DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-76/14
August 1976

Atomic Character of the 4d-Absorption of Ce metal: An Experimental Proof

by

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Abstract:

The photoabsorption of atomic Ce has been determined in the energy range from 100 eV to 150 eV. Except for very small deviations, the 4d-spectra of atomic and metallic Ce are identical. The resonances near the 4d-threshold are ascribed to $4d^{10}4f \rightarrow 4d^{9}4f^{2}$ transitions.

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The soft x-ray spectra of the rare-earth metals show a discrete line structure at the 4d-threshold followed by a giant resonance ≈10 - 20 eV above.[1-3] Fomichev et al.[2] suggested that the sharp lines at the onset are due to ionic transitions of the type $4d^{10}4f^{n} \rightarrow 4d^{9}4f^{n+1}$. Calculations[4-6] of the $4d^{10}4f^{n} \rightarrow 4d^{9}4f^{n+1}$ transitions for free rare-earth ions, from which the outer 5d and 6s electrons have been removed, support this suggestion. These calculations were able to account for the discrete lines at threshold and for the prominent maximum above. The interaction between the 4f electrons and the 4d vacancy splits the $4d^{9}4f^{n+1}$ configuration and raises some levels by ≈20 eV. Autoionization of the high levels, which comprise most of the oscillator strength, gives rise to the giant, approximately 10 eV wide resonance.

In order to test the validity of this interpretation we investigated the 4d-absorption of atomic Ce by means of synchrotron radiation. Atomic Ce was maintained inside a new resistance heated tubular furnace mounted in front of a 2m grazing incidence Rowland type spectrograph. The temperatures ranged from 1900° C to 2200° C. The length of the vapour column was ≈60 cm. 140 Å thick carbon films separated the vapour region from the high vacuum of the beam pipe and the spectrograph. A He buffer gas prevented the Ce atoms from reaching the windows. The spectra were recorded on photographic plates. The spectrograph was calibrated by means of the known lines of atomic rare gases.[9] The energy resolution at the 4d-threshold was better than 0.09 eV.

The 4d-spectrum of atomic Ce in the energy range from 100 eV to 150 eV is shown in Fig. 1. Because of the uncertainties involved in the determination of the vapour pressure and the lack of data on the concentration of molecules present in the vapour only the relative spectral dependence is presented. The spectrum is dominated by the strong ≈15 eV wide maximum peaking at 124 eV. For comparison the spectrum of metallic Ce[1,3,10] is included in Fig. 1. There is an excellent agreement between the spectra of both phases. Details of the fine structure at the 4d-threshold of atomic and metallic Ce are given in Fig. 2. The agreement between the two spectra is almost perfect. The energies of most of the maxima showing up in the spectra of atomic and metallic Ce agree within the experimental errors (see Table 1). The ground state of Ce is $4d^{10}4f5s^{2}5p^{6}\ 5d6s^{2}\ (^{1}G_{4})$.[11] At the elevated temperatures of our experiment also low excited states of the configurations 4f 5d $6s^{2}$ and 4f $5d^{2}$6s are populated. The excellent agreement between the 4d spectra of solid and atomic Ce demonstrates that the arrangement of the outer 5d and 6s electrons hardly influences the spectra. This finding is confirmed by the results for the Ce-halides.[12] The deviations reported for the Ce-oxide spectra[3] are probably due

to the presence of Ce^{4+} ions. The 5d and 6s radial wavefunctions scarcely overlap with 4d and 4f mainly located inside the closed $5s^2 5p^6$ shell. For the discussion of the main features of the spectra, therefore, it is justified to neglect the outer electrons. Dehmer et al.[4] and Sugar[6] have calculated the multiplet splitting and the relative oscillator strength for the Ce^{3+} $4d^{10}4f \rightarrow 4d^9 4f^2$ transitions. The results of their scaled calculations, included in Fig. 1 and Fig. 2, are in good agreement with the observed spectra. The same holds for the results of our calculations (intermediate coupling) of the multiplet splitting and the relative oscillator strength for the Ce $4d^{10}4f5s^2 5p^6 5d6s^2$ ($^1G_4$) $\rightarrow 4d^9 4f^2 5s^2 5p^6 5d6s^2$ transitions to all J = 3,4,5 final states, which are also shown in Fig. 1 and Fig. 2. The Slater- and spin-orbit parameters have been obtained from Hartree-Fock calculations. A scaling factor of 0.75 has been applied to the F and G parameters. The centre of gravity of the configuration has been shifted to give best agreement with the spectrum of atomic Ce. To facilitate comparison with the experimental data the 461 lines have been convoluted with a Lorentzian of 0.5 eV half width. It is obvious that the $4d^{10}4f \rightarrow 4d^9 4f^2$ transitions determine the main structure of the spectra. For a more detailed analysis correlation effects have to be taken into account.[5,7,8] Our results prove that the rearrangement of the outer electrons when going from the atom to the solid does not cause any considerable modifications.

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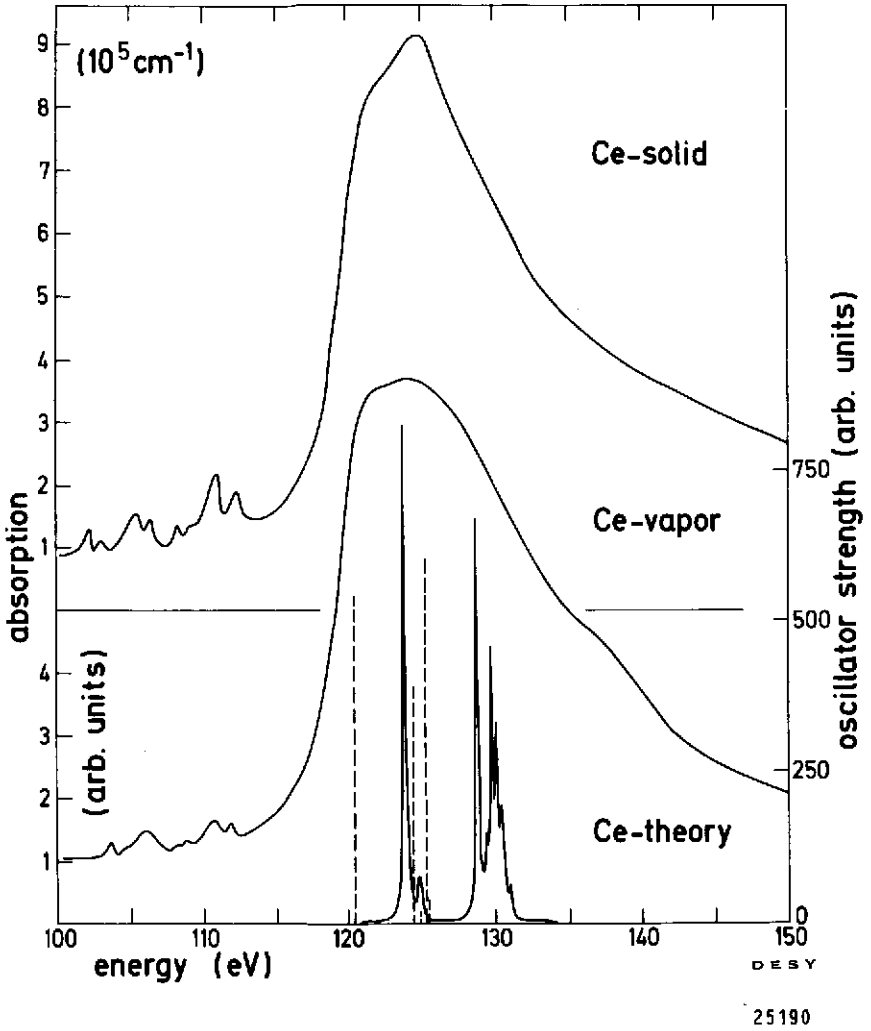
Table 1 Energies (in eV) of the maxima found at the 4d-threshold of atomic and metallic[3] Ce.

	Ce atom		Ce metal
a	101.46 ± 0.1	A	101.25 ± 0.2
b	103.38 ± 0.1	B	103.48 ± 0.1
c	104.34 ± 0.1	C	104.56 ± 0.1
d	105.55 ± 0.1	D	105.77 ± 0.1
e	105.83 ± 0.15	E	106.06 ± 0.1
f	106.38 ± 0.15	F	106.58 ± 0.1
g	107.82 ± 0.15	G	108.06 ± 0.1
h	108.42 ± 0.15		
		H	108.93 ± 0.1
i	109.12 ± 0.25		
		I	109.70 ± 0.15
j	109.97 ± 0.2		
k	110.52 ± 0.15	K	110.36 ± 0.1
l	111.76 ± 0.1	L	111.52 ± 0.1
m	112.95 ± 0.2		

Fig. 1 4d-absorption of atomic and metallic Ce in the energy range from 100 eV to 150 eV. (The zero line for the spectrum of Ce vapour may be shifted by one unit.) The calculated spectra Ce $4d^{10}4f5s^25p^65d6s^2 \rightarrow 4d^94f^75s^25p^65d6s^2$ (solid line) and Ce^{3+} $4d^{10}4f5s^25p^6 \rightarrow 4d^94f^25s^25p^6$ (Ref. 6, dashed line) are included.

Fig. 2 Fine structure at the 4d-threshold of atomic and metallic Ce. The calculated spectra Ce $4d^{10}4f5s^25p^65d6s^2 \rightarrow 4d^94f^25s^26p^65d6s^2$ (solid line) and Ce^{3+} $4d^{10}4f5s^25p^6 \rightarrow 4d^94f^25s^25p^6$ (Ref. 6, multiplied by 0.5, dashed line) are included.


(10^5 cm^-1)
Ce-solid
Ce-vapor
Ce-theory
absorption (arb. units)
oscillator strength (arb. units)
energy (eV)
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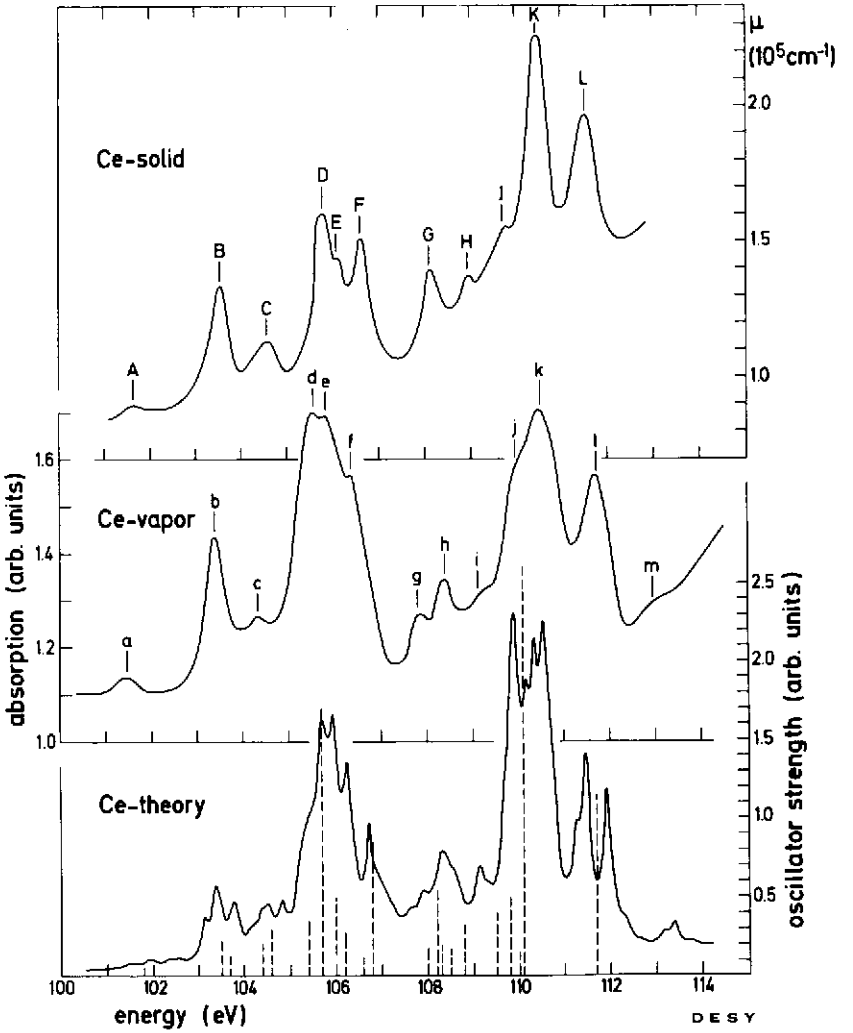
μ (10^5 cm^-1)
Ce-solid
Ce-vapor
Ce-theory
absorption (arb. units)
oscillator strength (arb. units)
energy (eV)
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