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June 1974

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MULTIPLET SPLITTING OF THE 4s and 5s CORE LEVELS IN THE RARE EARTH METALS

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June 1974

The multiplet splittings of the 4s and 5s levels in the rare earth metal series La through Lu are reported and discussed.

Since the first observation of multiplet splitting of core levels in X-ray Photoemission (XPS) spectra of solids by Fadley, et. al [1,2] many interesting applications have been made [3-7] and a deeper understanding of this phenomenon has developed [8-11]. In this Letter, we report the observation of multiplet splitting of the 4s and 5s core levels in the rare earth metal series La through Lu.

The samples were prepared by in situ evaporation under ultra high vacuum conditions (< 9 x 10^-9 torr.) and high resolution spectra were obtained with a Hewlett-Packard 5950A electron spectrometer with an analyzer vacuum of 3 x 10^-10 torr or better. A fuller description of the experimental details will be given elsewhere:

Our measured 4s and 5s splitting of the metals are given in Table 1 and compared with earlier work on several trifluorides [5]. The values for the splittings were obtained by least-squares fitting of Lorenztian or Gaussian functions to the spectra. The good agreement of the metal results with those of the trivalent ions is not surprising, since it has been shown

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† IBM fellow.
earlier that the XPS spectra of the 4f region of the metals compare well with optical data of the trivalent ions and with XPS results on the trifluorides [12].

The simplest estimate of the splitting $\Delta E(ns)$ is obtained by invoking Van Vleck's theorem [13] which yields

$$\Delta E_{\text{VV}}(\text{ns}) = \frac{(2S+1)}{7} G^3(\text{ns},4f)$$

where $S$ is the initial-state spin. These results are given in Table 1 and plotted in Fig. 1 along with the experimental results. The use of Mann's [14] atomic Slater integrals, $G^3$, is justified because the 4f states are essentially core-like. Equation 1 reproduces $\Delta E(5s)$ quite well; however, it systematically predicts a value that is 80% too high for $\Delta E(4s)$. This result is analogous to that in the 3d metal ion series, where it has been theoretically shown [10] and experimentally verified [8] that intra-shell correlations are extremely important, while inter-shell correlations are much smaller because elections in different principal shells are already spatially correlated. The reason for the overestimate of $\Delta E(4s)$ by Van Vleck's theorem is quite simple. In the high-spin final state, the 4s and 4f elections are spatially separated by the antisymmetry requirements of the Pauli Principle. Thus inclusion of correlation will lower the energy of the low-spin final state more than of the high-spin final state, reducing the splitting. To obtain an accurate theoretical value for $\Delta E(4s)$, it would be necessary to do a configuration interaction calculation on the final state as was done for the transition metal ions [10].
Figure 1 confirms the divalent character of metallic Eu and Yb cores, and demonstrates that at room temperature Ce is trivalent rather than tetravalent.
References

Table 1
Experimental and Calculated 4s and 5s Splittings (ev) of the Rare Earth Metals and Trifluorides.

<table>
<thead>
<tr>
<th>2S+1</th>
<th>ΔE(4s)(^a)</th>
<th>ΔE(4s)(^b)</th>
<th>ΔE(_{vv})(4s)(^c)</th>
<th>Full</th>
<th>X0.55</th>
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<tr>
<td>2</td>
<td>1.4(3)</td>
<td>--</td>
<td>2.85</td>
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<tr>
<td>3</td>
<td>2.0(3)</td>
<td>--</td>
<td>4.14</td>
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<td>1.2</td>
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<tr>
<td>4</td>
<td>2.7(3)</td>
<td>--</td>
<td>5.78</td>
<td>1.6(2)</td>
<td>1.7</td>
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<tr>
<td>5</td>
<td>--</td>
<td>--</td>
<td>7.52</td>
<td>--</td>
<td>2.38</td>
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<tr>
<td>6</td>
<td>5.4(3)</td>
<td>--</td>
<td>9.35</td>
<td>2.9(2)</td>
<td>2.8</td>
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<tr>
<td>8,7</td>
<td>7.4(3)</td>
<td>--</td>
<td>12.88,11.27</td>
<td>7.03,6.15</td>
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<tr>
<td>8</td>
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<td>8.2</td>
<td>13.91</td>
<td>7.59</td>
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<tr>
<td>7</td>
<td>d</td>
<td>7.5</td>
<td>12.17</td>
<td>6.64</td>
<td>3.2(3)</td>
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<tr>
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<td>5.74</td>
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<tr>
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<td>4.01</td>
<td>d</td>
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<tr>
<td>3</td>
<td>d</td>
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<td>5.51</td>
<td>3.01</td>
<td>d</td>
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<tr>
<td>1,2</td>
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<td>--</td>
<td>0.0,3.84,0.0,2.10</td>
<td>0.0(1)</td>
<td>--</td>
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<td>--</td>
<td>0.0(2)</td>
<td>--</td>
<td>0.00</td>
<td>0.00</td>
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</table>

\(^a\)This work. \(^b\)Reference 5. \(^c\)Equation 1. \(^d\)These values could not be obtained due to intense Auger transistions in the energy region of interest.
Figure Caption

Fig. 1. Comparison of the experimental values of the 4s and 5s multiplet splitting with the Van Vleck theorem values (Eq. 1). Filled circles are for the metals (this work), while open circles are trifluoride values (Ref. 5).
Fig. 1
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