DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-82-02
April 1982

DOUBLE EXCITATION STRUCTURE IN THE L-EDGE X-RAY ABSORPTION SPECTRA OF α-CERIUM

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PACS 78.70.Dm, 71.20.tc

ABSTRACT

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. The white line and the EXAFS of α-Ce are correctly described by the single particle picture. We deduce that α-Ce is not valence fluctuating, and that it has the same valence (3^+) as γ-Ce. We suggest that the α-peak arises from a process in which the 2p and the 4f electrons are simultaneously excited into empty 5d states.

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 valence fluctuating [2,3]. Johansson has explained the phase transition as a Mott transition in which the 4f state changes from localized (γ-Ce) to band-like (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 letter we report X-ray absorption measurements of the L_1, L_2 and L_3 spectra for α- and γ-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 many valence fluctuating systems relative valences have been deduced by interpreting it as the superposition of two independent spectra with different binding energy arising from each of the valence configurations[2]. For the case of γ- and α-Ce, however, we show that such an interpretation is not correct, and we suggest that the α-peak arises from an excitation in which both the 2p and the 4f electrons are involved.

The measurements were done at the spectrometer ROEMO at HASYLAB (DESY Hamburg). We have used a Si(111) double crystal monochromator optimized for small harmonic content[8] with an energy resolution of 1.5 eV at 6 keV. The experiments were done in transmission at room temperature for γ-Ce and at 77K for α-Ce. We have used cerium of 99.99% purity supplied by Rare Earths Ltd. Foils 8x20 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 hours 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 77K, and by finally releasing the pressure.

Figure 1 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 $(E-E_o)(a/a_\gamma)^2$, where E_o is the energy of the inflection point on the low energy flank of the edge. Note that the value of E_o turned out to be the same in γ- and 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 alignes 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.

The phase purity of α-Ce was checked by measuring the 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 77K. Figure 2 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 compared to 4.85 Å from lattice parameter measurements. The fit gives within 0.03 eV the same value for the zero of kinetic energy E_o = 5720 eV, for α-Ce and for CeH_2.

Next, we demonstrate that the EXAFS points unambiguously to a single binding energy in α-Ce. Indeed, changing the 4f occupation from 1 to 0 increases the binding energy of a 2p electron by roughly 9 eV[11]. Thus, if α-Ce in the ground state had a fraction A of its atoms in a configuration $4f^1$ and a fraction (1-A) in the configuration $4f^o$, the EXAFS should contain two contributions in which the zero of kinetic energy of the photoelectron differs by 9 eV. This is in contradiction to the experiment. Figure 2 shows calculated EXAFS with two values of E_o (5720.0 eV and 5729.0 eV) for A = 0.3 (valence of α-Ce assumed to be 3.7) and A = 0.8 (if the α-peak is interpreted as arising from valence fluctuations). It is obvious that the experiment can be fitted best with a unique binding energy. Thus we conclude that all the atoms in α-Ce have the same configuration.

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_γ = 5.16 Å and a_α = 4.85 Å. In both cases we used the same frozen $4f^1$ configuration. The energy axis has been normalized as in figure 1. The effect of the change of lattice parameter on the spectra is twofold: (i) the energy axis rescales by the factor $(a_\gamma/a_\alpha)^2$ 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. Thus we conclude that the basic absorption process at energy E_γ is the same in γ-Ce and α-Ce. A fundamental departure from the single particle picture occurs in the energy range between 9 eV and 26 eV above threshold, where an additional broader peak appears in α-Ce.

Figure 4 illustrates a possible mechanism for the α-peak. According to Compton scattering data[6] the 4f level is occupied with one electron both in the γ- and α-Ce ground states. In agreement with the EXAFS results discussed above the 2p core level has the same binding energy in γ- and α-Ce. Channel 1 which is possible in γ- and α-Ce represents a single-particle excitation of a 2p electron into empty d-states. Its contribution to $\tilde{\mu}$ is shown in Fig. 3. Channel 2 represents a process in which the 4f electron is promoted into the 5d band as the 2p electron is excited. This channel is only realized in α-Ce where the 4f state is band like. Channel 2 does not occur in γ-Ce where the 4f state is atomic like and does not mix with the 5d states. The energy to promote a 4f electron to an empty 5d state is Δ = 9 eV.[11] Thus, channel 2 opens at 9 eV above threshold. The 5d band width is B = 8 eV[12]. Therefore channel 2 remains open over an energy interval of $B + \Delta = 17$ eV, as observed. The structures of the L_1 edges show only minor differences. The initial and final states in L_1 and $L_{2,3}$ being different, there is no reason to expect the occurence of similar double excitations in L_1 as in $L_{2,3}$. The L_1 edges of Ce are similar to those of the heavy rare earths[10].

Finally, we notice that we have found no experimental evidence for a $4f^2$ final state configuration in X-ray absorption as claimed by Bianconi et al[13]. In X-ray photoemission, on the other hand, a $4f^2$ final state configuration has been found in Ce compounds[14]. This is not in contradiction to the present result because in our investigation the photoelectron is excited into d states just above the Fermi level in which the electron is able to screen the nucleus much more effectively than in XPS, where the photoelectron has a kinetic energy of 600 eV.

The combination of X-ray absorption and Compton scattering results leads us to the following conclusions: (i) γ- and α-Ce have the same valence in the ground state (3^+). (ii) α-Ce is not valence fluctuating in the ground state nor is the 4f electron promoted fully or partially into a 5d band state. (iii) The X-ray absorption mechanism for γ- and α-Ce differ only in a limited energy range of about 17 eV around E_α. We suggest that here a double excitation occurs in which the 4f electron in the presence of the 2p core hole makes a transition to the 5d band.

ACKNOWLEDMENTS

We would like to thank Dr. A. Bringer and Prof. B. Sonntag for many helpful discussions.

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11. Hartree-Fock calculations for atomic Ce with configurations $4f^1 5d^2 6s$ and $4f^0 5d^3 6s$ show that changing the 4f occupation from 1 to 0 increases the binding energy of a 2p electron by roughly 9 eV.

12. The width of the unoccupied 5d band is 7 eV. Inclusion of a 2p core hole width of 4 eV yields B = 8 eV for the white line width.

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FIGURE CAPTIONS

1. 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.

2. 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 to 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 EXAFS in contradiction with the experiment.

3. Calculated near edge structure of Ce with a_γ = 5.16 Å (full line) and a_α = 4.85 Å (dashed line) and the experimental γ-Ce data (dots).

4. Two channel excitation for the α-peak. In channel 1 absorption occurs by one-electron transitions from a 2p core state into empty d-band states. In channel 2 an extra energy is absorbed to promote the 4f electron into the 5d band.

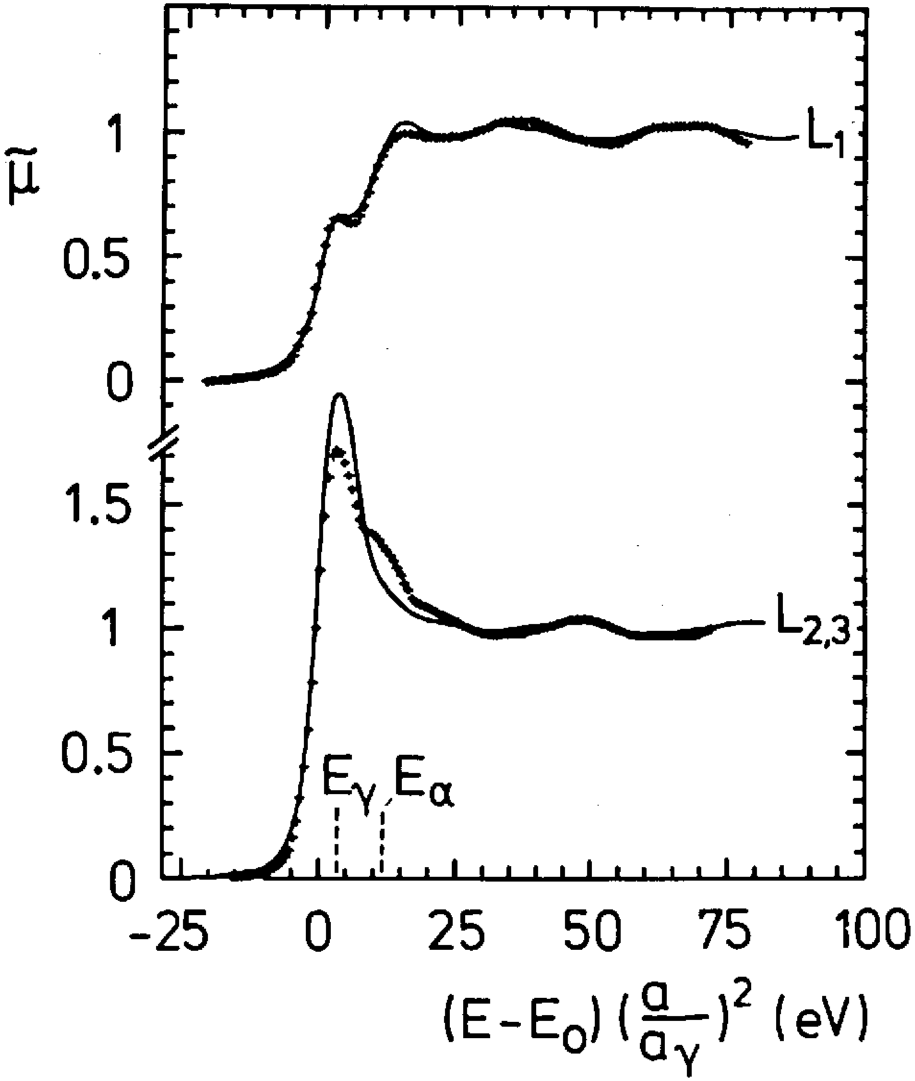


Fig. 1

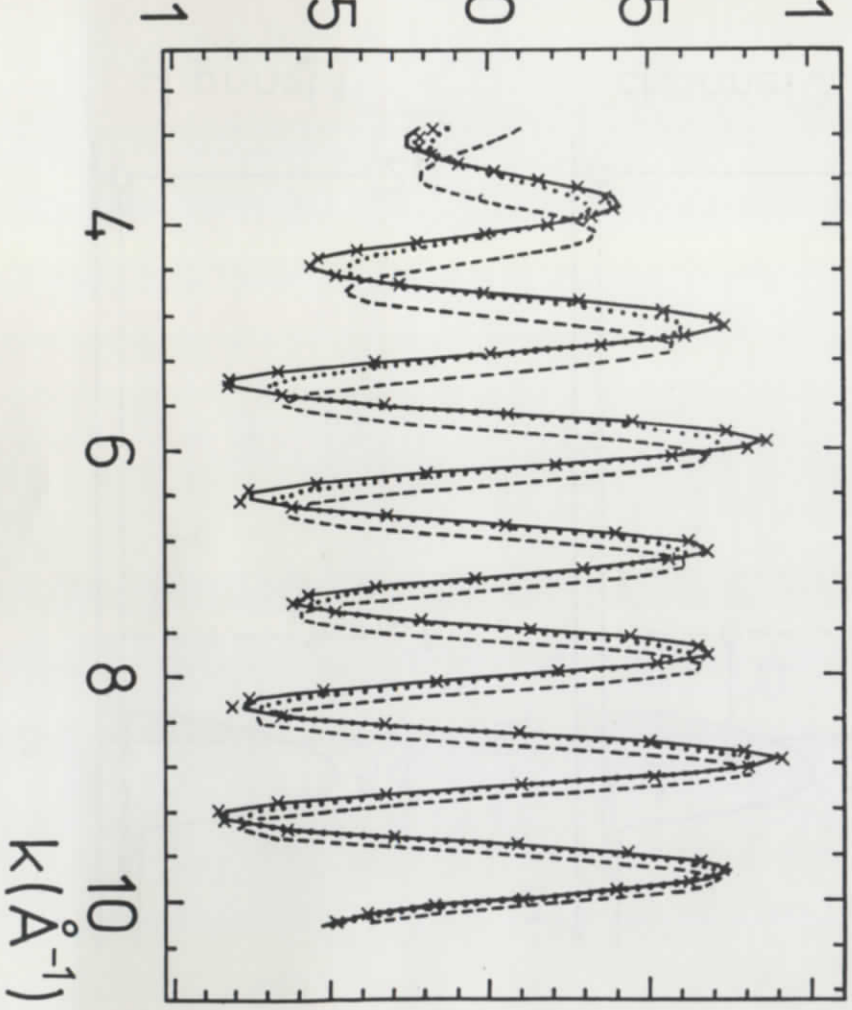
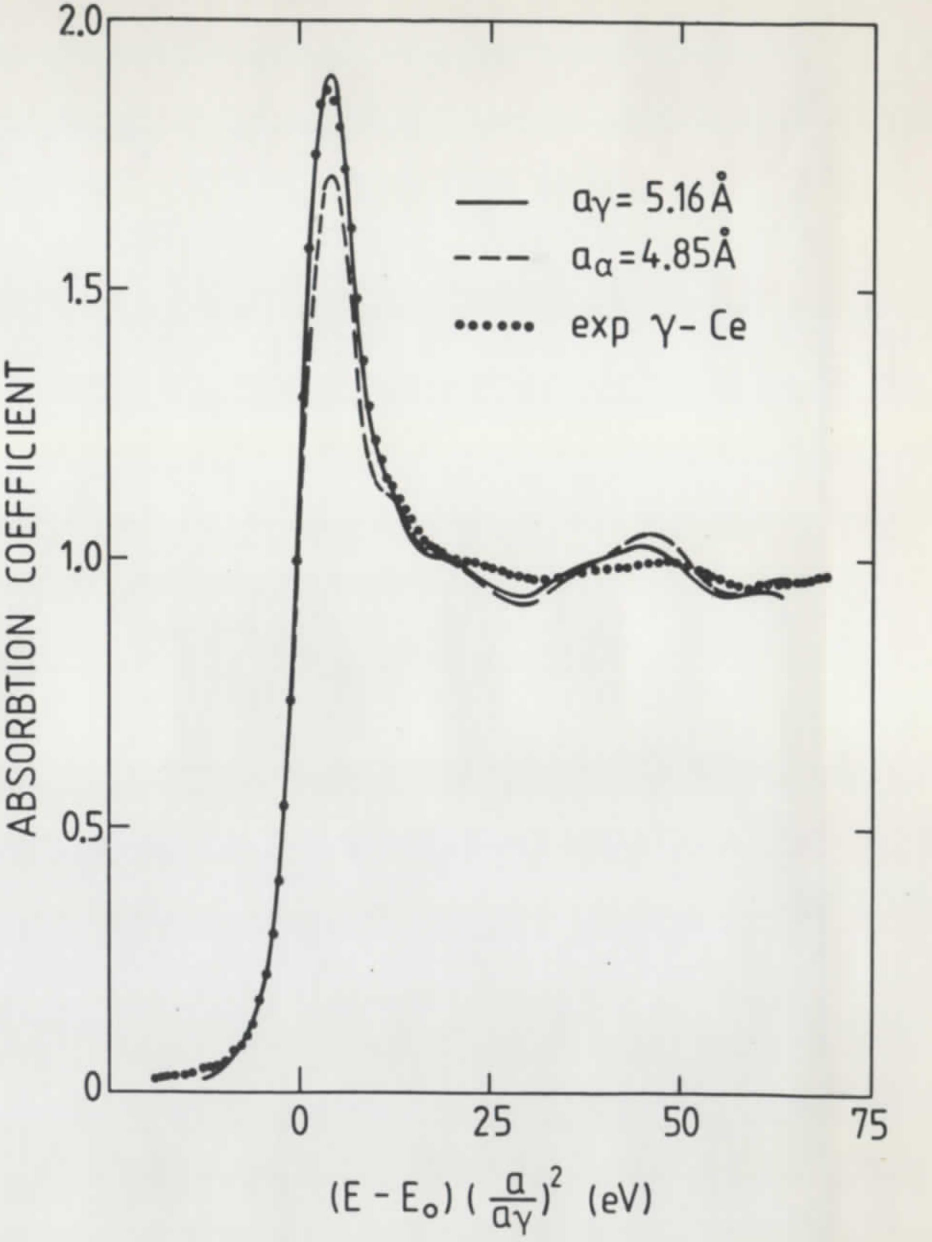

χ·k²
1
0.5
0
-0.5
-1
4
6
8
10
k(Å⁻¹)

Fig. 2


2.0
1.5
1.0
0.5
0
ABSORBTION COEFFICIENT
aγ = 5.16 Å
aα = 4.85 Å
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0
25
50
75
(E - E₀) (a/aγ)² (eV)

Fig. 3

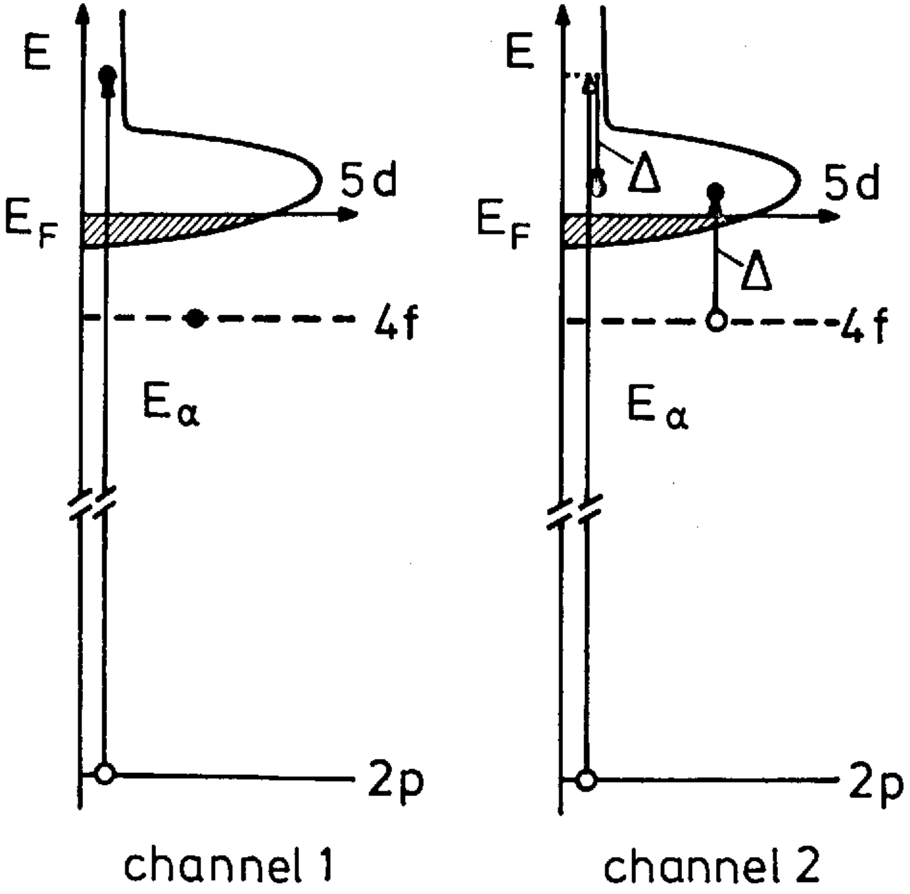
E
5d
E_F
4f
E_α
2p
channel 1
E
Δ
5d
E_F
Δ
4f
E_α
2p
channel 2

Fig. 4