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L-edge x-ray absorption spectra of γ- and α-cerium

B. Lengeler
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, Germany

G. Materlik
Hamburger Synchrotronstrahlungslabor am Deutschen Elektronen-Synchrotron, D-2000 Hamburg, Germany

J. E. Müller
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, Germany
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The L absorption spectra of γ- and α-Ce have been measured. The L_2 and L_3 spectra of both systems show white lines, but α-Ce exhibits an additional peak 9 eV above the white line. In a mixed-valence model α-Ce has a ratio $[Ce^{3+}]$ to $[Ce^{4+}]$ of about 0.8 to 0.2. However, this interpretation is in conflict with Compton scattering. The measured extended x-ray–absorption fine-structure (EXAFS) spectra of α-Ce allow only for one value E_0 (zero of photoelectron energy). It is an open question why only one value E_0 is observed in the EXAFS of mixed-valent systems.

Much experimental and theoretical evidence[1] indicates that the isostructural γ-α phase transition in Ce is due to changes in the localized $4f$ states. The first model of the transition was the promotional model which proposes that the occupation of the $4f$ level changes from 1 to 0.3 when Ce collapses into the α phase. Later, it was suggested that α-Ce is mixed valent.[2,3] Johansson has explained the phase transition as a Mott transition in which the $4f$ state changes from localized (γ-Ce) to bandlike (α-Ce) without change in the $4f$ occupation.[1-3] Band-structure calculations which gave almost the same $4f$ occupation in both phases support this picture.[4,5] These results also agree with Compton scattering data[6] which exclude any promotion or valence fluctuation larger than 0.05 electron per atom. The problems in explaining the driving mechanism for the phase transition purely by band-structure calculations have been discussed by Bringer.[7] Up to now it has not been possible to determine unambiguously the position of the $4f$ levels in γ- and α-Ce.[3]

In this paper we report x-ray absorption measurments of the L_1 and $L_{2,3}$ spectra for γ- and α-Ce. These spectra probe the unoccupied p and d projected densities of states, respectively. The $L_{2,3}$ spectra exhibit large peaks at threshold (γ peak) due to large empty $5d$ densities of states. The $L_{2,3}$ spectra of α-Ce exhibit an additional peak (α peak) 9 eV above the γ peak. From a similar double structure found in the L_3 edges of mixed-valent systems relative valences have been deduced by interpreting the spectrum as the superposition of two independent spectra with different binding energies arising from each of the valence configurations.[2]

The measurements were done at the spectrometer ROEMO at Hamburger Synchrotronstrahlungslabor (Deutsches Elektronen-Synchrotron, Hamburg). We have used a Si(111) double-crystal monochromator optimized for small harmonic content[8] with an energy resolution of about 1.5 eV at 6 keV. The experiments were done in transmission at room temperature for γ-Ce and at 77 K for α-Ce. We have used cerium of 99.99% purity supplied by Rare Earths Ltd. Foils 8×20 mm^2 in size and 4.5 μm thick without pinholes were prepared by rolling. Pure γ-Ce samples have been obtained by annealing the foils for 24 h in ultrahigh vacuum at 500 °C. Two of these samples were then transformed into α-phase Ce by compressing them up to 1 GPa at room temperature in a He atmosphere, by subsequently cooling them to 77 K, and by finally releasing the pressure.

The phase purity of α-Ce was checked by measuring the extended x-ray absorption fine strucutre (EXAFS) above the L_3 edge. In order to determine the nearest-neighbor distance in α-Ce we have used the Ce-Ce backscattering amplitudes and phases deduced from the EXAFS of CeH_2 measured at 77 K. Figure 1 shows the EXAFS of α-Ce and the result of the fit for the first-neighbor shell. The lattice parameter for α-Ce deduced from the EXAFS is 4.847 Å, in excellent agreement with the value 4.85 Å from lattice parameter measurements. The fit gives within 0.1 eV the same value for the zero of kinetic energy $E_0=5720$ eV, for α-Ce, and for CeH_2.

Figure 2 shows the measured L_1 and $L_{2,3}$ spectra of γ- and α-Ce. The absorption steps were normalized to one taking the average over the EXAFS. The normalized data $\tilde{\mu}$ are plotted versus $(E-E_0)(a/a_\gamma)^2$, where E_0 is the energy

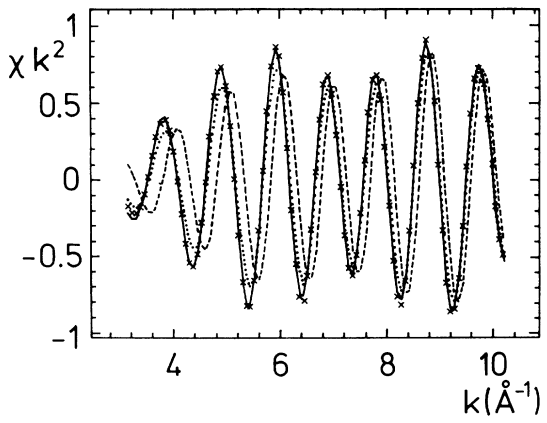

FIG. 1. Nearest-neighbor contribution in the EXAFS above the L_3 edge of α-Ce (crosses). A fit (full line) with backscattering phases and amplitudes from CeH_2 gives a lattice parameter of 4.847 Å for α-Ce compared with a known value of 4.85 Å.[1] A ground-state $4f$ occupation of 0.8 (dotted curve) and of 0.3 (dashed curve) gives the EXAFS in contradiction with the experiment.

of the inflection point on the low-energy flank of the edge. We found that the value of E_0 is the same in γ- ad α-Ce for all three edges. The square of the lattice parameter ratio $(a/a_\gamma)^2$, being one for γ-Ce and 0.883 for α-Ce, has been included in order to correct for the atomic volume dependence of the electron energy.[9] This rescaling aligns the structures in the absorption spectra above the edge. γ- and α-Ce show strong white lines at threshold. This feature is characteristic of all rare-earth metals.[10] The most outstanding difference between the $L_{2,3}$ spectra of γ- and α-Ce is the appearance of another peak 9 eV above the white line in α-Ce. In addition, the white line of α-Ce is smaller by 13% than that of γ-Ce.

If we interpret the shape of the $L_{2,3}$ edges in α-Ce in a mixed-valent picture we deduce a valence ratio $[Ce^{3+}]$ to $[Ce^{4+}]$ of about 0.8 to 0.2, as well as an unusually large broadening of the Ce^{4+} peak which is two times broader than the γ peak.

We notice also that a promotion of 0.20 electron/atom is not reconcilable with Compton scattering measurements on γ- and α-Ce,[6] which assert that no more than 0.05 electron/atom are promoted from the $4f$ level to the conduction band in the ground state.

Figure 3 presents the results of a band-structure calculation of the L_2 spectra of fcc cerium for the two different lattice parameters $a_\gamma = 5.16$ Å and $a_\alpha = 4.85$ Å. In both cases we used the same frozen $4f^1$ configuration. The energy axis has been normalized as in Fig. 2. The effect of the change of the lattice parameter on the spectra is twofold: (i) The energy axis rescales by the factor $(a/a_\gamma)^2$ and (ii) the size of the white line is reduced by 12%. Observe that the single-particle calculation correctly describes the measured near-edge structure of γ-Ce, as well as the γ peak in α-Ce.

It is likely that the two-peak structure in α-Ce is a ground-state effect. The two final states leading to the γ and α peaks are separated in energy by $\Delta = 9$ eV. In order

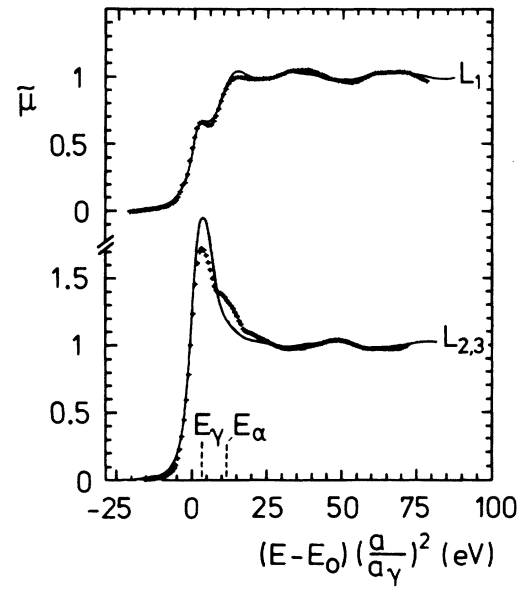

FIG. 2. Absorption coefficients of γ-Ce (full line) and α-Ce (crosses) near the L_1 and $L_{2,3}$ edges. A white line E_γ in $L_{2,3}$ is observed in both phases. α-Ce shows a second peak (E_α) 9 eV above E_γ.

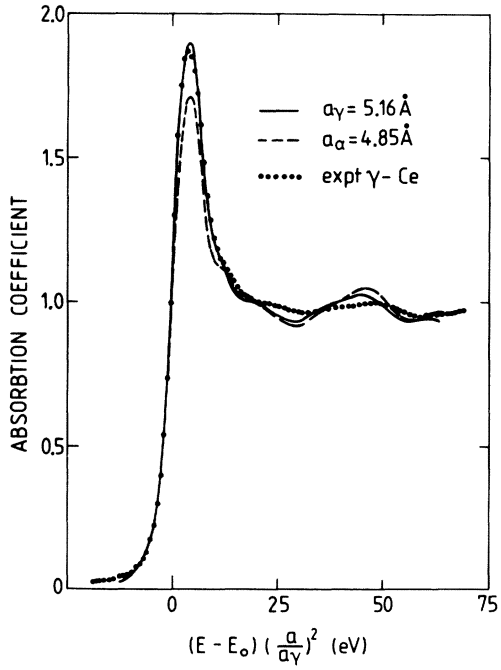

FIG. 3. Calculated near-edge structure for the L_2 spectrum of Ce with $a_\gamma = 5.16$ Å (full line) and $a_\alpha = 4.85$ Å (dashed line) and the experimental γ-Ce data (dots).

to obtain a transfer of 0.2 electrons from $4f$ to $5d$ the hybridization matrix elements V_α should be[11]

$$V_\alpha \geq \sqrt{0.2}\,\Delta \simeq 4 \text{ eV} ,$$

while our calculation indicates that the $4f$-$5d$ hybridization is two orders of magnitude smaller. This is supported by the spectrum measured on *Pd*Ce with 2 at.% Ce which shows an even stronger increase of the α peak.[12]

Although these arguments favor the mixed-valence approach to the two-peak structure in α-Ce, a quantitative interpretation of the sizes of the two peaks as relative valence is by no means straightforward. The reduction and broadening of the white line in our calculation is a consequence of the increased overlap of the $5d$ states in the collapsed phase. In addition, we found that the exact amplitude and width of the white line is very sensitive to the occupation and the degree of localization of the $4f$ states. The EXAFS spectra in Fig. 3 are not correctly reproduced by the band-structure calculation. While the discrepancies in amplitude (due to the neglect of the finite mean free path of the excited electron) are trivial, the discrepancies in the energy placement of the features of the spectrum have been attributed to using a periodic potential.[10]

The L_1 spectra of γ- and α-Ce show only minor differences, and are similar to the L_1 spectra of the heavy rare earths.[10] Due to the absence of sharp features in the unoccupied p states, the two-peak structure would be here much less conspicuous than in the $L_{2,3}$ spectra. The peak at the edge, a hybridization effect of the $5d$ states,[9] is somewhat more pronounced in α-Ce, as a consequence of the broader $5d$ band. On the other hand, the reduction in the amplitude of the second peak of the L_1 spectrum which is correlated with the α peak is not reproduced by the single-particle calculation.

In the mixed-valence model we expect two values E_0 for the kinetic energy of the photoelectrons in the EXAFS of α-Ce. If α-Ce in the ground state has a fraction A of its atoms in a configuration $4f^1$ and a fraction $(1-A)$ in the configuration $4f^0$, the EXAFS should contain two contributions in which the zero of kinetic energy of the photoelectron differs by 9 eV. Figure 1 shows a calculated EXAFS with two values of E_0 (5720.0 and 5729.0 eV) for $A=0.3$ (valence of α-Ce assumed to be 3.7) and $A=0.8$ (mixed valence). It is apparent that the experiment can be fitted best with a unique binding energy which is in favor of a nonpromotional model in Ce. However, it has been claimed that the EXAFS of the mixed-valent systems TmSe and $Sm_{0.75}Y_{0.25}S$ allow also only for one value of E_0.[13-15] Why this is so is still an open question.

In conclusion, we have measured the x-ray absorption of the L edges of γ- and α-Ce. In addition to the white line in $L_{2,3}$, α-Ce shows a second peak 9 eV above the white line. When this double structure in α-Ce is interpreted as due to mixed valence a ratio $[Ce^{3+}]$ to $[Ce^{4+}]$ of about 0.8 to 0.2 is obtained. This interpretation is in conflict with Compton scattering. Furthermore, the reduction of the white line during the phase transition is at least partly due to the increased overlap of the $5d$ states in the collapsed phase. Finally, it is still an open question why in EXAFS spectroscopy mixed-valent systems show only one value E_0 for the zero of kinetic energy of the photoelectrons.

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