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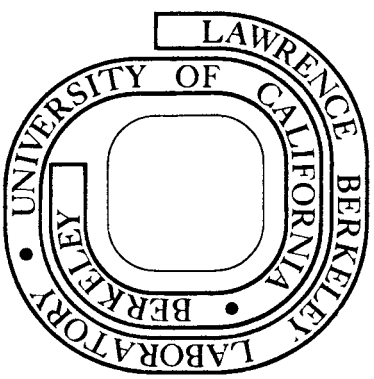

LBL-1691

DISCLAIMER

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

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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.

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High-resolution 4f-shell and valence-band spectra of metallic Gd, Tb, and Dy have been observed under ultrahigh vacuum conditions (8×10^{-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.[1] 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 <u>in-situ</u> 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 9×10^{-9} Torr during evaporation, but it returned immediately to 8×10^{-11} Torr,

*Work performed under the auspices of the U. S. Atomic Energy Commission.

the operating pressure. In-situ monitoring of the oxygen 1s region revealed a fractional monolayer of adsorbed oxygen as the only detectable contaminant on Gd and Dy. No oxygen 1s signal was detected on the Tb sample.

Valence-band and 4f spectra are shown in Fig. 1. The use of monochromatized Al $K\alpha_{1,2}$ 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 metals[2] and trifluorides.[3] The results of Hagström and co-workers[2] 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 $Z^{4+}(4f^n)$ final state is one greater than for the comparison optical ion $(Z = 1)^{3+}(4f^n)$. Herbst, Lowy, and Watson[5] 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 energy[6] of 7 - 10 eV for 4f photoemission from rare-earth metals, in good agreement with their quantity $(\Delta_- - \epsilon_{4f})$. 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 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 $4f^7(^8S)$, with all seven 4f spins parallel. The final state can only be ^7F, which is the lowest term in $Eu^{3+}(4f^6)$, and indeed only one narrow peak is observed, at E_B = 8.62 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 $0 \leqslant J \leqslant 7$ (in the optical spectrum of 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 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 ^6P, ^6I, and ^6D terms between 32,000 and 41,000 cm^{-1} in the optical spectrum of 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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Table I. Binding energies (eV) and FWHM of characteristic features of 4f-VB spectra of Gd, Tb, and Dy.[c]

		VB Maximum	$4f_{\downarrow}$	$4f_{\uparrow}(1)$	$4f_{\uparrow}(2)$	$4f_{\uparrow}(3)$	Intensity Ratio $\Sigma\ 4f_{\uparrow}/4f_{\downarrow}$
Gd	E_B^F	1.08(10)[a]	--	8.62(10); ^7F[b]	--	--	∞
	FWHM	1.50(5)	--	1.25(10)	--	--	
Tb	E_B^F	--	2.63(10); ^8S	7.80(10) ^6P, ^6I, ^6D	9.53(10)	10.51(10)	7.4 ± 0.4
	FWHM	--	0.80(5)	1.20(5)	1.36(5)	1.32(5)	
Dy	E_B^F	--	4.47(10); ^7F	8.23(10); ^5D, ^5L	9.53(10)	12.82(10)	2.7 ± 0.4
	FWHM	--	1.8(1)	1.8(1)	2.5(1)	2.2(1)	

[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.

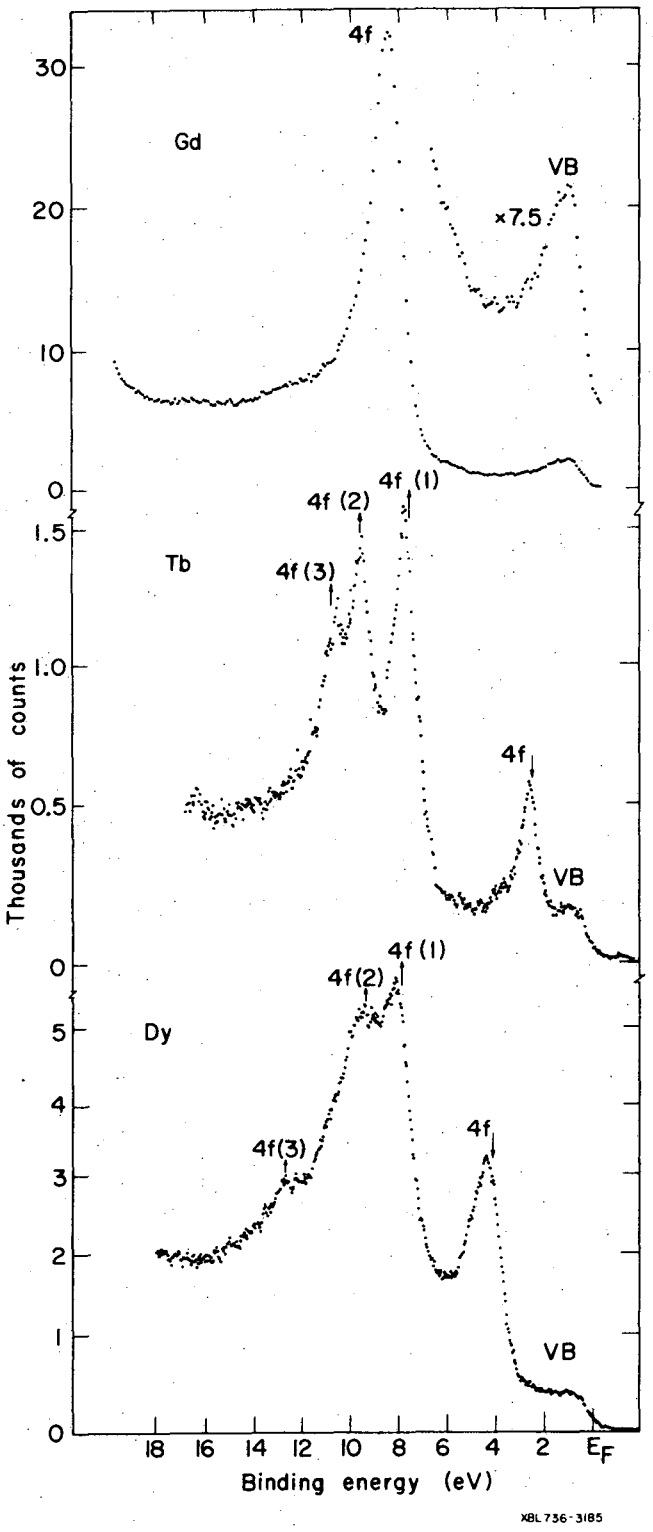
4f
Gd
VB
×7.5
4f (2)
4f (1)
4f (3)
Tb
4f
VB
4f (1)
4f(2)
Dy
4f(3)
4f
VB
Thousands of counts
30
20
10
0
1.5
1.0
0.5
0
0
5
4
3
2
1
0
18 16 14 12 10 8 6 4 2 E_F
Binding energy (eV)
XBL 736-3185

Fig. 1

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