

Mean valence of Yb metal in the pressure range 0 to 340 kbar

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The mean valence of Yb metal was investigated in the pressure range 0 to 340 kbar at room temperature by L_{III} -edge spectroscopy using a diamond-anvil cell and a focusing x-ray absorption spectrometer. Structure and position of the observed L_{III} edges show that Yb metal is divalent in the fcc phase (0–40 kbar) and trivalent in the hcp phase (above 300 kbar). In the bcc phase (40–300 kbar) a continuous valence transition towards 3+ is observed.

Yb metal, when exposed to high external pressures at room temperature, undergoes two structural phase transitions^{1–3}: At 40 kbar the ambient-pressure fcc phase transforms to a bcc structure, which is stable up to about 300 kbar, and at still higher pressures it becomes hcp. While Yb metal is divalent ($4f^{14}$ configuration) under ambient conditions, very little and even controversial experimental information exists on its valence in the high-pressure phases. A valence transition to the trivalent state was theoretically predicted by Johansson and Rosengren at pressures around 130 kbar,⁴ which is in contradiction to earlier equation-of-state data obtained from shock-wave experiments.⁵ More recent x-ray diffraction measurements, however, revealed an anomalously strong pressure dependence of the lattice constant in the bcc phase, which was interpreted as an indication for a continuous valence transition.²

We have studied the Yb L_{III} x-ray absorption edge at pressures up to 340 kbar in order to clarify the question of a valence transition in the high-pressure phases of Yb metal. As is by now well established, structure and energetic position of L_{III} edges contain quantitative information on the valence of rare-earth atoms.^{6,7} By combining the method of L_{III} -edge spectroscopy on a laboratory x-ray absorption spectrometer with ultrahigh pressure techniques (using a diamond-anvil cell) we have established a powerful tool for studying pressure-induced valence transitions in rare-earth systems. For Yb metal we clearly identify a continuous valence transition extending over the whole range of the bcc phase (from 40 to \approx 300 kbar) and we find that Yb is trivalent in the hcp phase above 300 kbar.

The experiments were performed with a conventional laboratory x-ray absorption spectrometer based on a Rowland-type focusing monochromator on a 2-kW Mo x-ray source. A Johansson-type Ge(220) crystal produced a tunable monochromatic x-ray beam with an energy width of \approx 4.5 eV [full width at half maximum (FWHM)] at 8 keV. Details of the x-ray absorption spectrometer are presented elsewhere.⁸ The high-pressure setup involved a

diamond-anvil cell of the Syassen-Holzappel type⁹ using an inconel gasket and silicon oil as pressure-transmitting medium. The pressure applied to the Yb absorber foil (5 μ m thick, 99.9% pure) was measured *in situ* with the ruby-fluorescence method to an accuracy of 3%. Even at the highest-pressure values achieved, the pressure varied by less than \pm 5% over the area of the sample. Due to the small sample size (\approx 0.05 mm²) and a high photoabsorption in the diamond anvils the x-ray flux was reduced by a factor of \approx 10⁴ as compared to ambient-pressure absorption experiments.

Some typical L_{III} -edge x-ray absorption spectra of Yb metal at room temperature and at various external pressures are presented in Fig. 1. The spectra exhibit a peaked structure at the absorption edge ("white line"), which is characteristic for L_{II} and L_{III} edges of $4f$ systems. It is due to atomiclike transitions from $2p_{3/2}$ states to empty $5d$ states slightly above the Fermi level.¹⁰ The energy position of the L_{III} edge of Yb metal at ambient pressure [Fig. 1(a)] is characteristic for divalent Yb systems.¹¹ At a pressure of 340 kbar the L_{III} -edge peak [Fig. 1(d)] has shifted by 6.5 ± 0.5 eV to higher energies characteristic for trivalent Yb systems.¹¹ This increase of the $2p_{3/2}$ -binding energy by \pm 6.5 eV is caused by an increase of the effective nuclear potential when a $4f$ electron is promoted to the conduction band.¹² The L_{III} -edge spectra of Figs. 1(a) and 1(d) thus clearly show that Yb metal has transformed from the divalent state [$4f^{14}(5d6s)^2$] at ambient conditions to the trivalent (or almost trivalent) state [$4f^{13}(5d6s)^3$] at 340 kbar.

In the bcc phase of Yb metal the observed L_{III} edges [Figs. 1(b) and 1(c)] exhibit features characteristic for a mixed-valent state. At these pressures the L_{III} -edge structures can be described by a superposition of two peaked edges originating from divalent and trivalent Yb ions, respectively. From the relative intensities of the two subspectra a value for the mean valence \bar{v} is derived.^{6,7,10,11}

The solid lines in Fig. 1 represent the results of least-squares-fit analyses using a superposition of two

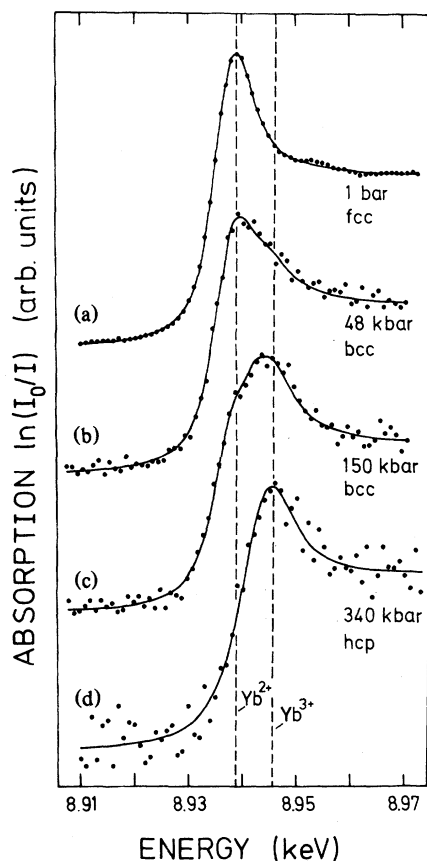


FIG. 1. L_{III} -edge absorption spectra of Yb metal at room temperature and at various pressures. The solid lines represent the results of a least-squares-fit analysis (see text). The dashed vertical lines indicate characteristic positions of the L_{III} -edge peak for divalent and trivalent metallic Yb systems, respectively.

L_{III} -edge subspectra. Each subspectrum is described by the sum of an arctan function (corresponding to the L edge) and a Lorentzian of variable width and peak height (corresponding to the white line). The spectral parameters for the divalent subspectrum were adjusted from the Yb metal spectrum at ambient pressure [Fig. 1(a)], while those for the trivalent subspectrum were obtained from the 340-kbar spectrum and additional spectra taken from trivalent Yb compounds.⁸ The total widths of the white lines were found to be $\cong 8$ eV (FWHM) for divalent Yb and $\cong 10$ eV (FWHM) for trivalent Yb. These spectral parameters were used to fit the L_{III} -edge spectra in the mixed-valent region resulting in values for the mean valence \bar{v} as a function of external pressure. The spectrum at 30 kbar could be fitted equally well with only a single subspectrum corresponding to divalent Yb.

The results for \bar{v} of Yb metal as a function of external pressure are summarized in Fig. 2. We find

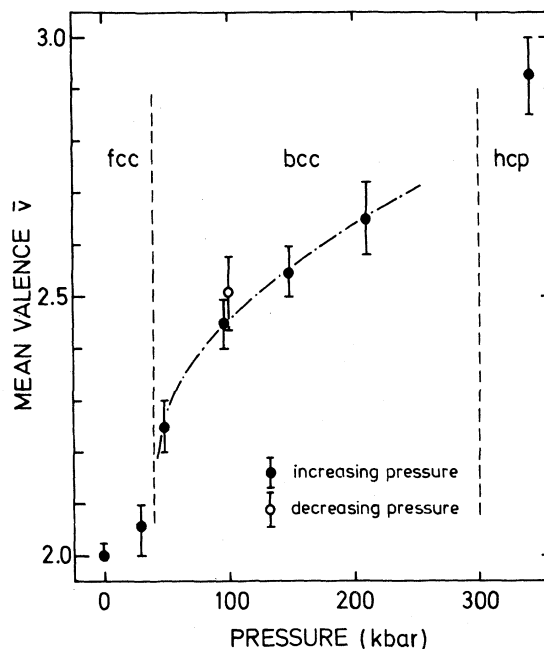


FIG. 2. Pressure dependence of the mean valence of Yb metal in its various phases at room temperature. The dashed lines represent the phase boundaries as known from x-ray diffraction work (Refs. 1–3).

that within the accuracy of the present measurements Yb metal stays divalent in the fcc phase up to the fcc \rightarrow bcc phase transition at 40 kbar. This is in agreement with previous findings.^{1,13} In the bcc phase a continuous pressure-induced valence transition is found, which extends over the whole range from 40 to $\cong 300$ kbar. The valence change with pressure, which is most dramatic just above the fcc \rightarrow bcc phase transition, slows down with increasing pressure and even does not seem to get completed in the bcc phase. In the hcp phase the only data point taken at 340 kbar indicates a trivalent (or nearly trivalent) state of Yb.

Previous high-pressure studies of transport properties of Yb metal in the bcc phase at pressures up to 160 kbar, however, were interpreted as evidence against a valence transition.^{1,13} The conclusions concerning \bar{v} of these previous measurements were based on the observed transport properties at low temperatures, while the present data describe the pressure dependence of \bar{v} at room temperature. The apparent discrepancy between these transport measurements and the present results might originate in a temperature dependence of the mean valence. A strong influence of temperature on \bar{v} in mixed-valent Yb systems can, in fact, be anticipated from several experimental findings: (i) $YbAl_2$ is mixed valent at room temperature^{11,14} with a valence increasing with temperature¹⁵; (ii) temperature-induced valence

changes are also known for systems like YbCuAl and YbCu₂Si₂, which are trivalent (or near to trivalent) at room temperature¹¹ and which show strong anomalies in their thermal expansion coefficients and their magnetic behavior reflecting an increase of the divalent state at low temperatures.¹⁶ This temperature behavior of mixed-valent Yb systems, which is opposite to, e.g., mixed-valent Eu systems,¹⁷ may be understood on the basis of an interconfigurational fluctuation model, taking into account the high degeneracy of the trivalent $4f^{13}$ configuration.¹⁶ If the same temperature influence on \bar{v} is also operative in the mixed-valent bcc phase of Yb metal the discussed discrepancy would be resolved, since the transport measurements of Refs. 1 and 13 were performed at relatively low temperatures and/or low pressures, where a divalent or almost divalent state can be expected for bcc-Yb metal. So it is still an open question whether bcc Yb is already mixed valent at low temperatures and pressures just above the fcc-bcc phase transition. It should be mentioned that a previous Mössbauer study of Yb metal at 4.2 K indicates a mean valence of $\cong 2.3$ at pressures between 60 and 70 kbar.¹⁸

Finally, we like to give some general comments on the reliability and accuracy of valences derived from L_{III} -edge spectra, i.e., to what extent the double-edge structure represents the initial-state valence mixture. In a variety of L -edge studies of heavy rare-earth systems, where the $4f$ states are well localized, no discrepancies between the observed L -edge structures and the mean valences derived from other measurements (Mössbauer isomer shift, valence-band photoemission,¹⁹ etc.) have been found.^{10,16,20} The white lines observed for the heavy rare-earth metals, in particular, are well described by a single-particle pic-

ture based on transition from $2p$ states into empty $5d$ states.²⁰ The situation is different in deep core-level x-ray photoemission spectroscopy measurements, where the initially unscreened positive core hole has been found to cause both shake-up and shake-down processes in Eu systems completely masking the initial-state valence.²¹ The absence of such final-state satellites in the L_{III} -edge spectra is qualitatively understandable, since in this absorption process the electron is excited into quasibound $5d$ states screening the $2p$ hole with respect to more itinerant valence and conduction electrons. Despite the observed correspondence between L -edge structure and mean valence, the absolute accuracy of the derived \bar{v} values is limited by the employed line-fitting procedure and is estimated as $\Delta\bar{v} = \pm 0.05$ (in addition to statistical inaccuracies). The relative change of \bar{v} , however, (e.g., as a function of pressure) can be derived with far better accuracy from the L -edge spectra. It should be emphasized that the above arguments may not apply to the case of Ce systems, where the $4f$ electrons are less localized.

In summary, we have shown that L -edge x-ray absorption spectroscopy, in combination with conventional ultrahigh pressure techniques, is a widely applicable tool for studying pressure-induced valence transitions in rare-earth systems. A continuous valence transition was found for the bcc phase of Yb metal, while it was shown to be trivalent in its high-pressure hcp phase.

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