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X-RAY PHOTOEMISSION SPECTRA OF THE 4d LEVELS IN RARE EARTH METALS*

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High resolution photoemission spectra of the 4d levels in the rare earth metals are reported. The metals with partially filled 4f shells display very complicated structure due to multiplet splitting, while those with the $4f^0$ or $4f^{14}$ configuration exhibit only spin-orbit splitting. A detailed analysis is given for the $4f^7$ metals europium and gadolinium.

- - -

The photoemission spectra of core levels in materials possessing unpaired electrons often exhibit satellite structure. This phenomenon, which is usually attributed to multiplet splitting, was first observed in x-ray photoemission spectra (XPS) of solids by Fadley et al.[1,2] It is interpreted as arising from the multiplicity of final states formed by the coupling of an open core shell with partially filled outer shells. Rare-earth metals and rare earth compounds, with their large number of unpaired 4f electrons, should present particularly interesting cases for study of multiplet structure. Earlier XPS studies have in fact revealed multiplet structure in rare earths. Early work on gaseous Eu showed an anomalous 4d photoelectron spectrum.[2] Cohen, et al.[3] observed and assigned multiplet structure in rare-earth trifluorides. Recently Signorelli and Hayes[4] reported complex structure in the 4d spectra

of compounds of La, Ce, Pr, Eu, and Yb, which they attributed to "monopole excitation" (correlation peaks) and electrostatic coupling (multiplet structure). To further elucidate the origins of the rare-earth 4d photoemission spectra, we have studied the 4d regions in all the rare-earth metals, except Pm. The metals have certain advantages over compounds; in particular, ligand field effects should be negligible. In this letter, we report the 4d spectra of selected rare-earth metals near the middle and ends of the 4f series. These cases were chosen on the basis of their relative simplicity.

The measurements were made in a Hewlett-Packard 5950A ESCA Spectrometer that had been modified for ultra high vacuum operation.[5] The exciting radiation was the monochromatized AℓKα line, and the total instrumental line width was 0.55 eV FWHM.[6] Rare-earth metal samples were prepared by *in situ* evaporation from high-purity, well-outgassed charges spot-welded on tungsten filaments. During the evaporation the pressure was maintained at or below 9×10^{-9} torr; immediately thereafter it returned to 3×10^{-10} torr or lower. Monitoring of the oxygen 1s line revealed at most a small fraction of one monolayer of adsorbed oxygen, and in several cases no oxygen at all could be detected.

Figure 1 shows the 4d spectra of La and Lu, which have a completely empty and a completely filled 4f shell, respectively, These spectra exhibit only well-defined spin-orbit split doublets with separations of 2.85(10) and 10.0(2) eV, respectively, in reasonable agreement with theoretical values of 3.2 and 10.2 eV.[7] Also shown is the 4d spectrum of Yb, which is a divalent metal with a $4f^{14}$ ion-core configuration. Here again the 4d spectrum consists simply of a $4d_{5/2}$ - $4d_{7/2}$ spin-orbit doublet split by 8.90 (15) eV, in excellent agreement with the value 8.8 eV given by Hagström *et al.*,[8] but between the atomic value[2] 8.4 (1) eV and the theoretical

value of 9.5 eV.[7] The binding energies of the $4d_{5/2}$ lines in La, Yb, and Lu are 103.7 (1) eV, 181.4 (1) eV, and 196.1 (1) eV, respectively, relative to the Fermi energy. The simple spin-orbit doublet character of the 4d doublet in Yb is interpreted as further confirmation of the $4f^{14}$ configuration in this metal.

Figure 2 shows the XPS spectra in the 4d region of Ce, Sm, and Eu. These spectra are typical of the rest of the rare-earth series in exhibiting complex structure due to the $4d^9 4f^n$ interaction. We shall discuss only the $4d^9 4f^7$ cases, Eu and Gd, as only these have as yet been analyzed in detail. The discussion below applies particularly to Eu. The Gd spectrum has not been as well resolved as yet. For these two metals the initial open-shell configuration and level is $4f^7$; ^8S. Thus emission of an $n\ell$ electron can lead only to the two terms $n\ell^{4\ell+1}\ 4f^7$; ^9L and $n\ell^{4\ell+1}\ 4f^7$; ^7L, where $|L| = |\ell|$. For the $\ell = 2$ case of interest here, each term consists of five levels with J ranging from $|S-2|$ to $|S+2|$. The configuration $f^7(^8S)d^1$ was treated by Judd.[9] By reversing the sign of the d-shell spin-orbit coupling constant ζ, we can use his discussion essentially verbatim for $f^7(^8S)d^9$, noting that the d-f exchange terms require no modification because the 4f shell is exactly half full. Figure 3 is a plot of the level ordering within the ^9D and ^7D multiplets using the reduced variables η and ξ defined by Judd[9] (cf his Fig. 5). The parameter η scales as energy for any particular value of ξ, which is itself an index of the degree of j-j coupling in the 4f shell: $\xi = 0$ for pure L-S and -1 for j-j coupling.

The five-peak fine structure on our ^9D peak in the Eu spectrum (Fig. 2) shows excellent agreement with this interpretation, while the ^7D fine structure is unresolved. Judd attributed a similar effect in the GdI spectrum to a contraction of the ^7D multiplet through interaction with an excited term ^7D of f^7d, derived from the level ^6P of the core.

We can qualitatively explain the difference in appearance and structure of the ^7D and ^9D terms but cannot account quantitatively for the contraction of the ^7D term on the basis of our simple model. However we can set a lower limit on ξ of -0.47 (Fig. 3). The main uncertainty is in the value of G for which we can set a lower limit $G \geqslant 4.4$ eV. Energies calculated on Judd's model are compared with experimental values in Table 1. The derived value of the effective 4d spin-orbit coupling constant within the ^9D manifold is $\zeta_d = 1.4$ (2) eV. This is somewhat smaller than estimates based on theory ($\zeta_d = 2.2$ eV) or obtained by interpolation using the La, Yb, and Lu experimental values ($\zeta_d = 1.8$ (3) eV). Again this contraction within the ^9D manifold is probably attributable to interaction with excited states.

A noteworthy feature of the Eu spectrum is the apparent reduction in multiplet separation between the ^7D and ^9D terms. According to simple theory,[9] this separation would be given by

$$G = \frac{24}{35}\, G^1(4d,4f) + \frac{32}{105}\, G^3(4d,4f) + \frac{528}{1524.6}\, G^5(4d,4f) \quad ,$$

or 18.91 eV, using Mann's[10] exchange integrals. The lower limit we give for G is 4.4 eV, corresponding to a reduction factor of 0.23. A large reduction factor is expected for multiplet splitting cases involving two subshells with the same principal quantum number, because of the large intrashell

correlation energy. A factor of 0.6 has previously been observed for 4s 4f multiplets in rare-earth salts[3] and metals.[11] Closure of the multiplet energy gap arises primarily through configuration interaction of the low-spin term (^7D in this case) with excited states of the same symmetry. This should lead to two other observable spectral features: the $^7D/^9D$ intensity ratio should be less than the multiplet value of 7/9, and "correlation peaks" should be present at higher binding energies, as observed[12] in Mn^{2+}. Large background intensities in our spectra, arising from elastic scattering, preclude a really quantitative interpretation, but both of the above features appear to be present. Figure 4 shows a wider energy scan of the 4d region in Gd metal, showing peaks that can be tentatively assigned as correlation satellites of the ^7D multiplet.

It is ironic that the main ^9D and ^7D multiplet peaks resemble a $4d_{5/2} - 4d_{3/2}$ doublet so closely at lower resolution that they were so interpreted in two earlier studies, on atomic Eu[2] and on EuO[4].

Photoabsorption measurements in rare earths have also been analyzed in terms of multiplet effects,[13] but because of different selection rules these spectra are not directly comparable to ours. X-ray emission lines involving the 4d level should also reflect the various couplings of 4d and 4f electrons. Salem and Scott[14] recently interpreted the $L_{\beta 2,15}$ and L_{γ_1} emission lines as having multiplet structure, but they deconvoluted their spectra into only two discrete lines. It is obvious from our results that the situation is more complicated. It seems probable that even more structure will be resolable when higher-resolution photoemission experiments become possible.

FOOTNOTES AND REFERENCES

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†IBM Fellow.

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Table I. The $4d^9 4f^7$; ^9D Multiplet Energies in Eu Metal (in eV)

Level	E(expt)	E(fitted)[a]
$^9D_6$[b]	0	0.1
$^9D_5$	0.78(04)	0.8
$^9D_4$	1.52(04)	1.4
$^9D_3$	2.22(04)	2.2
$^9D_2$	2.85(08)	2.9
^7D[c]	6.33(10)	6.3

a) After Ref. 9.

b) The binding energy of $^9D_6$ relative to the Fermi energy is 127.70 (15) eV.

c) Mean energy only.

FIGURE CAPTIONS

Figure 1. XPS spectra of the 4d levels of La, Yb, and Lu metals, showing only spin-orbit doublets.

Figure 2. XPS spectra of the 4d regions of Ce, Sm, and Eu metals exhibiting structure due to final-state coupling. The Eu spectrum has been analyzed as discussed in text.

Figure 3. Levels of the configuration f^7d^9 that derive from the core level $^8S_{7/2}$. The axes are labelled as follows: $\eta = (E(J) - \frac{35}{80} G) [G^2 + (\frac{5}{2} \rho)^2]^{-1/2}$; $\xi = \frac{\chi}{1 + |\chi|}$, where $\chi = \frac{5}{2} \zeta/G$. The matrix elements were calculated for the f^7d configuration so, for our case, $\zeta \leqslant 0$, $G \geqslant 0$, and therefore $-1 \leqslant \xi \leqslant 0$. The LS extreme is given for $\xi = 0$ on the left, and the Jj extreme is given for $\xi = -1.0$ on the right.

Figure 4. Wider energy scan of the 4d region in the x-ray photoemission of Gd metal, showing probable correlation lines of ^7D (upper panel) and narrow energy scan (lower panel).

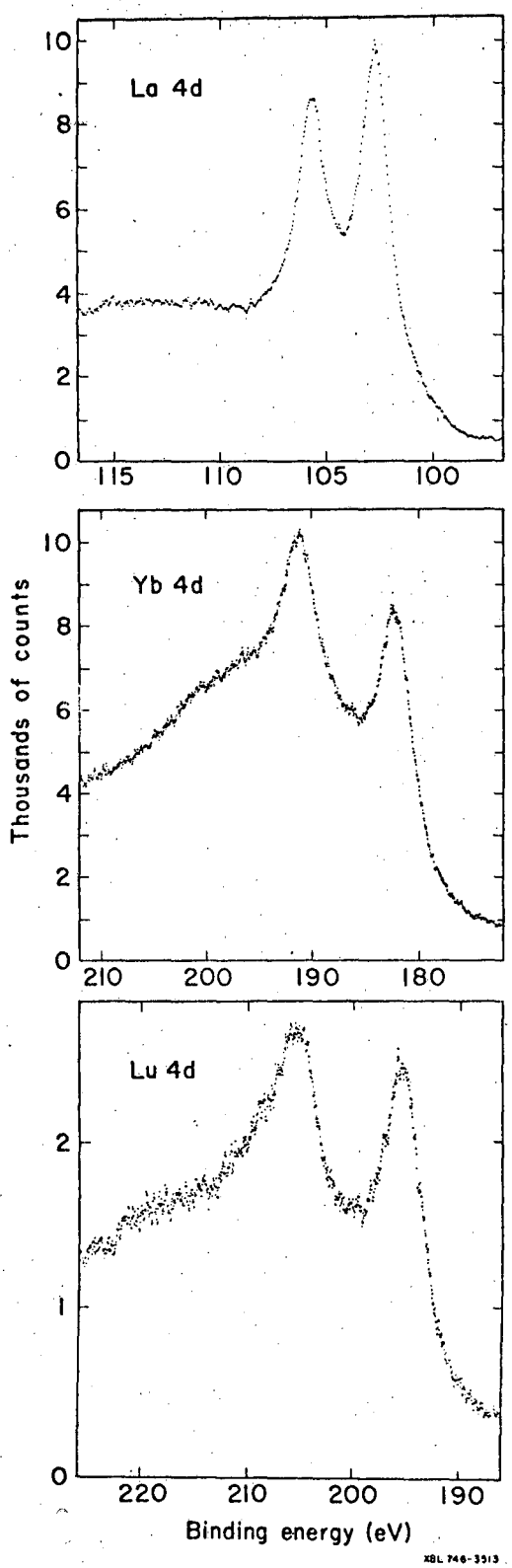

La 4d
Yb 4d
Lu 4d
Thousands of counts
Binding energy (eV)
XBL 746-3513

Fig. 1

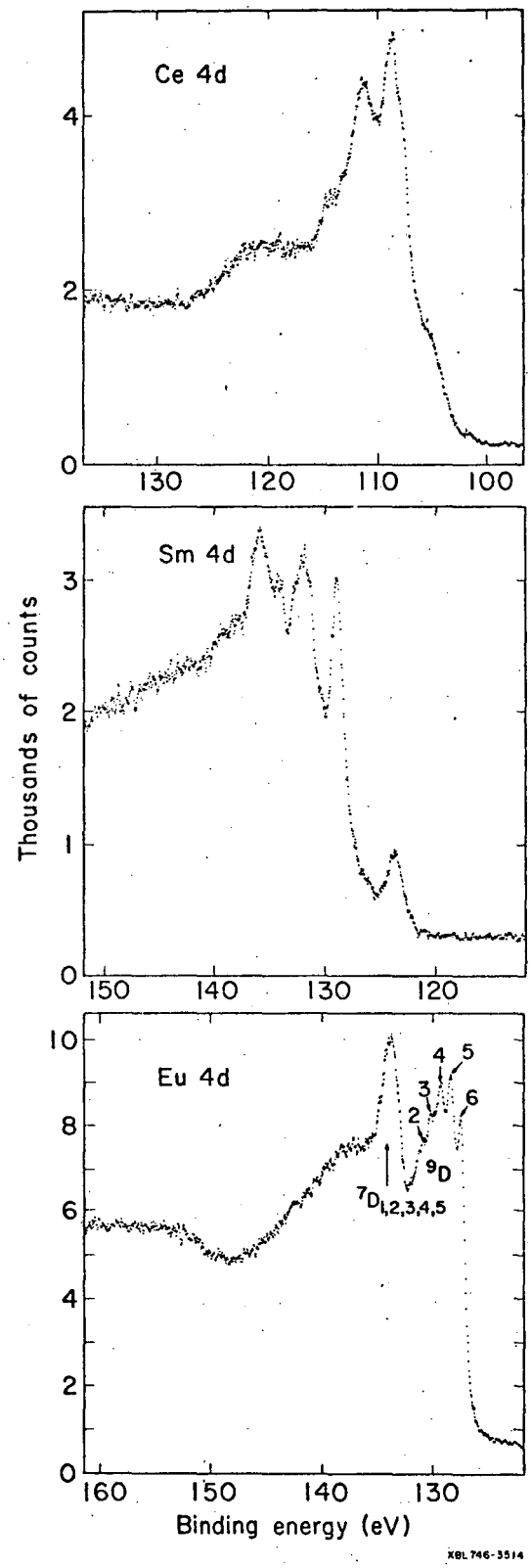
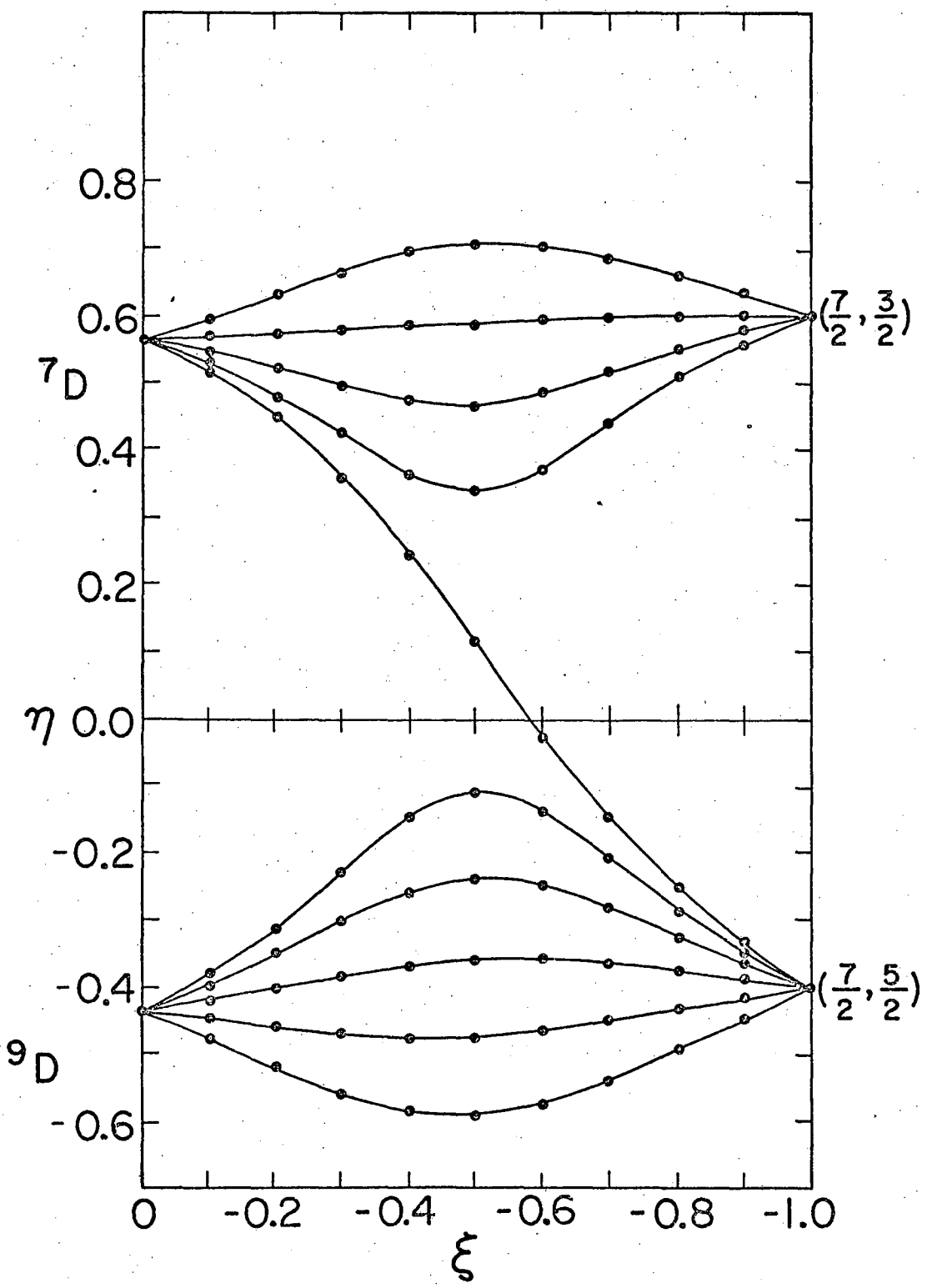

Ce 4d
Sm 4d
Eu 4d
Thousands of counts
Binding energy (eV)
$^7D_{1,2,3,4,5}$
^9D
1
2
3
4
5
6
XBL 746-3514

Fig. 2



XBL746-3551

Fig. 3

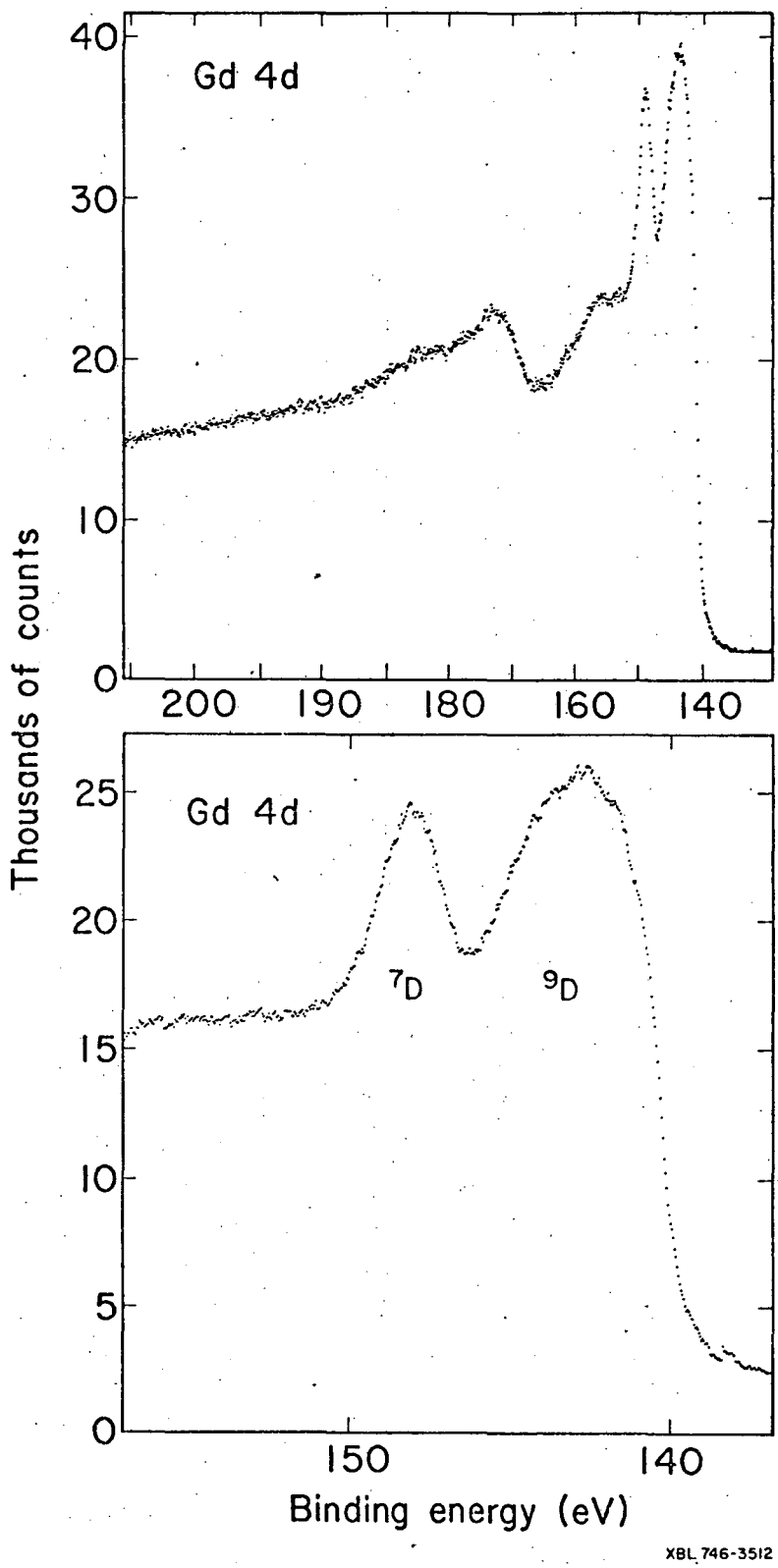

Gd 4d
Gd 4d
^7D
^9D
Thousands of counts
Binding energy (eV)
XBL 746-3512

Fig. 4

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