

X-ray-absorption spectroscopy study of the heavy-fermion superconductor PrOs₄Sb₁₂

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(Received 24 January 2003; published 30 May 2003)

X-ray-absorption fine-structure (XAFS) measurements have been carried out at the Pr L_{III} and Os L_{III} edges on the Pr-based heavy-fermion superconductor PrOs₄Sb₁₂. The x-ray absorption near-edge structure results suggest that the Pr valence is very close to 3+ with at most a small amount of Pr⁴⁺ [$\nu_{Pr} \sim 3.019(3)$], while Os is close to metallic in this material. The extended XAFS results show that the Pr ions rattle inside the Sb cage characterized by a low Einstein temperature ($\Theta_E \sim 75$ K), with a possible very small off-center displacement. They also indicate that the Os₄Sb₁₂ framework in PrOs₄Sb₁₂ is quite stiff.

DOI: 10.1103/PhysRevB.67.180511

PACS number(s): 74.70.Tx, 61.10.Ht

Superconductivity has recently been discovered in the filled skutterudite PrOs₄Sb₁₂; this material is the first example of a Pr-based heavy-fermion superconductor.^{1,2} Specific heat measurements reveal a Schottky anomaly with a peak at $T \sim 3$ K,¹⁻³ which is consistent with a Γ_3 nonmagnetic, quadrupolar ground state and a low-lying Γ_5 excited state separated by $\Delta \sim 8$ K, in the cubic crystalline electric field (CEF). Low-temperature inelastic neutron scattering measurements are in excellent agreement with this CEF energy-level scheme.² Anders proposed that the superconductivity in this material is mediated via the quadrupolar fluctuations of the Γ_3 ground state by applying a two-channel Anderson lattice model.^{4,5} However, this theory requires that Pr ions in PrOs₄Sb₁₂ have an intermediate valence. Recent x-ray photoelectron spectroscopy (XPS) measurement suggested that there is little evidence of a mixed valence for Pr, but the uncertainty of the amount of Pr⁴⁺ is 6% (Ref. 6) in this material and therefore does not preclude this model. In order to further probe the local electronic configuration of Pr, we carried out x-ray absorption near-edge structure (XANES) experiments to elucidate the Pr valence state.

With the filled skutterudite structure, PrOs₄Sb₁₂ is also a potential thermoelectric material. Most other filled skutterudites have low thermal conductivity due to a “rattling” of the rare-earth atom (such as Ce, Eu, Yb in other skutterudites), while the other atoms are assumed to be responsible for the metallic conductivity. Therefore, we applied the extended x-ray absorption fine structure (EXAFS) technique at both Pr L_{III} and Os L_{III} edges to compare PrOs₄Sb₁₂ as a thermoelectric material with other filled skutterudite systems.

Single crystals of PrOs₄Sb₁₂ were grown in an Sb flux as described in Ref. 1; these crystals were ground and then sifted through a 400-mesh sieve. The resulting very fine powder was then brushed onto scotch tape and loaded into a liquid He cryostat. The XAFS experiments were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 4-3 using Si $\langle 220 \rangle$ monochromator crystals. The Pr L_{III} -edge data were collected in fluorescence mode with the sample aligned 45° with respect to the beam, while the Os L_{III} -edge data were collected in transmission mode (step height ~ 0.34) with the sample perpendicular to the beam.

The Pr L_{III} -edge XANES data for PrOs₄Sb₁₂ and Pr₂O₃ are shown in Fig. 1(a) with the edge step height normalized to 1.0. In the normalization procedure, two points above the edge (energies = 6005 eV and 6300 eV in this case) are selected and a straight line is drawn through the data. The amplitude at the point where this straight line crosses the main edge is set to 1.0. The Pr L_{III} -edge data for PrOs₄Sb₁₂ clearly show a single-peak structure, which is very similar to that of Pr₂O₃; the positions of these two edges are also nearly identical. It has been shown in previous XANES studies that the Pr³⁺ L_{III} -edge has a single peak structure, while

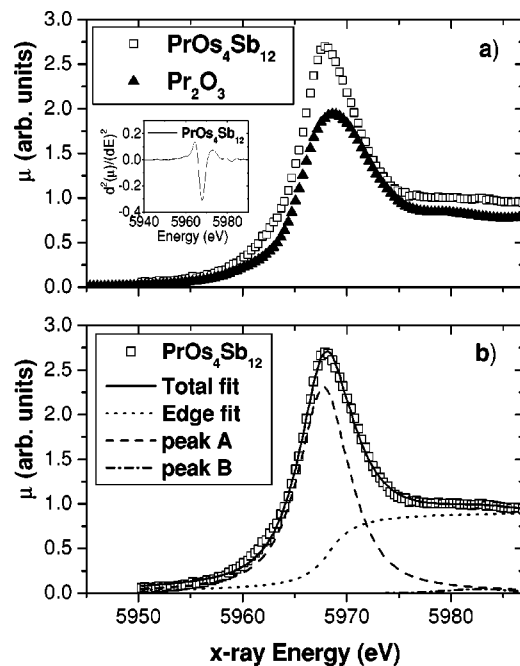


FIG. 1. (a) Pr L_{III} -edge XANES data for PrOs₄Sb₁₂ and Pr₂O₃ (Pr³⁺ standard). Both edges were normalized to an edge step height of 1. The energy range selected to normalize the edge is 6005 to 6300 eV. The inset shows the second derivative of the Pr L_{III} -edge data for PrOs₄Sb₁₂. (b) A fit of the Pr L_{III} -edge data for PrOs₄Sb₁₂. The solid line is the overall fit result, while the dotted line shows the edge fit using the “arctan” function. The dashed and dot-dashed lines are the fit results to peaks A and B, respectively.

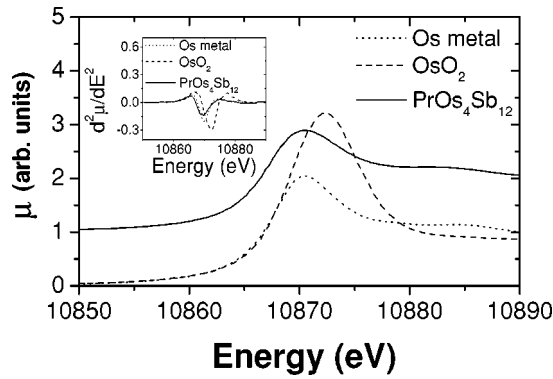


FIG. 2. Os L_{III} -edge XANES data for $\text{PrOs}_4\text{Sb}_{12}$ (vertically shifted by 1.0 unit), Os metal, and OsO_2 , a poor metal. All edges were normalized so that the edge step height is 1. The two energy points selected to normalize the edge are at 10950 and 11500 eV. Inset shows the second derivative: $d^2\mu/dE^2$.

a secondary peak would appear when Pr^{4+} ions are present, usually about 4 eV above the Pr^{3+} peak.⁷⁻⁹ We see no evidence for such a peak (also see $d^2\mu/dE^2$ in inset of Fig. 1) and consequently, no clear evidence for the existence of Pr^{4+} in $\text{PrOs}_4\text{Sb}_{12}$. However, for small Pr^{4+} concentrations another peak occurs, about 12~14 eV above the Pr^{3+} edge that has been attributed to Pr^{4+} ;¹⁰ the position of this second peak shifts to lower energy as the Pr valence increases.¹⁰ Since there is a tiny peak about 14 eV above the Pr L_{III} edge, there is a small possibility that this tiny second peak could indicate the presence of a very small amount of Pr^{4+} . Note the Pr_2O_3 XANES data also have a very small second peak (~12 eV above the first peak), which might indicate that there is a very small amount of Pr^{4+} ions in this reference sample.

Bianconi *et al.* suggested that the valence state of Pr in an intermediate valence regime can be determined as $V_{\text{Pr}} = 3 + I_B / (I_A + I_B)$, where I_A and I_B are the amplitudes for peak A (main peak) and peak B (second peak 14 eV above A peak).⁹ In order to obtain a quantitative measure of the Pr valence in $\text{PrOs}_4\text{Sb}_{12}$, we carried out an edge fit to the Pr L_{III} -edge XANES data. The edge function used in the fit was a standard “arctan” function, plus two Lorentzian peaks to fit the A and B peaks. The fit result is plotted in Fig. 1(b). It is clear that the second peak at ~5982 eV is very tiny; the Pr valence obtained from this approach is 3.019(0.003), or 1.9% of Pr^{4+} . This value provides an upper limit for the Pr^{4+} concentration.

XPS results suggests that there is no Pr^{4+} in $\text{PrOs}_4\text{Sb}_{12}$, but the accuracy of this result is limited by the signal-to-noise ratio, which is about 5%.⁶ Therefore, this XPS measurement could not detect a small amount of Pr^{4+} . The main edge in the Pr XANES data indicates that the Pr valence is very close to 3.0. Even allowing for the possibility that the weak peak 14 eV above the edge corresponds to Pr^{4+} , the amount is at most 2%—a much more stringent constraint on the Pr^{4+} concentration. This result questions the validity of using the two-channel Anderson lattice model, as proposed by Anders,^{4,5} to describe superconductivity in $\text{PrOs}_4\text{Sb}_{12}$.

Figure 2 presents the Os L_{III} -edge data for $\text{PrOs}_4\text{Sb}_{12}$, Os

metal (metallic standard), and OsO_2 , a poor metal that shows not only some metallic character, but also a shifted “white line.” Both μ and $d^2\mu/dE^2$ vs E plots (inset) show that the Os L_{III} -edge data for $\text{PrOs}_4\text{Sb}_{12}$ and Os metal are very similar; however, the peak position in the second derivative for OsO_2 is shifted ≈ 2 eV upwards compared to the Os metal. This indicates that the local electronic structure of Os in $\text{PrOs}_4\text{Sb}_{12}$ is close to metallic as was found for $\text{CeOs}_4\text{Sb}_{12}$.¹¹

EXAFS analyses were also carried out at the Pr L_{III} and Os L_{III} edges to study the local structure around these two types of atoms in $\text{PrOs}_4\text{Sb}_{12}$. The E -space data (μ vs energy) were reduced using standard procedures.^{12,13} First, the pre-edge absorption from other atoms was removed and the post-edge background, μ_0 (embedded atom¹⁴) was determined. Then the XAFS function $\chi(k)$ can be obtained as $\chi(k) = \mu/\mu_0 - 1$, where $k = \sqrt{2m_e(E - E_0)/\hbar^2}$ and E_0 is the binding energy of the L_{III} shell electrons of the excited atom.

The Fourier transform (FT) of $\chi(k)$ yields the r -space data, which have peaks corresponding to different atomic shells. Theoretical standards for each peak in r space can be calculated using the FEFF code.¹⁵ These standards and a Gaussian pair distribution function are used to fit the corresponding peak in r -space data, from which the width of the pair distribution function, σ , can be extracted. Since σ indicates the fluctuation of the distance between two atoms, it is a quantitative measurement of the local distortions of the bond lengths.

The Pr L_{III} -edge r -space data at three different temperatures and the extracted σ^2 for the Pr-Sb bond as a function of temperature are shown in Fig. 3. It is clear that the Pr-Sb peak [near 3.4 Å in Fig. 3(a)] has a very large temperature dependence; the amplitude of this peak drops more than 70% as the temperature increases from 3 to 310 K. This indicates that the Pr-Sb bond in $\text{PrOs}_4\text{Sb}_{12}$ is very soft. $\sigma^2(T)$ for the Pr-Sb bond also shows this strong temperature dependence [Fig. 3(b)]; it increases from 0.006 Å² to ~0.023 Å² (about a threefold increase) as the temperature increases to 300 K.

With the filled skutterudite structure, $\text{PrOs}_4\text{Sb}_{12}$ is also a potential thermoelectric material. In a filled skutterudite, the rattling filler ion is assumed to scatter phonons and, therefore, to lower its thermal conductivity.^{16,17} Keppens *et al.* also suggest that this rattling filler ion is a localized vibrational mode, which can be modeled as an Einstein oscillator for $\text{LaFe}_4\text{Sb}_{12}$.¹⁶ The large temperature dependence of σ^2 for the nearest Pr-Sb bond clearly indicates that this bond is very weak and the vibration amplitude of the Pr ion inside the Sb cage is very large, which agrees with the idea of a “rattling filler ion.”

For an Einstein oscillation, $\sigma_{Einstein}^2$ of an atom pair can be expressed in term of the Einstein temperature Θ_E :

$$\sigma_{Einstein}^2(T) = \frac{\hbar^2}{2M_R k_B \Theta_E} \coth \frac{\Theta_E}{2T}. \quad (1)$$

Here, M_R is the reduced mass. In this case, we set M_R equal to the atomic mass of the Pr atom: ~141 g/mol because of the relative stiffness of the $\text{Os}_4\text{Sb}_{12}$ framework, as discussed later in this paper. In a real system, there is also a static distortion, from vacancies and interstitial atoms, plus the

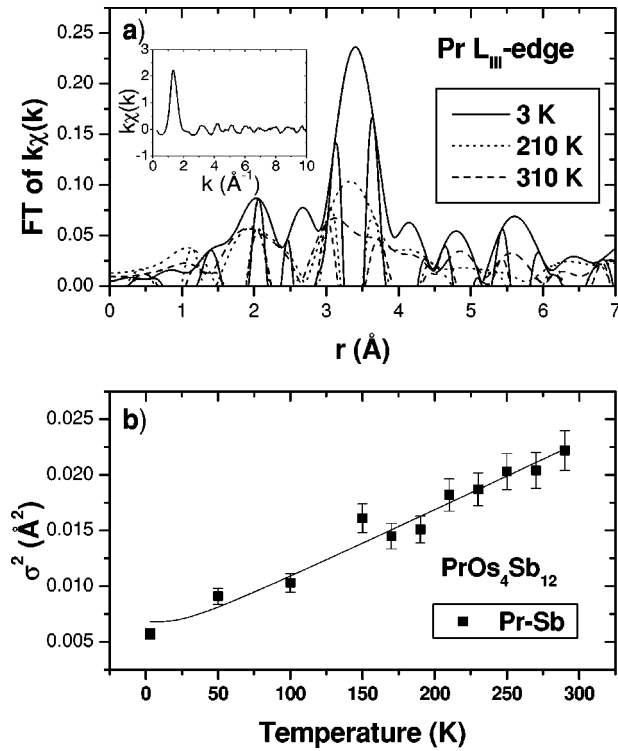


FIG. 3. (a) The Pr L_{III} -edge r -space data for $\text{PrOs}_4\text{Sb}_{12}$ at 3, 210, and 310 K. The Fourier transform (FT) range is from 3.3 to 9.05 \AA^{-1} , with 0.3 \AA^{-1} Gaussian broadening. The high-frequency curve inside the envelope is the real part of the Fourier transform (FT_R). The envelope is defined as $\pm \sqrt{FT_R^2 + FT_I^2}$, where FT_I is the imaginary part of the transform. The inset is the k -space data at the Pr L_{III} edge for $\text{PrOs}_4\text{Sb}_{12}$ at 3 K. (b) σ^2 as a function of temperature for the nearest Pr-Sb bond (peak at 3.4 \AA). The solid line shows the fit result for $\sigma^2(T)$ using an Einstein model.

possibility of an off-center displacement, which will contribute to the total σ^2 . Since a static distortion has no temperature dependence, we can therefore write the total σ^2 for an atom pair in terms of a static distortion and an Einstein contribution:

$$\sigma^2 = \sigma_{static}^2 + \sigma_{Einstein}^2(T). \quad (2)$$

By fitting σ^2 vs T in Fig. 3 to Eq. (2), we can extract both σ_{static}^2 and Θ_E for the rattling Pr atom. The solid curve in Fig. 3 shows that $\sigma^2(T)$ can be well fit by an Einstein model; σ_{static}^2 and Θ_E are 0.0045 \AA^2 and 75.4 K , respectively. Such a low Einstein temperature indicates that the Pr ion rattling will have a rather large amplitude at 300 K, which is comparable to other types of filler ions, such as Ce, Eu, and Yb¹⁸.

Single-crystal x-ray diffraction results give a U_{iso} parameter for Pr of 0.0363 \AA^2 (Ref. 19) at 300 K. Including the static distortion obtained from our XAFS result (0.0045 \AA^2 , assuming all of it comes from a Pr off-center displacement), the extracted Einstein temperature Θ_E from the diffraction result would be $\sim 57 \text{ K}$ for the localized Pr vibration. This result is about 18 K smaller than that obtained from the XAFS results. Note that XAFS measures the Pr vibrations along the Pr-Sb bond direction; however, it is also possible

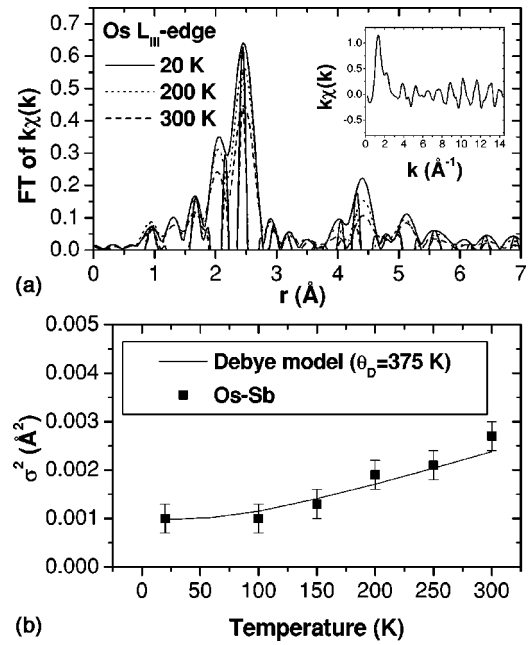


FIG. 4. (a) Os L_{III} -edge r -space data for $\text{PrOs}_4\text{Sb}_{12}$ at 20, 200, and 300 K. The FT range is from 3.3 to 13.5 \AA^{-1} , with 0.3 \AA^{-1} Gaussian broadening. The inset shows the corresponding k -space data at 20 K. (b) σ^2 as a function of temperature for the nearest Os-Sb bond. The solid line shows the fit result using a correlated Debye model.

for the Pr to vibrate in a direction towards a void. Such vibrations would have a lower Einstein temperature than that obtained from XAFS and would contribute to the isotropic diffraction result. However, both diffraction and XAFS agree that the low Einstein temperature indicates that the Pr is acting as a rattler atom.

Similar fits have been carried out for other filled antimonide skutterudites, and the values of σ_{static}^2 obtained for the nearest Ln-Sb bond (Ln: Ce, Eu, Yb) range from 0.0010 to 0.0020 \AA^2 , which is reasonable for such a complicated system.¹⁸ However, σ_{static}^2 for $\text{PrOs}_4\text{Sb}_{12}$ is 0.0045 \AA^2 , about two times larger than that for $\text{CeOs}_4\text{Sb}_{12}$ ($\sigma_{static}^2 \sim 0.0020 \text{ \AA}^2$ for $\text{CeOs}_4\text{Sb}_{12}$, Ref. 18). This larger static distortion for the Pr-Sb bond may indicate that Pr is very close to being off-center. Compared to $\text{CeOs}_4\text{Sb}_{12}$, $\text{PrOs}_4\text{Sb}_{12}$ has a slightly larger lattice constant ($\text{PrOs}_4\text{Sb}_{12}$, 9.3068 \AA ;¹⁹ $\text{CeOs}_4\text{Sb}_{12}$, 9.302 \AA , Ref. 20). XANES studies of these two materials suggests that both Pr and Ce are mainly +3 ions.²¹ The ionic radius of Pr^{3+} is $\sim 1.13 \text{ \AA}$, which is 0.02 \AA smaller than that for Ce^{3+} .²² Therefore, the $\text{PrOs}_4\text{Sb}_{12}$ system has a relatively larger cage with a smaller rattling ion, which can possibly lead to an off-center instability for the Pr ion. If we assume that the static distortion obtained for the Pr-Sb bond is caused solely by a Pr off-center displacement, then we can estimate an upper limit for this off-center displacement of $\sim 0.07 \text{ \AA}$ ($\sqrt{0.0045}$).

In discussing the Pr-Sb bond, we have assumed that the $\text{Os}_4\text{Sb}_{12}$ framework forms a relatively stiff cage for the rattling Pr ion in $\text{PrOs}_4\text{Sb}_{12}$. This leads to a localized vibration of the Pr ion in this material. To check this behavior, we have

carried out Os EXAFS experiments. Figure 4 shows the Os L_{III} -edge r -space data for $\text{PrOs}_4\text{Sb}_{12}$ as well as the extracted σ^2 as a function of temperature for the nearest Os-Sb bond, from which one can obtain information about the local distortion of the $\text{Os}_4\text{Sb}_{12}$ framework. The first main peak in Fig. 4(a), near 2.5 Å, corresponds to the nearest Os-Sb peak; its amplitude drops about 30% as the temperature increases from 20 to 300 K. This is much less than the 70% amplitude drop for the nearest Pr-Sb peak obtained from Fig. 3(a), which indicates that the nearest Os-Sb bond is significantly stronger than that of the nearest Pr-Sb bond.

σ^2 is plotted as a function of temperature in Fig. 4(b). The net change in σ^2 for the Os-Sb pair as T increases from 20 to 300 K is only about 0.0018 Å², which is far less than that for the nearest Pr-Sb pair (Fig. 3). Since the Os-Sb bond is a part of the unit crystal structure, we expect the T dependence of σ^2 to be better modeled by the Debye model. Using the built-in Debye card in the FEFF7 code, the correlated Debye temperature Θ_D for this Os-Sb pair vibration can be extracted by fitting the σ^2 vs T curve. The fit result yields $\Theta_D \sim 375$ K, which is more than four times the value of Θ_E for the Pr-Sb pair. This Debye temperature supports the assumption made earlier that the Os/Sb network forms a relatively stiff cage surrounding the Pr ion.

In summary, XANES and EXAFS experiments have been used to study the local electronic structure and the local lattice distortions of Pr and Os atoms in $\text{PrOs}_4\text{Sb}_{12}$. The XANES results indicate that the Pr ion is mainly in a 3+ valence state. The amount of Pr^{4+} in the system is very small with a maximum upper limit of $\sim 2\%$. Thus, it is unlikely that the fluctuating valence, two-channel Anderson lattice model is the mechanism for superconductivity in $\text{PrOs}_4\text{Sb}_{12}$. From the Os XANES, the Os atoms have a mainly metallic character when compared with Os metal and OsO_2 . The EXAFS data clearly support the idea of a rattling Pr filler ion ($\Theta_E \sim 75$ K) within a fairly stiff cage in this material. However, the extra static distortion in the Pr-Sb bond compared to other filled skutterudites may suggest that Pr in this material is close to the on-center to off-center transition; an upper limit of a possible off-center displacement is about 0.07 Å.

The work at UCSC was supported by NSF Grant No. DMR0071863; the work at UCSD was supported by the Department of Energy, under Grant No. DE FG03-86ER-45230, and under the NEDO International Joint Research Program. The experiments were performed at SSRL, which is operated by the DOE, Division of Chemical Sciences, and by the NIH, Biomedical Resource Technology Program, Division of Research Resources.

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²²The ionic radii are obtained at a website named WebElements™ Periodic Table, <http://www.webelements.com/>.