Unusual field-driven anisotropy of the low-lying ferromagnetic state in NdOs$_4$As$_{12}$

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Abstract. We present the low-temperature specific heat $C(T)$ of the filled skutterudite compound NdOs$_4$As$_{12}$, which undergoes a ferromagnetic transition at $T_C = 1.10$ K. In the absence of an external field $B$, the $C(T)$ results show a Schottky-like anomaly at 0.93 K whose origin is attributed to a lowering of the $T_0$ cubic point symmetry of the Nd$^{3+}$ ions rather than to an impact of the molecular field. More intriguingly, however, for $B = 0.25$ T applied parallel to the [111] direction, a sharp peak in $C(T)$ occurs at $T^* \approx 0.7$ K. This is in striking contrast to $B \parallel [100]$ where the Curie temperature is essentially unchanged. While more experimental input is needed to resolve the nature of a $T^*$ phase, our observations point at anomalous field-driven ground-state properties of ferromagnetic NdOs$_4$As$_{12}$.

1. Introduction

Unique crystal structure of the filled skutterudites is the basis of their intriguing physical properties. The $MT_4Pn_{12}$ materials are composed of rigid covalently bonded cage-forming frameworks $T_4Pn_{12}$ enclosing differently bonded guest atoms $M$, where $M$ is an electropositive element like alkali, alkaline-earth, lanthanide, light actinide or thallium metal, $T$ a transition metal of the 8-th group, and $Pn$ a pnictogen (P, As, or Sb). For the $M$ atom with partially filled 4$f$ orbitals, the $MT_4Pn_{12}$ compounds exhibit a large variety of emergent quantum phenomena such as, e.g., metal-insulator transition, BCS-type and unconventional superconductivity, magnetic and quadrupole order, and heavy-fermion behavior [1].

In the case of $M = $ Nd, all compounds exhibit ferromagnetic (FM) phase transition. Whereas NdFe$_4$Sb$_{12}$ orders ferromagnetically below 16.5 K, one order of magnitude lower critical temperatures have been found in other neodymium-filled phosphide and antimonide skutterudites [1]. Among them, NdOs$_4$Sb$_{12}$ with the Curie temperature $T_C \approx 0.9$ K has attracted considerable attention. For this low-$T_C$ ferromagnet, a possible heavy-fermion behavior was suggested because of a large electronic specific heat coefficient $\gamma = 520$ mJ/molK$^2$, but a mechanism that could lead to composed quasiparticles remains unsolved [2]. Recent progress in the synthesis of arsenide skutterudites enable studies of their transport and thermodynamic properties. A salient feature of NdFe$_4$As$_{12}$ with $T_C = 14.6$ K is a Schottky-like anomaly deep inside the ferromagnetic state which is caused by the Zeeman splitting of a quasi-degenerate sextet ground state of the Nd$^{3+}$ multiplet in the presence of a molecular field [3]. In contrast, a Schottky-like anomaly in NdOs$_4$As$_{12}$ ($T_C = 1.10$ K) occurs on the border of the FM order and shifts to the paramagnetic state upon small external fields [4]. We suppose that low-lying
thermal excitations in NdOs$_4$As$_{12}$ originate from a structural rearrangement rather than from the splitting in a molecular field. Finally, NdRu$_4$As$_{12}$ shows the ferromagnetic transition at a Curie point $T_C \approx 2.3$ K. For this compound, our preliminary experiments suggest that a quartet is the Nd$^{3+}$ ground state [5].

2. Experimental

Single crystals of NdOs$_4$As$_{12}$ were grown utilizing a molten Cd:As flux and an enhanced pressure as described elsewhere [4]. Single crystals of the Sb-based counterpart were grown using an Sb flux method [2]. High-temperature magnetic susceptibility measurements point at an effective moment $\mu_{\text{eff}} \approx 3.52 \mu_B$ and 3.47 $\mu_B$ for NdOs$_4$As$_{12}$ and NdOs$_3$Sb$_{12}$, respectively. These values, being very close to the Nd$^{3+}$ free-ion value of $\mu_{\text{eff}} = 3.62 \mu_B$, indicate almost a complete filling of the skutterudite structure with the guest Nd atoms in both materials. Specific heat $C(T)$ was determined with the aid of the thermal-relaxation method utilizing a commercial $^3$He microcalorimeter (PPMS). In-field measurements were performed for $B = 0.25$ T aligned parallel to the [100] and [111] directions of the same single crystal.

3. Results and discussion

A recent study showed that, similarly to the phosphide and antimonide counterparts, NdOs$_4$As$_{12}$ orders ferromagnetically due to a well-localized character of the $4f$ electron states [4]. However, unlike other neodymium-filled skutterudites, NdOs$_4$As$_{12}$ shows a Schottky-like anomaly in the vicinity of the Curie temperature. In addition, enhanced values of the specific heat are observed at liquid-helium temperatures where both phonon excitations and magnetic fluctuations were found to be negligible. With small applied fields such that $\mu_B B \ll k_B T_C$, a maximum of the Schottky-like peak shifts above the ferromagnetic transition and thus, provides evidence for an anomalous origin of low-lying thermal excitations in NdOs$_4$As$_{12}$. We suppose that the Schottky-like effect with an energy separation $\Delta/k_B \approx 2.2$ K is caused by a lowering of the $T_h$ cubic point symmetry of the Nd$^{3+}$ ion due structural disorder. A plausible possibility concerns a small distortion of the Os cubes. Indications for such a disorder have been observed in the closely related compound NdOs$_4$Sb$_{12}$ [6]. Because an unusual local disorder in NdOs$_4$Sb$_{12}$ is mainly restricted to the Nd–Os species with a minor significance of the Sb$_{12}$ cage, it is reasonable to assume a similar Os–Os distortion in NdOs$_4$As$_{12}$ [4].

Figure 1 presents the specific heat of NdOs$_4$As$_{12}$ in the vicinity of the ferromagnetic phase transition at $T_C \approx 1.10$ K. The zero-field data are in perfect agreement with our previous results for a collection of several single crystals. In particular, we observed a hump in $C(T)$ at around $T = 0.93$ K due to the Schottky-like effect whose anomalous origin is evidenced by the measurement in a magnetic field applied along the [100] easy magnetization axis [4]. Indeed, while our findings indicate a weak $T_C(B)$ dependence in the small field range, the application of an external field rapidly shifts the Schottky-like anomaly to higher temperatures. However, for $B \parallel [111]$ we have found a qualitatively different behavior of the specific heat. Though the Schottky-like anomaly is substantially smaller and its maximum is shifted to somewhat higher temperatures, the FM peak is not resolved at around 1 K. Most remarkably, a sharp anomaly is observed at $T^* \approx 0.7$ K. Interesting that the zero-field and $B \parallel [111]$ dependences are essentially the same below $T^*$. Finally, we note that differences between various $C(T, B)$ curves tend to disappear above 3 K.

The temperature dependence of the magnetic entropy $S_{\text{mag}}$ for NdOs$_4$As$_{12}$ is depicted in the inset of Fig. 1. The $S_{\text{mag}}(T)$ behavior can be simply obtained after subtraction of the electronic term with the coefficient $\gamma = 125$ mJ/molK$^2$ (cf. the solid line in Fig.1), since the lattice contributions $C_{\text{lat}}$ to the specific heat are negligible at $T \lesssim 5$ K [4]. We additionally assumed that the specific heat at $T < 0.4$ K follows the $C(T)$ dependence expected for a simple isotropic ferromagnet. At around 0.7 K, $S_{\text{mag}}(T)$ reaches a value of $\approx 0.6 R \ln 2$. Upon heating above $T^*$,
Figure 1. (Color online) Low-temperature specific heat of NdOs$_4$As$_{12}$ in the vicinity of the ferromagnetic phase transition at $T_C = 1.10$ K. In-field measurements were preformed for $B$ aligned parallel to the [100] and [111] directions. $T^* \approx 0.7$ K marks a position of unknown phase transition for $B \parallel [111]$. The solid line represents the electronic specific heat with a coefficient $\gamma = 125$ mJ/molK$^2$. Inset: Influence of a magnetic field of 0.25 T on the temperature dependence of the magnetic entropy at $T \leq 3$K.

the $S_{\text{mag}}$ data shows a much weaker temperature dependence for $B = 0.25$ T applied along the [111] direction then in the absence of an external magnetic filed. For $B = 0.25$ T applied along the easy direction of magnetization, the magnetic entropy starts to increase at slightly higher temperatures, but no feature at the Curie point is resolved. We also note that the zero-field magnetic entropy in NdOs$_4$As$_{12}$ levels off above $\approx 2.5$ K at a value of $\approx 12.3$ J/molK, i.e., only by a few percent larger than $R\ln4$ and thus, suggestive of a fourfold degeneracy of the ground state.

At this stage of research, a nature of the $T^*$ anomaly is unclear. Forthcoming experiments should uncover interactions leading to anomalous low-$T$ physical properties of NdOs$_4$As$_{12}$. Obviously, a large field-induced anisotropy is driven from the partially filled 4f orbitals. If the magnetic dipoles are involved in the phase transition at $T^* \approx 0.7$ K in $B = 0.25$ T, then an exciting possibility concerns a FM quantum critical (end) point accessed by tuning pressure and magnetic field applied along the [111] direction. Such a scenario seems to be supported by the lack of a FM anomaly in the specific heat at around 1 K. If high-rank multipole moments of the 4f shell interact with the main conduction band, then a phase transition could be governed by a nondipolar order parameter. Note that phase transitions driven by electric quadrupole relatively often occur in lanthanide-filled skutterudites but, in general, a multiopolar order parameter of higher rank is very rare. A comparison with the closely related ferromagnet NdOs$_4$Sb$_{12}$ seems to support an existence of sizable multipolar interactions in NdOs$_4$As$_{12}$.

In Fig. 2 we show the specific heat of NdOs$_4$Sb$_{12}$ in the vicinity of the ferromagnetic phase transition at $T_C \approx 0.9$ K. The zero-field $C(T)$ results are in satisfactory agreement with the literature data for a collection of several single crystals [2]. This holds true for enhanced
values of the specific heat in the low-$T$ paramagnetic state as well as a temperature of about 0.78 K at which a FM peak occurs. Moreover, a simple model based on the relation $C(T) = \gamma T + C_{\text{lat}}$ leads to a coefficient $\gamma$ as large as $\approx 500 \text{ mJ/molK}^2$. (Note that, alike for NdOs$_4$As$_{12}$, the phonon specific heat is negligible below 3 K.) On the other hand, the magnitude of a FM anomaly in our NdOs$_4$Sb$_{12}$ single crystal has been found to be smaller than in previous studies. As a consequence, there is a relatively large dissimilarity in zero-field $S_{\text{mag}}(T)$. As shown in the inset of Fig.2, the magnetic entropy saturates at a value of $0.87R$ ($\approx 1.25R\ln2$) which is substantially smaller than 1.14$R$ ($\approx R\ln3$) reported previously [2]. Such a difference is puzzling, especially that a large difference in the occupancies of the Nd site is unlikely. Indeed, both NdOs$_4$Sb$_{12}$ specimens, being obtained in various crystal-growth processes, show the high-temperature effective magnetic moments close to the Nd$^{3+}$ free-ion value [2, 4]. Nevertheless, magnetic entropy consideration lead to the suggestion that the $\Gamma^{(5)}$ doublet rather then the $\Gamma^{(2)}$ quartet is the ground state of the Nd$^{3+}$ multiplet in NdOs$_4$Sb$_{12}$. Additionally shown in Fig. 2 are the low-temperature $C(T)$ data taken at $B = 0.25$ T applied parallel to the [100] and [111] directions. In a sharp contrast to NdOs$_4$As$_{12}$, the antimony-based compound exhibits an isotropic response to externally applied fields. Down to 0.4 K, both $C(T)$ dependencies are virtually the same. In particular, FM anomalies are clearly seen at around 1 K, in accord with the resistivity data [2].

4. Conclusions
We measured the specific heat of NdOs$_4$As$_{12}$ and NdOs$_4$Sb$_{12}$ in the vicinity of the ferromagnetic phase transition at $T_C = 1.10$ K and $T_C \approx 0.9$ K, respectively. These closely related compounds display qualitatively different response of $C(T)$ to externally applied fields. Solely for the arsenic-
based compound, we observed a pronounced anomaly at \( T^* \approx 0.7 \text{ K} \) in \( B = 0.25 \text{ T} \) applied parallel to the [111] direction. We tentatively attribute an anomalous field-induced anisotropy of the ferromagnetic state in \( \text{NdOs}_4\text{As}_{12} \) to characteristics of fourfold degenerated ground state of the \( \text{Nd}^{3+} \) multiplet.

4.1. Acknowledgments
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