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5f-Electron Excitation Energies and the Coulomb Term, U, in the Light Actinide Metals

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Relativistic Hartree-Fock-Wigner-Seitz band calculations have been performed for the actinide metals Ac through Am in order to estimate 5f excitation energies. Our calculations predict that the tetravalent state (i.e., four s-d conduction electrons) is favored for the lighter elements with a crossover to a trivalent ground state occurring near uranium. We find the Coulomb energy, U, for 5f electron hopping to increase from 2–3 eV at Th to 4–5 eV at Am.

The 5f electrons of the actinide metals are of considerable interest for the study of magnetism since they are less localized than the 4f states of the rare earths but less itinerant than transition-metal 3d electrons. One quantity particularly relevant to magnetic behavior is the Coulomb term U, the energy required for an extra magnetic electron to hop onto an atomic site. In this Letter we report the first theoretical estimates of U for the light actinides, Ac through Am. U is found to increase across the series, consistent with the view[1] that the 5f electrons become more localized with increasing atomic number. Essential to the calculations are estimates of 5f excitation energies, which are interesting in light of recent x-ray photoemission studies[2] of thorium, uranium, and some of their oxides; in anticipation of further experimental progress we also report estimates of these 5f excitation energies. We employ a computational scheme[3] which has been quite successful in predicting 4f excitations in the rare-earth metals and, as experimental data become available, it will be interesting to assess the applicability of the method to the actinides.

Central to the present investigation is the ne-

glect of hybridization between the 5f and the 6d-7s conduction electrons. The 5f states are degenerate with the conduction bands and hybridization is assuredly significant in these metals[1]; but our aim is to estimate the excitation energy of a single 5f electron as a function of 5f occupation number, and for this purpose it is essential to keep the 5f's distinct from the conduction electrons by setting hybridization equal to zero. The atomic configuration $5f^n 6d^{m=1} 7s$ is assumed appropriate to the metal, and we perform calculations for varying 5f occupancy n (with a concomitant change in the valence m to preserve charge neutrality). n is confined to integral values so that atomic spectral data may be used to estimate correlation effects. Band calculations[4-6] are performed, and by permitting the 6d and 7s counts to be nonintegral, the bands and their associated charge densities are iterated to crude self-consistency.[6] The total Hartree-Fock band energy E_{band} and one-electron energies ϵ_i are evaluated. During the calculations the positions and widths of the *occupied* f levels are monitored. The level widths decrease with increasing atomic number; for example, they are 2 eV and 0.7 eV for trivalent Th and Am, respectively.

Depending on $5f$ count and atomic number the f levels lie either above or below the Fermi energy, ϵ_F, indicating whether the configuration is stable, as we will see in Fig. 1.

In estimating the excitation energy of a $5f$ electron we make the assumption, invoked[3] in analogous calculations for the rare earths, that the hole created by the removal of an f electron (either in a photoemission event or when the f electron hops to an adjacent site) will be "completely" screened, i.e., that the final state of the atomic cell is electrically neutral. We estimate the energy of the final state through a band calculation for a metal with one fewer $5f$ electron and one more conduction electron than the initial state. The description of the final state is crude but has the virtue of being well defined and computatinally tractable. Identifying Δ_- as the energy necessary to so excite a $5f$ electron into the conduction bands, we have

$$\Delta_- = E_{metal}\left(f^{n-1}(ds)^{m+1}\right) - E_{metal}\left(f^n(ds)^m\right), \quad (1)$$

where E_{metal} represents the total energy per atom of the metal. Since we are not capable of calculating correlation in the metallic state, we make use of the free-atom correlation-energy difference, ξ:

FIG. 1. Values of $\Delta_-(f^n \to f^{n-1})$ and $\epsilon_F - \epsilon_{5f}$ for the divalent, trivalent, and tetravalent configurations of the actinides. Reliability of the spectral information entering the Δ_- estimates is indicated by the different circles.

$$\xi \equiv E_{corr}\left(f^{n-1}d^m s\right) - E_{corr}\left(f^n d^{m-1} s\right)$$

$$= \left[E\left(f^{n-1}d^m s\right)_{expt} - E\left(f^{n-1}d^m s\right)_{RHF\ calc}\right] - \left[E\left(f^n d^{m-1} s\right)_{expt} - E\left(f^n d^{m-1} s\right)_{RHF\ calc}\right]$$

$$= \left[E\left(f^{n-1}d^m s\right) - E\left(f^n d^{m-1} s\right)\right]_{expt} - \left[E\left(f^{n-1}d^m s\right) - E\left(f^n d^{m-1} s\right)\right]_{RHF\ calc}. \quad (2)$$

The first bracket in the last line of Eq. (2) is supplied by experimental spectral data for atomic configurations of integral s and d (as well as f) counts most closely corresponding to the band results. Under the assumption that ξ is a good approximation for correlation effects in the metal and with use of our relativistic Hartree-Fock (RHF) band calculations of the total energy, Eq. (1) becomes

$$\Delta_- = \xi + E_{band}\left(f^{n-1}(ds)^{m+1}\right) - E_{band}\left(f^n(ds)^m\right). \quad (1a)$$

Δ_- results for both divalent and trivalent initial states are shown in Fig. 1. A striking aspect of the figure is that Δ_- based on the trivalent configuration changes sign from negative to positive between uranium and neptunium, implying that the tetravalent metallic state is stable relative to the trivalent from thorium to uranium and that thereafter the trivalent state is favored. Thus, noting the predicted ground-state valence, a well-defined $5f$ level does not appear before Pa, in contrast to the progressive filling of the $4f$ shell
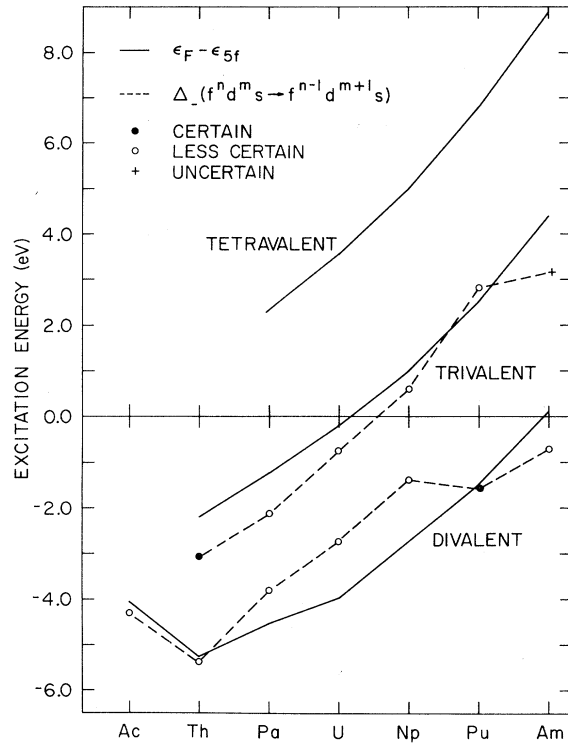
from Ce onward in the lanthanide series. Figure 1 predicts the energies of empty $5f$ states as well; the negative of $\Delta_-(f^{n+1} \to f^n)$ is to be interpreted in our scheme as the energy above ϵ_F of an unoccupied $5f$ level (f^n denoting the ground state).

The spectroscopic data[7] are uncertain for many configurations; this affects the reliability of the ξ[8] and Δ_- values, as Fig. 1 indicates; for tetravalent states the data are too poor for Δ_- esti-
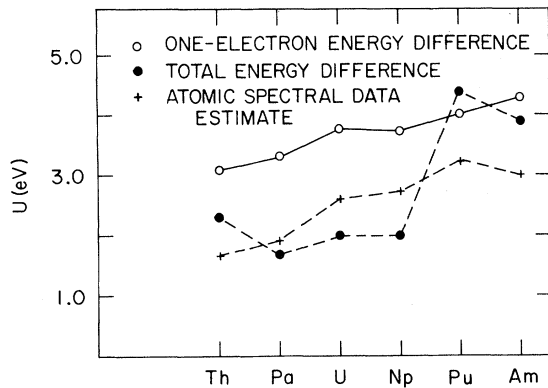
FIG. 2. Values for the Coulomb term, U, based on trivalent reference states. U_{atomic} is obtained from atomic spectral data. Estimates of U for the metals are obtained from Fig. 1 and are based on the Δ_- results or their one-electron analogs, $\epsilon_F - \epsilon_{5f}$.

mates. The center of gravity of the *occupied* $5f$ levels is ϵ_{5f}; measured with respect to the Fermi energy it provides an alternative approximation for the excitation energy. Except perhaps for Am, the most rare-earth-like of the elements studied here, Fig. 1 shows rather good agreement between $\epsilon_F - \epsilon_{5f}$ and Δ_-. This is in contrast to the rare earths, for which $\epsilon_F - \epsilon_{4f}$ predicts much larger excitation energies than Δ_-; of the two predictions, Δ_- agrees with experiment for the rare earths.

The energy cost[9] for a $5f$ electron to hop from one atom to another while maintaining charge neutrality is, for a trivalent reference state,

$$U_{\text{atomic}}$$
$$= E(f^{n-1}d^3s) + E(f^{n+1}ds) - 2E(f^n d^3 s); \quad (3)$$

this is readily obtained from the spectral information. Our estimate for the metal is

$$U = \Delta_-(f^n \to f^{n-1}) - \Delta_-(f^{n+1} \to f^n), \quad (4)$$

which is simply the distance between adjacent curves in Fig. 1. U_{atomic} values, obtained from experimental spectral data, and U values, obtained from Fig. 1, are presented in Fig. 2. Both estimates are seen to increase from Th to Am. Johansson[10] has also estimated U_{atomic}; his results agree with ours except for Am. Herring made use of atomic data to estimate $U \sim 5-6$ eV for the rare earths, in accord with experiment.[11] Consequently, the present results reinforce the view that the $5f$ electrons of the lightest actinides are similar to the itinerant $3d$ electrons of the transition metals, while at Am the local character of the rare-earth $4f$ states is almost attained.

Finally, we note that the main effect of hybridization will be to change the $5f$ occupancy to some nonintegral value. If the occupancy were determined, the corresponding $5f$ excitation energy could be deduced by simple interpolation of the results appearing in Fig. 1. Hybridization is not expected to modify significantly our conclusions in regard to U.

Enthusiastic conversations with D. J. Lam and J. W. Wilkins are acknowledged, and we are indeed grateful to Professor I. Lindgren for providing advice and his relativistic atomic program.

[1]See, for example, *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974), Vols. I and II.

[2]J. Verbist *et al.*, J. Electron Spectrosc. Relat. Phenomena 5, 193 (1974); B. W. Veal and D. J. Lam, Phys. Rev. B 10, 4902 (1974), and references therein.

[3]J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B 6, 1913 (1972); self-consistent relativistic calculations for the rare earths have also been made and will be reported presently.

[4]Following L. Hodges, R. E. Watson, and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972), we employ the renormalized-atom approach in which radial wave functions are defined within r_{WS}, the Wigner-Seitz radius of the metal. Relativistic Hartree-Fock free-atom wave functions are computed, truncated at r_{WS}, and normalized to unity within the Wigner-Seitz sphere; initial band-structure potentials are then constructed with the truncated wave functions. $6d$ and $7s$ band extrema are determined by imposing Wigner-Seitz boundary conditions at r_{WS} on the large components of the wave functions obtained from integration of the Dirac-Fock equations.

[5]Since the metals under consideration have minuscule paramagnetic moments, the computations utilize I. Lindgren's LS average-of-configuration scheme (to be published) in which the L, S, M_L, and M_S quantum numbers of an open shell are averaged over.

[6]The Fermi level, ϵ_F, is determined by assuming a parabolic s-band and a rectangular d-band density of states. Though crude, this suffices for the almost unfilled d bands treated here. Average energies for the $6d$ and $7s$ electrons in the occupied bands are chosen; wave functions are found at those energies and used to estimate the $6d$ and $7s$ contributions to the band poten-

tials. Band extrema are again determined and the procedure repeated until the conduction-band minimum and the d-band extrema have converged to within 0.005 eV. Calculations using other approximations suggest an uncertainty of $\lesssim 0.3$ eV and E_{band} and $\lesssim 1$ eV in $\epsilon_F - \epsilon_{5f}$.

[7]Summarized by L. Brewer, J. Opt. Soc. Amer. **61**, 1101 (1971).

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[10]B. Johansson, Phys. Rev. B **11**, 2740 (1975).

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Is the Deformation Parameter β Different for Different Kinds of Transitions?

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It is shown on the basis of isospin arguments that the deformation parameter β_2 for 2^+ first excited states is expected to be a function of the external field producing the transition. This is contrary to the usual assumption based on the collective model that β is an intrinsic property of the nucleus and is, therefore, the same for all kinds of transitions. Data available in the literature support the expectation.

It is usually assumed *a priori* for lack of better information that the deformation parameter β for excitation of a collective state is independent of the means of excitation. This idea stems directly from the usual collective model, where the neutron and proton matter distributions are assumed to have the same shape. The purpose of this note is to point out, however, that a systematic difference in the deformation parameter β_2 is expected when the first excited 2^+ collective state of nuclei is excited by different external fields. Several authors[1] have pointed out from the point of view of a microscopic model that (p,p') and (n,n') might be rather different because of a difference between $n\text{-}n$ or $p\text{-}p$ and $n\text{-}p$ forces. Spin-dependent forces are not very effective in exciting the these states, and the spin-independent $n\text{-}p$ force is much stronger than the $n\text{-}n$ or $p\text{-}p$ forces. This fact is taken into account in the optical model of elastic scattering by the Lane potential[2] $\hat{V}_1 \vec{T} \cdot \vec{t}/A$, which has the effect of making the nuclear potential deeper for protons than for neutrons in neutron-excess nuclei. However, when the collective model is then applied to inelastic scattering of 2^+ states, the deformed optical potential may fail badly in describing the excitation process.

As an example of the expected failure consider a nucleus like ^{90}Zr, which has the $N = 50$ neutron shell closed. In an extreme shell-model picture the 2^+ vibration would involve just the protons filling the 29–50 shell, which would be excited much more strongly by neutrons than by protons. On the other hand the deformed optical potential would inappropriately describe the difference between (n,n') and (p,p') in terms of the neutron excess and would therefore be greater for proton projectiles. In reality both the neutron and proton closed shells participate rather strongly through $\Delta N = 2$ transitions, and these transitions give rise to large corrections to the shell-model amplitudes expressed in terms of polarization charges. Because core polarization reduces the isovector amplitude and enhances the isoscalar amplitude, the collective-model picture of the excitation, whose strength is represented by the intrinsic parameter β, is nearly recovered. However, it is expected that some residue of the shell effect will remain, so that the parameter β will be different when measured by different kind kinds of transitions.

A convenient parametrization of the expected differences based on the collective model can be made by use of different deformation parameters