

## Article

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# Valence of cerium ions in selected ternary compounds from the system Ce-Rh-Sn

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Over the last years, intermetallic compounds from the system Ce–Rh–Sn have attracted a considerable attention owing to a rich variety of strongly correlated electron phenomena they exhibit. CeRhSn<sub>2</sub>, Ce<sub>5</sub>Rh<sub>4</sub>Sn<sub>10</sub>, Ce<sub>2</sub>Rh<sub>3</sub>Sn<sub>5</sub> and Ce<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub> are magnetically ordered heavy fermion systems [1-5]. Interestingly, for Ce<sub>3+x</sub>Rh<sub>4</sub>Sn<sub>13-x</sub> (0.2<x<0.6) no sign of Kondo effect and long range magnetic order was found down to the temperature of 0.4 K [5]. In turn, CeRhSn shows non-Fermi liquid-type thermodynamic and transport properties at low temperatures [6-7] accompanied by an intermediate valence state of the Ce ions. Further, for CeRhSn, CeRhSn<sub>2</sub> and CeRh<sub>2</sub>Sn<sub>4</sub> spin fluctuations due to the Rh 4d electrons were also suggested [1,7-8]. The possible coexistence of magnetic phenomena originating from Ce and Rh makes the unequivocal interpretation of experimental data for these compounds very difficult. Consequently, a detailed understanding of the very complex physical properties/behavior requires the use of a broad spectrum of experimental methods, including extended thermodynamic and transport measurements as well as careful investigations of electronic structure. For these systems the full characterization of Ce 4f states in regard to their occupancy, localization in a conduction band and hybridization with the other valence band states is crucial for an unambiguous determination of ground state properties and the low energy excitations. Thus, X-ray absorption spectroscopy (XAS) is here of great use as a bulk probe which is highly sensitive on chemical states of elements. Furthermore, absorption measurements at the Ce L<sub>III</sub> edge results in spectra with minimized lifetime broadening, largely unaffected by complicated many-electron final state effects. These spectra can be used to estimate the numbers for the fractional valence of Ce which originates from the strong hybridization between the Ce 4f and the other valence band states related to the valence fluctuation phenomena and/or to the formation of covalent bonds.

The Ce L<sub>III</sub> XAS spectra were recorded in a transmission arrangement at the EXAFS beamlines A1 and C of the HASYLAB at DESY. The wavelength selection was realized using the Si (111) double crystal monochromator which yielded an experimental resolution of approximately 1.5 eV (FWHM) at the Ce L<sub>III</sub> threshold of 5723 eV (C), or using the two-crystal mode (A1). The powdered materials were mixed with small amounts of B<sub>4</sub>C and mounted on a 1cm<sup>2</sup> window sample holder using the paraffin wax. Measurements were performed at ambient temperature and at low temperatures down to 5 K using a He-gas flow cryostat. Experimental data were recorded using CePO<sub>4</sub> or CeO<sub>2</sub> as external reference compounds with Ce ions in a trivalent or in a tetravalent state, respectively.

The Ce L<sub>III</sub> XAS spectra for the compounds Ce<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub>, Ce<sub>3.2</sub>Rh<sub>4</sub>Sn<sub>12.8</sub>, Ce<sub>3.5</sub>Rh<sub>4</sub>Sn<sub>12.5</sub>, CeRh<sub>2</sub>Sn<sub>4</sub>, Ce<sub>1.2</sub>Rh<sub>2</sub>Sn<sub>3.8</sub> and Ce<sub>2.1</sub>Rh<sub>3.1</sub>Sn<sub>4.8</sub> (Fig. 1) show only a single ‘white line’ at the energy of ~5722 eV. These maxima correspond to 4f<sup>4</sup>(5d6s)<sup>3</sup> configuration of the Ce<sup>3+</sup>. There is no evidence for additional peaks in the measured spectra, distributed analogously to the maxima observed in the spectrum for the CeO<sub>2</sub> standard. Thus one can conclude that Ce ions in the investigated systems are exclusively in a trivalent state. Furthermore, there is basically no difference between the spectra measured at ambient conditions and at low temperatures. This indicates that the trivalent electronic configuration

of Ce in these compounds is stable over the examined temperature range. In case of  $\text{Ce}_2\text{Rh}_3\text{Sn}_5$ , however, there is also a weak additional peak in the Ce  $L_{\text{III}}$  XAS spectra at the energy of nearly +9 eV above the ‘white line’, which can be ascribed to  $4f^0(5d6s)^4$  configuration of the  $\text{Ce}^{4+}$ . This minor contribution diminishes with increasing temperature, as often observed for Ce-based intermediate valence systems [9]. Further, the presence of this additional maximum in the measured Ce  $L_{\text{III}}$  XAS spectra was found to be very sensitive on chemical composition. For  $\text{Ce}_{2.1}\text{Rh}_{3.1}\text{Sn}_{4.8}$  a stable trivalent state of Ce ions has been observed within the whole investigated temperature range (Fig. 1).

Quantitative evaluation of the Ce  $L_{\text{III}}$  XAS spectra for  $\text{Ce}_2\text{Rh}_3\text{Sn}_5$  was performed using the Athena program package [10]. Deconvolution of the normalized spectra was carried out considering two Gaussian functions representing the defined transitions and an arctan step function to account for the transitions of photoelectrons ejected from  $2p_{3/2}$  states to the continuum. Analysis of the relative decrease of the  $4f^0(5d6s)^4$  peak with increasing temperature leads to the rough estimate of the mean valence of Ce ions in  $\text{Ce}_2\text{Rh}_3\text{Sn}_5$  changing from +3.10 at 6 K to +3.05 at ambient temperature.

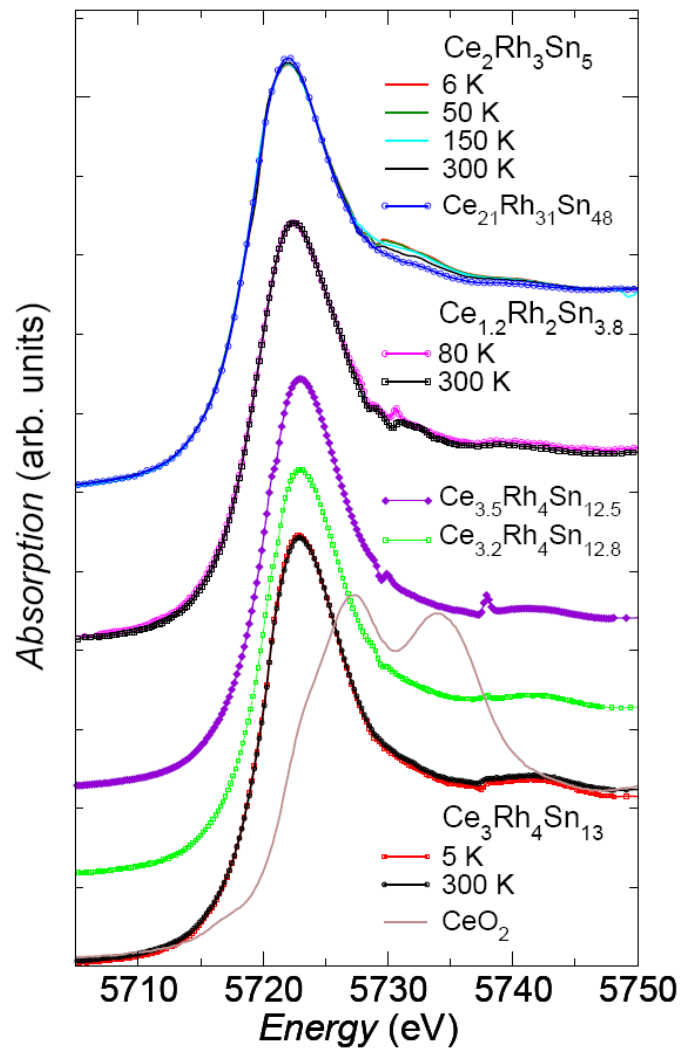


Figure 1: The normalized Ce  $L_{\text{III}}$  XAS spectra.

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