Ferromagnetism and possible heavy fermion behavior in single crystals of NdOs$_4$Sb$_{12}$

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Single crystals of the filled-skutterudite compound NdOs$_4$Sb$_{12}$ have been investigated by means of electrical resistivity, magnetization, and specific heat measurements. The NdOs$_4$Sb$_{12}$ crystals have the LaFe$_4$P$_{12}$-type cubic structure with a lattice parameter of 9.3 Å. Possible heavy-fermion behavior is inferred from specific heat measurements, which reveal a large electronic specific heat coefficient $\gamma \approx 520\,\text{mJ/mol-K}^2$, corresponding to an effective mass $m^* \approx 98\,m_e$. Features related to a ferromagnetic transition at $\sim 0.9\,\text{K}$ can be observed in electrical resistivity, magnetization, and specific heat. Conventional Arrott-plot analysis indicates that NdOs$_4$Sb$_{12}$ conforms to mean-field ferromagnetism.

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I. INTRODUCTION

The filled skutterudite compounds have the chemical formula MT$_4$X$_{12}$, where M is an alkali (Na or K), alkaline earth (Ca, Sr, Ba), lanthanide or actinide atom; T is a transition-metal atom (Fe, Ru, Os); and X is a pnictogen atom (P, As, Sb). The compounds crystallize in a LaFe$_4$P$_{12}$-type structure with the space group Im$ar{3}$. Due to the strong hybridization between f- and conduction electrons and their unique crystal structure, the lanthanide- and actinide-based filled skutterudite materials display a wide range of strongly-correlated-electron phenomena, such as BCS-like superconductivity (e.g., PrRu$_4$Sb$_{12}$)\footnote{\textcopyright J. B. Betts and A. H. Lacerda, version, currently submit to Physical Review B} heavy fermion behavior (e.g., PrFe$_4$P$_{12}$)\footnote{P.-C. Ho, W. M. Yuhasz, N. P. Butch, N. A. Frederick, T. A. Sayles, J. R. Jeffries, and M. B. Maple, version, currently submit to Physical Review B} heavy fermion superconductivity (e.g., PrOs$_4$Sb$_{12}$)\footnote{G. Giester, version, currently submit to Physical Review B} ferromagnetism (e.g., PrFe$_4$Sb$_{12}$)$^2$ metal-insulator transitions (e.g., PrRu$_4$P$_{12}$)$^3$ Kondo-insulator behavior (e.g., UFe$_4$P$_{12}$ and CeFe$_4$P$_{12}$)$^4$ valence fluctuation behavior (e.g., YbFe$_4$Sb$_{12}$)$^{10,11}$ and non-Fermi-liquid behavior (e.g., CeRu$_4$Sb$_{12}$)$^{12,13}$

Previous studies have shown ferromagnetic ordering in Nd-based filled skutterudites. Measurements of NdFe$_4$Sb$_{12}$ revealed ferromagnetic order below 16.5 K with a Nd ordered moment of 2.04 $\mu_B$ and a Fe collinear moment of 0.27 $\mu_B$. Lower ferromagnetic transition temperatures were found in NdFe$_4$P$_{12}$ at 2 K$^4$ NdRu$_4$P$_{12}$ at 1.6 K$^6$ NdRu$_4$Sb$_{12}$ at 1.3 K$^5$ and NdOs$_4$Sb$_{12}$ at 0.8 K$^6$. Since NdOs$_4$Sb$_{12}$ displays ferromagnetism with a low Curie temperature and its neighboring compound PrOs$_4$Sb$_{12}$ shows heavy fermion behavior and unconventional superconductivity\footnote{\textcopyright J. B. Betts and A. H. Lacerda, version, currently submit to Physical Review B}, possibly involving triplet spin pairing of electrons, there is a strong likelihood that PrOs$_4$Sb$_{12}$ is near a ferromagnetic quantum critical point. Thus, by thoroughly characterizing the physical properties of NdOs$_4$Sb$_{12}$, a deeper insight into the unusual behavior of PrOs$_4$Sb$_{12}$ may be attained. Earlier studies of the compound NdOs$_4$Sb$_{12}$ only reported the results of structural refinement\footnote{\textcopyright J. B. Betts and A. H. Lacerda, version, currently submit to Physical Review B} and the value of the Curie temperature.\footnote{G. Giester, version, currently submit to Physical Review B} In this report, we present a new and detailed investigation of NdOs$_4$Sb$_{12}$ single crystals, including measurements of X-ray diffraction, electrical resistivity, magnetization, and specific heat. We also discuss possible heavy fermion behavior in this Nd-based filled skutterudite compound.

II. EXPERIMENTAL DETAILS

NdOs$_4$Sb$_{12}$ single crystals were grown in a molten Sb flux as described previously\footnote{P.-C. Ho, W. M. Yuhasz, N. P. Butch, N. A. Frederick, T. A. Sayles, J. R. Jeffries, and M. B. Maple, version, currently submit to Physical Review B} using high purity Nd, Os (3.5N), and Sb (6N). X-ray powder diffraction measurements were performed with a Rigaku D/MAX B x-ray machine on a powder prepared by grinding several single crystals, which indicated single phase NdOs$_4$Sb$_{12}$ with a minor impurity peak of Sb (\lesssim 10%). The crystals had a LaFe$_4$P$_{12}$-type BCC structure\footnote{G. Giester, version, currently submit to Physical Review B} with a lattice parameter $a = 9.30\,\text{Å}$. Two single crystals of similar dimension were selected for single crystal X-ray diffraction measurements. The data were collected on a four-circle Nonius Kappa diffractometer at 296 K using Mo $K_\alpha$ radiation ($\lambda = 0.071073\,\text{nm}$). No absorption corrections were necessary because of the rather regular crystal shape and small dimensions of the investigated crystals. The structure was refined with the SHELXS-97 program\footnote{G. Giester, version, currently submit to Physical Review B}.
Electrical resistivity $\rho(T, H)$ was measured using the standard 4-wire technique in a Quantum Design PPMS system and in a $^3$He-$^4$He dilution refrigerator in fields up to 8 T. The low temperature (0.02 K - 2.6 K) and high-field (8 T - 18 T) $\rho(T, H)$ measurements were performed in the National High Magnetic Field Laboratory at Los Alamos National Laboratory. The electrical current applied to the sample was perpendicular to the applied magnetic field, which was along the [001] direction, in all $\rho(T, H)$ measurements. Measurements of $\rho(T, P)$ were made under hydrostatic pressures up to 28 kbar in a beryllium-copper piston-cylinder clamp and a $^4$He cryostat. The pressure was determined inductively from the pressure-dependent superconducting transition of a Pb manometer.

DC magnetic susceptibility from 2 K to 300 K was measured in a Quantum Design MPMS SQUID magnetometer. The magnetization $M(H, T)$ measurements were carried out in a $^3$He Faraday magnetometer with a gradient field of $\sim 0.05 - 0.1$ T/cm in external fields up to 5.5 T and at temperatures between 0.4 K and 2 K. For the Faraday magnetometer measurements, several single crystals (total mass of 21.3 mg) were combined in a mosaic fashion with magnetic field applied along the [001] axis. Specific heat $C(T)$ of multiple single crystals (total mass of 42.15 mg) was measured between 0.5 K and 70 K in a $^3$He calorimeter using a semiadiabatic heat-pulse technique.

III. RESULTS AND DISCUSSION

A. Single crystal structural refinement

Structural refinement was performed on X-ray diffraction data collected from single crystals of NdOs$_4$Sb$_{12}$; the results are listed in Table I. The thermal displacement parameters $U_{11}$ of the Nd atoms are isotropic and have large values compared with the $U_{ii}$ for the Os and Sb atoms, a common feature in the filled skutterudites. The Nd sites are fully occupied, which is not always the case for filled skutterudites, such as Pr$_{0.75}$Fe$_4$Sb$_{12}$ and Eu$_{0.95}$Fe$_4$Sb$_{12}$\cite{22}. If the NdOs$_4$Sb$_{12}$ crystal is considered to be a simple Debye solid with the Nd atoms behaving like Einstein oscillators, the thermal displacement and the Einstein temperature $\Theta_E$ are related by

$$U = \frac{h^2}{2m_{Nd}k_B\Theta_E}\coth\left(\frac{\Theta_E}{2T}\right),$$  \hspace{1cm} (1)

where $m_{Nd}$ is the atomic mass of Nd. For NdOs$_4$Sb$_{12}$, $\Theta_E$ is estimated as $\sim 45$ K, which is close to the values found for thallium-filled antimony skutterudites such as Tl$_{0.22}$Co$_4$Sb$_{12}$, Tl$_{0.5}$Co$_{3.5}$Fe$_{0.5}$Sb$_{12}$, Tl$_{0.8}$Co$_3$FeSb$_{12}$, and Tl$_{0.8}$Co$_4$Sb$_{11}$Sn\cite{23,24}.

B. Magnetic Properties

The dc magnetic susceptibility $\chi_{dc}(T)$ of NdOs$_4$Sb$_{12}$ was measured at 500 Oe and is displayed in Fig. 1(a). The $\chi_{dc}^{-1}(T)$ data (Fig. 1(b)) exhibit different slopes at high and low temperatures. The linear slope of $\chi_{dc}^{-1}(T)$ between 65 K and 300 K yields a Curie constant ($C_{CW}$) \cite{25} $\sim 1.39$ Nd-mol/cm$^3$, a positive $\Theta_{CW}$ of 596 K, and a value of $\mu_{eff} \sim 3.84 \mu_B$, which is close to the Nd$^{3+}$ free ion value of 3.62 $\mu_B$. The Curie-Weiss fit to the low-temperature range of $\chi_{dc}^{-1}(T)$ (Fig. 1(c)) gives $C_{CW} \sim 0.69$ cm$^3$/mol, a positive $\Theta_{CW} \sim 1$ K, and a value of $\mu_{eff} \sim 2.35 \mu_B$. The curvature in $\chi_{dc}^{-1}(T)$ is due to the influence of the crystalline electric field (CEF), and the positive $\Theta_{CW}$ from the low-temperature fit indicates ferromagnetic order developing below 1 K.

Although the crystal structure of NdOs$_4$Sb$_{12}$ has tetrahedral symmetry ($T_d$)\cite{26}, this is only a slight deviation from cubic symmetry ($O_h$). Thus, to simplify the CEF analysis, only $O_h$ symmetry was considered. In an ionic (localized) model with cubic symmetry, the Nd$^{3+}$ tenfold degenerate $J = 9/2$ Hund’s rule ground state multiplet splits into a $\Gamma_6$ doublet and two $\Gamma_8$ ($\Gamma_8^{(1)}$, $\Gamma_8^{(2)}$) quartet states. In the treatment of Lea, Leask, and Wolf\cite{27} these energy levels and their corresponding wave functions in cubic $O_h$ symmetry can be parameterized by the variables $x_{LLW}$ and $W$, where $x_{LLW}$ is the ratio of the
TABLE I: Single crystal structural data measured at $T = 296$ K for NdOs$_4$Sb$_{12}$. The crystal structure is LaFe$_2$P$_{12}$-type with the space group Im$3$ (No. 204). The range of X-ray scattering angle is $2^\circ < 2\theta < 80^\circ$.

| NdOs$_4$Sb$_{12}$ | |
|------------------|-----------------|
| Crystal size     | $84 \times 78 \times 84$ $\mu$m$^3$ |
| Lattice parameter $a$ [Å] | 9.3075(2) |
| Reflection in refinements | $473 \leq 4\sigma(F_2)$ of 482 |
| Number of variables | 11 |
| Goodness of fit | 1.265 |
| Nd in 2a (0, 0, 0); Occupancy | 1.00(1) |
| Thermal displacement [Å] | Nd: $U_{11} = U_{22} = U_{33}$ 0.0482(5) |
| Interatomic distances [Å] | Nd - 12 Sb 3.4831 |
| Os in 8c (1/4, 1/4, 1/4); Occupancy | 1.00(1) |
| Thermal displacement [Å] | Os: $U_{11} = U_{22} = U_{33}$ 0.0025(1) |
| Interatomic distances [Å] | Os - 6 Sb 2.6239 |
| Sb in 24g (0, y, z); y: 0.15597(3); z: 0.34017(3); Occupancy | 1.00(1) |
| Thermal displacement [Å] | Sb: $U_{11}$ 0.0026(1) |
| Interatomic distances [Å] | Sb - 1 Sb 2.9033 |

The ground state of Nd is a conventional Arrott plot consisting of $M^2$ vs $H/M$ isotherms plotted versus $T$. Positive values correspond to the spontaneous magnetization $M_{sp}$.

![FIG. 2: (a) Magnetization $M$ vs magnetic field $H$ isotherms and the saturation magnetization $M_{sat}$ determined from $M$ vs $H$ isotherms below the Curie temperature $\Theta_C$. (b) $M^2$ vs $H/M$ isotherms (Arrott plot) for NdOs$_4$Sb$_{12}$. (c) Inverse initial magnetic susceptibility (open circles) determined from $M^2 = 0$ intercepts of $M^2$ vs $H/M$ isotherms, compared to the $\chi_{sat}^{-1}(T)$ data (pluses). The line is a Curie-Weiss fit. (d) $H/M = 0$ intercepts of $M^2$ vs $H/M$ isotherms plotted versus $T$. Positive values correspond to the spontaneous magnetization $M_{sp}$.](image)

The intercepts of the linear fits to the $(H/M)$ axis ($\equiv$ the inverse initial magnetic susceptibility) agree well with the low-temperature $\chi_{sat}^{-1}(T)$ data (Fig. 2(c)). The intercepts of the linear fit to the $M^2$ axis are shown in Fig. 2(d), where zero identifies $\Theta_C = 0.93$ K. Below $\Theta_C$, the intercept of the $M^2$-axis corresponds to the square of the spontaneous magnetization $(M_{sp}^2)$, which levels off and results in a small value of $M_{sp} \sim 0.7 \mu_B/$f.u.. However, a linear extrapolation of the negative $M^2$-axis intercept back to zero temperature yields a much larger value of $\sim 1.76 \mu_B/$f.u., which is comparable to the saturation magnetization $M_{sat}$ of $\sim 1.73 \mu_B$/f.u. determined.
The value of $M$ magnetization found in NdFe$_3$T directly from the 6 T, 8 T, 9 T.ing the width of the transition at $T \sim 0$ K indicates that the single crystal studied is of good metallurgi-

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r resistivity $\rho$ vs $T$ for magnetic fields $H$ between 8 T and 18 T for NdOs$_4$Sb$_{12}$. The solid lines are guides to the eye. (c) Position of the shoulder $T_d$ in $\rho(T)$ (which corresponds to $\Theta_C$) vs $H$, with vertical bars indicating the width of the transition at $T_d$ as described in the text. (d) High-$T$ resistivity $\rho$ vs $T$ at $H = 0$ T, 0.5 T, 1 T, 2 T, 4 T, 6 T, 8 T, 9 T.

directly from the $M(H)$ data of NdOs$_4$Sb$_{12}$ (Fig. 2(a)). The value of $M_{sat}$ is also consistent with the saturation magnetization found in NdFe$_4$P$_{12}$ ($1.72 \mu_B$/f.u.).

C. Electrical Resistivity

Low-temperature electrical resistivity $\rho(T)$ data for NdOs$_4$Sb$_{12}$ in various magnetic fields from 0 T to 18 T are shown in Figs. 3(a) and (b). The zero-field residual resistivity ratio $\rho(300 K)/\rho(0.02 K)$ of $\sim 45$ indicates that the single crystal studied is of good metallurgical quality (Fig. 3(a) and (d)). A shoulder occurs in the zero-field $\rho(T)$ curve at $\sim 1.2$ K, below which $\rho(T)$ has a sharp drop, indicating the development of an ordered state. The temperature $T_d$ at which this drop occurs is defined as the intercept of two lines, one of which is a linear fit to the data above the transition while the other is a linear fit to the data below the transition. The upper and lower limits of the transition are defined as the temperatures midway between $T_d$ and the temperatures at which the data deviate from the linear fits. Shown in Fig. 3(c) is the field dependence of $T_d$, which increases with increasing field up to 6 T, and is no longer observed in the $\rho(T)$ data at higher fields. The temperature $T_d$ correlates with the onset of ferromagnetic order at 0.9 K det-

determined from magnetization and specific heat measure-

ments. Displayed in Fig. 4(d) are the high-temperature $\rho(T, 0 T \leq H \leq 9 T)$ data for NdOs$_4$Sb$_{12}$, which show a slight increase in $\rho(T)$ with increasing field.

In order to analyze the behavior of the resistivity be-

low $\Theta_C$, the $\rho(T)$ data were fit with a power-law of the form $\rho(T) = \rho_0 + BT^n$. The fitting curves are plotted as dashed lines in Fig. 4(a). The residual resistivity $\rho_0$ increases with increasing field and has a linear $H$-dependence above 8 T (Fig. 4(b)). Between 0 T and 18 T, the exponent $n$ varies from 3 to 4, which indicates that NdOs$_4$Sb$_{12}$ exhibits neither typical Fermi-liquid $(n \sim 2)$ nor typical non-Fermi-liquid $(n < 2)$ behavior (Fig. 4(c)). Since ferromagnetic ordering occurs below $\Theta_C$, electron-spin wave scattering was considered with the form:

$$\rho(T) = \rho_0 + A T \frac{T}{\Delta_{spw}} (1 + 2 \frac{T}{\Delta_{spw}}) \exp \left( \frac{-\Delta_{spw}}{T} \right),$$  

where $\Delta_{spw}$ is the spin wave energy gap, which may result either from magnetic anisotropy or from broken symmetry due to presence of a CEF. This formula describes the $\rho(T, H)$ data well, and the fitting curves are shown as solid lines in Fig. 4(a). As determined from these fits, the spin-wave energy gap $\Delta_{spw}$ is $\sim 0.75$ K at 0 T, increases approximately linearly to $\sim 4.5$ K as the field increases to 12 T, and then drops to $\sim 3.4$ K at 18 T (Fig. 4(d)).

Figure 4(a) displays the zero-field $\rho(T)$ data, which have a slight negative curvature at $\sim 130$ K that may be related to scattering from the CEF levels. In order to analyze the CEF contribution to $\rho(T)$ at 0 T, it is necessary to subtract a lattice contribution $\rho_{lat}(T)$ and an impurity contribution $\rho_{imp}$ ($\sim 9.4 \mu\Omega\cdot$cm) from the resistivity data. Usually, $\rho_{lat}(T)$ is estimated from an isostructural nonmagnetic reference compound; in the
excited states in that compound. Thus it is reasonable to due to electron-phonon scattering and use it as an case of NdOs$_4$Sb$_{12}$, the resistivity of LaOs$_4$Sb$_{12}$, which has an empty 4f shell, was used. However, above 100 K, $\rho(T)$ of LaOs$_4$Sb$_{12}$ exhibits a significant negative curvature that is common in La-based compounds such as LaAl$_2$. This curvature is generally less pronounced in Sc-, Y-, and Lu-based compounds, which have completely empty or filled 4f-electron shells. However, the compounds ScOs$_4$Sb$_{12}$, YOs$_4$Sb$_{12}$ and LuOs$_4$Sb$_{12}$ have not yet been synthesized. Above 100 K, $\rho_{\text{lat}}(T)$ was estimated from SmOs$_4$Sb$_{12}$, as $\rho(T)$ of SmOs$_4$Sb$_{12}$ has an approximately linear-$T$ dependence between 100 K and 300 K. The s-f exchange scattering effect in $\rho(T)$ of SmOs$_4$Sb$_{12}$ only appears below 80 K due to the small energy splitting ($\sim 35$ K) between the ground and the first excited states in that compound. Thus it is reasonable to assume that $\rho(T)$ of SmOs$_4$Sb$_{12}$ for 100 K $\leq T \leq 300$ K is due to electron-phonon scattering and use it as an estimate of the high-temperature portion of $\rho_{\text{lat}}(T)$ for NdOs$_4$Sb$_{12}$.

The incremental resistivity $\Delta\rho(T) = \rho(T) - \rho_{\text{lat}}(T) - \rho_{\text{imp}}$ (Fig. 5(b)) is best described by two energy-level schemes that are consistent with the CEF analysis of $\chi(T)$ discussed previously. During the CEF analysis of $\Delta\rho(T)$, it was also found that s-f exchange scattering alone could not entirely account for $\Delta\rho(T)$; otherwise, $\rho_{\text{imp}}$ would always be negative, which is unphysical. Thus, the effect of aspherical Coulomb scattering was also considered, with the ratio between the s-f exchange scattering and the aspherical Coulomb scattering defined as $x : (1-x)$. In Fig. 5(b), the fit curves representing the two best-fit energy schemes are plotted in comparison with $\Delta\rho(T)$, which is described well by both fits above 40 K. The departure of $\Delta\rho(T)$ from the fits below 40 K may be due to a reduction of the electron scattering, resulting from the development of the coherent heavy-fermion ground state in NdOs$_4$Sb$_{12}$ as the temperature is lowered. The $\rho(H)$ isotherms are displayed in Fig. 6(a) and qualitatively agree with the $\rho(H)$ isotherms generated using the cubic-CEF parameters determined from the zero-field fits to $\Delta\rho(T)$ (Figs. 5(b) and (c)).

Measurements of $\rho(T)$ were performed from 1 K to 300 K under nearly hydrostatic pressure $P$ between 0 kbar and 28 kbar (Fig. 7). In Fig. 7 it can clearly be seen that the pressure-induced change in the high-$T$ electrical resistivity is much more pronounced than the resistivity change induced by high field (Fig. 3(c)), in the pressure and temperature ranges of this investigation. However, at low temperatures, the value of $T_d$ is more strongly influenced by an increase in field $H$ (Fig. 3(b)) than by variation of $P$ (Fig. 7 inset (b)).

### D. Specific Heat

Specific heat divided by temperature $C/T$ vs $T$ data for NdOs$_4$Sb$_{12}$ are shown in Fig. 8(a). The data reveal a pronounced peak at $\sim 0.8$ K that correlates well with the magnetic ordering temperature $\Theta_C$ inferred from the shoulder of $\rho(T)$, the divergence of $\chi_{dc}(T)$, and the Arrott-plot analysis. No obvious Schottky anomaly associated with CEF energy splitting was observed in the $C(T)$ data below 20 K. This is consistent with the fact

FIG. 5: (a) Zero-field resistivity $\rho$ and the estimated $\rho_{\text{lat}} + \rho_{\text{imp}}$ vs temperature $T$ for NdOs$_4$Sb$_{12}$, where $\rho_{\text{imp}} \sim 9.4 \mu\Omega$-cm. (b) Temperature dependence of the incremental resistivity $\Delta\rho = \rho - \rho_{\text{lat}} - \rho_{\text{imp}}$ and CEF fits for two different ground states: $\Gamma_6$ (dashed line) and $\Gamma_8^{(2)}$ (solid line), where $x/(1-x)$ is the ratio of s-f exchange to aspherical Coulomb scattering for NdOs$_4$Sb$_{12}$.

FIG. 6: (a) Isotherms of electrical resistivity $\rho$ vs magnetic field $H$ for NdOs$_4$Sb$_{12}$, (b) and (c) Calculated $\rho$ vs $H$ isotherms including the effects of s-f exchange and aspherical Coulomb scattering using the CEF parameters determined from zero-field data.
strong evidence against the possibility of a CEF Schottky effect in NdOs$_4$Sb$_{12}$ at various pressures $P$ up to 28 kbar. Inset (a): Expanded view of the resistive ferromagnetic transitions. Inset (b): Temperature of the drop in $\rho(T)$ due to the onset of ferromagnetism $T_d$ (approximately corresponding to the Curie temperature $\Theta_C$) vs $P$ with vertical bars indicating the width of the transition.

that all the fits to the dc magnetic susceptibility data imply that the CEF splitting between the ground and first excited states is greater than 120 K. The Schottky anomaly due to 120 K CEF splitting would exhibit a peak at $\sim$ 40 K and make a negligible contribution to $C(T)$ below 20 K. Such a peak would also be difficult to resolve against the large lattice background.

In Fig. 7a, the specific heat of LaOs$_4$Sb$_{12}$ is displayed in comparison with that of NdOs$_4$Sb$_{12}$, where the electronic specific heat coefficient $\gamma$ and the Debye temperature $\Theta_D$ of LaOs$_4$Sb$_{12}$ are $\sim$ 36 mJ/mol-K$^2$ and $\sim$ 280 K, respectively. After the specific heat of nonmagnetic LaOs$_4$Sb$_{12}$ (an estimate of the lattice heat capacity of NdOs$_4$Sb$_{12}$) is subtracted from the specific heat of NdOs$_4$Sb$_{12}$, the difference divided by temperature $\delta C/T$ is plotted against $T^2$ and shown in the inset of Fig. 7a. The value of $\gamma$ for NdOs$_4$Sb$_{12}$ estimated from the $\delta C/T$ vs $T^2$ plot ranges from $\sim$ 436 mJ/mol-K$^2$ to $\sim$ 530 mJ/mol-K$^2$. Below 13 K, $\delta C/T$ vs $T^2$ is not constant, which could be due to a difference between the actual lattice heat capacities of NdOs$_4$Sb$_{12}$ and LaOs$_4$Sb$_{12}$. Nevertheless, the curvature in $C/T$ vs $T^2$ of NdOs$_4$Sb$_{12}$ (inset of Fig. 7b) and the magnetic transition occurring at $\sim$ 1 K cause difficulties in the analysis of the data using the typical formula $C/T = \gamma + \beta T^2$. Since we have strong evidence against the possibility of a CEF Schottky contribution from the analysis of the $\chi(T)$ data, the curvature in $C/T$ vs $T^2$ is possibly due to either the rattling motion of the Nd atoms or a narrow peak in the density of electronic states near Fermi energy, such as a Kondo resonance. However, we do not consider the application of the resonance level model (RLM) to be appropriate, because the magnetization data above $\Theta_C$ are fit well by a Brillouin function and no obvious Kondo effect is observed in the $\rho(T)$ data of NdOs$_4$Sb$_{12}$.

FIG. 7: Electrical resistivity $\rho$ vs temperature $T$ for NdOs$_4$Sb$_{12}$ at various pressures $P$ up to 28 kbar. Inset (a): Expanded view of the resistive ferromagnetic transitions. Inset (b): Temperature of the drop in $\rho(T)$ due to the onset of ferromagnetism $T_d$ (approximately corresponding to the Curie temperature $\Theta_C$) vs $P$ with vertical bars indicating the width of the transition.

FIG. 8: (a) Zero-field $C$ vs $T$ for NdOs$_4$Sb$_{12}$ and LaOs$_4$Sb$_{12}$ below 20 K. Inset: $\delta C/T$ vs $T^2$ below 20 K, where $\delta C = C(NdOs_4Sb_{12}) - C(LaOs_4Sb_{12})$. The extrapolated values of the two dashed lines at 0 K set the lower and upper limits of $\gamma(NdOs_4Sb_{12}) - \gamma(LaOs_4Sb_{12})$. (b) A comparison between $C$ of NdOs$_4$Sb$_{12}$ and a fit of $C_{el} + C_{lat}$, where $C_{el} = \gamma T$ and $C_{lat}$ is composed of $C_{Deb}$ and $C_{Ein}$ as described in the text. The electronic specific heat coefficient $\gamma$, the Debye temperature ($\Theta_D$), the Einstein temperature ($\Theta_E$), and the coupling constant $r$ for the Einstein oscillator are estimated as 520 mJ/mol-K$^2$, 255 K, 39 K, and 0.48 respectively. Inset: $C/T$ vs $T^2$ for NdOs$_4$Sb$_{12}$ below 20 K for NdOs$_4$Sb$_{12}$.
FIG. 9: (a) Incremental specific heat $\Delta C (\Delta C \equiv C - C_{el} - C_{lat})$ (left axis) and the magnetic entropy $S_{mag}$ (right axis) vs temperature $T$. (b) Logarithmic plot of the power-law fit (dotted line) and the anisotropic-spin-wave fit (dashed line) to the incremental specific heat $\Delta C(T)$ after the electronic and lattice contributions have been removed (in a very limited measuring range below $\Theta_C$).

\[
\Delta C = C_{el} + C_{Deb},
\]

\[
C_{Ein} = r \left[ 3R \frac{(\Theta_E/T)^2 \exp(\Theta_E/T)}{\exp(\Theta_E/T) - 1} \right],
\]

\[
C_{Deb} = (17 - r) \cdot \frac{12\pi^4}{5} \frac{R}{\Theta_D} T^{3/2},
\]

where $R$ is the universal gas constant, $\Theta_D$ represents the Debye temperature, and $r \leq 1$. The effective Debye temperature is $(17 - r)/r$ times bigger than that of the Einstein-like $N_d$ rattling motion due to the participation of the rest of the atoms in the unit cell. Below 20 K, a least squares fit of $C_{el} + C_{lat}$ to the $C(T)$ data was performed, where $C_{el} = \gamma T$ is the electronic specific heat, from which estimated values of $\gamma, \Theta_D, \Theta_E$, and $r$ were derived. The fitting curve is plotted in Fig. 9(b) along with the $C(T)$ data of NdOs$_4$Sb$_{12}$ as a comparison. The values obtained for $\gamma, \Theta_D, \Theta_E$, and $r$ are estimated as 520 mJ/mol-K$^2$, 255 K, 39 K, and 0.48, respectively. The value of $\Theta_D$ is close to the Debye temperature of LaOs$_4$Sb$_{12}$, the value of $\Theta_E$ is comparable to that determined from the X-ray data, and the value of $\gamma$ is close to that estimated from the simple subtraction of the LaOs$_4$Sb$_{12}$ specific heat data, suggesting that NdOs$_4$Sb$_{12}$ is possibly a heavy fermion compound.

The temperature dependence of the magnetic entropy $S_{mag}$ was derived from the integration of $\Delta C/T$ vs $T$ and is shown in Fig. 9(a), where $\Delta C \equiv C - C_{el} - C_{lat}$. The magnetic entropy ($S_{mag}$) in NdOs$_4$Sb$_{12}$ reaches 0.69R ($\approx Rn2$) at 0.85 K and levels off at a value of $\sim 1.14R$ ($\approx Rln3$). The magnetic entropy reaches $\sim 74\%$ of its full value at $\Theta_C$, and a noticeable magnetic contribution persists up to $\sim 3K$, revealing the existence of magnetic fluctuations above $\Theta_C$. It has been argued for the antiferromagnetic system Gd$_{1-x}$Y$_x$Ni$_2$Sb$_4$ that magnetic fluctuations can contribute to $C(T)$ at temperatures up to 5 times the Neél temperature. Thus, we cannot completely rule out the possibility that the short range magnetic correlations near the ferromagnetic transition temperature regime give rise to enhancement of the specific heat of NdOs$_4$Sb$_{12}$

However, it is unlikely that they would account for a large fraction of the enhanced specific heat, due to the following arguments: (i) The paramagnetic-state $M(H)$ isotherm data (2 - 5 K) scale well with a Brillouin function. The $M(H)$ data at 2 K and 3 K, and the $\chi^{-1}(T)$ data along with the initial $\chi^{-1}$ from the Arrott Plot analysis do not show obvious evidence of magnetic fluctuations above 2 K (displayed in Fig. 9(a) and (b)). (ii) The value estimated for $\gamma$ (520 mJ/mol-K$^2$) is within the upper and lower limits of $\gamma$ (436 - 530 mJ/mol-K$^2$) estimated from the analysis done by comparing the specific heat of NdOs$_4$Sb$_{12}$ with that of the nonmagnetic compound LaOs$_4$Sb$_{12}$ suggesting that our analysis is justified. (iii) The lower limit (4 K) of the fitting range used to determine $\gamma$ from the formula $C = C_{el} + C_{lat}$ is four times the Curie temperature, which is safely higher than the temperature at which the calculated $S_{mag}$ saturates. (iv) Heavy fermion behavior has been found in the neighboring compounds PrOs$_4$Sb$_{12}$ ($\gamma \sim 600$ mJ/mol-K$^2$) and SmOs$_4$Sb$_{12}$ ($\gamma \approx 880$ mJ/mol-K$^2$) earlier studies of the related compound NdFe$_4$Sb$_{12}$ also reported possible evidence for an enhanced electron mass. Considering all of these points, it seems likely that NdOs$_4$Sb$_{12}$ displays heavy fermion behavior.

Since $S_{mag}$ lies between Rn2 ($= 0.69R$) and Rn4 ($= 1.39R$), it is difficult to determine conclusively whether the $\Gamma_6$ doublet or $\Gamma_8^{(2)}$ quartet is the Nd$^{3+}$ ground state. If the $\Gamma_6$ doublet is the ground state, then the extra entropy may result from another degree of freedom, such as a tunnelling mode or off-center mode of Nd$^{3+}$. If the $\Gamma_8^{(2)}$ doublet is the ground state, the smaller entropy may be due to an overestimated lattice contribution to the specific heat or transfer of entropy to the conduction electron system.

Figure 9(b) displays the incremental specific heat $\Delta C(T)$ after the electronic and lattice contributions have been removed. Even though the range of the $\Delta C(T)$ data below $\Theta_C$ is very limited, the data were fit with spin-wave formulas $\Delta C(T) \propto T^n$ for magnetically isotropic metals and $\Delta C(T) \propto T^{3/2} \exp(-\Delta_{spw}/T)$ for magnetically anisotropic metals. From the first formula, the value of the exponent $n \approx 2.3$ is higher than the value of
1.5 expected from a spin wave in an isotropic metal. The spin-wave energy gap $\Delta_{\text{sw}}$ determined from the second formula is $\sim 0.54\,\text{K}$, consistent with the value of 0.75 K determined from the zero-field resistivity data.

IV. SUMMARY

We have performed X-ray diffraction, electrical resistivity, magnetization, and specific heat studies of NdOs$_4$Sb$_{12}$ single crystals, which exhibit interesting strongly-correlated-electron behavior. X-ray experiments have revealed full occupancy of Nd sites and a large mean square displacement of Nd ions in NdOs$_4$Sb$_{12}$. The compound NdOs$_4$Sb$_{12}$ exhibits mean-field-type ferromagnetism with $\Theta_C \sim 0.9\,\text{K}$. The value of $\gamma$ estimated from the analysis of the specific heat is large, $\sim 520\,\text{mJ/mol-K}^2$ ($m^* \sim 98\,\text{m_e}$), indicating that NdOs$_4$Sb$_{12}$ is a possible heavy fermion compound. A cubic CEF analysis suggests two best-fit energy level schemes: (I) $\Gamma_6$ (0 K), $\Gamma_8^{(1)}$ (180 K), $\Gamma_8^{(2)}$ (420 K); (II) $\Gamma_8^{(2)}$ (0 K), $\Gamma_8^{(1)}$ (220 K), $\Gamma_6$ (600 K), both with a molecular field parameter $\Lambda = 1.39\,\text{Nd-mol/cm}^3$. The electrical resistivity data indicate that both $s$-$f$ exchange and aspherical Coulomb scattering are present in NdOs$_4$Sb$_{12}$. Low-temperature electrical resistivity data suggest the possible existence of spin-wave excitations below $\Theta_C$. The uncertainty in the CEF-energy-level scheme ground state and the possible existence of spin-wave excitations may be resolved by further neutron scattering experiments.

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