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June 1973

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X-RAY PHOTOEMISSION STUDY OF Gd, Tb, AND Dy 4f AND VALENCE BANDS*

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June 1973

High-resolution XPS spectra of 4f electrons further support trivalent ion-core assignments for Gd, Tb, and Dy. Fermi edges were observed in all three metals, but the valence-band spectra are surprisingly different.

High-resolution 4f-shell and valence-band spectra of metallic Gd, Tb, and Dy have been observed under ultrahigh vacuum conditions (8 x 10^{-11} Torr). Detailed structure in the 4f-shell final states identifies the transitions as (4f^7 \rightarrow 4f^6) in Gd, (4f^8 \rightarrow 4f^7) in Tb, and (4f^9 \rightarrow 4f^8) in Dy, thereby further confirming the tripositive character of the ion cores in rare-earth metals. However, large differences were observed in the valence-band spectra of these three metals, in contrast to the very similar initial-state densities obtained from APW calculations. In the Gd valence-band spectrum a peak appears near the Fermi energy E_F, while both Tb and Dy show free-electron-like plateaus.

Samples were prepared by in-situ evaporation in the preparation chamber of a Hewlett-Packard 5950A ESCA Spectrometer that had been modified for ultrahigh vacuum operation. The pressure rose momentarily as high as 9 x 10^{-9} Torr during evaporation, but it returned immediately to 8 x 10^{-11} Torr.

* Work performed under the auspices of the U. S. Atomic Energy Commission.
the operating pressure. **In-situ** monitoring of the oxygen ls region revealed a fractional monolayer of adsorbed oxygen as the only detectable contaminant on Gd and Dy. No oxygen ls signal was detected on the Tb sample.

Valence-band and 4f spectra are shown in Fig. 1. The use of monochromatized Al Kα₁,₂ x-rays permitted direct observation of the Fermi edge and resolution of valence-band and 4f structural features not observed in previous XPS studies of rare-earth metals² and trifluorides.³ The results of Hagström and co-workers² on these metals were completely confirmed. The overall shapes and energy spacings of the 4f peaks agreed well with the trifluoride results of Wertheim, *et al.*,³ which were used diagnostically in conjunction with optical data.⁴

Table I lists the binding energies of major features in the spectra and final-state assignments for the 4f peaks. The relative positions of the component 4f peaks in each spectrum agree well with optical levels, which have been assigned up to 40,000 cm⁻¹ (5 eV). The peaks are spaced slightly more widely in the XPS spectra, as expected, because the ionic charge in the \( Z^{1+} (4f^{N}) \) final state is one greater than for the comparison optical ion \( (Z = 1)^{3+} (4f^{N}) \). Herbst, Lowy, and Watson⁵ have thoroughly discussed the absolute binding energies of 4f electrons in rare-earth metals. Our 4f binding energies agree well with their calculated values. The 4f binding energies agree well for Tb but there is a discrepancy of about 0.8 eV for Gd and Dy with earlier experimental work.² This is probably due to the fact that we could determine the Fermi level directly. We have also independently estimated a relaxation energy⁶ of 7 - 10 eV for 4f photoemission from rare-earth metals, in good agreement with their quantity \( (Δ - ε_{4f}) \). It should be emphasized that the 4f structure that appears practically in the valence bands in the spectra in Fig. 1 isn't really there in the initial-state density, where the 4f shell would be a single peak.
\( \sim 10 \text{ eV} \) further below \( E_F \). The \( 4f \) hole states are "intruders" that invade the valence-band region on photoemission via a larger relaxation energy.

The \( 4f \) structure is most conveniently interpreted in terms of exchange splitting, as discussed by Wertheim, et al. \(^3\) Thus in Gd the initial state is \( 4f^7(6s) \), with all seven \( 4f \) spins parallel. The final state can only be \( 7F \), which is the lowest term in \( \text{Eu}^{3+}(4f^6) \), and indeed only one narrow peak is observed, at \( E_B = 8.62 \text{ eV} \). The width of this peak (1.25 eV FWHM) must arise in part from splitting of the \( 7F \) term into the seven levels \( 7F_J \), with \( 0 \leq J \leq 7 \) (in the optical spectrum of \( \text{Eu}^{3+} \) these levels are distributed over about 0.6 eV).

The valence-band spectrum of Gd shows a well-resolved peak of \( \sim 1.5 \text{ eV} \) FWHM after a (rather uncertain) correction for inelastic scattering. This peak has its maximum within 0.5 eV of \( E_F \) and is in good agreement both with APW theory\(^1\) and with Eastman's UPS results.\(^7\) This high density of states at \( E_F \) in Gd is important in explaining both the large saturation magnetization and the electronic heat capacity.\(^1\)

The Tb \( 4f \) sextet structure (or majority-spin structure, in the terminology of Wertheim, et al.\(^3\)) shows the distinct peaks and a shoulder. Probably the peak at 7.8 eV is the analog of the \( 6F, 6I, \) and \( 6D \) terms between 32,000 and 41,000 cm\(^{-1}\) in the optical spectrum of \( \text{Gd}^{3+} \) (Ref. 4). The other peak and shoulder must arise from higher, as yet unassigned, levels.

The valence-band XPS spectrum of Tb does not show a definite maximum near \( E_F \), but instead is completely flat for at least 1 eV. The valence-band XPS spectrum of Dy is flat for 3 eV below \( E_F \), in striking contrast to the APW valence-band density of states. It is even clearer in Dy than in Tb that there is no peak in the spectrum near \( E_F \), because the interfering \( 4f \) minority-spin peak is farther below \( E_F \).
The Dy $^4f$ spectrum shows a strong resemblance to the optical spectrum of Tb$^{3+}(4f^8)$. There is a well-resolved minority-spin peak (the $^7F$ term) at $E_F - 4.5$ eV, and a majority-spin (quintet) structure of at least three peaks, the first lies $3.7$ eV from the $^7F$-term peak, in good agreement with the $\sim 26,000$ cm$^{-1}$ (3.2 eV) gap in the Tb$^{3+}$ optical levels between the mean energy of the $^7F$ term and a group of levels near $28,000$ cm$^{-1}$ of $^5D$ and $^5L$ character. Additional optical levels in the $33,000 - 36,000$ cm$^{-1}$ region in Tb$^{3+}$ are probably responsible for at least part of the other major component of the quintet peak. A third, smaller component presumably corresponds to as-yet-unassigned optical levels.

In summary, the rare-earth metals Gd, Tb, and Dy are clearly shown to have tripositive $4f^7$, $4f^8$, and $4f^9$ ion-core configurations, in agreement with earlier XPS studies and other measurements. The valence-band spectra, however, vary markedly, in contrast to expectations based on band-structure calculations.
FOOTNOTES AND REFERENCES


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<th>VB Maximum</th>
<th>$4f_{\uparrow}$</th>
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<th>$4f_{\uparrow}(2)$</th>
<th>$4f_{\uparrow}(3)$</th>
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<td>9.53(10)</td>
<td>10.51(10)</td>
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<td>1.20(5)</td>
<td>1.36(5)</td>
<td>1.32(5)</td>
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<td>4.47(10); $^7_5$</td>
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<td>12.82(10)</td>
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<td>2.2(1)</td>
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$^a$Value in parenthesis is the absolute error in the last place.

$^b$Assignments from optical data (Ref. 4).

$^c$Relative energies difference between features are accurate to within 0.05 eV.
FIGURE CAPTION

Fig. 1. X-ray photoemission spectra of the $4f$ and valence band region of Gd, Tb, and Dy.
Fig. 1
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