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by

G. Materlik

*Hamburger Synchrotronstrahlungslabor HASYLAB at DESY*

B. Sonntag and M. Tausch

*II. Institut für Experimentalphysik, Universität Hamburg*

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G. Materlik

Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches  
Elektronen-Synchrotron DESY, D-2000 Hamburg 52, Germany

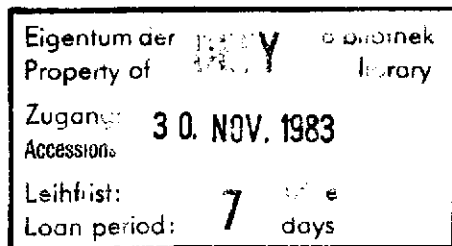
and

B. Sonntag and M. Tausch

II. Institut für Experimentalphysik, Universität Hamburg,  
D-2000 Hamburg 50, Germany

Abstract

The X-ray L absorption spectra were measured for the atomic rare earths Ce, Sm, Gd and Er. From the energy positions of well resolved absorption lines at threshold in comparison to the corresponding solid state spectra the atom-to-metal shifts of the core level binding energies have been determined. For Sm and Er which undergo a valence change on formation of the solid shifts differ by more than 6 eV from those of Ce and Gd which have the same configuration in the atom and the solid.



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Introduction

Shifts of core level binding energies of atoms in different chemical environments reflect changes in valence orbitals and in the valence configuration and differences in the relaxation processes. The fingerprint character of these shifts explains the considerable experimental and theoretical effort devoted to the investigation of this subject<sup>1,2</sup>. Especially the atom-to-metal shifts of the rare earth elements recently have attracted much interest. This interest has been stimulated by the valence fluctuations detected in pure rare earths and rare earth compounds<sup>3,4,5</sup>. One of the major problems encountered in this field is the lack of experimental data on free metal atoms in the X-ray region. There are almost no X-ray absorption, X-ray emission and X-ray photoemission data on free metal atoms, from which core-level binding energies, transition probabilities, core-hole lifetimes and indications of the importance of many electron effects can be obtained. In addition to being important for atomic physics, all these values are necessary for a thorough assessment of the influence of the chemical environment. Oscillations in the differential optical oscillator strength<sup>6</sup> or more important, multiple electron excitations<sup>7</sup> can cause structures in the absorption spectra above inner shell thresholds. These effects have to be considered in the analysis of the X-ray absorption near edge structure (XANES)<sup>8</sup> and the extended X-ray absorption fine structure (EXAFS)<sup>9</sup> of solids.

The high temperatures required for the preparation of free rare earth atoms and their low absorption cross sections render these experiments extremely difficult. Since a lot of basic information can be obtained from absorption spectra, we measured the L-absorption spectra of a representative set of atomic rare earth elements, Ce, Sm, Gd and Er.

The measurements were done at the X-ray spectrometer ROEMO at the Hamburger Synchrotron Radiation Laboratory HASYLAB. We have used a non dispersive Si double crystal monochromator optimized for small harmonic content<sup>10</sup>. To balance high energy resolution and higher order contamination, (111) Bragg reflection was used for Ce and Sm and (220) Bragg reflection for Gd and Er. The atomic metals were maintained inside a resistance heated tubular furnace<sup>11</sup> mounted behind the exit slit of the monochromator. The metal vapours were contained in a Ta tube except for Er where a W tube was used. The temperatures ranged from 1320 K to 2500 K namely  $1320 \pm 50$  K for Sm,  $2020 \pm 50$  K for Er,  $2250 \pm 50$  K for Gd and  $2500 \pm 50$  K for Ce, which according to vapour pressure data<sup>12</sup> correspond to pressures between 2 mbar and 16 mbar. The length of the vapour column was approximately 50 cm. Be windows (400  $\mu$ m thick) separated the vapour region from the surrounding air. A Ne buffer gas (20 mbar to 30 mbar) retarded the escape of the metal atoms from the hot zone of the furnace and prevented them from reaching the Be-windows. Charging the furnace with a sample of ~50 g made possible stable operation for ~4-6 hours. For the exact determination of the atom-to-metal shifts, the spectra of the rare earth metals were recorded simultaneously with the vapour spectra by using three ionisation chambers in a row. The metal sample was placed between the first and the second and the vapour between the second and third chamber. In some cases metal runs were taken immediately before or after each vapour measurement.

#### Experimental results and discussion

The  $L_3$  absorption spectra of atomic and metallic Ce, Sm, Gd and Er are presented in Fig. 1. Since the  $L_2$  spectra are very similar to the  $L_3$  spectra they are not shown. The prominent white lines at the threshold of the atomic  $L_2$  and  $L_3$  absorption are attributed to  $2p_{1/2,3/2} \rightarrow 5d$  transitions. As

demonstrated in Fig. 1 these lines can be very well fitted by a single Lorentzian. Autoionisation, which could cause an asymmetric line shape<sup>13</sup>, does not contribute significantly to the decay of the 2p core hole. The onset of transitions to higher excited states manifests itself on the high energy side in the deviation of the experimental curve from the Lorentzian. A break in the atomic absorption spectrum, which is clearly to be seen ~3 eV above the center of the white line, is most likely due to  $2p \rightarrow 6d$  transitions. On the formation of the solid the white lines are shifted and broadened by the interaction with the neighbouring atoms. Materlik et al.<sup>14</sup> demonstrated that the white line and the near edge structure can be well described by a single-particle band structure calculation. For Ce and Gd which have the same  $4f^n$  configuration (Ce  $4f^1$ , Gd  $4f^7$ ) in the atom and in the solid the centers of the white lines almost coincide (1-2 eV shift). In contrast to this, for Sm and Er, which undergo a change of the  $4f^n$  configuration on solidification (Sm  $4f^6 \rightarrow 4f^5$ ; Er  $4f^{12} \rightarrow 4f^{11}$ ) the peak of the white line is shifted towards higher energies by about 8 eV.

The  $L_1$  spectra of the atomic and metallic samples are given in Fig. 2. The atomic spectra display a clearly discernible line at threshold due to  $2s \rightarrow 6p$  transitions. The strength of this line is comparable to the strength of the  $2s \rightarrow \epsilon p$  continuum transitions. Therefore the line is harder to disentangle from the transitions to higher excited states than the  $2p \rightarrow 5d$  absorption lines discussed above. In the solid the hybridisation of the outer s, p and d symmetric orbitals changes the spectra at threshold completely. The metal spectra show a steep rise at threshold followed by a further increase of the cross section towards the maximum located approximately 20 eV above the onset. The experimental spectrum is well reproduced by one-electron band structure cal-

culations<sup>14</sup>. The shoulder at threshold and the dominant maximum at higher energies reflect the structure of the p-projected density of conduction band states. Again the atoms undergoing a valence change (Sm, Er) on solidification and those which do not (Ce, Gd) are easily distinguished. For Ce and Gd the steep rise at threshold of the metal spectra almost coincides with the rise of the atomic cross section whereas for Sm and Er they are separated by more than 5 eV.

From the area under the Lorentzian lines the ratio of the cross sections  $\sigma(2p_{3/2} \rightarrow 5d) / \sigma(2p_{1/2} \rightarrow 5d)$  has been determined to be  $2.1 \pm 0.1$ . Within the error limits this ratio agrees with the statistical ratio of 2 and indicates only small differences between the respective matrix elements. The cross section  $\sigma(2s \rightarrow 6p)$ , determined in an analogous way is approximately a factor of 6 smaller than  $\sigma(2p_{3/2} \rightarrow 5d)$ .

From the comparison of the experimental and the calculated spectra<sup>14</sup> the metal core level binding energies referred to the Fermi level  $E_{2s,F}^M$ ,  $E_{2p,F}^M$  have been inferred<sup>15</sup>. The positions of the maxima of the atomic absorption lines are used to determine the  $2p \rightarrow 5d$  and  $2s \rightarrow 6p$  excitation energies  $E_{2p \rightarrow 5d}^A$  and  $E_{2s \rightarrow 6p}^A$ . The energy differences

$$\Delta E = E_{ex}^A - E_{cF}^M$$

between the atomic excitation energies  $E_{ex}^A$  and the metal core level binding energies  $E_{cF}^M$  are listed in Table 1. Valence changes on solidification can be well identified with the help of these  $\Delta E$  values. In order to compare our energy shift  $\Delta E$  with the calculated core-level binding energy shifts

$$\delta E = E_c^A - E_{cF}^M = E_{ex}^A + E_c^{*A} - E_{cF}^M$$

we have to correct for the atomic binding energy of a 5d ( $E_{5d}^{*A}$ ) or 6p ( $E_{6p}^{*A}$ ) electron in the presence of a 2p or 2s hole respectively. Since the 2s and 2p ionisation energies cannot be directly read off from the spectra, values for the binding energies  $E_{5d}^{*A}$  were used from atomic relativistic Hartree-Fock calculations<sup>16</sup> to determine  $\delta E_{L_2}$  and  $\delta E_{L_3}$ . For  $\delta E_{L_1}$  no such values were available so that we had recourse to the Z+1 model. Therefore in table 1 approximate values for  $E_{5d}^{*A}$  and  $E_{6p}^{*A}$  are listed also, which have been obtained from tabulated energy levels of the Z+1 atoms<sup>17,18,19</sup>. As seen, values obtained from either method show very good agreement. In this context we want to remind the reader that the interaction of the atomic valence electrons results in a multiplet splitting of 0.5 eV to 1.0 eV<sup>17,18,19</sup> which can modify the tabulated shifts correspondingly.

For each element the differences between the  $\delta E_{L_1}$ ,  $\delta E_{L_2}$  and  $\delta E_{L_3}$  shifts are within the error limits. In view of the discussion above, the atom-to-metal core-level-independent binding energy shifts calculated by Johanssen and Martensson<sup>2</sup> are in good agreement with the experimental values. The values reported from the ab-initio calculation by Herbst<sup>1</sup> also agree reasonably well with our measurements and show, even at these deep core states, only small differences. Both experimental and theoretical values show clearly the strong influence of the atom-to-metal valence change.

#### Acknowledgement

We like to thank Dr. J.F. Herbst for making his calculated atomic binding energies  $E_c^{*A}$  available to us.

References

- 1) J.F. Herbst, Phys. Rev. Lett. 49, 1586 (1983)(and references therein)
- 2) B. Johansson and N. Martensson, Phys. Rev. B21, 4427 (1980)
- 3) H. Launois, M. Rawiso, E. Holland-Moritz, R. Pott and D. Wohlleben, Phys. Rev. Lett. 44, 1271 (1980)
- 4) L.M. Falicov, W. Hanke, M.B. Maple eds. Valence Fluctuations in Solids, North Holland Publ. Co., Amsterdam,(1981)
- 5) P. Wachter and H. Boppert eds. Valence Instabilities, North Holland Publ. Co., Amsterdam, (1982)
- 6) S.T. Manson and M. Inokuti in Inner-Shell and X-Ray Physics of Atoms and Solids eds. D.J. Fabian, H.Kleinpoppen and L.M. Watson, Plenum Press, New York and London, 1981, page 273
- 7) W. Malzfeldt, W. Niemann and P. Rabe, to be published
- 8) see e.g.: M. Belli, A. Scafati, A. Bianconi, S. Mobilio, L. Palladino, A. Reale and E. Burattini, Solid State Comm. 35, 355 (1980)
- 9) see e.g.: G.S. Brown and S. Doniach, in Synchrotron Radiation Research, eds. H. Winick and S. Doniach, Plenum Press, New York and London, 1980,page 353
- 10) G. Materlik and V.O. Kostroun, Rev. Sci. Instr. 51, 86 (1980)
- 11) R. Bruhn, B. Sonntag and H.W. Wolff, J. Phys. B12, 203 (1979)
- 12) W.F. Brunner and T.H. Batzer, Practical Vacuum Techniques, Reinhold Publ. Corp.,New York,(1965)
- 13) A.F. Starace in: Handbuch der Physik Vol. 31,1, ed. W. Mehlhorn, Springer Verlag, Berlin, Heidelberg, New York,(1982)
- 14) G. Materlik, J.F. Müller and J.W. Wilkins, Phys. Rev. Lett. 50, 267 (1983)
- 15) With respect to the inflection point of the experimental spectra, following values were used for  $E_{CF}^K - E_O^m$  given in eV in the sequence  $L_3, L_2, L_1$ :  
Ce: -0,3, -0,3, +0,5; Sm: -0,5, -0,5, +0,6; Gd: -0,4, -0,4, +0,6;  
Er: -0,3, -0,5, +1,6
- 16) J.F. Herbst, private communication
- 17) L. Brewer, J. Optic. Soc. Am. 61, 1101 (1971)
- 18) L. Brewer, J. Optic. Soc. Am. 61, 1666 (1971)
- 19) W.C. Martin, R. Zalubas and L. Hagan, Atomic Energy Levels - The Rare Earth Elements, National Bureau of Standards NSRDS-NBS 60 (1978)

Table 1: Experimental energy separation  $\Delta E_L = E_{ex}^A - E_{CF}^M$  and experimental  $\delta E_L$  and theoretical<sup>1,2</sup>  $\delta E^{calc}$  atom-to-metal core-level binding energy shifts. The atomic 5d and 6p binding energies  $E_{5d}^{*A}$  and  $E_{6p}^{*A}$  are given in the sequence: reference 16 / Z+1 model.  $\delta E_{L_{2,3}}$  and  $\delta E_{L_1}$  were calculated with values from reference 16 and from the Z+1 model respectively.

Note that the tabulated error only includes the uncertainty to determine  $E_{ex}^A$  and  $E_o^m$  from the experimental data.

	Ce	Sm	Gd	Er
$\Delta E_{L_3}$ (eV)	$2.6 \pm 0.3$	$-3.8 \pm 0.3$	$2.8 \pm 0.3$	$-3.7 \pm 0.3$
$E_{5d}^{*A}$ (eV)	7.6 / 7.4	6.3 / 6.7	7.6 / -	5.2 / 5.7
$\delta E_{L_3}$ (eV)	$10.2 \pm 0.3$	$2.5 \pm 0.3$	$10.4 \pm 0.5$	$1.5 \pm 0.3$
$\Delta E_{L_2}$ (eV)	$2.6 \pm 0.3$	$-3.9 \pm 0.3$	$2.9 \pm 0.3$	$-3.4 \pm 0.3$
$E_{5d}^{*A}$ (eV)	7.6 / 7.4	6.3 / 6.7	7.6 / -	5.2 / 5.7
$\delta E_{L_2}$ (eV)	$10.2 \pm 0.3$	$2.4 \pm 0.3$	$10.5 \pm 0.3$	$1.8 \pm 0.3$
$\Delta E_{L_1}$ (eV)	$5.3 \pm 0.6$	$-2.5 \pm 0.5$	$4.7 \pm 0.4$	$-3.6 \pm 0.7$
$E_{6p}^{*A}$ (eV)	- / -	- / 5.0	- / -	- / 4.9
$\delta E_{L_1}$ (eV)	---	$2.5 \pm 0.5$	---	$1.3 \pm 0.7$
$\delta E_{ref.1}^{calc}$ (eV)	9.3	0.4	8.4	0
$\delta E_{ref.2}^{calc}$ (eV)	9.7	1.8	9.1	1.5

### Figure Captions

Fig. 1

$L_3$  absorption spectra of atomic (dotted line) and metallic (solid line) Ce, Sm, Gd and Er. A background, determined by extrapolating the absorption spectrum below the 2p threshold towards higher energies by a straight line, has been subtracted. The positions of the Fermi levels  $E_F^M$ , the atomic 5d excitation energies  $E^A$  and the ionisation energies  $E_{5d}^{*A}$  are indicated. The dashed line gives a Lorentzian absorption profile. The edge heights are normalized. The inflection point  $E_o^m$  of the absorption edge of the solid state spectrum is chosen as origin of the energy scale.

Fig. 2

$L_1$  absorption spectra of atomic (dotted line) and metallic (solid line) Ce, Sm, Gd and Er. A background, determined by extrapolating the absorption spectrum below the 2s threshold towards higher energies by a straight line, has been subtracted. The positions of the Fermi levels  $E_F^M$ , the atomic 6p excitation energies  $E^A$  and the ionisation energies  $E_{6p}^{*A}$  are indicated. The edge heights are normalized. The inflection point  $E_o^m$  of the absorption edge of the solid state spectrum is chosen as origin of the energy scale.

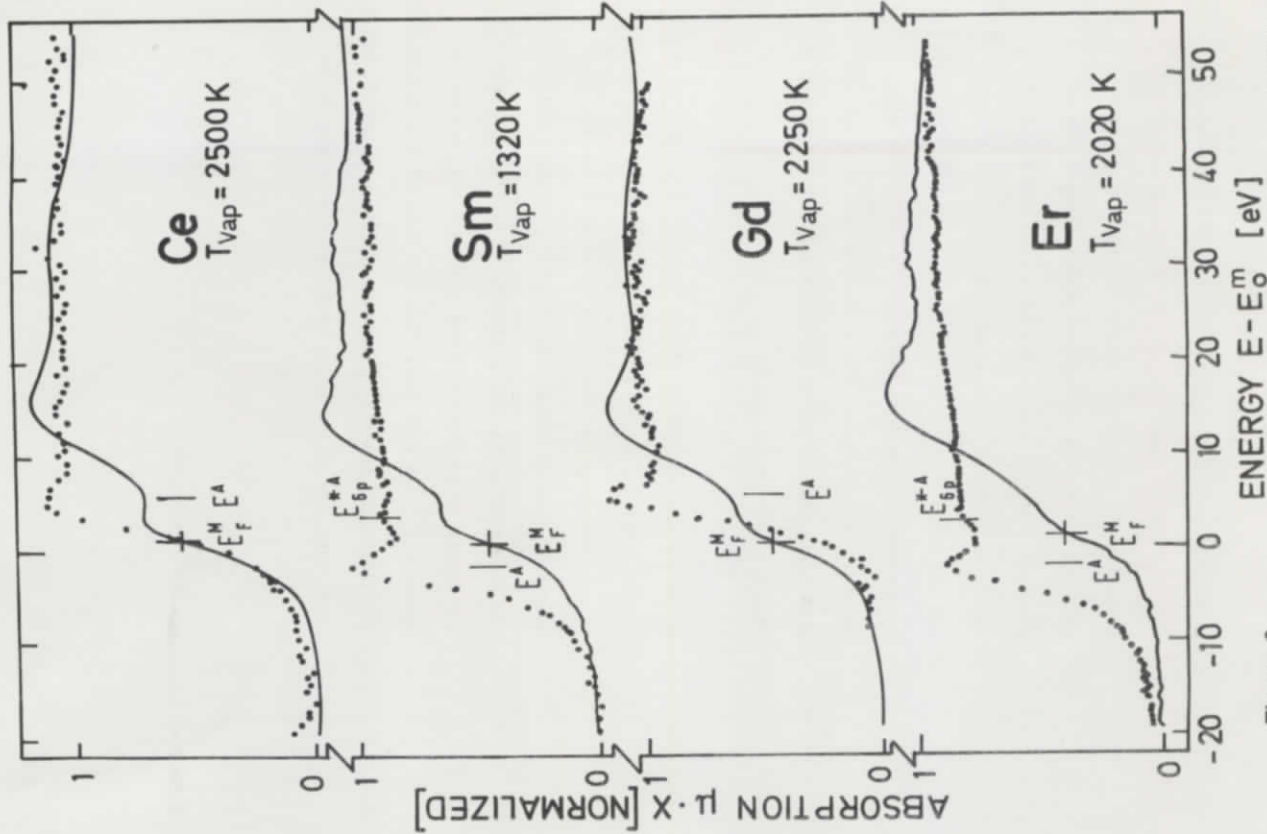


Figure 2

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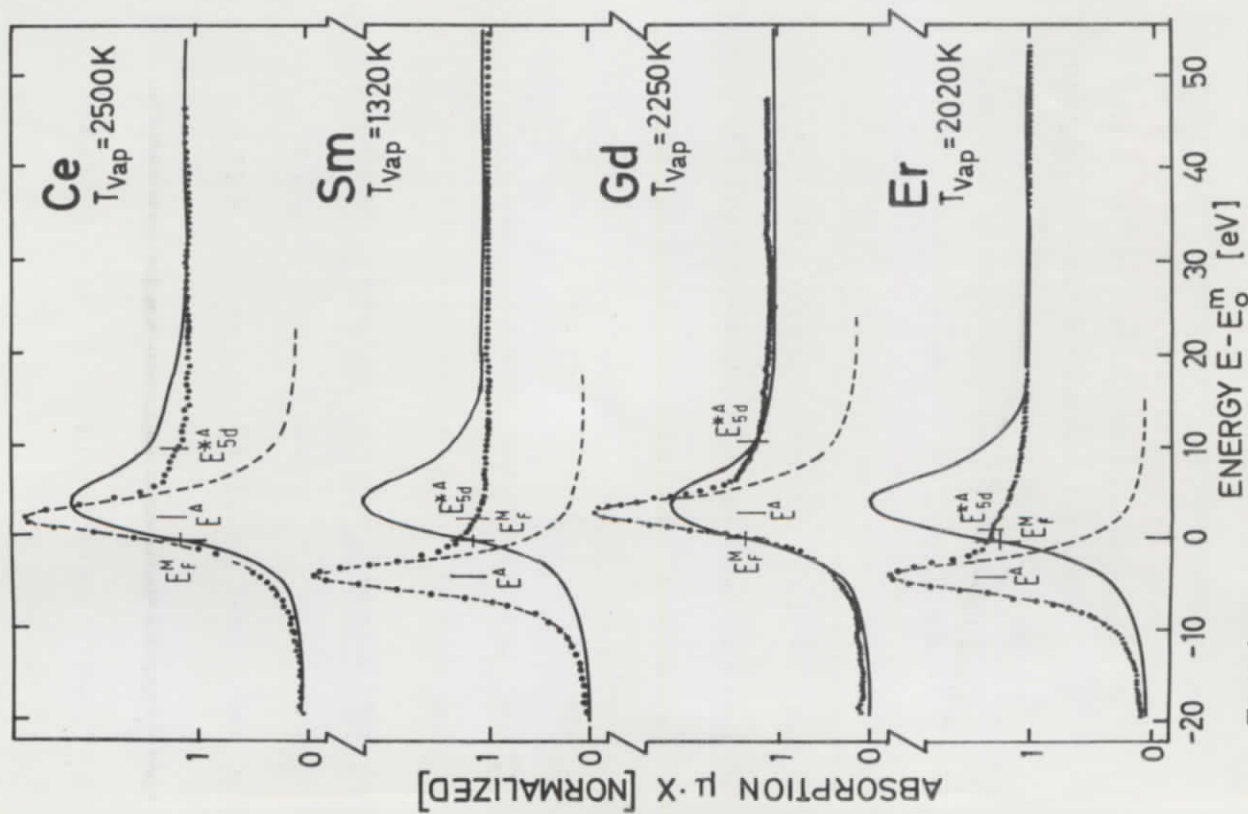


Figure 1

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