

particular, the experimental peak located just below  $\omega_{x-y}$  is explained by the continuum of states we have found below the threshold frequency.

The sagittal SDPS is split, in Fig. 3, into its longitudinal and transverse components. We point out the different behavior of these contributions at the longitudinal threshold, where  $\rho_{x+y}$  vanishes but  $\rho_{x-y}$  exhibits a maximum. When elasto-optic scattering occurs, as in semiconductors with  $n_2 < 1$ , both  $\rho_{x+y}$  and  $\rho_{x-y}$  contribute to the Brillouin spectrum and the most significant structure is the peak in  $\rho_{x-y}$ . On the contrary, if  $n_2 > 1$  the surface reflection coefficient is large, the ripple mechanism becomes dominant and only the orthogonal projections of the displacements ( $\rho_{x+y}$ ) contribute to the spectrum.<sup>4</sup> This mechanism should be also observable in GaAs by lowering the wavelength of the incident light.

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## Calculated Bulk Properties of the Actinide Metals

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Self-consistent relativistic calculations of the electronic properties for seven actinides (Ac-Am) have been performed using the linear muffin-tin orbitals method within the atomic-sphere approximation. Exchange and correlation were included in the local spin-density scheme. The theory explains the variation of the atomic volume and the bulk modulus through the 5f series in terms of an increasing 5f binding up to plutonium followed by a sudden localization (through complete spin polarization) in americium.

The variation of the atomic volume in the actinide series of elements, shown in Fig. 1, was originally accounted for in terms of a valence picture<sup>1,2</sup> where the 5f electrons were considered to be nonbonding just as the 4f electrons are in the rare-earth metals. However, more recently it has become increasingly clear, both

from experimental and theoretical work,<sup>3</sup> that this is not a valid picture of the real behavior exhibited by the 5f electrons. Kmetko and Hill<sup>4</sup> made band-structure calculations for the lighter actinides and found that the width of the 5f band is comparable to the d-band width of the heavier 3d elements. Subsequent extensions of this work,<sup>5</sup>

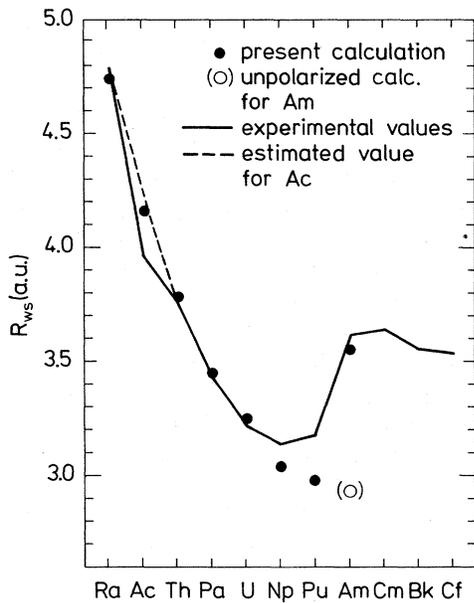


FIG. 1. Comparison between the experimental and the calculated atomic Wigner-Seitz radius,  $R_{WS}$ , for the actinide metals. The dashed line corresponds to an estimated value for Ac derived by Zachariasen, Ref. 2.

where relativistic effects were incorporated, essentially confirmed these results. By a careful examination of the experimental cohesive energies, it was possible to demonstrate that the  $5f$  electrons do take part in the bonding.<sup>6-8</sup> Thus for the earlier actinides the  $5f$  electrons must be considered itinerant and the original valence picture has to be abandoned.

A variety of experimental evidence, which has now accumulated, shows that americium is the first  $5f$  element which behaves as a normal trivalent rare-earth metal.<sup>9</sup> This means that in this element the  $5f$  electrons are localized and non-bonding and that the magnetic moment associated with the  $f^6$  configuration is zero. The most recent experimental verification of this is the discovery of superconductivity in americium.<sup>10</sup> For the following element, curium, a rare-earth type of behavior is found, as for example demonstrated by its magnetic properties.<sup>11</sup> We therefore have to conclude that the  $5f$  electrons are itinerant (metallic) for the lighter elements but localized for the heavier ones ( $\geq$ Am). This may be looked upon as a Mott transition within the  $5f$  shell taking place as a function of the atomic number.<sup>12</sup> This behavior is closely related to that of the  $3d$  monoxides, where the  $3d$  electrons undergo a Mott transition as a function of the atomic

number.<sup>13</sup>

In recent years it has become clear<sup>14,15</sup> that a number of ground-state properties of metals can be described accurately using a *one-electron picture*<sup>16</sup> and a local approximation for the exchange-correlation energy functional.<sup>17</sup> Starting from this reduction of the original many-body problem to a self-consistent band-structure problem, further computational and conceptual simplifications may be introduced. Thus, e.g., the so-called atomic-sphere approximation (ASA)<sup>18</sup> had been applied successfully to calculate various bulk properties of the transition metals<sup>15,19</sup> and in the present Letter we apply this method to the actinide metals.<sup>20</sup> Thereby, as should be clear from the description of the actinides given above, we encounter a situation where the band theory is pushed to its limits of applicability. However, in order to simulate the possibility of a localization of the  $5f$  electrons, we allow for a (ferromagnetic) spin polarization. A similar procedure has earlier been used to study the onset of magnetism and its influence on the atomic volume and bulk modulus in the  $3d$  transition metals.<sup>15,21</sup>

In Fig. 1 we compare the calculated equilibrium atomic volumes with those found experimentally in the most dense crystal structures. As can be seen, for Th, Pa, and U the agreement is most satisfactory. It is first when we come to Np and Pu that we can notice significant deviations between the calculated and experimental values. The deviations are most easily interpreted as due to correlation effects not included in the present one-particle scheme, and it is significant that we overestimate the binding. Both neptunium and plutonium are known to behave anomalously in most of their physical properties and are, in fact, close to being magnetic,<sup>9</sup> indicative of strong  $f$ -electron correlations. In agreement with experiments<sup>9,22</sup> the present calculations give no spin-polarized solution for Np and Pu at zero pressure, but for somewhat expanded volumes (negative pressures) a net magnetization is calculated.

Arriving at americium, we find that the *fully* spin-polarized solution exists at normal pressure and has the lowest energy. In Fig. 1 we show the calculated equilibrium volumes for both the non-polarized and polarized state in Am. From this we notice the drastic effect that spin polarization has on the atomic volume, indicating an almost nonbonding character of the  $5f$  electrons. Furthermore, we observe that, allowing for this polarization, the calculated atomic volume agrees well with the experimental value.

In Fig. 2 we compare the calculated bulk modulus with experiment. Again, a good general agreement is obtained. We note in particular that the spin-polarized calculations for Am give a bulk modulus close to the experimental value, a value which is also close to those typical for rare-earth metals.

In the ASA the partial contributions to the pressure may readily be investigated and the results are displayed in Fig. 3. First we notice that even in thorium the  $f$  states seem to have some significance for the bonding. However, it should be kept in mind that this does not necessarily imply that the  $f$  orbitals are occupied, and instead is due to the fact that the partial-wave analysis of the tails of the  $s$ ,  $p$ , and  $d$  orbitals will give rise to small  $f$ -partial-wave contributions. But as we proceed through the series the importance of the  $f$  contribution to the binding increases strongly as a result of the progressive occupation of the orbitals. Because of the narrowing of the  $f$  band, this tendency saturates between Np and Pu. For the unpolarized calculation in Am we still find an appreciable  $f$  contribution to the binding, whereas the spin-polarized  $f$  state has an essentially nonbonding character. Thus, from this point of view the totally polarized solution represents correctly the localized nonbonding  $f^6$  state in americium.

From the calculated state density we find essentially no occupation of the  $f$  band in thorium. For the next element, protactinium, the  $f$  band

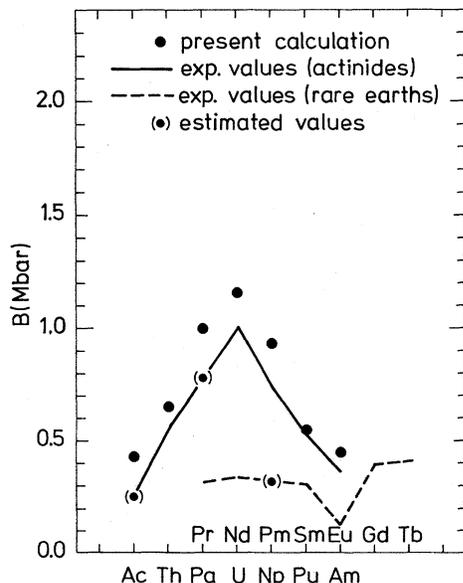


FIG. 2. Comparison between the experimental and calculated bulk modulus for the actinide metals.

intersects the Fermi energy and the  $f$  occupation number,  $n_f$ , is approximately 1. In uranium the calculated value of  $n_f$  is somewhat larger than 2. For Np and Pu the  $n_f$  numbers are of the order of 4 and 5, respectively. These occupation numbers agree very well with those estimated from renormalized-atom calculations<sup>23</sup> and also with those obtained from thermodynamical arguments.<sup>7</sup> It is also found that the occupation numbers are practically unchanged for all the elements when calculated as a function of volume. For the spin-polarized solution in Am we obtain an occupation number  $n_{f\uparrow} \approx 6$  and  $n_{f\downarrow} = 0$ . If the corresponding spin moment is combined with the orbital moment, the total moment is equal to zero.

The  $f$ -band width is about 5 eV in Ac, of the order of 3 eV for Th-Np, and somewhat larger than 2 eV for Pu. In Am, finally, it is less than 1 eV. These widths are consistent with those listed in Ref. 23. The effective Stoner interaction parameter,  $I_f$ , is calculated to be fairly constant through the series as well as to be rather volume independent with a value  $I_f \approx 0.5$  eV.

Exactly the same type of calculation as presented here has been performed for metallic cerium<sup>24</sup> in order to elucidate the nature of the electronically driven  $\gamma$ - $\alpha$  transition. The results obtained for cerium allow us to identify  $\alpha$ -Ce with plutonium and  $\gamma$ -Ce with americium, thus supporting the Mott-transition interpretation of the  $\gamma$ - $\alpha$  transition.<sup>25</sup>

The calculated equilibrium volume for actinium shows a quite substantial deviation from the recently reported value,<sup>26</sup> but agrees quite well with an estimated value given by Zachariassen.<sup>2</sup> This point will be discussed in a forthcoming article

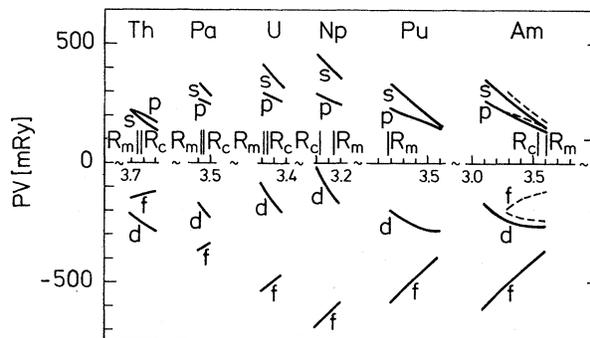


FIG. 3. Partial contributions of the  $s$ ,  $p$ ,  $d$ , and  $f$  partial waves to the pressure. The dashed lines correspond to the spin-polarized calculations for Am. The measured and calculated Wigner-Seitz radii are denoted by  $R_m$  and  $R_c$ , respectively.

where a more detailed account of the present work will be presented.

To summarize, the present calculations have shown that it is possible to account theoretically for the variation of the atomic volume in the actinide series. Thereby the importance of the 5f-electron contribution to the binding has been clearly demonstrated (Fig. 3). Moreover, it was possible to account for the localization within the f shell, which takes place as a function of atomic number.

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