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Cerium L_{III} -edge x-ray absorption study of the $Ce_xFe_{4-y}Co_ySb_{12}$ skutterudites

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The cerium L_{III} -edge x-ray absorption near-edge spectra of the $Ce_xFe_{4-y}Co_ySb_{12}$ compounds have been obtained at 295 K and unambiguously indicate that cerium is in the $4f^1$ electronic ground state for all values of $0.22 \leq x \leq 0.98$ and $0.0 \leq y \leq 3.5$. This stable trivalent state of cerium is in agreement with the proposed $(CeFe_4Sb_{12})_{1-\alpha}(□Co_4Sb_{12})_\alpha$ solid solution structure, in which the cerium atoms are always surrounded by twelve antimony first neighbors and six iron second neighbors, the observed magnetic properties of $CeFe_4Sb_{12}$ and $Ce_{0.9}Fe_3CoSb_{12}$, and the electronic structure of $CeFe_4Sb_{12}$ obtained from band-structure calculations.

I. INTRODUCTION

The valence of cerium in the filled skutterudite $CeFe_4X_{12}$ compounds, where X is P, As, or Sb, has been the subject of many discussions and much recent speculation. A cerium valence of four in $CeFe_4P_{12}$ and of three in $CeFe_4Sb_{12}$ has been postulated¹ from their unit-cell volumes. A trivalent state for cerium in $CeFe_4Sb_{12}$ was also predicted² from band-structure calculations. In contrast, a cerium valence of 3.74 at 4.2 K was deduced³ from electrical conductivity measurements. The concept of the cerium valence in these compounds requires some explanation.² In no case is the cerium atom oxidized to the cerium(III) or cerium(IV) oxidation state in these intermetallic compounds. Rather, the concept of the cerium valence refers to the electronic ground state of the cerium atom; the $4f^0$ and $4f^1$ ground states are usually referred to as tetravalent and trivalent cerium, respectively.

In order to better understand and predict the technologically important thermoelectric properties⁴ of the filled skutterudite compounds, it is necessary to obtain a good description of their electronic structure and, particularly, of the electronic configuration of cerium in these materials. X-ray absorption spectroscopy at the cerium L_{III} edge is a unique technique⁵ for obtaining this information, because it is element and electronic transition specific. Recently, the cerium L_{III} -edge x-ray absorption near-edge structure spectrum (XANES spectrum) of $CeRu_4P_{12}$ at room temperature has been reported,⁶ and the results indicate that cerium is predominantly trivalent, i.e., cerium is in the $4f^1$ electronic ground state in this filled skutterudite. We present herein a cerium L_{III} -edge XANES study of the $Ce_xFe_{4-y}Co_ySb_{12}$ se-

ries of compounds and we discuss the results in the framework of their electronic structure.

II. EXPERIMENT

The samples studied herein are identical to those prepared⁷ and studied^{8,9} previously. The powder absorbers had thicknesses of ~ 15 mg/cm². The cerium L_{III} -edge XANES spectra were obtained at 295 K on the D21 station at LURE. The ring was operating at 1.85 GeV and a stored current of 200 mA. Detailed preliminary measurements indicated that better XANES spectra were obtained in transmission mode than in fluorescence detection mode. Thus the measurements were carried out in transmission mode with a Si(311) double-crystal monochromator using ion chambers filled with a mixture of nitrogen and helium, both in front and behind the sample. Harmonic contamination was rejected by using a total reflection mirror with a cut off at 9 keV. The resolution calculated from the width of the two slits located in front of the monochromator and in front of the first ion chamber is estimated to be 1.4 eV. The spectra were recorded with a step of 2 eV below 5710 eV and of 0.2 eV between 5710 and 5760 eV. Because of the extensive scattering produced by the presence of large amounts of antimony in the absorbers, the jump in absorption at the cerium L_{III} edge is smaller than desirable and the quality of the XANES spectra is somewhat lower than usually obtained^{6,10,11} with other cerium-containing intermetallic compounds. The K -edge absorption spectrum of a thin metallic foil of chromium was used for energy calibration.

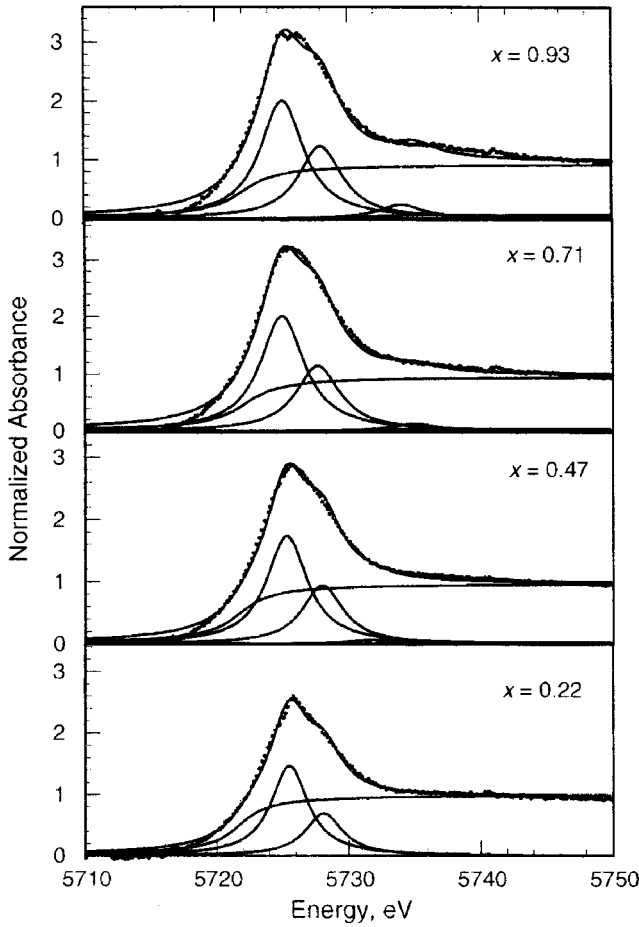


FIG. 1. The 295 K cerium L_{III} -edge XANES spectra of $Ce_xFe_{4-y}Co_ySb_{12}$, with $x=0.93, 0.71, 0.47, 0.22$ and their fits as described in the text.

III. RESULTS AND DISCUSSION

The cerium L_{III} -edge XANES spectra of $Ce_xFe_{4-y}Co_ySb_{12}$ are shown in Fig. 1 for $x=0.93, 0.71, 0.47,$ and 0.22 and the y values given in Table I. The spectra obtained for $x=0.98, 0.82, 0.60,$ and $0.35,$ are not shown herein but are very similar. All the spectra have been analyzed in the fashion discussed below. It is obvious that all the spectra are characterized by a main absorption peak at ~ 5725 eV and a minor broader absorption peak at ~ 5735 eV. Further, these spectra are very similar to that observed⁶ for $CeRu_4P_{12}$. Hence, a simple visual inspection indicates a

TABLE I. Cerium L_{III} -edge XANES energies, and core-hole lifetimes. Γ in eV, and the cerium valence for $Ce_xFe_{4-y}Co_ySb_{12}$.

x	y	E_0	E_1	Δ	Γ	Ce valence
0.22	3.5	5721.7	5725.5	2.58	3.40	3.00
0.35	3.0	5721.4	5725.3	2.76	3.62	3.02
0.47	2.5	5721.7	5725.3	2.70	3.74	3.02
0.60	2.0	5721.8	5725.2	2.80	3.84	3.04
0.71	1.5	5722.2	5725.0	2.71	4.06	3.04
0.82	1.0	5722.3	5725.0	2.79	4.12	3.06
0.93	0.5	5722.1	5725.1	2.86	4.00	3.07
0.98	0.0	5722.1	5725.4	2.62	3.94	3.03

predominately trivalent state, i.e., a $4f^1$ electronic ground state for cerium in $Ce_xFe_{4-y}Co_ySb_{12}$.

A more detailed analysis of the spectra shown in Fig. 1 and a search for any trend with composition requires a more sophisticated fit of the absorption profile and several different models for fitting the cerium L_{III} -edge XANES spectra have been reported.^{6,10-12} The common points between these models are the following. The continuum absorption is represented by an arctangent function superimposed on a linear background and the absorption lines corresponding to the $2p_{3/2} \rightarrow 5d$ transitions are represented by Lorentzian lines. Hence, the cerium L_{III} -edge XANES spectrum of $CeAl_2$, a typical trivalent cerium compound, is well fitted¹¹ by equation.

$$\mu(E) = B_0 + B_1 E + \left\{ 0.5 + \frac{1}{\pi} \arctan \left(\frac{E - (E_1 + \delta)}{\Gamma/2} \right) \right\} + \frac{A(\Gamma/2)^2}{(E - E_1)^2 + (\Gamma/2)^2}, \quad (1)$$

where B_0 and B_1 are the linear background parameters, E_1 is the energy at which the $2p_{3/2} \rightarrow 5d$ transition occurs. Γ is the core-hole lifetime for the transition. A is the area of the Lorentzian peak, and δ is the shift between the onset of the continuum and bound-state transitions. For the spectrum of $CeAl_2$, δ is positive.

The cerium L_{III} -edge XANES spectra of intermediate-valent cerium compounds show^{10,12-15} two Lorentzian absorption peaks separated by the replicate splitting of 9 to 10 eV, and they have been analyzed^{12,14} with two arctangent functions and two Lorentzian peaks representing the continuum absorption and the $2p_{3/2} \rightarrow 5d$ transitions for the trivalent and tetravalent cerium states, respectively. In the case of the $CeFe_{11}TiH_y$ compounds,¹² it should be noted that the fit shown is poor and the parameter δ is negative for both valence states, in disagreement with the analysis of Croft *et al.*¹¹ for $CeAl_2$. In this model the cerium XANES spectra have been fitted with the equation

$$\mu(E) = B_0 + B_1 E + \frac{A_1}{A_1 + A_2} \left\{ 0.5 + \frac{1}{\pi} \arctan \left(\frac{E - (E_1 + \delta)}{\Gamma/2} \right) \right\} + \frac{A_2}{A_1 + A_2} \left\{ 0.5 + \frac{1}{\pi} \arctan \left(\frac{E - (E_2 + \delta)}{\Gamma/2} \right) \right\} + \frac{(\Gamma/2)^2 A_1}{(E - E_1)^2 + (\Gamma/2)^2} + \frac{(\Gamma/2)^2 A_2}{(E - E_2)^2 + (\Gamma/2)^2}, \quad (2)$$

where E_1 and E_2 are the energies at which the $2p_{3/2} \rightarrow 5d$ transitions occur for the trivalent and the tetravalent cerium, respectively. Γ is the core hole lifetime for the transition. A_1 and A_2 are the areas of the Lorentzian peaks, and δ is the energy shift between the onset of the continuum and the bound state. All our attempts to fit the spectra in Fig. 1 with Eq. (2) lead to a poor fit of the main peak and we conclude, in agreement with Lee *et al.*,⁶ that the peak at ~ 5725 eV is not a simple Lorentzian peak.

Hence, after subtraction of a linear background, the cerium L_{III} -edge XANES spectra of $Ce_xFe_{4-y}Co_ySb_{12}$ have been fitted with a model that uses two arctangent functions to fit the continuum and three Lorentzian peaks, two for the

main peak at ~ 5725 eV and one for the minor peak at ~ 5735 eV, i.e., with the equation

$$\begin{aligned} \mu(E) = & (A_1 + A_2)/(A_1 + A_2 + A_3) \left\{ 0.5 + \frac{1}{\pi} \arctan \left(\frac{E - E_0}{\Gamma/2} \right) \right\} \\ & + \frac{A_1(\Gamma/2)^2}{(E - E_1)^2 + (\Gamma/2)^2} + \frac{A_2(\Gamma/2)^2}{(E - E_1 - \Delta)^2 + (\Gamma/2)^2} \\ & + A_3/(A_1 + A_2 + A_3) \left\{ 0.5 + \frac{1}{\pi} \arctan \left(\frac{E - E_0 - 10}{\Gamma/2} \right) \right\} \\ & + \frac{A_3(\Gamma/2)^2}{(E - E_1 - 10)^2 + (\Gamma/2)^2}, \end{aligned} \quad (3)$$

where E_0 is the energy of the onset of the continuum. E_1 and $E_1 + \Delta$ are the energies at which the $2p_{3/2} \rightarrow 5d$ transitions occur for the trivalent cerium. Γ is the core-hole lifetime for the transition, and A_1 , A_2 , and A_3 are the areas of the Lorentzian peaks. Because the peak at ~ 5235 eV is very weak, a replicate splitting of 10 eV has been assumed in Eq. (3).

The fits with Eq. (3) are good and the resulting parameters are given in Table I. The predominant peak at ~ 5725 eV is well fitted with two Lorentzian peaks at ~ 5725 and 5728 eV. This double Lorentzian absorption is assigned to the $2p_{3/2}4f^1 \rightarrow 4f^15d$ transitions in which the $5d$ orbitals are split into e_g and t_{2g} orbitals by the crystal field of the twelve antimony atoms surrounding the cerium atom. A splitting, Δ , of ~ 2.6 eV corresponds to a $10Dq$ of $21\,000\text{ cm}^{-1}$, a very reasonable value for this type of electronic environment. The Lorentzian peak at ~ 5735 eV is assigned to the $2p_{3/2}4f^0 \rightarrow 4f^05d$ transition. As indicated in Table I, the linewidth Γ or the core-hole lifetime is essentially independent of composition and is similar to that measured by Lee *et al.*⁶ in $\text{CeRu}_4\text{P}_{12}$.

The cerium valence obtained from the areas A_1 , A_2 , and A_3 is also given in Table I and is shown in Fig. 2 as a function of the cerium content. The samples for $x=0.93$ and 0.98 have been measured at two different times on the same absorber and the two values are both plotted in Fig. 2. These duplicate measurements give an estimate of ± 0.03 for the error on the cerium valence. Hence, we conclude that the cerium valence is 3.03 ± 0.03 and cerium is in the $4f^1$ ground state in all the $\text{Ce}_x\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ compounds. The slight increase in cerium valence with cerium content is may be due to a trivial amount of oxidation of surface cerium atoms in the grains.

IV. CONCLUSIONS

Our experimental measurements indicate that cerium is trivalent in all the $\text{Ce}_x\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ compounds and is independent of both x and y , an independence which is in agreement with theoretical predictions from band-structure calculations of Nordström and Singh² on $\text{CeFe}_4\text{Sb}_{12}$. Unfortunately, the band-structure calculations extend at most

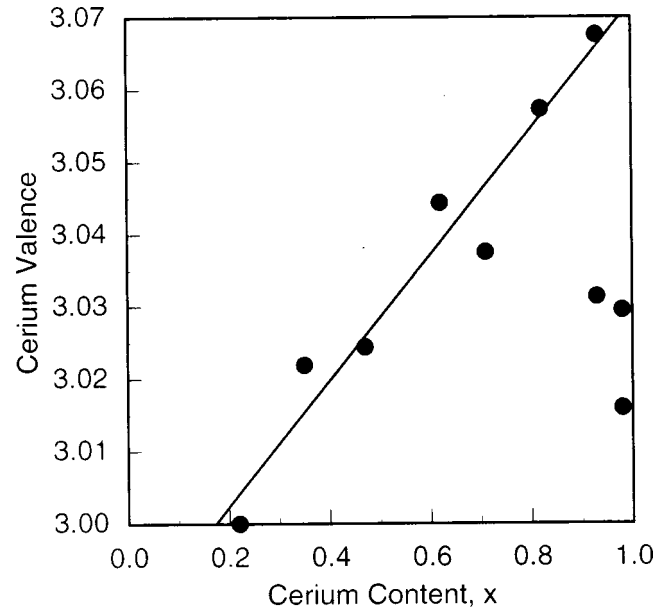


FIG. 2. The cerium valence in $\text{Ce}_x\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ as a function of cerium content. It should be noted that the ± 0.03 error bars are almost the size of the vertical axis of the plot and that no true correlation between the cerium valence and the cerium content exists.

to only 4 eV above the Fermi level, and hence the energies of the unoccupied $5d$ levels probed by XANES cannot be compared with the band-structure calculations. The independence of the cerium valence on composition agrees with the proposal⁸ that the $\text{Ce}_x\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ compounds consist of solid solutions $(\text{CeFe}_4\text{Sb}_{12})_{1-\alpha}(\text{Co}_4\text{Sb}_{12})_\alpha$, in which the cerium atoms are surrounded by twelve antimony first neighbors and six iron second neighbors. The effective magnetic moments¹⁶ of $3.8\mu_B$ and $2.6\mu_B$ in $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ are also in agreement with the trivalent state of cerium whose free ion magnetic moment is $2.54\mu_B$.

The stable trivalent state of cerium in $\text{Ce}_x\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ contrasts with the intermediate-valent state¹⁷ of ytterbium in $\text{YbFe}_4\text{Sb}_{12}$. Steric arguments may be used to understand this difference. The unit cell volume of $\text{YbFe}_4\text{Sb}_{12}$ is larger than that of $\text{CeFe}_4\text{Sb}_{12}$ and hence the void in which the ytterbium atom resides is larger than that available for the cerium. In addition, because of the lanthanide contraction ytterbium, with a 12-coordinate metallic radius of 1.75 \AA , is smaller than cerium, with a 12-coordinate metallic radius of 1.81 \AA . Hence, in order to better fill in the available void in the structure, ytterbium tends to be divalent.

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