S_{mag} was derived from the integration of C_{mag}/T vs T and is shown in the inset of Fig. 3, where a magnetic contribution to the heat capacity $C_{mag} = C - \gamma T - C_{lat}$. As for other local-moment ferromagnets NdT_4Pn_{12} [4,6,8], we have assumed that itinerant electrons do not contribute to the FM ordering. [Note that uncertainties due to an unknown $C(T)$ dependence at $T < 0.4$ K have a negligible effect on the overall S_{mag} behavior.] We found that the magnetic entropy in $NdRu_4As_{12}$ levels off at close to $R\ln 4$ and thus, suggestive of a quartet ground state in the CEF level scheme. In addition to our entropy analysis, the low-temperature susceptibility and magnetization data support this conclusion. Indeed, both the characteristic structure of $\chi_{dc}^{-1}(T)$ around 50 K and the value of $\mu_{eff}^{LT} = 2.21$ μ_B are consistent with a $\Gamma_{67}^{(2)}$ quartet as the ground state of the Nd^{3+} multiplet [17,6].

Basic physical properties of $NdRu_4As_{12}$ and its homologue $NdOs_4As_{12}$ [8] demonstrate far-reaching similarities. This holds