Theoretical aspects of the 5f delocalization of americium under pressure

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(Received 29 July 1991)

Americium is the first element of the actinide series with localized and chemically inert 5f electrons. It has earlier been demonstrated that with applied pressure the 5f electrons in Am become itinerant, and therefore bonding. The crystal structure of americium has been experimentally determined to change with increasing pressure; it changes from double hcp→fcc→monoclinic or distorted fcc→the α-uranium structure (orthorhombic), or a related structure. The experimentally observed volume collapse associated with 5f delocalization is very small. In contrast, previous theoretical calculations have predicted a volume collapse between 25% and 40%. We present the total energy versus volume of americium in the fcc and in the experimentally reported α-uranium structure obtained from fully relativistic, full-potential, linear-muffin-tin-orbital calculations based on the local-density approximation. In combination with previous calculations for the low-pressure phase, our calculations predict that *the delocalization of the 5f electrons in americium is accompanied by a ~34% volume collapse.*

I. INTRODUCTION

Most of the experimental data on the actinide elements can best be understood by assuming that the 5f electrons are itinerant and bonding in the early part of the series (Ac–Pu), but localized and chemically inert in americium and the subsequent elements.[1] An indication that this picture is essentially correct is the good agreement between the experimentally and theoretically determined (assuming delocalized 5f states) equilibrium volumes, bulk moduli and cohesive energies of the early actinides (Ac–Pu).[2] Furthermore, calculations (also assuming itinerant 5f electrons) of the thermal expansion coefficients yield good agreement with experimental data for the early actinides.[3] Early studies of the electronic structure of the actinides showed that the 5f states form a band pinned to the Fermi level (E_F) in the early part of the series,[4] and the bonding properties of the 5f band were shown to explain the parabolic trend in the equilibrium volumes of the early actinides.[2] Moreover, the unusual crystal structures found in protactinium (body-centered tetragonal), uranium (orthorhombic, two atoms per cell), neptunium (orthorhombic, eight atoms per cell), and plutonium (monoclinic, sixteen atoms per cell) have long been argued to reflect the itinerary of the 5f states. This speculation was quantified by Wills and Eriksson,[5] who used a fully relativistic, full-potential linear-muffin-tin-orbital (LMTO) method to calculate the equation of state of thorium, protactinium, and uranium, and obtained the correct crystal structures for these elements, with a clear correlation between open, low-symmetry structures and 5f occupation.

Americium (Am) and the following elements stand in sharp contrast to the earlier actinides. The volume of americium is ~40% larger than the element preceding it, plutonium (Pu). The volumes of Am, curium (Cm), berkelium (Bk), and californium (Cf) are close to the volumes of the trivalent rare-earth elements. Furthermore, the crystal structure is the same as in some of the rare-earth elements [double hexagonal close packed (dhcp)]. This suggests that the 5f electrons are localized and chemically inert in Am, Cm, Bk, and Cf (as well as in the subsequent actinides).[6] Hence the jump in volume between Pu and Am has been argued to be a Mott transition, with the 5f electrons being nonbonding and localized in Am.[7] Further, it has been suggested that americium is trivalent, with an $[f^6]$ configuration and a $J=0$ ground state.[7] Therefore, in agreement with experiments, Am is expected to be nonmagnetic, and was even predicted to be superconducting,[8] a prediction that was later verified.[9]

Since Am is on the low-density side of a Mott transition, whereas the preceding element, Pu, is on the high-density side, it is interesting to speculate whether the ground state of these elements can be pushed to "the other side" by an appropriate external parameter. This has indeed been shown to be the case, since high-pressure experiments on Am (as well as Cm, Bk, and Cf) show several interesting crystallographic phase transitions, indicating a delocalization of the 5f electrons.[10] We show the experimental data on Am (Ref. 10) in Fig. 1 (curve marked 1). The zero-pressure crystal structure of Am is dhcp. At ~50 kbar the fcc structure is stabilized, and at ~100 kbar a monoclinic or distorted fcc structure is stable. Finally, at ~150 kbar, there is another crystallographic transition; the structure stable above this pressure has been suggested to be the same as in uranium at low temperatures (α-U structure) or a related structure.[10] This type of behavior is also found in Cm, Bk, and Cf.[10] The dhcp→fcc transition has been shown to be governed by the 6d electrons, using LMTO calculations with the atomic-sphere-approximation (ASA) and the 5f electrons treated as core states.[11] Similar phase transitions are found in the rare-earth elements.[12] This transition is therefore not thought to be associated with a delocalization of the 5f shell. It is, however, tempting to correlate

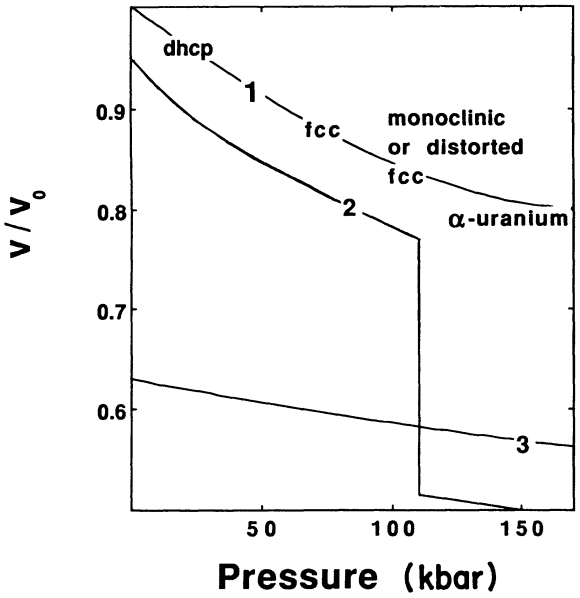

FIG. 1. High-pressure data on Am. V_0 is the experimental volume at zero pressure and V is the measured/calculated volume. Curve 1 is the experimental curve of Benedict (Ref. 10), curve 2 is the calculated curve of Skriver, Johansson, and Andersen (Ref. 2), and curve 3 is the calculated curve of Brooks (Ref. 2). We have also indicated the experimentally determined structure types.

the onset of open, low-symmetry structures with $5f$ delocalization, especially since the high-pressure structure of Am is reported to be the same as in the low-temperature phase of uranium (known to have delocalized $5f$ states). If the transition to the low-symmetry structure is driven by the onset of $5f$ delocalization, a substantial volume collapse through the transition would be expected, and in Cm, Bk, and Cf a substantial volume collapse has been observed.[10] The experimental results for Am (Fig. 1) are unusual in this regard; the volume collapse observed in the transition to the low-symmetry structure is very small.

Calculations of Am under pressure support the picture of delocalized $5f$ states in the high-pressure phases.[2] Using spin-polarized LMTO-ASA calculations, in a hypothetical fcc structure, Skriver, Johansson, and Andersen[2] found that, at the experimental volume, the $5f$ band spin-polarized to saturation, i.e., the spin-up band was almost completely filled and the spin-down band was almost completely empty. Since, for filled bands, Bloch and Wannier representations are equivalent,[13] they argued that their calculations represented localized $5f$ electrons. As a function of pressure, it was found that the theoretical equation of state reproduced the experimental data fairly well (we have reproduced this result in Fig. 1, curve marked 2).[2] The calculated equation of state showed a van der Waals loop and a Maxwell equal-area construction gave a phase transition from localized, polarized to itinerant, nonpolarized $5f$ electrons. The calculated transition pressure was in fairly good agreement with experiment. The calculated volume collapse, however, due to the onset of itinerant and bonding $5f$ electrons, was $\sim 40\%$, in agreement with intuition (and experience in the later actinides), but in sharp disagreement with experimental results. Brooks subsequently performed fully relativistic calculations for paramagnetic Am (using a hypothetical fcc structure).[2] His results (the curve marked 3 in Fig. 2) may be viewed as a modified (and improved) equation of state for the paramagnetic phase of Am. The resulting phase diagram is thus the curve marked 2 in Fig. 1 for pressures lower than the phase transition (~ 100 kbar) and the curve marked 3 in Fig. 1 for pressures higher than the phase transition. The volume collapse through the transition in this modified phase diagram is $\sim 25\%$, somewhat reduced over curve 2, but still in substantial disagreement with experiment.

The agreement between experiment and theory is fairly good for the low-pressure phases, but poor for the high-pressure phases. Because the true crystal structure of the low-pressure phases is the same (or very similar to) the one used in the calculations,[2] while the experimentally observed high-pressure structure is very different from the fcc structure, we have been motivated to investigate whether the fcc structure used for the high-pressure phase in all previous calculations[2] is too crude an approximation, and if an improved calculation, using the reported α-U structure, of the high-pressure phase would yield an equation of state in better agreement with experiment. We have therefore performed fully relativistic, full-potential local-density approximation (LDA) total-energy calculations of the phase diagram of Am in the α-U structure and, for comparison, in the fcc structure, assuming itinerant $5f$ electrons, to compare with the high-pressure experiments.[10]

II. DETAILS OF CALCULATIONS

In this work we have used a full-potential linear-muffin-tin-orbital technique.[14] The calculations were all-electron, fully relativistic (with the spin-orbit coupling included at each variational step[15]), and employed no shape approximation to the charge density or potential. Exchange and correlation were treated in the LDA using the Hedin-Lundqvist exchange-correlation functional. The base geometry was a muffin-tin geometry with a true interstitial; the basis functions, charge density, and potential were expanded in spherical-harmonic series within the muffin tins and in Fourier series in the interstitial. The volume in the muffin-tin spheres was kept the same in all structures and was a fixed fraction (approximately 0.50) of the total volume. The basis set was comprised of augmented linear-muffin-tin orbitals.[15,16] The tails of the basis functions (the extension of the bases outside their parent spheres) were linear combinations of Hankel or Neuman functions with nonzero kinetic energy; three tail functions were used for each basis. The basis set contained $6s$, $6p$, $7s$, $7p$, $6d$, and $5f$ orbitals; all orbitals were contained in the same energy panel, and were thus allowed to hybridize, with a separate set of energy parameters for the $6s$, the $6p$, and the rest of the basis functions.

Integration over the Brillouin zone was done using "special point" sampling.[17] The results reported here

used 10–60 points in the irreducible wedge of the fcc Brillouin zone and 16–100 points in the irreducible wedge of the orthorhombic Brillouin zone. The number of points was increased until the total energy did not change with more than 1 mRy. Furthermore, we tested the orthorhombic structure by setting the positional parameters and the cube axes of the orthorhombic lattice so that it described the fcc lattice. The calculated energy was the same as for fcc (within 0.05 mRy). Spherical harmonic expansions were carried out through $l=8$ for the bases, charge density, and potential. The Fourier series for the basis functions contained 369 plane waves for the fcc structure and 1053 plane waves for the orthorhombic structure; the Fourier series for the charge density and potential contained 1695 plane waves for the fcc structure and 5175 plane waves for the orthorhombic structure. The difference in energy between the different structures was converged to less than 0.1 mRy with these expansion sets.

III. RESULTS

The calculated total energy as a function of Wigner-Seitz radius is displayed in Fig. 2. Notice that , although the energy difference between the two structures is quite large ($\sim$0.4 eV per atom with the α-U structure being stable), the two energy curves show very similar volume dependence. The electronic pressure is therefore very similar in the two structures; the two pressure curves (not shown) corresponding to Fig. 2 lie on top of one another. The zero pressure volume is approximately 16 Å^3 and is consistent with our previous calculations of the volumes of the light actinides.[5] This value is, of course, much too low compared to the experimental (trivalent) result. Our calculated electronic pressure at volumes lower than the experimentally observed phase transition ($\sim$20% volume compression) agrees well with the results of Skriver, Johannson, and Andersen,[2] and lies only marginally above curve 2 in Fig. 1.

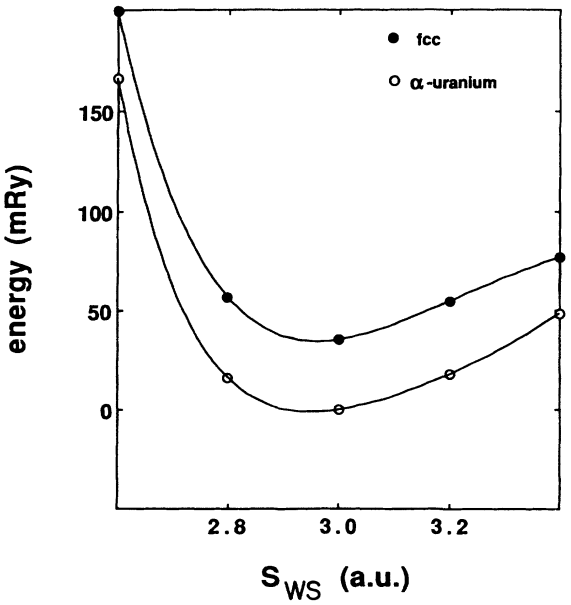

FIG. 2. Calculated total energy as a function of Wigner-Seitz radius for Am.

Our results therefore show that the assumed fcc structure in the calculations of the high-pressure phase of Am (Ref. 2) is a good approximation for the pressure-volume dependence, and that using the experimentally reported structure together with the spin-orbit interaction only marginally modifies the zero-temperature equation of state of Am found by Skriver, Johansson, and Andersen.[2] It was previously found that the spin-orbit interaction modifies the theoretical equation of state, decreasing the predicted volume collapse from the $\sim$40% found by Skriver, Johansson, and Andersen to $\sim$25%.[2] We find that the effect of including the full crystal potential is to cancel most of the effect of the spin-orbit interaction. Instead of improving the agreement between the LDA prediction and experiment, we have restored the applicability of the original calculations of Skriver, Johansson, and Andersen,[2] and we therefore conclude that calculations of the zero-temperature phase diagram of Am, based on the LDA, yield an $\sim$34% volume collapse at $\sim$110 kbar, in disagreement with experiments. Furthermore, our calculations show that itinerant $5f$ electrons favor low-symmetry structures, just as in the light actinides.[5] In the following section we will discuss the basic electronic structure, to try to distinguish features that favor these open structures.

IV. ELECTRONIC STRUCTURE

The calculated density of states (DOS) of Am in the fcc and α-U structures are displayed in Fig. 3. The DOS was generated at a volume of 13.6 Å^3. The upper curve is the total DOS and the shaded area is the $5f$ partial DOS. The α-U structure has two atoms per cell, but since these atoms have almost identical $5f$ partial DOS, we show the contribution for only one of them in Fig. 3. Notice that the total DOS is dominated by the $5f$ contribution (cross-hatched area) and that at these volumes the $5f$ (and total) bandwidth is fairly large, $\sim$5 eV. The bandwidth at these volumes is comparable to the zero-pressure bandwidths of some of the light actinides and the transition metals. It is therefore not surprising that, at these volumes, $5f$ bonding has overcome localization energies due to spin polarization.[18] Notice in Fig. 3 that the bandwidths of the fcc and α-U structures are quite similar. The main difference between the two structures is that the DOS of the α-U structure has fewer sharp features, such as van Hove singularities. The low-symmetry, α-U structure has fewer degenerate bands and therefore shows a more smeared DOS. This can be seen more clearly in Fig. 4, where we plot the energy bands that correspond to the DOS in Fig. 3. Notice also that at these contracted volumes the $7s$ band has moved up in energy, so that the lowest eigenvalue in the fcc structure is not at the Γ point but at the X point, and has mostly $6d$ character. Similarly, in the α-U structure the lowest eigenvalue is not at the Γ point but between the Y and T points. This type of effect was first noticed for transition-metal systems, where it is referred to as an $s \rightarrow d$ transfer.[19] For actinides the notation should be $s \rightarrow d,f$ transfer.

The conclusion from Figs. 3 and 4 is therefore that the α-U structure has a broader DOS, with fewer degenerate bands. This structure also has the lower energy of the

two. A plausible argument for this is that degeneracies in the partially occupied $5f$ bands of the fcc structure may be broken by lowering the crystal symmetry. Occupied, degenerate states, in the fcc phase, which are close to E_F can therefore lower the total energy by lowering the crystal symmetry, since by doing this one band is pushed up above E_F (and therefore does not contribute to the total energy) and one band is pushed down, lowering the total energy. For the lower-symmetry structure to be favored, this gain in energy must be greater than the loss of Madelung energy due to the lowered symmetry.

V. CHARGE-DENSITY CONTOURS

In Fig. 5 we show the calculated charge-density contours for the two structures at the above-mentioned volume. The total density is shown in the upper part of the figure. In the lower part of the figure we have plotted the density obtained when subtracting the spherical-averaged density from the muffin-tin region and the planar-averaged part from the interstitial. The density shown in the lower part of the figure therefore shows some discontinuities, since the spherical component inside the muffin tins does not equal the interstitial planar average. These discontinuities are, of course, absent in the plot of the total density (upper figure). Both the fcc and α-U contour plots are cuts in the (100) planes. Notice that the interstitial density is much less symmetric in the α-U structure. Here the three almost-spherical features in the interstitial reflect the atoms lying one crystal plane below the plane in which the cut was made. In contrast, the interstitial density of the fcc structure is quite featureless and flat. The nonspherical component of the charge density inside the muffin-tin spheres is quite

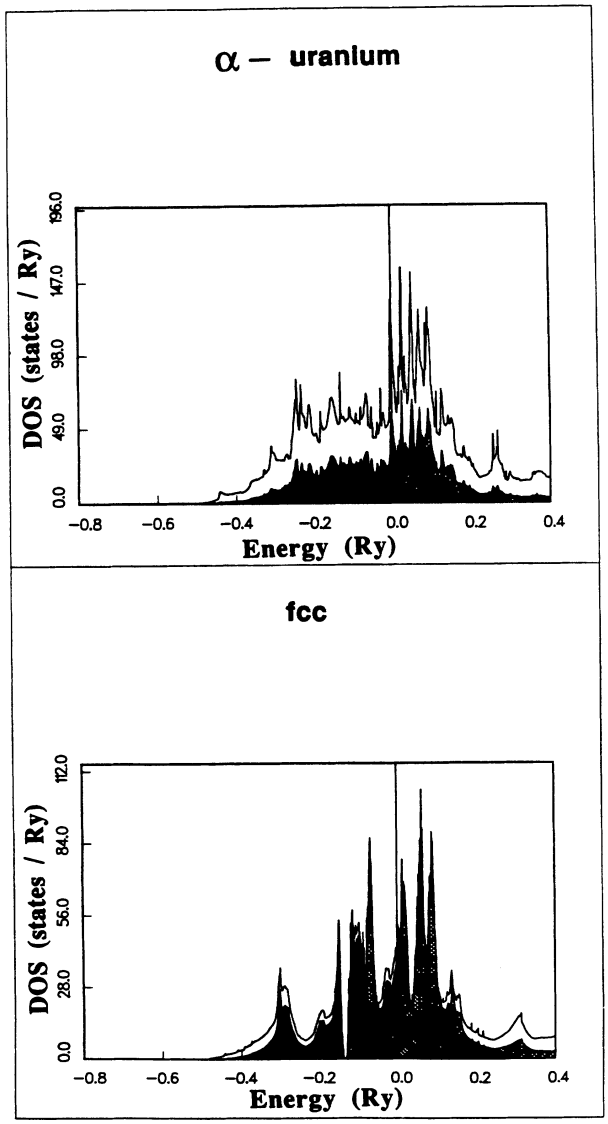

FIG. 3. Calculated DOS for Am in the fcc (lower curve) and α-U structure (upper curve). Energies are in eV and the Fermi level is at zero and is marked with a vertical line. The cross hatched area represents the $5f$ partial DOS.

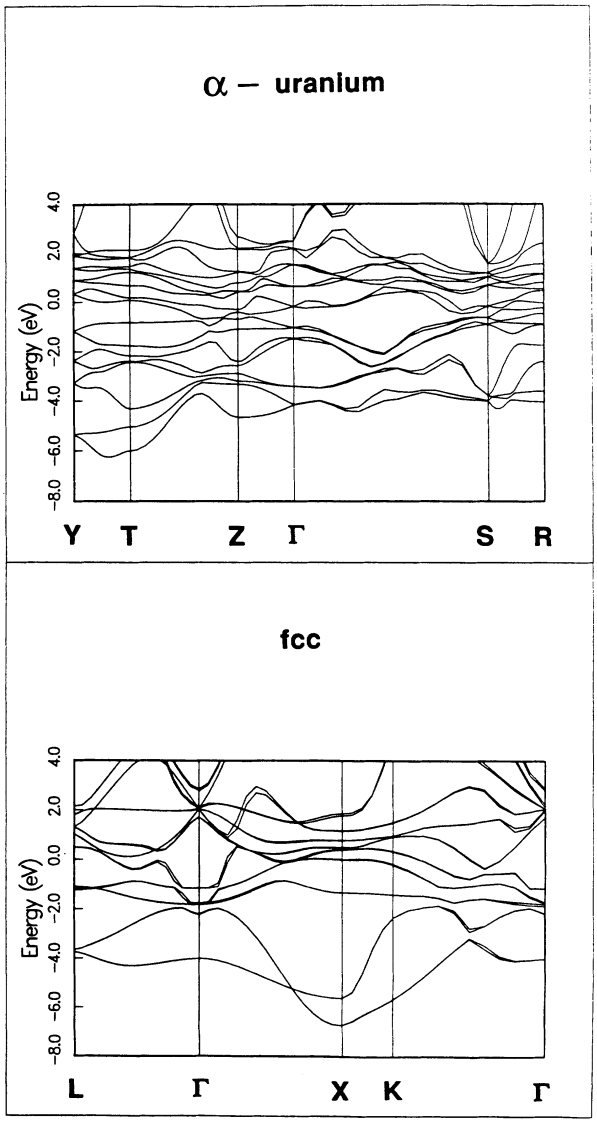

FIG. 4. Calculated energy bands for Am in the fcc (lower curve) and α-U structure (upper curve). Energies are in eV and the Fermi level is a zero.

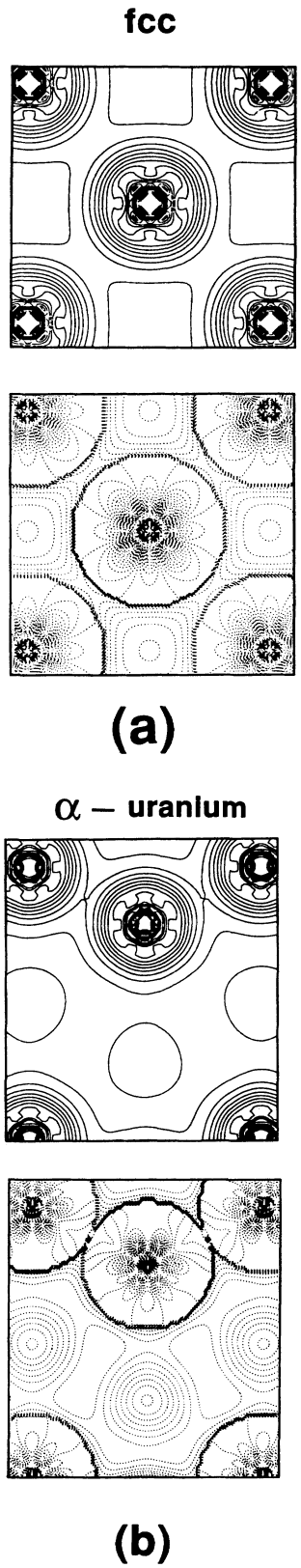

FIG. 5. Charge-density contours (in e^-/a.u.^{3}) for Am in the (a) fcc and (b) α-U structure. The total density is shown in the upper part and the nonspherical density in the lower part. The spacing between the solid lines is 0.07, and between the dotted lines it is 0.01.

pronounced both in the fcc and the α-U structure. This is because the $5f$ electrons are substantially localized within the muffin-tin spheres and the f spherical harmonics have a multidirectional character. The nonspherical contribution of the $5f$ density is larger in Am than in the light actinides[5] due to the greater number of $5f$ electrons in Am. The number of $5f$ electrons in the present calculations on Am is approximately 6 for all volumes, with slightly larger $5f$ occupation for the lower volumes.

VI. CONCLUSION

The present work reports on the total energy of Am in the fcc and α-U structures as a function of the Wigner-Seitz radius, obtained from a very accurate computational technique.[14] The calculations have no shape approximation to the charge density or potential, and the only approximations made are (i) truncation in basis functions and in the expansions of potentials and densities (we have been quite careful in checking the convergence of these) and (ii) perhaps most important of all, the local density approximation for treating exchange and correlation. Our calculated results, combined with the earlier work of Skriver, Johansson, and Andersen,[2] *give a ~34% volume collapse at 110 kbar,* in disagreement with experimental data but in good agreement with previous theories, as well as theoretical and intuitive ideas about $5f$ delocalization.

There are two possibilities for the observed disagreement. The present results show either that LDA cannot explain the high-pressure phases of Am, or that the measured equation of state at these pressures is wrong. Clearly, using LDA for narrow-band systems can be doubtful. On one hand, calculations based on LDA for the earlier actinides yield good agreement for the lattice constants,[2] the cohesive energies,[2] the bulk moduli,[2] as well as the crystal structures.[5] On the other hand, calculations on the high-temperature (fcc) phase of Pu, the δ phase, do not reproduce the lattice constant with sufficient accuracy.[20,5] Namely, the calculated volume obtained for fcc Pu is close to the α-Pu volume, and much smaller than the volume of the δ phase. It has been suggested that the phonon pressure stabilizes this phase of Pu.[20] Also, calculations of δ-Pu at the experimental volume give a spin-polarized ground state,[2,21] which has not been observed experimentally. The present results might be a similar breakdown of LDA, in describing the electronic structure of Am at higher pressures. However, the calculated bandwidth of δ-Pu at the experimental volume is only $\sim$2.5 eV broad, whereas the bandwidths for the early actinides at the low-temperature volumes are larger, $\sim$4–5 eV. The bandwidth of Am at volumes corresponding to where the α-U structure is stable is comparable to the earlier actinides at the low temperature, and it is known that for these systems LDA works rather well.[2,3,5] It would therefore seem that LDA should be able to describe the electronic structure, and the equation of state, reasonably well for Am at these volumes.

The other possible reason for the large disagreement between experiment and the present theory might be that the measured x-ray data on Am is not quite compatible

with the α-U structure, and that the high-pressure phase has a different structure and volume. This was pointed out in Ref. 10; not all of the measured data could be fitted assuming the α-U structure. If the wrong structure was used to fit the experimental data, the corresponding volume is also wrong.

The present results do support the experimental suggestion that the high-pressure phase of Am has delocalized $5f$ electrons. If the high-pressure phase of Am is trivalent (and therefore a $6d$ metal), the reported experimental, and the present theoretical, low-symmetry crystal structure (α-U) is highly anomalous. It is known that d electrons favor bcc, fcc, hcp, or related structures.[12] Also, experimental data on Cm, Bk, and Cf (where a volume collapse is associated with the transition to low-symmetry structures, and where the high-pressure phase is believed to have delocalized $5f$ states) give the expectation that the high-pressure phase of Am also has delocalized $5f$ electrons.

We finally note that more work (both theoretical and experimental) is desirable for the high-pressure phase of Am, since we cannot rule out the possibility of LDA not being applicable for describing this phase. If our results (and the results of Ref. 2) are shown to be accurate by comparing with other theoretical approaches, the experimental data must be questioned.

ACKNOWLEDGMENTS

One of us (O.E.) is grateful to Börje Johansson, Uppsala, for suggesting this problem. We also want to thank A. M. Boring for a critical reading of this paper. The support from the Nuclear Materials Division at Los Alamos is highly appreciated. Valuable discussions with Bob Albers and B. R. Cooper are acknowledged.

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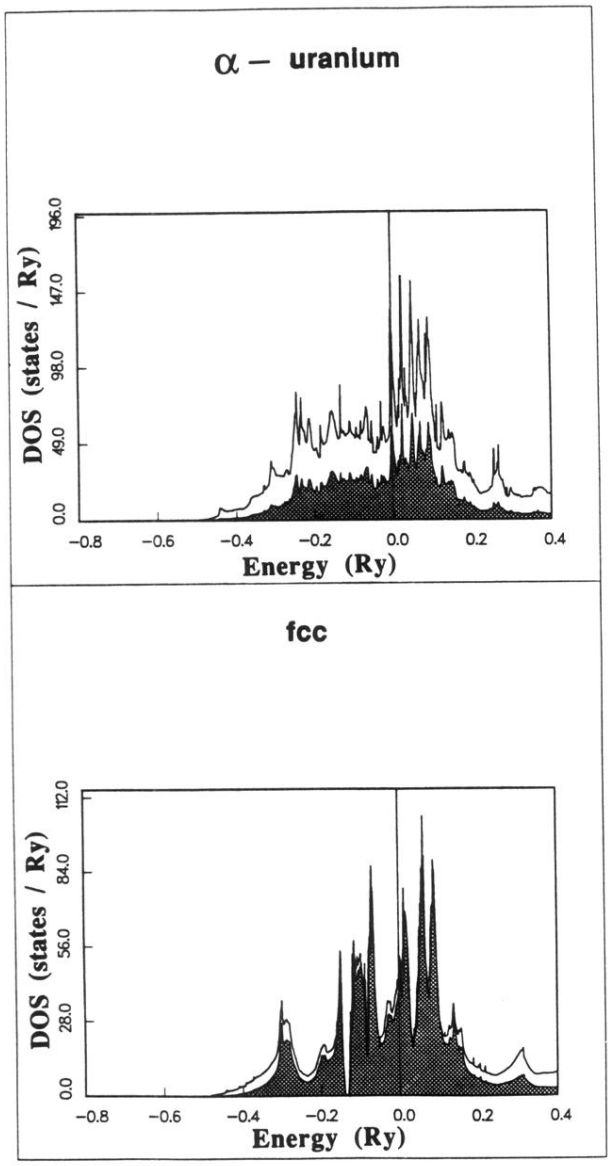

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