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

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(Received 18 July 1983)

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.

PACS numbers: 78.70.Dm, 32.30.Hj, 71.50.+t

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. 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. 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 or, more important, multiple-electron excitations 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) and the extended x-ray-absorption fine structure (EXAFS) 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. 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 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 data correspond to pressures between 2 and 16 mbar. The length of the vapor column was approximately 50 cm. Be windows (400 μm 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 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 \( \sim 3 \) 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 Wilkins\(^{14} \) 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 \( 4f^{11} \), Gd \( 4f^{13} \)) in the atom and in the solid the centers of the white lines almost coincide (1\( \rightarrow 2 \)-eV shift). In contrast to this, for Sm and Er, which undergo a change of the \( 4f^n \) configuration on solidification (Sm \( 4f^6 \rightarrow 4f^{12} \); 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 \( 2s \rightarrow 6p \) 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 \( d \) absorption lines discussed above. In the solid the hybridization of the outer \( s, p, \) and \( d \) absorption lines discussed above. In the solid the hybridization of the outer \( s, p, \) and \( d \) absorption lines discussed above.

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 \( E_{F}^{\text{B}} \), the atomic \( 5d \) excitation energies \( E_{5d}^{\text{A}} \), and the ionization energies \( E_{1d}^{\text{A}} \) are indicated. The dashed line gives a Lorentzian absorption profile. The edge heights are normalized. The inflection point \( E_0^{\text{m}} \) of the absorption edge of the solid-state spectrum is chosen as the origin of the energy scale.

The area under the Lorentzian lines is proportional to the ratio of the cross sections \( c(2p_{3/2} \rightarrow 5d)/c(2p_{1/2} \rightarrow 5d) \) 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 \( c(2s \rightarrow 6p) \), determined in an analogous way, is approximately a factor of 6
smaller than $\alpha(2p_{3/2} - 5d)$.

From the comparison of the experimental and the calculated spectra, we have inferred, in the solid state, the metal core-level binding energies referred to the Fermi level $E_{2s, f}^M$, $E_{2p, f}^M$ have been inferred, in the solid state. The positions of the Fermi levels $E_F^M$, the atomic $6p$ excitation energies $E_{6p}^M$, and the ionization energies $E_{6p}^{*\,M}$ 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.

The energy differences

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

between the atomic excitation energies $E_{ex}^M$ and the metal core-level binding energies $E_{cM}^M$ are

listed in Table I. 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

$$\delta E = E_{cA} - E_{cM} = E_{cA} + E_{6p}^{*A} - E_{cM}$$

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 calculations to determine $\Delta E_{L_{23}}$. For $\Delta E_{L_1}$, 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. 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, 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

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta E_{L_3}$</th>
<th>$\Delta E_{L_2}$</th>
<th>$\Delta E_{L_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>2.6 ± 0.3</td>
<td>2.8 ± 0.3</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>Sm</td>
<td>10.2 ± 0.3</td>
<td>10.4 ± 0.5</td>
<td>1.5 ± 0.3</td>
</tr>
<tr>
<td>Gd</td>
<td>5.3 ± 0.6</td>
<td>4.7 ± 0.4</td>
<td>3.6 ± 0.7</td>
</tr>
<tr>
<td>Er</td>
<td>9.7</td>
<td>9.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>$\delta E_{6p}^{cal A}$</th>
<th>$\delta E_{6p}^{cal B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>9.3</td>
<td>0</td>
</tr>
<tr>
<td>Sm</td>
<td>0.4</td>
<td>8.4</td>
</tr>
<tr>
<td>Gd</td>
<td>9.7</td>
<td>9.1</td>
</tr>
<tr>
<td>Er</td>
<td>1.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$Ref. 1. $^b$Ref. 2.
limits. In view of the discussion above, the atom-
to-metal core-level-independent binding-energy
shifts calculated by Johansson and Martensson are
in good agreement with the experimental val-
ues. The values reported from the ab initio cal-
culation by Herbst also agree reasonably well
with our measurements and show, even at these
depth core states, only small differences. Both
experimental and theoretical values show clearly
the strong influence of the atom-to-metal valence
change.

We would like to thank Dr. J. F. Herbst for
making his calculated atomic binding energies $E_c$ available to us.

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mental spectra, the following values were used for $E_c$ given in electronvolts 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.
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