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Low-binding-energy satellites in rare-earth-metal 3*d* spectra: An exception at Eu

J. F. Herbst and J. M. Burkstrand
Physics Department, General Motors Research Laboratories, Warren, Michigan 48090

J. W. Wilkins
Laboratory of Atomic and Solid State Physics, Materials Science Center, Cornell University, Ithaca, New York 14853

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Photoejection of a 3*d* core electron in a rare-earth metal can result in the filling of an unoccupied 4*f* level, leading to a satellite structure of lower binding energy than the most intense 3*d* lines. We calculate the positions of these satellites for La to Tm. No such structure is predicted for Eu, in accord with our photoemission measurements. Results for the other elements agree well with the observed satellite positions.

I. INTRODUCTION

X-ray photoemission (XPS) spectra of 3*d* electrons in the rare-earth metals[1-3] generally feature two major peaks which correspond to the spin-orbit-split $3d_{3/2}$ and $3d_{5/2}$ levels. The final state associated with these peaks consists of a 3*d* hole screened by the 5*d*-6*s* conduction electrons with no change in the 4*f* occupancy, as theoretical work[4] based on this assumption has shown. Recent XPS measurements[2,3] for La, Ce, Pr, Nd, and Sm have revealed novel satellites with binding energies less than the most intense 3*d* lines. Wertheim and co-workers have proposed[2,3] that the mechanism responsible for the satellites is the filling of an unoccupied 4*f* level at the photoionized site. This process involves an energy gain which leads to a structure having *smaller* binding energy. Such energy-gain satellites are not observed in photoemission spectra of most metals.

In this paper we describe calculations of the satellite positions; a final state having one more 4*f* electron than the initial state is assumed. Our calculations predict satellite energies below those of the dominant structures for La through Tm with the notable *exception* of Eu. The results indicate that it is energetically impossible to populate the Eu $4f^8$ level even in the presence of a 3*d* core hole. Furthermore, we report 3*d* XPS spectra for Eu and Gd (as well as Pr and Nd) which are consistent with our theoretical work. In particular, it is significant that the satellite is not observed in Eu but reappears for the next element in the series, Gd.

II. CALCULATION SCHEME

We estimate satellite positions by a technique we have successfully applied[4-6] to 3*d* and 4*f* levels in the rare-earth metals. The procedure begins with relativistic Hartree-Fock (RHF) calculations for atomic configurations approximating those of the solids, and crystal potentials are then constructed from the computed wave functions by the renormalized atom method. Band calculations for appropriate final as well as initial states are iterated to crude self-consistency, and level energies are obtained from differences in total band energies.

The multiplicity-weighted average of the principal $3d_{3/2}$ and $3d_{5/2}$ binding energies $\tilde{\Delta}_-(3d)$ is given[4] by

$$\tilde{\Delta}_-(3d) = E^{\mathrm{RHF}}_{\mathrm{metal}}[3d^9 4f^n (5d-6s)^{m+1}] - E^{\mathrm{RHF}}_{\mathrm{metal}}[3d^{10} 4f^n (5d-6s)^m], \quad (1)$$

where m is the valence, and $E^{\mathrm{RHF}}_{\mathrm{metal}}$ represents the total RHF energy of all the electrons in a Wigner-Seitz sphere of the metal. If the low-energy satellite corresponds to a final state in which the $4f^{n+1}$ configuration is occupied, its position $\tilde{\Delta}(\mathrm{sat})$ is given by

$$\tilde{\Delta}(\mathrm{sat}) = E^{\mathrm{RHF}}_{\mathrm{metal}}[3d^9 4f^{n+1} (5d-6s)^m] - E^{\mathrm{RHF}}_{\mathrm{metal}}[3d^{10} 4f^n (5d-6s)^m]. \quad (2)$$

All states entering Eqs. (1) and (2) are constrained to be electrically neutral, and the 4*f* electrons are placed into the Hund's-rule ground levels via multiplet theory. The separation $\tilde{\delta}$ between a major peak and its satellite is then

$$\tilde{\delta} \equiv \tilde{\Delta}(\mathrm{sat}) - \tilde{\Delta}_-(3d) = E^{\mathrm{RHF}}_{\mathrm{metal}}[3d^9 4f^{n+1} (5d-6s)^m] - E^{\mathrm{RHF}}_{\mathrm{metal}}[3d^9 4f^n (5d-6s)^{m+1}]. \quad (3)$$

The tildes in Eq. (1)–(3) signify neglect of correlation and 3*d*-4*f* multiplet effects.

III. RESULTS AND COMPARISON WITH EXPERIMENT

Values of $\tilde{\Delta}_-(3d)$, $\tilde{\Delta}(\mathrm{sat})$, and $\tilde{\delta}$ are presented in Table I for La through Tm; Yb and Lu have filled

TABLE I. Theoretical $[\tilde{\Delta}_-(3d)]$ and experimental $[\langle E_B(3d)\rangle]$ average $3d$ binding energies; satellite positions $[\tilde{\Delta}(\text{sat})]$ and separations $(\tilde{\delta})$ in the absence of correlation effects [see Eqs. (2) and (3)]; estimates of the correlation contribution ξ; and satellite separations δ. All $4f$ states are Hund's rule levels; all energies in eV. Note that $\tilde{\delta}$ and δ are *positive* for Eu.

Element	$\tilde{\Delta}_-(3d)$	$\langle E_B(3d)\rangle$	$\tilde{\Delta}(\text{sat})$	$\tilde{\delta}$	ξ	δ
La	844.1	842.3(3)[a]	840.8	−3.3	−1.0	−4.4
Ce	892.5	891.1(4)[a]	887.4	−5.1	−0.9	−5.9
Pr	941.7	940.4(4)[c]	935.3	−6.4	−1.0	−7.4
Nd	991.7	990.1(4)[c]	985.4	−6.3	−1.4	−7.7
Sm	1094.7	1092.1(?)[a]	1087.6	−7.1	−1.8	−8.9
Eu	1139.1	1137.3(6)[c]	1143.6	+4.5	−3.1	+1.4
Gd	1201.6	1199.7(6)[c]	1199.8	−1.8	−3.6	−5.5
Tb	1256.8	1257.4(8)[b]	1254.4	−2.4	−3.1	−5.5
Dy	1313.5		1308.8	−4.7	−2.7	−7.4
Ho	1370.8		1366.7	−4.1	−3.2	−7.3
Er	1429.3		1425.9	−3.4	−3.8	−7.2
Tm	1489.0		1484.6	−4.4	−3.8	−8.1

[a] Reference 3.
[b] Reference 1.
[c] This work.

$4f$ shells and cannot exhibit satellites of this nature. $\tilde{\Delta}_-(3d)$ agrees with experiment to within about 2 eV (see Table I), and estimates show that correlation will add at most that amount to the calculated $3d$ binding energies.[4] The relatively small impact of correlation on $\tilde{\Delta}_-(3d)$ results from the extreme localization of the $3d$ shell, leading to increased accuracy of the Hartree-Fock binding energies, and the maintenance of the $4f$ occupancy in the two states appearing in Eq. (1). The situation differs for $\tilde{\delta}$, a quantity on the order of 5 eV while $\tilde{\Delta}_-(3d) \sim 10^3$ eV. In the absence of relevant atomic spectral information, we estimate the correlation addition ξ to $\tilde{\delta}$ by modifying the analogous quantity ξ_+ entering Δ_+, the unoccupied $4f$ level position (see Table I of Ref. 6). ξ_+ involves the same $4f$ transition appearing in $\tilde{\delta}$, and we reduce it by 2–8% to account for the slightly higher $4f$ density in the presence of a $3d$ hole.[7] Values of ξ so derived are given in Table I, as well as the resulting satellite separations δ:

$$\delta \equiv \xi + \tilde{\delta} . \tag{4}$$

An essential feature of Table I is that all δ (and $\tilde{\delta}$) values are negative (i.e., corresponding to a satellite at lower energy than the principal lines) with the exception of europium. The unoccupied $4f$ level in Eu metal is located (Refs. 8 and 9) 8.6 eV above the Fermi energy, and a $3d$ core hole is incapable of forcing occupation of that level. Since $\delta \simeq 1.4$ eV for Eu, a value much less than the 5–6 eV width of the major lines, our work predicts *no* observable satellite for that element.

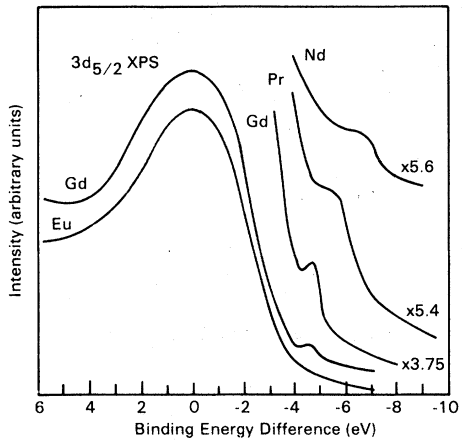

FIG. 1. X-ray-photoemission spectra in the $3d_{5/2}$ region for Eu, Gd, Pr, and Nd. The major peaks have been aligned and their intensities normalized to that for Eu. For the sake of clarity the spectra have been vertically offset.

We have examined this point through XPS measurements for Eu, in addition to Pr, Nd, and Gd. The experiments were carried out in a standard ultrahigh vacuum system[10] (base pressure ~ 9 $\times 10^{-9}$ Pa) equipped with an Al $K\alpha$ source. The high-purity (99.99%) polycrystalline samples were cleaned by repeated sequences of argon-ion bombardment (100 μA/cm^2, 2000 V) and annealing ($T \leq 300$ °C).

Surface cleanliness was monitored by Auger electron spectroscopy; oxygen and carbon contamination were always $\lesssim 0.2$ at.%. Figure 1 shows Eu and Gd $3d_{5/2}$ spectra (0.4 eV resolution) and the satellite spectra for Pr and Nd (0.8 eV resolution). Although the satellites are indeed weak (especially for Nd), we nevertheless find no evidence for such structures in Eu in consonance with our theoretical work.

Table II compares our results with the available

TABLE II. Comparison of predicted satellite separations δ with experimental values ΔE.

Element	δ	ΔE (expt)	
		a	b
La	−4.4	−3.2	
Ce	−5.9	−4.9	
Pr	−7.4	−4.9	−5.6(6)
Nd	−7.7	−5.3	−6.3(6)
Sm	−8.9	−8.2	
Eu	+1.4		none
Gd	−5.5		−4.6(6)

[a] References 2 and 3.
[b] This work.

data. Given the small satellite intensities, the two sets of measurements are in good agreement with each other; qualitative agreement with theory is excellent. We emphasize that our calculations are for Hund's rule $4f$ states, whereas the experimental values ΔE represent the midpeak satellite separations; $|\delta|$ thus represents an upper limit for $|\Delta E|$, so that the quantitative accord is actually better than Table II indicates. Since the fine structure is unresolved, it is impossible to extract the energy more accurately corresponding to the calculations, which obviates more detailed comparison. The overall accord between theory and experiment, however, is strongly suggestive that the mechanism responsible for the satellites is the occupation of the $4f^{n+1}$ level in the presence of a $3d$ core hole. We note that in the case of Sm, however, there is now substantial experimental[11] and theoretical[12] evidence that its satellite, which is noticeably larger than those of the other rare earths, is primarily due to a divalent surface layer.

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