Experimental Atom-To-Solid *L*-Level Shifts for Ce, Sm, Gd, and Er

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The x-ray *L* absorption spectra were measured for the atomic rare-earth elements 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 the 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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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.^{1,2} 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-earth elements and rare-earth compounds.³⁻⁵ 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 strength⁶ or, more important, multiple-electron excitations⁷ 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)⁸ and the extended x-ray-absorption fine structure (EXAFS)⁹ 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 nondispersive Si double-crystal monochromator optimized for small harmonic content.¹⁰ 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 furnace¹¹ mounted behind the exit slit of the monochromator. The metal vapors were contained in a Ta tube except for Er where a W tube was used. The temperatures ranged from 1320 to 2500 K, namely, 1320 ± 50 K for Sm, 2020 ± 50 K for Er, 2250 ± 50 K for Gd, and 2500 ± 50 K for Ce, which according to vapor-pressure data¹² correspond to pressures between 2 and 16 mbar. The length of the vapor column was approximately 50 cm. Be windows (400 μ m thick) separated the vapor region from the surrounding air. A Ne buffer gas (20 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 h. For the exact determination of the atom-to-metal shifts, the spectra of the rare-earth metals were recorded simultaneously with the vapor spectra by use of three ionization chambers in a row. The metal sample was placed between the first and the second and the vapor between the second and third chambers. In some cases metal runs were taken immediately before or after each

vapor measurement.

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. Autoionization, which could cause an asymmetric line shape,¹³ does not contribute significantly to the decay of the $2p$ core hole. The onset of transitions to higher excited states manifests itself

FIG. 1. L_3 absorption spectra of atomic (dotted lines) and metallic (solid lines) 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 ionization energies E_{5d}^{*A} are indicated. The dashed line gives a Lorentzian absorption profile. The edge heights are normalized. The inflection point E_0^m of the absorption edge of the solid-state spectrum is chosen as the origin of the energy scale.

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 neighboring atoms. Materlik, Müller, and Wilkins¹⁴ 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 hybridization 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 calculations.¹⁴ 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 ± 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

FIG. 2. L_1 absorption spectra of atomic (dotted lines) and metallic (solid lines) 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 ionization energies E_{6p}^{*A} are indicated. The edge heights are normalized. The inflection point E_0^m of the absorption edge of the solid-state spectrum is chosen as the origin of the energy scale.

smaller than $\sigma(2p_{3/2} - 5d)$.

From the comparison of the experimental and the calculated spectra¹⁴ the metal core-level binding energies referred to the Fermi level $E_{2s,F}^M$, $E_{2p,F}^M$ have been inferred.¹⁵ 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

TABLE I. Experimental energy separation $\Delta E_L = E_{ex}^A - E_{cF}^M$ and experimental δE_L and theoretical (Refs. 1 and 2) δE^{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 following sequence: (Ref. 16 value)/($Z+1$ model value). $\delta E_{L2,3}$ and δE_{L1} were calculated with values from Ref. 16 and from the $Z+1$ model, respectively. Note that the tabulated error only includes the uncertainty to determine E_{ex}^A and E_0^m from the experimental data. All energies are in electronvolts.

	Ce	Sm	Gd	Er
ΔE_{L3}	2.6 ± 0.3	-3.8 ± 0.3	2.8 ± 0.3	-3.7 ± 0.3
E_{5d}^{*A}	7.6 / 7.4	6.3 / 6.7	7.6 / ...	5.2 / 5.7
δE_{L3}	10.2 ± 0.3	2.5 ± 0.3	10.4 ± 0.5	1.5 ± 0.3
ΔE_{L2}	2.6 ± 0.3	-3.9 ± 0.3	2.9 ± 0.3	-3.4 ± 0.3
E_{5d}^{*A}	7.6 / 7.4	6.3 / 6.7	7.6 / ...	5.2 / 5.7
δE_{L2}	10.2 ± 0.3	2.4 ± 0.3	10.5 ± 0.3	1.8 ± 0.3
ΔE_{L1}	5.3 ± 0.6	-2.5 ± 0.5	4.7 ± 0.4	-3.6 ± 0.7
E_{6p}^{*A}	... / ...	... / 5.0	... / ...	... / 4.9
δE_{L1}	...	2.5 ± 0.5	...	1.3 ± 0.7
$\delta E^{calc a}$	9.3	0.4	8.4	0
$\delta E^{calc b}$	9.7	1.8	9.1	1.5

^aRef. 1.

^bRef. 2.

listed in Table I. Valence changes on solidification can be well identified with the help of these ΔE values. In order to compare our energy shift ΔE 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 $2p$ ionization energies cannot be directly read off from the spectra, values for the binding energies E_{5d}^{*A} were used from atomic relativistic Hartree-Fock calculations¹⁶ to determine δE_{L2} and δE_{L3} . For δE_{L1} no such values were available so that we had recourse to the $Z+1$ model. Therefore in Table I 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.¹⁷⁻¹⁹ 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 to 1.0 eV,¹⁷⁻¹⁹ which can modify the tabulated shifts correspondingly.

For each element the differences between the δE_{L1} , δE_{L2} , and δE_{L3} shifts are within the error

limits. In view of the discussion above, the atom-to-metal core-level-independent binding-energy shifts calculated by Johansson and Martensson² are in good agreement with the experimental values. The values reported from the *ab initio* calculation by Herbst¹ 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.

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