Applicability of the Spin-Orbit Sum Rule for the Actinide 5*f* States

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The branching ratio of core-valence transitions in electron energy-loss spectroscopy and x-ray absorption spectroscopy is linearly related to the expectation value of the spin-orbit operator of the valence states. Here, we analyze the branching ratio of the $N_{4,5}$ edges in the actinides and find that the spin-orbit sum rule gives an accurate result without the need to include the core-valence interactions. The branching ratio is not only useful to study the variations in the 5*f* spin-orbit interaction, it also allows us to constrain the 5*f* count for given angular-momentum coupling conditions.

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Spin-orbit coupling plays an integral role in the behavior of narrow-band materials. Nowhere is there such a strong example as in the actinides, where the 5*f* bands are known to be narrow [1–4] and have a large spin-orbit interaction [5,6], leading to behaviors such as itinerant magnetism, heavy fermions and superconductivity [7–11]. In the actinides the outer *s* and *d* electron orbitals are broad and overlap strongly, while the atomiclike 5*f* orbitals have a smaller radius with less overlap. In the actinide series the lightest elements have metalliclike *f* electrons, whereas the heavier actinides have atomiclike *f* electrons. The change in shape of the *f* orbitals from overlapping to nonoverlapping is very prominent for increasing atomic number of the nucleus and is also seen under certain chemical and physical circumstances. Such a change can reduce the hybridization and crystal-field interaction; hence we can expect a more atomic character with larger spin-orbit interaction, where the $f_{5/2}$ population is increased at the cost of the $f_{7/2}$. The relative occupation of these spin-orbit split levels may be investigated using the sum rule for core-valence transitions in electron energy-loss spectroscopy (EELS) or x-ray absorption spectroscopy (XAS) [12–15], potentially explaining the origin of the above-mentioned behaviors observed in the 5*f* states.

In the excitation of an electron from a core level into the valence band, the electric-dipole transition gives two final-state multiplets which are separated in energy by the spin-orbit interaction of the core hole. Transition metals, rare earths, and actinides exhibit this set of high-intensity peaks, often called white lines, at the threshold of absorption edges. As an illustration, Fig. 1 shows the $N_{4,5}$ ($4d \rightarrow 5f$) spectra obtained by EELS [16] for α-Th, α-U, and α-Pu, each accompanied by a single-crystal diffraction pattern that confirms the phase being examined. Also, the XAS [17] spectrum for α-Pu is presented to show that this gives a similar result as EELS. The pronounced white lines for each metal are due to the spin-orbit split $4d_{3/2}$ and $4d_{5/2}$ multiplets, where the detailed structure is not resolved due to the intrinsic core-hole lifetime broadening of ~2 eV [12,18]. Along the actinide series from Th to Pu the $4d_{3/2}$ peak progressively reduces in intensity, since the electric-dipole selection rules govern that a $d_{3/2}$ core electron can be excited into an $f_{5/2}$, but not into an $f_{7/2}$ level [12]. This suggests that the intensity ratio of the white lines depends on the spin-orbit interaction of the 5*f* states. This dependence has been explained using many-electron spectral calculations, where the spin-orbit, Coulomb, and exchange interactions are treated on equal footing [13,14], and a spin-orbit sum rule has been derived using angular-momentum algebra

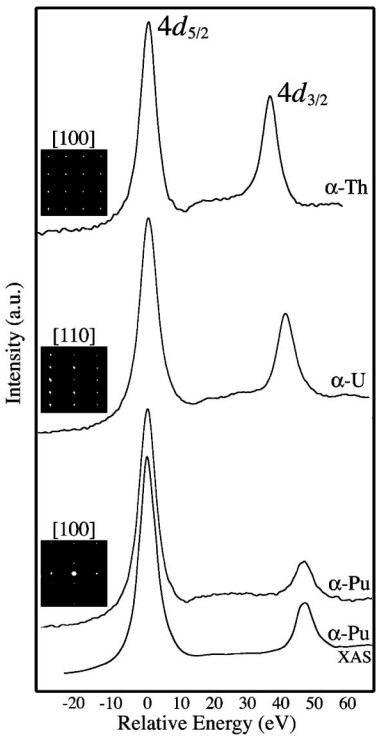

FIG. 1. The $N_{4,5}$ ($4d \rightarrow 5f$) edges from α-Th, α-U, and α-Pu acquired by EELS in a TEM and from α-Pu acquired by XAS. A single-crystal diffraction pattern from each metal is presented, confirming the phase being examined by EELS.

[12,15]. While it was shown that this sum rule works very well for $4d$ and $5d$ metals, the $3d$ and $4f$ metals suffer from the presence of strong core-valence interactions [13].

In this Letter, we show that the spin-orbit sum rule can be applied successfully to the actinides, using the $N_{4,5}$ edges in Th, U, and Pu metal, and UF_4 as a standard with a known number of $5f$ electrons. Application of the sum rule yields accurate values of the spin-orbit interaction *per hole*. Even when the number of holes is not precisely known, the sum-rule analysis can be extremely useful, since it puts a constraint on the relation between the spin-orbit interaction and the number of f electrons. This provides a way to restrict the range allowed for the f count, thereby supplying useful criteria for calculational schemes.

For $d \rightarrow f$ transitions [19], the branching ratio is defined as $B \equiv A_{5/2}/(A_{5/2} + A_{3/2})$, where $A_{5/2}$ and $A_{3/2}$ are the areas underneath the core level $d_{5/2}$ and $d_{3/2}$ peaks, respectively. The sum rule [12–15] gives the relation

$$\frac{\langle w^{110} \rangle}{n_h} = -\frac{5}{2}(B - B_0), \tag{1}$$

where $\langle w^{110} \rangle$ is the expectation value for the angular part of the $5f$ spin-orbit electron operator, n_h is the number of $5f$ holes, and B_0 is the value of the branching ratio without spin-orbit interaction in the f shell. As for all XAS sum rules [12,20], the expectation value is obtained per hole, since the core electron is excited into the unoccupied valence states. The values per electron can be obtained by multiplying both sides of Eq. (1) by n_h/n.

In order to relate the results to physical quantities we need to know the precise meaning of $\langle w^{110} \rangle$. Spin-orbit interaction is given by a Hamiltonian $(l \cdot s)\zeta_l$, where $l \cdot s$ and ζ_l are the angular and radial parts, respectively, of the spin-orbit operator for the l shell. The spin-orbit parameter ζ_l depends on the effective Z (atomic) number, whereas the expectation value of the angular part $\langle l \cdot s \rangle = \frac{3}{2}\langle w^{110} \rangle$ for the f shell depends on the electron distribution over the angular-momentum levels, $j = l \pm 1/2$. It can be expressed in the electron occupation numbers $n_{7/2}$ and $n_{5/2}$ of the $j = 7/2$ and $5/2$ levels,

$$\langle w^{110} \rangle = n_{7/2} - \tfrac{4}{3} n_{5/2}, \tag{2}$$

where $n = n_{7/2} + n_{5/2}$ is the total number of f electrons [21]. Thus $\langle w^{110} \rangle$ is $-4/3$ for a $j = 5/2$ electron and 1 for a $j = 7/2$ electron, while $\langle w^{110} \rangle = 0$ corresponds to the statistical distribution, $n_{7/2}$:$n_{5/2} = 4$:3.

Equation (1) shows that in order to extract the value of $\langle w^{110} \rangle / n_h$ from the branching ratio, B, we need to know the value of B_0. It has been shown that B_0 depends on the core-valence interaction [13]. If this interaction can be neglected, the sum rule is exact and B_0 is equal to the statistical value of $\frac{3}{5}$ for a d core hole. However, when the spin-orbit-split core levels are mixed due to core-valence interactions, we need to add a correction term Δ, which is proportional to the difference between B_0 and the statistical value, such that

$$\frac{\langle w^{110} \rangle}{n_h} = -\frac{5}{2}\left(B - \frac{3}{5}\right) + \Delta, \tag{3}$$

$$\Delta \equiv \frac{5}{2}\left(B_0 - \frac{3}{5}\right). \tag{4}$$

It can be shown using first-order perturbation theory that Δ is proportional to the ratio between the core-valence exchange interaction $G^1(c, l)$ and the energy splitting between the white lines, which is determined by the core spin-orbit parameter ζ_c. Table I shows that there is a remarkable proportionality between $G^1(c, l)/\zeta_c$ and Δ over a wide range of different edges in $3d$, $4d$, $4f$, $5d$, and $5f$ metals. These values were obtained from relativistic atomic Hartree-Fock calculations using Cowan's code [22], where B_0 was calculated using the weighted average over the different J levels in the ground state.

From Table I we can make the following observations. For $3d$ transition metals the application of the spin-orbit sum rule for the $L_{2,3}$ branching ratio is severely hampered by the large $(2p, 3d)$ exchange interaction, which is of similar size as the $2p$ spin-orbit interaction [13]. The same is true for the $M_{4,5}$ edges of the lanthanides, where the $(3d, 4f)$ exchange interaction is strong compared to the $3d$ spin-orbit interaction [23]. On the other hand, the sum rule holds quite well for the $L_{2,3}$ edges of $4d$ and $5d$ transition metals, as might be expected for a deep $2p$ core level which has small $G^1(c, l)$ and large ζ_c. The situation is also favorable for the $M_{4,5}$ and $N_{4,5}$ edges of the actinides, giving a small $G^1(c, 5f)/\zeta_c$ for the $3d$ and $4d$ core levels. The latter result is quite surprising: in spite of the fact that the Th $4d$ core level is shallower than the Zr $2p$ or Hf $2p$ and lies in between the Ti $2p$ and La $3d$, the core-valence interactions do not spoil the sum rule.

The theoretical values of B, $\langle w^{110} \rangle / n_h$, and Δ for the $N_{4,5}$ edges are given in Table II for the different $5f^n$ ground-state configurations, which were calculated in

TABLE I. The calculated values for $G^1(c, l)/\zeta_c$ and the correction term Δ for a range of different absorption edges in $3d$, $4d$, and $5d$ transition metals, lanthanide, and actinides [19]. The linear relation between both quantities is evident from the numbers.

	$c \rightarrow l$	$G^1(c, l)/\zeta_c$	Δ
Ti $3d^0$	$L_{2,3}$ $(2p \rightarrow 3d)$	0.981	−0.895
La $4f^0$	$M_{4,5}$ $(3d \rightarrow 4f)$	0.557	−0.485
Th $5f^0$	$N_{4,5}$ $(4d \rightarrow 5f)$	0.041	−0.020
Th $5f^0$	$M_{4,5}$ $(3d \rightarrow 5f)$	0.021	−0.018
Zr $4d^0$	$L_{2,3}$ $(2p \rightarrow 4d)$	0.018	−0.015
Hf $5d^0$	$L_{2,3}$ $(2p \rightarrow 5d)$	0.002	−0.002

TABLE II. Relativistic atomic Hartree-Fock calculations in intermediate coupling (IC) for different $5f^n$ configurations. The branching ratio, B, of the $N_{4,5}$ edge spectra; the expectation value of the $5f$ spin-orbit interaction per hole, $\langle w^{110}\rangle/n_h$; the branching ratio without $5f$ spin-orbit interaction, B_0; and the resulting $\Delta = \frac{5}{2}(B_0 - \frac{3}{5})$.

n	B	$\langle w^{110}\rangle/n_h$	B_0	Δ
0	0.592	0	0.592	−0.020
1	0.634	−0.1026	0.593	−0.017
2	0.680	−0.2145	0.594	−0.014
3	0.723	−0.3184	0.596	−0.010
4	0.760	−0.4043	0.598	−0.005
5	0.817	−0.5419	0.600	0
6	0.918	−0.7888	0.602	0.005

intermediate coupling (IC) using Cowan's code [22]. The gradual decrease of Δ along the series is caused by the increasing core spin-orbit interaction ζ_c [13]. As long as $\langle w^{110}\rangle/n_h \gg \Delta$, the relative error in the sum rule is small. In the analysis of the experimental branching ratios we explicitly keep track of the error in the sum rule by including the calculated value of Δ, and we shall solve the problem for the case that the number of $5f$ electrons per atom is unknown.

The experimental values of B for Th, U, UF_4, and Pu metal are given in Table III. They were obtained using the integrals of the measured N_4 and N_5 peak intensities (Fig. 1) after removal of a fitted background. The values of B were converted to $\langle w^{110}\rangle/n_h - \Delta$ using Eq. (3), and $\langle w^{110}\rangle/n_h$ was plotted in Fig. 2 versus the number of f electrons. The thick line (blue) shows the interpolated $\langle w^{110}\rangle/n_h$ using the IC values of Δ given in Table II for each f^n. For comparison the thin horizontal line (red) shows $\langle w^{110}\rangle/n_h$ assuming $\Delta = 0$ (no core-valence interactions). This shows that only for Th the relative error would be significant. Clearly, the accuracy of the analysis is not limited by the theoretical correction term Δ but by the experimental error bar, which should typically be in the order the difference between the XAS and EELS results.

TABLE III. Experimental values for the branching ratio, B, of the $N_{4,5}$ edge spectra of different actinides and resulting value of $\langle w^{110}\rangle/n_h - \Delta = \frac{5}{2}(B - \frac{3}{5})$.

	B	$\langle w^{110}\rangle/n_h - \Delta$
α-Th (EELS)[a]	0.623	−0.058
α-U (XAS)[b]	0.676	−0.190
α-U (EELS)[a]	0.685	−0.213
UF_4 (XAS)[b]	0.677	−0.194
α-Pu (XAS)[a]	0.813	−0.533
α-Pu (EELS)[a]	0.826	−0.565

[a]This work (experimental data in Fig. 1).
[b]From Kalkowski *et al.*, Ref. [18].

Precise numbers for the $5f$ electrons quoted in the literature should be viewed with suspicion, since different calculational schemes can give different f counts. Interestingly, when the experimental value of B is known, Eq. (3) becomes a relation between the f count and the spin-orbit expectation value. The smaller the value of Δ, the more precise this relation is. We demonstrate graphically with the aid of Fig. 2 that it is indeed possible to relate the angular-momentum coupling of the $5f$ states with the number of electrons. For this purpose Fig. 2 shows the theoretical curves for the three atomic coupling schemes, jj, LS, and IC [12]. Equation (2) allows a straightforward interpretation of these curves in terms of the occupation numbers of the ground-state j levels. In all cases the negative values confirm the predominant occupation of the $j = 5/2$ levels. The jj and LS coupling schemes give the atomic extremes. In jj coupling, the $5f$ spin-orbit interaction forces, for $n \leq 6$, all electrons in the $j = 5/2$ level, giving $\langle w^{110}\rangle/n_h = -\frac{4}{3}n/n_h$. In LS coupling, the Coulomb and exchange interactions give an increase in $n_{7/2}$ at the cost of $n_{5/2}$, thereby increasing the value of $\langle w^{110}\rangle$. In the atomic ground state, the electrostatic and spin-orbit interaction compete with each other,

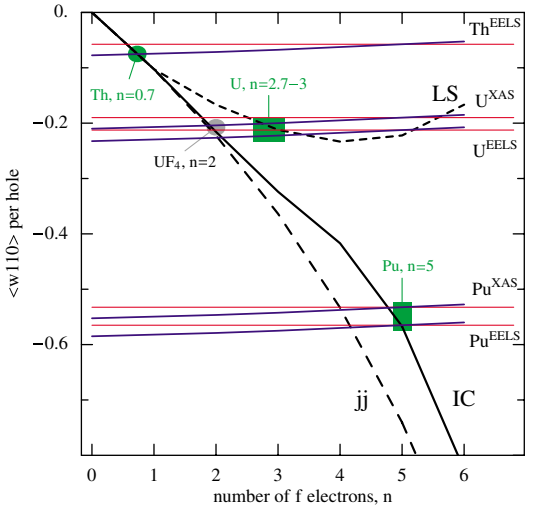

FIG. 2 (color online). The spin-orbit expectation value per hole versus the number of $5f$ electrons (n). The experimental solutions obtained from EELS and XAS are given by $\langle w^{110}\rangle/n_h = -\frac{5}{2}(B - \frac{3}{5}) + \Delta$ for α-Th, α-U, and α-Pu (see Table III) with $\Delta = 0$ (thin horizontal, red lines) and using Δ for each n from Table II (thick, blue lines). Also plotted are the theoretical curves for the different coupling schemes; LS (short dashed line), jj (long dashed line) and intermediate coupling (IC) (solid line). The control sample UF_4 with $n = 2$ (gray circle) falls directly on the IC curve, exactly as the spin-orbit sum rule predicts. The filled (green) circle and boxes represent α-Th, α-U, and α-Pu with their most probable f count, as discussed in the text.

resulting in IC (with values given in Table II). For actinide atoms the IC ground state is close to the jj coupling limit, as can be verified from the curves in Fig. 2, while for lanthanide atoms it is closer to the LS coupling limit, due to the smaller $4f$ spin-orbit interaction. The values of the IC ground state can be regarded as the limit for a localized atom in the solid, while the symmetry breaking in a more itinerant system can mix the $f_{7/2}$ and $f_{5/2}$ states, which increases $\langle w^{110}\rangle$. The value of $\langle w^{110}\rangle/n_h$ for a control sample UF_4, where $n = 2$, is plotted in Fig. 2 (gray circle). Because of the atomic character of UF_4, it falls directly on the IC curve. This result might be taken as evidence for the spin-orbit sum rule.

The experimental solution for each of the metals is given by the nearly horizontal lines in Fig. 2. α-Th falls on the IC curve for $n = 0.75$ (filled circle), but if we assume $n \approx 1$ then the spin-orbit interaction would be somewhat reduced. For α-Pu the case is clear cut: the measured $\langle w^{110}\rangle/n_h$ is well outside the range of LS coupling and satisfies IC for $n \approx 5$ (filled box). Even if α-Pu would be $n = 6$, the result is still much closer to IC than to LS coupling. However, for α-U there is a choice ranging from IC for $n = 2$ (and $n_{7/2}/n \approx 2\%$) to resembling LS coupling for $n = 3$ (and $n_{7/2}/n \approx 25\%$). This actually shows that there is a severe restriction for the f count if a specific choice of angular-momentum coupling is imposed. Therefore, the results obtained from a sum-rule analysis can provide important guidance for theoretical calculations. If we adopt the most commonly encountered f counts in the literature, namely, Pu f^5 and U $f^{2.7}$ to f^3, this implies IC for Pu and a resemblance to LS coupling for U.

In conclusion, our results show that the spin-orbit sum rule works excellently for the actinide metals, where the error caused by the core-valence exchange interaction is minimal. This means we now have an unambiguous probe for the $5f$ spin-orbit interaction per hole. In cases where the f count is not precisely known, application of the sum rule allows a restriction of the range possible for the f count, thereby providing useful criteria for calculational schemes.

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