

Schottky-like anomaly on the border of localized ferromagnetism in the filled skutterudite $\text{NdOs}_4\text{As}_{12}$

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We present some physical properties of the filled skutterudite compound $\text{NdOs}_4\text{As}_{12}$, which exhibits a ferromagnetic transition at $T_C \approx 1.1$ K, evidenced by distinct anomalies in susceptibility, electrical resistivity, and specific-heat $C(T)$ measurements. At $B = 0$, the heat capacity displays a Schottky-like term with maximum values at about 0.93 K. Additionally, the $C(T)$ data show enhanced values in the low-temperature paramagnetic state. Upon small external fields $B \leq 0.25$ T, a Schottky-like peak shifts above the ferromagnetic transition. Anomalous low-energy excitations of a quartet ground state of the Nd^{3+} multiplet are attributed to a lowering of the T_h cubic point symmetry due to structural disorder rather than to the Zeeman splitting due to a molecular field. We expect that our findings will be also relevant for the study of exotic heavy-fermion behavior in filled skutterudites.

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I. INTRODUCTION

The 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 such as alkali, alkaline-earth, lanthanide, light actinide, or thallium metal, T a transition metal of the 8th group, and Pn a pnictogen (P, As, or Sb). Because the filler atom resides in the large icosahedron cage composed of twelve Pn atoms, the guest atom can move around potential minima or the wide bottom of the potential inside the pnictogen cage. For the M atom with partially filled $4f$ orbitals, the MT_4Pn_{12} compounds exhibit a large variety of emergent quantum phenomena such as metal-insulator transition, BCS-type and unconventional superconductivity, magnetic and quadrupole order, and heavy-fermion behavior [1].

Previous studies have shown ferromagnetic (FM) phase transition in all the Nd-filled skutterudites known so far. Whereas $\text{NdFe}_4\text{Sb}_{12}$ orders ferromagnetically below 16.5 K [2], one order of magnitude lower critical temperatures have been found in other neodymium-filled phosphide and antimonide skutterudites [1]. Among them, $\text{NdOs}_4\text{Sb}_{12}$ 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/mol K², but a mechanism that could lead to composed quasiparticles remains unclear [3]. On the other hand, for the closely related compounds $\text{PrOs}_4\text{Sb}_{12}$ and $\text{SmOs}_4\text{Sb}_{12}$, a number of careful experiments revealed exotic heavy-fermion properties whose origins are very different from that induced through the screening of magnetic degrees of freedom, as usually observed in many cerium- and uranium-based intermetallic compounds. For $\text{PrOs}_4\text{Sb}_{12}$ with $\gamma = 310\text{--}750$ mJ/mol K², the existence of a superconducting phase adjacent to the field-induced antiferro-quadrupole order indicates a new class of heavy-fermion superconductivity [4–6]. Most likely, the scattering of conduction electrons off the unusually small singlet-triplet crystal electric field (CEF) excitations gives

rise to the large mass enhancement [7]. For $\text{SmOs}_4\text{Sb}_{12}$, the unprecedented feature is a magnetic-field-independent coefficient $\gamma \simeq 820\text{--}880$ mJ/mol K² [8,9]. Novel mechanisms involving positional degrees of freedom have been proposed to unravel a magnetically robust heavy-fermion state [10,11].

According to the extended x-ray absorption fine structure (EXAFS) analysis [12], the rare-earth ions in $\text{PrOs}_4\text{Sb}_{12}$ and $\text{NdOs}_4\text{Sb}_{12}$ are apparently on-center inside the pnictogen cage, although the ultrasonic measurements have suggested off-center motions [13]. Indeed, the Pr-Sb, Nd-Sb, and Sb-Sb pair distances were found to be very little disordered. Most importantly, however, the second-neighbor Pr-Os and Nd-Os peaks are highly disordered even at low temperatures and a structure of the Os-Os peak indicates some disorder as well. Considering all of these points, it was proposed that the Os cage distorts with some of the Os atoms moving either toward or away from the Pr or Nd atoms. Such a distortion can lead to long and short Pr(Nd)-Os distances, but no change in the Os-Os distances. An interesting possibility is that the Os cubes surrounding a Pr or Nd atom in the skutterudite structure are slightly sheared, so that two cube faces change from squares to rhombuses [12].

Difficulties inherent to the synthesis have hampered progress in investigations of arsenide skutterudites. This is particularly seen for the $MT_4\text{As}_{12}$ compounds where M is a rare-earth element different from La, Ce, and Pr. For example, only brief information about the lattice parameters [14] and crude estimations of the Curie temperatures [1] were reported for $\text{NdT}_4\text{As}_{12}$ until recently. Also, we recently became aware of interesting results for $\text{NdFe}_4\text{As}_{12}$, which shows a ferromagnetic transition at $T_C = 14.6$ K [15]. A salient feature of this material is a Schottky-like anomaly deep inside the ferromagnetic state which is caused by the Zeeman splitting of a quasidegenerate sextet ground state of the Nd^{3+} multiplet in the presence of a molecular field.

In this paper, we present a comprehensive study of the temperature and field dependence of both thermodynamic and transport properties of $\text{NdOs}_4\text{As}_{12}$ around its ferromagnetic transition at $T_C \approx 1.1$ K. Magnetic entropy considerations

indicate a fourfold-degenerate ground state of the Nd^{3+} ion. Unlike in $\text{NdFe}_4\text{As}_{12}$, a Schottky-like anomaly in $\text{NdOs}_4\text{As}_{12}$ occurs on the border of the FM order and shifts to the paramagnetic state upon small external fields. We hypothesize that low-lying thermal excitations in $\text{NdOs}_4\text{As}_{12}$ originate from a structural rearrangement rather than from the splitting in a molecular field.

II. EXPERIMENTAL

Single crystals of $\text{NdOs}_4\text{As}_{12}$ were grown from a molten Cd:As flux. To this aim, we slightly modified a method that has been successfully used to obtain crystals of the La-, Ce-, and Pr-filled arsenide skutterudites [16]. Elemental components in a molar ratio Nd:Os:As = 1.2:4:14:54 and with purities better than 99.9% were placed in a quartz ampoule, which inner part was covered with pyrolytic carbon to prevent a possible reaction with silica. An expected change of the flux composition due to the high vapor pressure of liquid arsenic was compensated by using a supplemental As in the amount of 120 mg per cm^3 of a free volume of the ampoule. Subsequently, the sealed ampoule was loaded in a home-built cell that allowed us to control an Ar pressure up to 40 atm. Its application was necessary to compensate the As vapor pressure acting on the inner part of the ampoule, when it was heated to 875 °C with a rate of 20 °C/hr, kept at this temperature for 3 hr, and cooled down to 730 °C with the rate of 1.2 °C/hr.

The solidified flux was removed by sublimation in high vacuum at 600 °C. It turned out that about one-fourth of Nd-Os-As substrates formed $\text{NdOs}_4\text{As}_{12}$ single crystals with dimensions up to 0.75 mm, whereas the rest formed binary Nd-As and Os-As compounds. (An efficiency was reduced even further to ~6% when the $\text{CdAs}_{2.5}$ flux was used.) The selected crystals were cleaned in acid to remove possible impurity phases from their surfaces.

The chemical composition of the crystals was examined by electron-probe microanalysis with energy-dispersive x-ray spectroscopy (EDXS) at 20 keV electron energy. Single-crystal x-ray diffraction (XRD) measurements were made on a 4-circle diffractometer X'calibur (Oxford Diffraction) equipped with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). For low-temperature XRD, an open flow helium cooler, Helijet (Oxford Diffraction), was used. Crystallographic calculations were made with the SHELX-97 program package [17]. The analytical absorption corrections were calculated using the package program of CrysAlis (version 171.33.42; Oxford Diffraction). The maximum (minimum) value amounts to 1.9532 (0.2122), 1.7843 (0.2821), and 1.7231 (0.2412) for the data taken at 11, 100, and 300 K, respectively.

Bulk magnetization $M(T)$ down to 0.47 K was measured in a Quantum Design magnetic properties measurement system equipped with the iHelium3 sub-kelvin option. For temperatures $0.47 < T < 10$ K, a mosaic of 10 crystals with a total mass of $m = 4.6$ mg was measured in a magnetic field $B = 0.05$ T aligned parallel to the [100] and [111] directions. At higher temperatures, $M(T)$ measurements were conducted in $B = 0.05$ T on a collection of hundreds of single crystals ($m = 140.1$ mg) with a random crystalline orientation. An automatic background subtraction procedure was used in order to account for a sample holder contribution

to the magnetization data. Low-temperature ac susceptibility $\chi_{\text{ac}}(T)$ experiments for a few single crystals ($m = 3.5$ mg) were performed with the drive field $B_{\text{ac}} = 0.1$ mT utilizing a ^3He - ^4He dilution refrigerator. Electrical resistivity $\rho(T)$ was studied by a standard four-point ac technique in zero and magnetic fields up to 2 T applied perpendicular to the electrical current. For low-temperature measurements $T < 4$ K, a Linear Research ac resistance bridge (model 700) was utilized applying electrical current of 500 μA in the mK temperature range. For measurements at $T \geq 4$ K in a Quantum Design physical properties measurement system (PPMS), the same specimen with a length of 0.68 mm and a cross section of 0.14×0.15 mm^2 was used. Electrical contacts were made by electrochemical deposition of copper. Zero-field thermopower $\alpha(T)$ for $T = 0.4$ –300 K was determined by a method described elsewhere [18]. Specific heat $C(T)$ for a few single crystals ($m = 2.1$ mg) was determined with the aid of the thermal-relaxation method utilizing a commercial ^3He microcalorimeter (PPMS).

III. RESULTS AND DISCUSSION

EDXS analyses were performed for several single crystals. All samples were found to be macroscopically homogeneous. Typical results for one single crystal, as a function of position, indicate that the average atomic ratio of the respective elements amounts to about 6.5 at. % for neodymium, 26.4 at. % for osmium, and 67.1 at. % arsenic. The maximum deviation at various points was not larger than 0.5 at. %. The relevant data of structural refinement for $\text{NdOs}_4\text{As}_{12}$ are listed in Table I. This compound crystallizes in the $\text{LaFe}_4\text{P}_{12}$ -type structure with the space group $Im\bar{3}$ (No. 204). The cubic lattice parameter $a = 8.5386(10)$ Å slightly differs from 8.5291 Å previously determined from the powder XRD experiments [14].

The $2a$ position appears to be fully occupied by the Nd atoms, whose atomic displacement parameters U_{ii} are isotropic and amount to 0.0198(2) Å² at room temperature. While this value is clearly higher than displacement parameters of the filler atoms in other arsenide skutterudites [19–21], twice as large $U_{ii} = 0.0482(5)$ Å² were reported for Nd in the Sb-based counterpart [3]. Upon cooling to 11 K, the atomic displacements decrease by a factor of 2.3. As a result, the Nd U_{ii} value at the lowest temperatures is only slightly larger compared to the atoms of the polyanion $[\text{Os}_4\text{As}_{12}]$. As expected, the atomic displacement parameters of Os and As show much weaker temperature dependence. For the arsenic atoms, the differences in U_{ii} at 11 K and 300 K are in the uncertainty limit of the structural refinement, though the data taken at 100 K seem to suggest their nonmonotonic temperature dependence. For the osmium atoms, an increase of U_{ii} at low temperatures appears to be somewhat better evidenced. Indeed, the 11 K value is about 25% larger than the U_{ii} value at room temperature, which difference is much above the uncertainty limit. These findings might indicate a structural disorder at the $8c$ Os site, as discussed later.

In Fig. 1, we summarize the magnetic properties of $\text{NdOs}_4\text{As}_{12}$. The inverse susceptibility $\chi_{\text{dc}}^{-1}(T)$, measured in $B = 0.05$ T for a randomly oriented collection of single crystals, is shown in Fig. 1(a). At high temperatures $T \gtrsim 200$ K,

TABLE I. Single-crystal structural data measured at various temperatures for NdOs₄As₁₂: structure type LaFe₄P₁₂; space group $Im\bar{3}$ (No. 204); $Z = 2$. The crystal size was $0.18 \times 0.15 \times 0.12$ mm³; occupancies refined for both the filler and framework atoms amount to 1.00(1). $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ and $wR_2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2}}$, where the subscripts o and c denote the experimentally measured and calculated structure factors, respectively.

NdOs ₄ As ₁₂			
Temperature (K)	11	100	300
Lattice parameter a (Å)	8.4898(15)	8.5062(14)	8.5386(13)
Calculated density ρ (Mgm ⁻³)	9.791(2)	9.735(2)	9.624(2)
Nd in $2a$ (0,0,0)			
Atomic displacement (Å ²)			
$U_{11} = U_{22} = U_{33}$	0.0087(3)	0.0100(2)	0.0198(2)
Os in $8c$ (1/4,1/4,1/4)			
Atomic displacement (Å ²)			
$U_{11} = U_{22} = U_{33}$	0.0067(2)	0.0048(1)	0.0053(1)
As in $24g$ (0,y,z)			
y	0.14819(2)	0.14337(1)	0.14840(4)
z	0.34853(1)	0.34837(1)	0.34829(5)
Atomic displacement (Å ²)			
U_{11}	0.0073(4)	0.0056(2)	0.0076(2)
U_{22}	0.0068(3)	0.0053(2)	0.0065(1)
U_{33}	0.0062(5)	0.0050(2)	0.0054(1)
Chemical bond length (Å)			
Nd-Nd	7.352(2)	7.367(2)	7.395(1)
Os-Os	4.245(1)	4.253(1)	4.269(1)
Nd-As	3.2153(12)	3.2208(7)	3.2326(6)
Os-As	2.4396(6)	2.4434(4)	2.4523(3)
Index ranges	$-17 \leq h \leq 17$ $-16 \leq k \leq 17$ $-17 \leq l \leq 13$	$-16 \leq h \leq 13$ $-14 \leq k \leq 17$ $-11 \leq l \leq 17$	$-11 \leq h \leq 11$ $-11 \leq k \leq 7$ $-13 \leq l \leq 11$
Reflections collected/unique	4800/257 [$R_{\text{int}} = 0.1199$]	5986/517 [$R_{\text{int}} = 0.1243$]	9341/545 [$R_{\text{int}} = 0.1080$]
Goodness of fit on F^2	1.333	1.354	1.269
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0653$, $wR_2 = 0.1307$	$R_1 = 0.0540$, $wR_2 = 0.1228$	$R_1 = 0.0484$, $wR_2 = 0.1204$

the linear slope of $\chi_{\text{dc}}^{-1}(T)$ yields a Curie constant 1.67(1) cm³ K/mol, a Weiss temperature $\Theta_{\text{W}} \approx -15.2(8)$ K, and an effective moment $\mu_{\text{eff}} \approx 3.66(2) \mu_{\text{B}}$ that is very close to the Nd³⁺ free-ion value of $\mu_{\text{eff}} = 3.62 \mu_{\text{B}}$. The latter finding indicates a complete filling of the skutterudite structure with the guest Nd atoms and highlights the absence of an Os $5d$ magnetic moment in NdOs₄As₁₂. Upon lowering temperature, an influence of the crystalline electric field (CEF) becomes evident. At low temperatures $T < 25$ K, the Curie-Weiss fit to $\chi_{\text{dc}}^{-1}(T)$ gives $\mu_{\text{eff}} \approx 2.50(1) \mu_{\text{B}}$. It is remarkable that a horizontal intercept of the low- T Curie-Weiss behavior is positive, thus suggesting a ferromagnetic order below about 1.2 K [cf. Fig. 1(b)].

Conclusive proof of ferromagnetism in NdOs₄As₁₂ comes from the temperature and magnetic field dependencies of the magnetization. Figure 1(c) displays $M(T)$ measured in a magnetic field of 0.05 T applied along the [100] and [111] directions. Below 2 K, both magnetization curves increase by more than one order of magnitude and show a tendency to saturation at the lowest temperatures. A Curie temperature $T_{\text{C}} \approx 1.10(2)$ K determined from an inflection point in the $M(T)$ data coincides very well with a peak in real part of the ac susceptibility [cf. the inset of Fig. 1(c)]. Below T_{C} , the magnetization values are significantly larger for $B \parallel [100]$ than for $B \parallel [111]$ and hence, the [100] direction

should be regarded as an easy direction of magnetization in NdOs₄As₁₂.

Figure 1(d) presents the magnetization data obtained at various temperatures ranging from 0.47 to 8 K. At $T = 0.47$ K, the magnetization shows a rapid increase with increasing magnetic field up to $B \approx 0.05$ T. (For better presentation, the B values of the $T = 0.47$ K data were multiplied by a factor of 10.) For $B > 0.1$ T, the $M(B)$ data display a weak increase with a tendency to saturation in higher fields. The M -axis intercept of a linear extrapolation of the $M(B)$ dependence for $B > 0.25$ T yields an ordered FM moment of $\mu_{\text{ord}} = 1.72(1) \mu_{\text{B}}/\text{f.u.}$ No hysteresis loop was observed at 0.47 K.

A well-localized nature of the $4f$ electrons and a substantial CEF splitting are characteristics of the neodymium-filled skutterudites [1]. The tenfold-degenerate $J = 9/2$ Hund's rule ground state of the Nd³⁺ ion splits into a Γ_5 doublet, and $\Gamma_{67}^{(1)}$ and $\Gamma_{67}^{(2)}$ quartets when placed in a cubic T_h crystalline environment [22]. For NdOs₄As₁₂, both the low- T effective moment $\mu_{\text{eff}} = 2.50 \mu_{\text{B}}$ and the spontaneously ordered moment $\mu_{\text{ord}} = 1.72 \mu_{\text{B}}/\text{f.u.}$ indicate that the ground state of Nd³⁺ is either Γ_5 or $\Gamma_{67}^{(2)}$. Similar values of $\mu_{\text{eff}} = 2.35 \mu_{\text{B}}$ and $\mu_{\text{ord}} = 1.73 \mu_{\text{B}}/\text{f.u.}$ were reported for NdOs₄Sb₁₂ with the energy separation of about 200 K between the ground state and the first excited state [3,23].

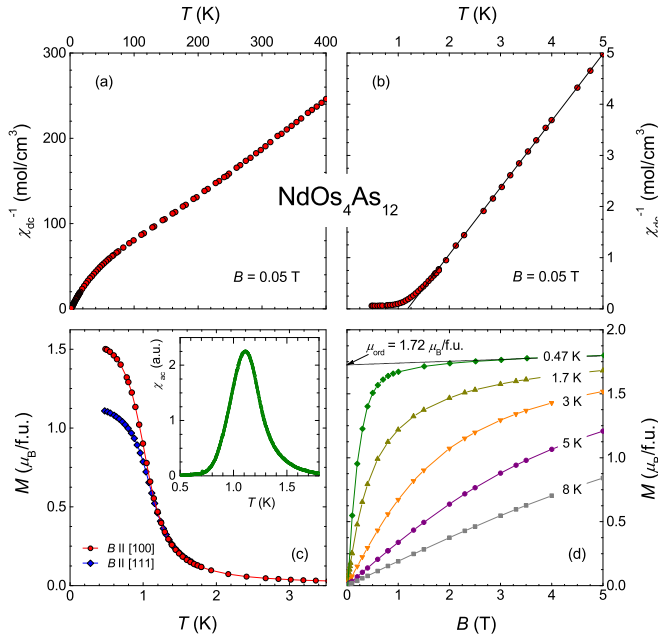


FIG. 1. (Color online) Magnetic properties of the filled skutterudite compound NdOs₄As₁₂. (a) Temperature dependence of inverse magnetic susceptibility. (b) Low-temperature $\chi_{dc}^{-1}(T)$ data indicating a ferromagnetic order below $\Theta_{CW} \approx 1.2$ K. An interval 1.8–25 K was chosen for the Curie-Weiss fit (solid line). (c) Temperature dependence of the magnetization measured in $B = 0.05$ T applied along the [100] and [111] direction. Inset: Real part of the ac susceptibility plotted as a function of temperature. (d) Magnetization isotherms for $B \parallel [100]$ at various temperatures. Note that the B values of the $T = 0.47$ K data were multiplied by a factor of 10.

A CEF splitting of comparable magnitude is expected for the closely related compound NdOs₄As₁₂, since further similarity between both low- T_C ferromagnets includes the downward deviation of $\chi_{dc}^{-1}(T)$ at comparable temperatures of about 50–65 K.

In Fig. 2(a), we compare the temperature dependence of the electrical resistivity $\rho(T)$ for NdOs₄As₁₂ and the nonmagnetic reference compound LaOs₄As₁₂ that superconducts below 3.2 K [24]. In spite of qualitatively different magnetic properties, the normalized $\rho(T)/\rho_{300\text{K}}$ dependence for these systems is very similar, including particularly a curvature at around 150 K. While a room-temperature resistivity of NdOs₄As₁₂ amounts to $\rho_{300\text{K}} = 400 \pm 80 \mu\Omega \text{ cm}$, a residual resistivity as small as $\rho_0 = 1.3 \pm 0.3 \mu\Omega \text{ cm}$ was measured at $T = 0.14$ K [25]. As a result, we obtained a residual resistivity ratio $\rho_{300\text{K}}/\rho_0 = 306$, the large value of which reflects the high quality of our NdOs₄As₁₂ single crystals.

Figure 2(b) presents the temperature dependence of the thermopower $\alpha(T)$ for NdOs₄As₁₂ and its La-filled counterpart. Except a narrow temperature window between 2 and 35 K, the thermopower of NdOs₄As₁₂ is positive. Its temperature dependence resembles that of LaOs₄As₁₂ [26]. The similarity is especially visible in a quasi- T -linear decrease upon cooling from 300 to about 200 K and a broad maximum at around 100 and 60 K for NdOs₄As₁₂ and LaOs₄As₁₂, respectively.

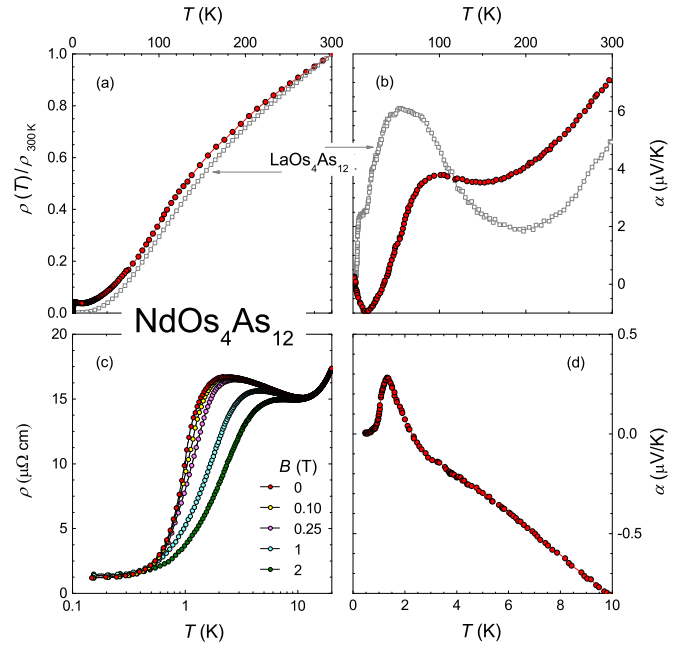


FIG. 2. (Color online) Comparison of the temperature dependencies of the electrical resistivity (a) and the thermoelectric power (b) of NdOs₄As₁₂ and the nonmagnetic reference compound LaOs₄As₁₂ [26]. (c) Low-temperature resistivity of NdOs₄As₁₂ in varying magnetic fields. (d) Low-temperature thermopower of NdOs₄As₁₂ showing a pronounced anomaly around the Curie temperature.

The $\rho(T)$ and $\alpha(T)$ results having similar characteristics for both homologues points out that the charge current is mainly transported by the itinerant As 4*p* and Os 5*d* electrons. In other words, the response of conduction electrons in NdOs₄As₁₂ to either thermal gradient and electric field provides further evidence for a localized character of the Nd 4*f* electrons and a large level spacing between the ground state and the first excited state. Note that similar conclusions were drawn for La- and NdFe₄As₁₂, in which the itinerant Fe 3*d* electrons additionally carry magnetic moments [15].

In the case of NdOs₄As₁₂, the ferromagnetic phase transition leads to a pronounced drop of $\rho(T)$ below about 1.7 K, as depicted in Fig. 2(c). A clear signature of the FM phase transition is also seen in the thermopower, though a maximum of the $\alpha(T)$ anomaly appears at a somewhat higher temperature of 1.30(6) K [cf. Fig. 2(d)]. Also shown in Fig. 2(c) are the low-temperature $\rho(T)$ data taken in various magnetic fields up to 2 T. In the paramagnetic region, the zero-field $\rho(T)$ results exhibit a local minimum at around 10 K followed by a logarithmic increase with decreasing temperature down to approximately 2 K. This $-\log T$ increase of $\rho(T)$ is strongly influenced by magnetic fields. At $B = 2$ T, the logarithmic term in $\rho(T)$ is suppressed and the resistivity levels off with a value of about $15 \pm 3 \mu\Omega \text{ cm}$. Interestingly, a $\rho(T) \propto -\log T$ behavior was reported for other Nd-filled skutterudites [1,27–29], but a logarithmic term is absent in the low- T resistivity of a possible heavy-fermion system NdOs₄Sb₁₂ [3].

The low-temperature dependence of the specific heat $C(T)$ of NdOs₄As₁₂ is given in Fig. 3. The $C(T)$ data display

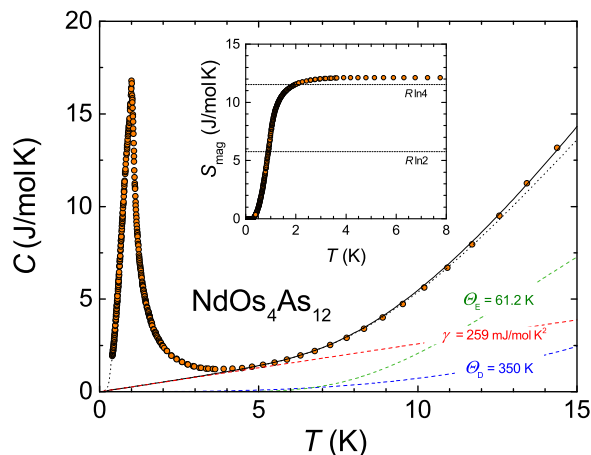


FIG. 3. (Color online) Low-temperature specific heat of $\text{NdOs}_4\text{As}_{12}$. The dashed lines represent contributions of individual terms of a fit (solid line) as described in the text. Note that a $C(T)$ behavior at $T < 0.4$ K (dotted line) was approximated by the dependence expected for isotropic ferromagnets [31]. Inset: Temperature dependence of the magnetic entropy at $T \leq 8$ K.

a very sharp peak with the maximum at $T = 1.00(2)$ K that signals the ferromagnetic phase transition. Unexpectedly, the paramagnetic-state specific heat shows large values (> 1.2 J/mol K) in the temperature range where both the magnetic and lattice contributions are negligible. Indeed, as presented in Fig. 1(d), the ferromagnetic correlations strongly diminish with increasing temperature. Thus, it is unlikely that they would account for a large fraction of the specific heat at $T \gtrsim 4T_C$. In turn, the lattice heat capacity C_{lat} of $\text{NdOs}_4\text{As}_{12}$ can be modeled by a combination of the Einstein mode C_E due to the filler Nd atom and the usual Debye βT^3 term (β is proportional to the Debye temperature Θ_D) due to the remaining 16 atoms of the polyanion $[\text{Os}_4\text{As}_{12}]$. Therefore, the Debye temperature was fixed to 350 K ($\beta = 0.724$ mJ/mol K⁴) in accord with $\Theta_D = 360$ K for $\text{LaOs}_4\text{As}_{12}$ [30]. We also assumed the full occupancy of the $2a$ lattice position by the Nd atoms, in fair agreement with the chemical analysis, the crystallographic data, and the magnetic susceptibility results. At $4 \leq T \leq 12$ K, a least-squares fit of $\gamma T + C_E + \beta T^3$ to $C(T)$ yields $\gamma = 259(3)$ mJ/mol K² and the Einstein temperature $\Theta_E = 61.2(2)$ K (cf. dotted line in Fig. 3). Finally, we point out that a sum of $\gamma T + C_E + \beta T^3$ shows small deviations from the measured specific heat above 12 K. This difference, however, can be removed by including the extra Debye δT^5 term with $\delta = 0.95$ $\mu\text{J/mol K}^6$ (cf. solid line in Fig. 3).

The temperature dependence of the magnetic entropy S_{mag} was derived from the integration of $\Delta C/T$ vs T and is shown in the inset of Fig. 3, where $\Delta C = C - \gamma T - C_{\text{lat}}$. Under such conditions, the magnetic entropy of $\text{NdOs}_4\text{As}_{12}$ levels off at close to $R \ln 4$. Thus, combining with the low- T magnetic susceptibility results, the $\Gamma_{67}^{(2)}$ quartet appears to be the ground state of the Nd^{3+} multiplet.

At first glance, the result of the simple fit presented in Fig. 3 might reflect a substantial electron mass enhancement in $\text{NdOs}_4\text{As}_{12}$. Note that the corresponding analysis of the low- T specific-heat data for the closely related ferromagnet

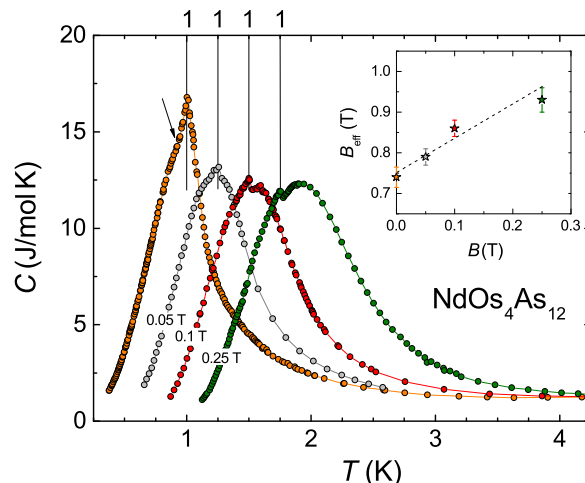


FIG. 4. (Color online) Impact of small applied fields on the specific heat of $\text{NdOs}_4\text{As}_{12}$ in the vicinity of the ferromagnetic phase transition. The in-field $C(T)$ curves are shifted by $\Delta T = 0.25$ K for clarity. The arrow marks a position of the hump-like anomaly in the $B = 0$ results. Inset: Magnetic-field dependence of an effective field B_{eff} , as concluded from the maximum of the Schottky-like anomaly (see text). The dashed line represents a linear-in- B increase of B_{eff} .

$\text{NdOs}_4\text{Sb}_{12}$ ($T_C \approx 0.9$ K) yielded an electronic specific-heat coefficient as large as $\gamma = 520$ mJ/mol K². Based on this estimate, possible heavy-fermion properties of $\text{NdOs}_4\text{Sb}_{12}$ were proposed [3] and further suggested by the results of soft x-ray spectroscopy [32]. For $\text{NdOs}_4\text{As}_{12}$, however, a formation of composite quasiparticles is unlikely because no additional indications of the electron mass enhancement were found. For example, its thermoelectric response is very different from those reported for heavy-fermion materials. Several experiments show a correlation between the low-temperature slope of the thermopower α/T and the coefficient γ [33–35]. Different data indicate the dimensionless quantity $q = (N_A e / \gamma)(\alpha/T) \approx \pm 1$ in the zero-temperature limit, where N_A is the Avogadro constant and e is the elementary charge [36,37]. This mutual relation between the charge and heat currents reflects a transport by the same quasiparticles. For $\text{NdOs}_4\text{As}_{12}$, except temperatures close to T_C , the diffusive $-\alpha/T$ values do not exceed 0.1 $\mu\text{V/K}^2$, as inferred from Fig. 2(d). The small thermopower implies $q \approx -0.01$ which is by two orders of magnitude smaller than the corresponding ratios for a variety of strongly correlated electron systems. Therefore, we came to a conclusion that the $\alpha(T)$ and $C(T)$ dependencies of $\text{NdOs}_4\text{As}_{12}$ are governed by electrons with very different effective masses or/and the enhanced specific heat in the low-temperature paramagnetic state needs another explanation.

Figure 4 presents the $C(T)$ dependence in the vicinity of the ferromagnetic phase transition. Experiments were performed both in zero and small external fields up to 0.25 T. A closer inspection into the zero-field results reveals a hump in $C(T)$ around $T = 0.93(2)$ K. An intrinsic nature of the anomaly located nearby the Curie temperature is highlighted by essentially the same $C(T)$ behavior at $T \simeq T_C$ for different ensembles of $\text{NdOs}_4\text{As}_{12}$ single crystals (not

plotted). Intuitively, our observation suggests the presence a low-lying Schottky effect in NdOs₄As₁₂ due to a splitting of the quartet ground state. However, a mechanism that gives rise to an energy separation $\Delta/k_B \simeq 2$ K cannot be simply attributed to the Zeeman splitting due to ferromagnetic order. Note that in the mean-field approximation, a molecular field B_{mol} shows a rapid increase on temperature close to T_C and a saturation at low temperatures. Therefore, in most cases, a splitting of the degenerate ground state usually occurs deep in the ferromagnetically ordered state. Such an effect is observed in, e.g., NdFe₄As₁₂, which displays the Schottky-like peak with a maximum value at about $T_m \approx 6$ K ($\approx 0.4T_C$) due to splitting of a quasidegenerate sextet (doublet and quartet) [15]. Furthermore, the position of the Schottky-like anomaly was found to be essentially field independent ($B < 9$ T) given the fact that the Zeeman splitting in the molecular field of 12.6 T is almost comparable to $k_B T_C$.

Considering the experimental value of $\mu_{\text{ord}} = 1.72 \mu_B/\text{f.u.}$ at $T = 0.47$ K [cf. Fig. 1(d)], for NdOs₄As₁₂ we estimate $B_{\text{mol}} \approx 1.5$ T in the limit $T = 0$. This rough calculation suggests that a magnitude of the molecular field would be sufficient to achieve the splitting of $\Delta/k_B \simeq 2$ K. Indeed, $B_{\text{mol}} \approx 0.74$ T, being the molecular field expected at $\approx 0.85T_C$, can produce the Schottky-like anomaly with a maximum at $T_m = 0.93$ K. Here, we assumed a relation $\Delta/2 = g_J^* J \mu_B B_{\text{eff}}$ where $g_J^* \approx 0.5$ is the effective Landé g factor at low temperatures, $J = 9/2$ is the total angular momentum for the Nd³⁺ ions, and B_{eff} is the effective field such that $B_{\text{eff}} = B + B_{\text{mol}}$. Without loss of generality, we also assumed that the Zeeman splitting of the quartet ground state leads to two nearly degenerate doublets and thus a relation $T_m = 0.417\Delta$ was considered.

Solid evidence for anomalous origin of low-lying thermal excitations in NdOs₄As₁₂ is obtained by specific-heat measurements in small external fields such that $g_J^* |J| \mu_B B$ is considerably smaller than $k_B T_C$. The $C(T, B)$ curves in Fig. 4 are shifted by constant offsets $\Delta T = 0.25$ K for clarity. Several observations are made at $T < 4.25$ K in $B \leq 0.25$ T: A position of the ferromagnetic anomaly is essentially B independent and the FM peak remains sharp up to 0.25 T. These findings indicate a weak $T_C(B)$ dependence in the small field range and are in striking contrast to an impact of B on the Schottky-like contribution C_{Sch} . The application of an external field rapidly shifts the Schottky-like anomaly to higher temperatures. In B as small as 0.05 T, both features are superimposed on each other. In fact, a rounded shape of $C_{\text{Sch}}(T)$ close to T_m is seen on both sides of the FM peak. At a slightly larger field of 0.1 T, the maximum of the $C_{\text{Sch}}(T)$ term entirely appears on the right side of the FM peak, i.e., at $T_m \approx 1.08(3)$ K. For $B = 0.25$ T, a large part of the Schottky-like anomaly with $T_m \approx 1.17(4)$ K occurs in the paramagnetic state. Finally, we note that upon increasing field, the $C_{\text{Sch}}(T)$ contribution to the specific heat becomes broader but its maximum value remains virtually unchanged.

The characteristics of the $C(T, B)$ curves shown in Fig. 4 imply that an external field increases the splitting of the quartet ground state but the number of degrees of freedom is unaltered [31]. Therefore, one can find B_{eff} values in finite fields using the same relations as for the $B = 0$ data. The results are

shown in the inset of Fig. 4. A linear increase of B_{eff} with increasing external field points to a nearly constant value of $B_{\text{mol}} \approx 0.74$ T in a rather wide temperature window close to the Curie temperature. Clearly, this conclusion strongly contrasts with expectations based on the Weiss molecular field theory of ferromagnetism. Indeed, in the presence of a small external field, it is predicted that induced magnetization curves are still characterized by a strong T dependence in the vicinity of T_C , although spin alignment occurs both below and above T_C . Furthermore, as long as the amplitude of the applied field is considerably smaller than $B_{\text{mol}}(0)$, the isothermal magnetization at $T \simeq T_C$ rapidly increases with B . For NdOs₄As₁₂, these predictions of the Weiss model were confirmed experimentally, as shown in Figs. 1(c) and 1(d). We thus conclude that the Schottky-like anomaly on the border of localized ferromagnetism in the filled skutterudite NdOs₄As₁₂ cannot be exclusively caused by the Zeeman splitting in the molecular field.

Besides magnetic properties, structural rearrangement is in principle an alternative phenomenon that can result in a splitting of the lowest CEF level. For NdOs₄As₁₂, this could happen if the T_h cubic point symmetry of the Nd³⁺ ions is lowered yielding a splitting of the quartet ground state. As far as some low-energy excitations of NdOs₄As₁₂ are considered, it is conceivable that rattling of the Nd atoms play an important role. Anharmonic motions around potential minima inside the pnictogen cage are frequently observed in the filled skutterudite family and depend on the cage size and/or the guest atoms. Relatively large U_{ii} factors for the filler Nd atoms in NdOs₄As₁₂ seem to support such a possibility. However, no clear ultrasonic dispersion due to rattling was found in the counterpart PrOs₄As₁₂ with similar displacement parameters [38]. Furthermore, off-center motions of Pr and Nd atoms in the larger Sb cage have been recently questioned [12].

A plausible possibility for the physical origin of the Schottky-like anomaly in NdOs₄As₁₂ concerns an unusual local disorder in the Os cubes. Indications for such a disorder have been observed in the closely related compound NdOs₄Sb₁₂ [12]. According to the extended x-ray absorption fine structure analysis, the second-neighbor peaks Nd-Os are anomalously small at 4 K and not observable at 300 K. The EXAFS experiments, supported by measurements at the Os L_{III} edge, suggest a distortion that can lead to long and short Nd-Os distances, but no change in the Os-Os distances. As a consequence, the Os cubes surrounding Nd atoms are slightly sheared so that two cube faces are distorted from squares to rhombuses giving rise to the lowering of the T_h cubic point symmetry. Whereas similar features were observed in PrOs₄Sb₁₂, neither the Eu-Sb, Eu-Os, or Os-Os peak is disordered for EuOs₄Sb₁₂. A lack of disorder in the structure of the Os/Sb cage network of the Eu-filled skutterudite is unclear. However, it is unlikely that valence of rare-earth elements plays an important role, since the bond lengths for Nd-Sb, Pr-Sb, and Eu-Sb differ by less than 0.01 Å [12].

As argued in Ref. [12], unusual local disorder in NdOs₄Sb₁₂ is mainly restricted to the Nd-Os species with a minor significance of the Sb₁₂ cage. Therefore, it is reasonable to assume a similar Os-Os distortion in NdOs₄As₁₂ [39]. If present, a number of the disordered Os cubes surrounding Nd

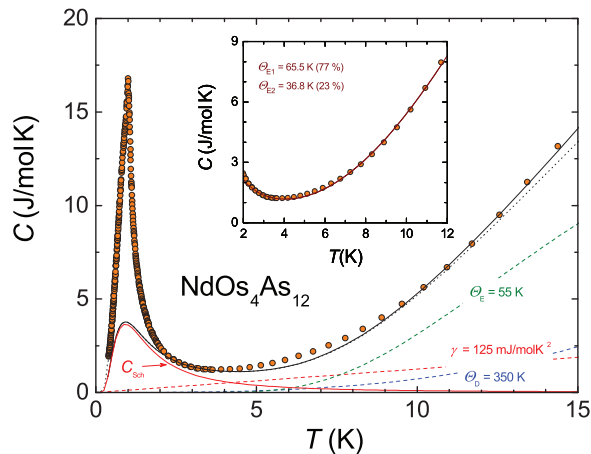


FIG. 5. (Color online) Low-temperature specific heat of $\text{NdOs}_4\text{As}_{12}$. Except for the red solid line describing the Schottky heat capacity of a two-level system with equal degeneracy and $\Delta/k_B = 2.2$ K, all the remaining lines have the same meaning as in Fig. 3. Inset: Comparison of the $C(T)$ result for models with $\Theta_E = 55$ K (dashed line) and two Einstein modes with different relative weights (solid line).

atoms is expected to be of the order of the Avogadro constant. Hence, they could account for a large fraction of the specific heat.

Low-lying thermal excitations in $\text{NdOs}_4\text{As}_{12}$, originating from a structural rearrangement rather than from the Zeeman splitting due to a molecular field, imply a substantial change of the simple model exemplified in Fig. 3. To this end, we performed a semiquantitative $C(T)$ analysis assuming the Schottky anomaly with the level splitting $\Delta/k_B = 2.2$ K between two levels of equal degeneracy. For simplicity, both Debye terms were fixed to the values determined earlier. The results are shown in Fig. 5. The Einstein temperature $\Theta_E = 55$ K is somewhat lower than the 61.2 K previously obtained. More importantly, however, the presence of the C_{Sch} term in the paramagnetic state results in a much smaller value of $\gamma \approx 125$ mJ/molK². This coefficient is similar to 134 mJ/molK² observed for $\text{NdFe}_4\text{As}_{12}$ [15] and only 2.5 times larger than 49 mJ/molK² observed for the nonmagnetic homologue $\text{LaOs}_4\text{As}_{12}$ [30]. Finally, we note that while the model with C_{Sch} captures the upward $C(T)$ curvature at $T \sim 4T_C$, it does not satisfactorily describe the specific-heat data between 5 and 9 K. Nevertheless, this misfit becomes smaller when two Einstein modes are taken into account, as shown in the inset of Fig. 5. There, we compare the result for $\Theta_E = 55$ K with a $C(T)$ dependence for a model with two different Einstein temperatures $\Theta_{E1} = 66.5$ K and $\Theta_{E2} = 36.8$ K of 77% and 23% relative weights, respectively. One can speculate that the latter model reflects an impact of a Os-Os distortion that leads to long and short Nd-Os distances.

For a possible heavy-fermion compound $\text{NdOs}_4\text{Sb}_{12}$, it was difficult to determine from magnetic entropy consideration ($R \ln 2 < S_{\text{mag}} < R \ln 4$) whether the Γ_5 doublet or $\Gamma_{67}^{(2)}$ quartet is the Nd^{3+} ground state [3]. If the Γ_5 doublet is the ground state, then the extra entropy may result from positional degrees of freedom. While Os-Os oscillations are one possibility, the EXAFS results make this scenario a very likely one. If the $\Gamma_{67}^{(2)}$

quartet is the ground state, the lowering of the T_h cubic point symmetry should lead to a low-lying Schottky effect with an energy separation close to that in $\text{NdOs}_4\text{As}_{12}$. Although no indications for a Schottky effect in $\text{NdOs}_4\text{Sb}_{12}$ have been found down to approximately $0.6T_C$ [3], in this particular case, the FM peak at $T \approx 0.8$ K can be superimposed on a Schottky anomaly and hence not easily seen in the zero-field $C(T)$ measurements. Such a situation would indicate the overestimated value of the electronic specific heat coefficient $\gamma = 520$ mJ/molK² and could imply a reexamination of a heavy-quasiparticle formation. Note that the results of inelastic neutron scattering experiment indicate the $\Gamma_{67}^{(2)}$ quartet as the ground state of the Nd^{3+} ion in $\text{NdOs}_4\text{Sb}_{12}$ [23].

For $\text{PrOs}_4\text{Sb}_{12}$, a distortion that keeps the Os-Os distance constant but splits the Pr-Os distances into four longer and four shorter distances can easily influence the energy splitting as small as ≈ 8 K between the two lowest CEF levels. Thus, this intrinsic disorder can be a key ingredient giving rise to various sample-dependent properties of $\text{PrOs}_4\text{Sb}_{12}$ such as a double structure in the $C(T)$ jump around the superconducting transition at ≈ 1.8 K and the Schottky anomaly with a maximum near 2 K [1,4,6]. For $\text{SmOs}_4\text{Sb}_{12}$, no EXAFS experiments were performed so far. We point out, however, that a possible Os-Os distortion and resultant positional degrees of freedom are in line with theoretical proposals to realize exotic heavy-fermion behavior with large and magnetically robust $\gamma \simeq 820\text{--}880$ mJ/molK² [10,11].

IV. SUMMARY

We succeeded in growing single crystals of $\text{NdOs}_4\text{As}_{12}$ large enough to determine low-temperature thermodynamic and transport properties. A large residual resistivity ratio, $\rho_{300\text{K}}/\rho_0 = 306$, demonstrates the high quality of our samples. Similarly to the phosphide and antimonide counterparts, $\text{NdOs}_4\text{As}_{12}$ orders ferromagnetically below $T_C \approx 1.1$ K due to a well-localized character of the $4f$ electron states. Magnetic entropy considerations indicate a quartet ground state of the Nd^{3+} multiplet.

Unlike other neodymium-filled skutterudites, $\text{NdOs}_4\text{As}_{12}$ 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, the maximum of the Schottky-like anomaly shifts above the ferromagnetic transition and thus provides evidence for an anomalous origin of low-lying thermal excitations in $\text{NdOs}_4\text{As}_{12}$. We attribute the Schottky-like effect with an energy separation $\Delta/k_B \simeq 2$ K to a lowering of the T_h cubic point symmetry of the Nd^{3+} ion due to structural disorder. We speculate that a small distortion of the Os cubes has an impact on the ground-state properties of $\text{NdOs}_4\text{As}_{12}$.

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- [1] H. Sato, H. Sugawara, Y. Aoki, and H. Harima, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 2009).
- [2] E. Bauer, S. Berger, A. Galatanu, C. Paul, M. D. Mea, H. Michor, G. Hilscher, A. Grytsiv, P. Rogl, D. Kaczorowski, L. Keller, T. Hermansdorfer, and P. Fischer, *Physica B* **312–313**, 840 (2002).
- [3] P.-C. Ho, W. M. Yuhasz, N. P. Butch, N. A. Frederick, T. A. Sayles, J. R. Jeffries, M. B. Maple, J. B. Betts, A. H. Lacerda, P. Rogl, and G. Giester, *Phys. Rev. B* **72**, 094410 (2005).
- [4] E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, *Phys. Rev. B* **65**, 100506(R) (2002).
- [5] T. Tayama, T. Sakakibara, H. Sugawara, Y. Aoki, and H. Sato, *J. Phys. Soc. Jpn.* **72**, 1516 (2003).
- [6] Y. Aoki, T. Namiki, S. Ohsaki, S. R. Saha, H. Sugawara, and H. Sato, *J. Phys. Soc. Jpn.* **71**, 2098 (2002).
- [7] H. Tou, Y. Inaoka, M. Doi, M. Sera, K. Asaki, H. Kotegawa, H. Sugawara, and H. Sato, *J. Phys. Soc. Jpn.* **80**, 074703 (2011).
- [8] W. M. Yuhasz, N. A. Frederick, P.-C. Ho, N. P. Butch, B. J. Taylor, T. A. Sayles, M. B. Maple, J. B. Betts, A. H. Lacerda, P. Rogl, and G. Giester, *Phys. Rev. B* **71**, 104402 (2005).
- [9] S. Sanada, Y. Aoki, H. Aoki, A. Tsuchiya, D. Kikuchi, H. Sugawara, and H. Sato, *J. Phys. Soc. Jpn.* **74**, 246 (2005).
- [10] T. Hotta, *J. Phys. Soc. Jpn.* **77**, 103711 (2008).
- [11] S. Tanikawa, H. Matsuura, and K. Miyake, *J. Phys. Soc. Jpn.* **78**, 034707 (2009).
- [12] T. Keiber, F. Bridges, R. E. Baumbach, and M. B. Maple, *Phys. Rev. B* **86**, 174106 (2012).
- [13] T. Yanagisawa, W. M. Yuhasz, P.-C. Ho, M. B. Maple, H. Watanabe, Y. Yasumoto, Y. Nemoto, and T. Goto, *Physica B* **403**, 735 (2008).
- [14] D. J. Braun and W. Jeitschko, *J. Solid State Chem.* **32**, 357 (1980).
- [15] R. Higashinaka, K. Takeda, T. Namiki, Y. Aoki, and H. Sato, *J. Phys. Soc. Jpn.* **82**, 114710 (2013).
- [16] Z. Henkie, M. B. Maple, A. Pietraszko, R. Wawryk, T. Cichorek, R. E. Baumbach, W. M. Yuhasz, and P.-C. Ho, *J. Phys. Soc. Jpn.* **77** (Suppl. A), 128 (2008).
- [17] G. M. Sheldrick, *Acta Crystallogr. A* **64**, 112 (2008).
- [18] R. Wawryk and Z. Henkie, *Philos. Mag. B* **81**, 223 (2001).
- [19] W. M. Yuhasz, N. P. Butch, T. A. Sayles, P.-C. Ho, J. R. Jeffries, T. Yanagisawa, N. A. Frederick, M. B. Maple, Z. Henkie, A. Pietraszko, S. K. McCall, M. W. McElfresh, and M. J. Fluss, *Phys. Rev. B* **73**, 144409 (2006).
- [20] R. E. Baumbach, P.-C. Ho, T. A. Sayles, M. B. Maple, R. Wawryk, T. Cichorek, A. Pietraszko, and Z. Henkie, *Proc. Natl. Acad. Sci. USA* **105**, 17307 (2008).
- [21] R. Wawryk, Z. Henkie, A. Pietraszko, T. Cichorek, L. Kepinski, A. Jezierski, J. Kaczkowski, R. E. Baumbach, and M. B. Maple, *Phys. Rev. B* **84**, 165109 (2011).
- [22] K. Takegahara, H. Harima, and A. Yanase, *J. Phys. Soc. Jpn.* **70**, 1190 (2001).
- [23] K. Kuwahara, M. Takagi, K. Iwasa, S. Itobe, D. Kikuchi, Y. Aoki, M. Kohgi, H. Sato, and H. Sugawara, *Physica B* **403**, 903 (2008).
- [24] I. Shirovani, K. Ohno, C. Sekine, T. Yagi, T. Kawakami, T. Nakanishi, H. Takahashi, J. Tang, A. Matsushita, and T. Matsumoto, *Physica B* **281–282**, 1021 (2000).
- [25] Unfortunately, we cannot provide the absolute values of the resistivity for much smaller crystals of $\text{LaOs}_4\text{As}_{12}$. However, assuming the same $d\rho/dT$ slopes at 300 K for both compounds, we have extracted a contribution of the $4f$ electron states to the resistivity of $\text{NdOs}_4\text{As}_{12}$. Such a crude estimate yields a ρ_{4f} term that is temperature independent above 150 K and as small as $30 \mu\Omega\text{cm}$.
- [26] R. Wawryk, O. Zogal, A. Pietraszko, S. Paluch, T. Cichorek, W. M. Yuhasz, T. A. Sayles, P.-C. Ho, T. Yanagisawa, N. P. Butch, M. B. Maple, and Z. Henkie, *J. Alloys Compd.* **451**, 454 (2008).
- [27] M. S. Torikachvili, J. W. Chen, Y. Dalichaouch, R. P. Guertin, M. W. McElfresh, C. Rossel, M. B. Maple, and G. P. Meisner, *Phys. Rev. B* **36**, 8660 (1987).
- [28] K. Abe, H. Sato, T. D. Matsuda, T. Namiki, H. Sugawara, and Y. Aoki, *J. Phys.: Condens. Matter* **14**, 11757 (2002).
- [29] K. Magishi, K. Nagata, Y. Iwahashi, H. Sugawara, T. Saito, and K. Koyama, *J. Phys.: Conf. Ser.* **200**, 012110 (2010).
- [30] K. Matsuhira, C. Sekine, M. Wakeshima, Y. Hinatsu, T. Namiki, K. Takeda, I. Shirovani, H. Sugawara, D. Kikuchi, and H. Sato, *J. Phys. Soc. Jpn.* **78**, 124601 (2009).
- [31] E. S. R. Gopal, *Specific Heat at Low Temperatures* (Plenum, London, 1966).
- [32] S. Imada, H. Higashimichi, A. Yamasaki, M. Yano, T. Muro, A. Sekiyama, S. Suga, H. Sugawara, D. Kikuchi, and H. Sato, *Phys. Rev. B* **76**, 153106 (2007).
- [33] K. Behnia, D. Jaccard, and J. Flouquet, *J. Phys.: Condens. Matter* **16**, 5187 (2004).
- [34] K. Izawa, K. Behnia, Y. Matsuda, H. Shishido, R. Settai, Y. Onuki, and J. Flouquet, *Phys. Rev. Lett.* **99**, 147005 (2007).
- [35] A. Pourret, K. Behnia, D. Kikuchi, Y. Aoki, H. Sugawara, and H. Sato, *Phys. Rev. Lett.* **96**, 176402 (2006).
- [36] K. Miyake and H. Kohno, *J. Phys. Soc. Jpn.* **74**, 254 (2005).
- [37] V. Zlatic, R. Monnier, J. K. Freericks, and K. W. Becker, *Phys. Rev. B* **76**, 085122 (2007).
- [38] T. Yanagisawa, W. M. Yuhasz, T. A. Sayles, P.-C. Ho, M. B. Maple, H. Watanabe, Y. Yasumoto, Y. Nemoto, T. Goto, Z. Henkie, and A. Pietraszko, *Phys. Rev. B* **77**, 094435 (2008).
- [39] A tentative analysis of the differential Fourier maps suggests an increasing disorder around the central position of the Os atoms with lowering temperature.