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Delocalization and new phase in americium: Density-functional electronic structure calculations

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Density-functional electronic structure calculations have been used to investigate the high pressure behavior of Am. At about 80 kbar (8 GPa) calculations reveal a monoclinic phase similar to the ground state structure of plutonium (α-Pu). The experimentally suggested α-U structure is found to be substantially higher in energy. The phase transition from fcc to the low symmetry structure is shown to originate from a drastic change in the nature of the electronic structure induced by the elevated pressure. A calculated volume collapse of about 25% is associated with the transition. For the low density phase, an orbital polarization correction to the local spin density theory was applied. Gradient terms of the electron density were included in the calculation of the exchange/correlation energy and potential, according to the generalized gradient approximation. The results are consistent with a Mott transition; the $5f$ electrons are delocalized and bonding on the high density side of the transition and chemically inert and nonbonding (localized) on the other.

I. INTRODUCTION

Americium belongs to the series of actinide metals. These elements have received considerable interest because of their nuclear properties but also because of their fascinating ground state electronic properties. The latter are perhaps best illuminated by their crystal structure and atomic volume behavior.[1] The crystal structures of the actinides are different from almost any other metal in the periodic table. Although the first two actinides, Ac and Th, have the fcc crystal structure, the crystal structures of the next four, Pa, U, Np, and Pu, show an increasing complexity, with plutonium attaining a monoclinic (16 atoms/cell) structure. Continuing in the actinide series a most peculiar observation is made; Am (next to Pu) has a close-packed crystal structure (dhcp) similar to the structure of the rare-earth metals and not at all similar to the open and low symmetry structures exhibited by the preceding actinides. The metals beyond Am also follow the example of Am with high symmetry and close-packed structures. Hence, the trend in the crystal structures is completely broken down between Pu and Am. As regards the atomic volumes, the behavior of the light actinides, up to Pu, is similar to that of the nonmagnetic d transition metals; the atomic volume decreases in a parabolic manner[2] as we proceed through Th, Pa, U, Np, and Pu. Actually, the volume of Pu is almost identical to that of Np. Again, we find a complete breakdown of this trend when continuing through Am, Bk, and Cf. The atomic volume of Am is about 40% larger than that of Pu and the following metals have also a much lower density than U, Np, and Pu. Thus, the trends of two important ground state properties, the crystal structure and the atomic volume, display a most obvious interruption between Pu and Am. Americium and the metals beyond form a second rare-earth series. Another key distinction between the itinerant and localized regimes could be attributed to the possible formation of magnetic moments on the f-electron sites. Generally, the localized phase of an f-electron metal shows magnetic ordering at low temperatures according to Russell-Saunders coupling for a free ion. However, for Am, the $f^6(J=0)$ ion configuration cancels the magnetic moment so that the localized phase cannot be distinguished from the itinerant phase by considering their respective magnetic properties.

The actinide metals are the first elements to populate the $5f$ orbitals in the periodic table. None of the electrons in Ac occupy a $5f$ state but the next element, Th, has a non-negligible amount of filled $5f$ states.[1,3] Proceeding through the actinide series the $5f$ occupation increases by about one electron per element and Pu has a total of about five and Am about six $5f$ states filled.[1] The experimental observations outlined in the previous paragraph could best be explained by a dramatic change in the electronic structure between Pu and Am. Specifically, it is believed that the $5f$ electrons of the lighter actinides, Th–Pu, have metallic or itinerant character greatly influencing the bonding characteristics, whereas for the heavier actinides, Am and on, the $5f$ electrons are localized and of minor importance for the chemical bonds between atoms in the solid. This makes sense because, first, the crystal structures of Am, Bk, and Cf are very similar to the rare-earth crystal structures, which in turn have been shown to originate from the bonding characteristics of their d electrons.[4] Secondly, the parabolic decrease of the atomic volume of the actinides up to Pu could be understood from consecutive filling of bonding (itinerant) $5f$ states, gradually increasing the interatomic bonds through Th–Pu, whereas the jump in volume to Am could be explained by the removal of some of the $5f$ contribution to the chemical bonding between the atoms. Hence, there is a transition between

TABLE I. A compilation of EOS data for americium. The equilibrium volume is given in Å^3 and the bulk modulus B in kbar. fcc results are obtained from spin polarized calculations including orbital polarization (GGA+OP) and with the $5f$ electrons treated as core electrons ($5f$ in core).

Crystal structure	V_0	B	B'
fcc (GGA+OP)	25.1	430	2.9
fcc ($5f$ in core)	26.6	460	3.4
α-Pu	16.9	1790	8.0
α-Np	17.0	1990	5.8
α-U	17.1	1540	5.7
α''	17.8	1210	6.4
bcc	16.5	1560	6.5
dhcp (expt)	29.3	400–450	6.0
fcc (expt)	29.3	294	3.0

Pu and Am that originates from a localization of the $5f$ electrons,[5] a so-called Mott transition. In fact, it has been argued[6] that such transitions already take place, partially or completely, in the phase diagram of Pu. At higher temperatures and expanded volumes a fcc phase (δ) of Pu shows similarities to both α-Pu and Am, and this may signal a Mott transition within Pu's phase diagram initiated by external parameters (pressure and temperature). This is to some extent in line with the picture of a Mott transition in Am (delocalization of the $5f$ electrons), induced by external pressure. Experimentally this has also been suggested in connection with the discovery of a low symmetry phase in Am at elevated pressure.

The experimental situation has been somewhat confusing for Am, arising from discrepancies in x-ray experiments. The equilibrium dhcp, structure (AM I) has not been a subject of controversy, but the second phase (AM II), fcc, has been observed at different pressures. Akella *et al.*[7] found a 50% mixture of dhcp and fcc at 52 kbar (5.2 GPa) and only fcc at 65 kbar. Roof *et al.*,[8] observed the same structural changes at similar pressures. Benedict *et al.*,[9] on the other hand, observed the dhcp up to 65 kbar. For the third phase, Am III, both Akella and Roof reported some variant of a monoclinic structure (α'') and they both suggested that AM IV had an orthorhombic sturcture (α', *α-U*). Later, Benedict and Dabos[10] observed dhcp up to 90 kbar and fcc at 95 kbar. Benedict also reported the AM IV phase as an orthorhombic structure (*α-U*) at about 150 kbar.[11] In this latter publication[11] various results for the bulk modulus and its pressure derivature were quoted and an average of $B_0=294$ kbar and $B_0'=3.0$ was calculated. These are the experimental results we have quoted in Table I. Even though there seems to be an experimental agreement regarding AM IV, the third phase of AM (Am III) has proven to be very difficult to characterize and several structures have been proposed for this phase. Different monoclinic structures, trigonal distorted fcc, and orthorhombic structures have all been suggested for Am III.[7–10] Benedict[11] concluded from his measurement that the Am III→Am IV transition took place at 150 kbar (15 GPa).

The motivation for the present study is mainly twofold. First, we believe that the new phase in Am proposed experimentally[8,11] (α-U) is questionable. Recently[12] the complex structures of the actinides were analyzed in terms of a simple model involving Pettifor's structural energy difference theorem.[13] These model calculations suggested that a likely candidate for the new phase in Am would be the monoclinic structure of α-Pu whereas the orthorhombic α-U structure was less likely. In the present study we calculate the total energy for several crystal structures, including those of α-U and α-Pu, in order to investigate this aspect further. Secondly, previous attempts at describing the Mott transition in Am from first-principles theory[14,15] have been less satisfactory in reproducing the details of the experimental data. In the present study we use improved theory with better approximations for the exchange/correlation energy and potential and we also introduce an orbital polarization (OP) correction to the exchange/correlation functional.[16,17] This scheme [generalized gradient approximation (GGA)+OP] was applied[18] for the Mott transition in Pr and compared favorably with self-interaction corrected local spin density theory (LSD-SIC) and experiments. Generally, density-functional calculations with a local spin density approximation are not able to accurately account for electron correlations that lead to localization effects of the electronic structure. This is a challenging problem and many attempts have been made to correct for this.

The localized (low density) phase of Am is here treated in the fcc crystal structure because this structure has been determined experimentally[11] for moderate pressures of Am and the body of experimental data is consistent for this structure. The transition from dhcp to fcc has been shown to be related to the *d*-band occupation in Am and involves only a few meV, and we do not consider this transition here. In the OP scheme the $5f$ localization is associated with the onset of a nearly saturated magnetic spin and orbital moment. The spin polarization energy is included in the LSD approximation and does not constitute a serious problem. The orbital polarization, however, is an effect that is present in open-shell Hartee-Fock theory and not in the LSD approximation. Here this effect is included through an energy shift of the $5f\{l,m_l,\sigma\}$ orbital equal to $-L_\sigma m_l E_\sigma^3$, where L_σ is the orbital moment for spin channel σ and E_σ^3 is the Racah parameter. When calculating the total energy an amount of $-1/2E_\sigma^3 L_\sigma^2$ is added to correct for double counting. The fcc phase of Am was treated in this way, whereas the calculations for the other structures of Am were paramagnetic with no spin or orbital moments.

The following sections contain computational details, results, and a discussion.

II. CALCULATION DETAILS

The total energy for the fcc, bcc, bcm (α''), α-U (α'), α-Np, and α-Pu structures[19] of americium was calculated as a function of volume. The α-U structure is orthorhombic with axial ratios $b/a=2.05$ and $c/a=1.76$ and an internal parameter $y=0.1125$. For this phase we made an effort to optimize these three parameters. The b/a was first optimized, and for that optimized value, the c/a was optimized. In a third step the internal parameter y was optimized. As a final step b/a and c/a were again allowed to relax for this new y. The α'' structure is a body centered monoclinic structure for which we chose $c/a=1.53$ and $b/a=1.03$ with the

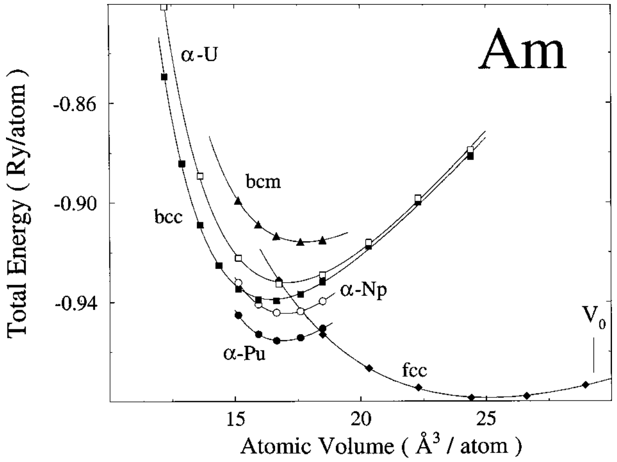

FIG. 1. Total energies (+61046 Ry/atom) for Am in the bcc, fcc, α'' (bcm), α-U, α-Np, and α-Pu structures. The fcc phase is calculated using spin and orbital polarization. The other structures are calculated assuming spin degeneracy. The ratios between the crystal structure parameters for the α'', α-U, α-Np, and α-Pu structures are kept equal to their equilibrium values for Ce (proposed), U, Np, and Pu.

angle β between the *a* and *c* axis equal to 92°. This is the same structure as was proposed by Olsen *et al.*[20] in the phase diagram of cerium. The α-Np structure is orthorhombic ($b/a=4.72$, $c/a=1.03$) with eight atoms per unit cell and the most complex, α-Pu, structure is monoclinic with 16 atoms per unit cell. For these calculations we used the full potential version of the linear muffin-tin orbital method.[21] This electronic structure method is an implementation of density-functional theory as applied for a bulk material. It is a first-principles method; no experimental numbers are used in the calculations except for the nuclear charge, which is 95 for Am. The approximations in this approach are limited to the approximation of the exchange/correlation energy functional, cutoffs in the expansion of basis functions, *k*-point sampling in integrations over the Brillouin zone, and the Born-Oppenheimer approximation. For the exchange/correlation approximation we used the generalized gradient approximation which has proven to be better for *f*-electron metals than the more commonly used local density approximations. In all calculations we used two energy tails associated with each basis orbital and for $6s$,$6p$, and the valence states ($7s$, $7p$, $6d$, and $5f$) these pairs were different. With this ''double basis'' approach we used a total of six energy tail parameters and a total of 12 basis functions per atom. Spherical harmonic expansions were carried out through $l_{\max}=6$ for the bases, potential, and charge density. The sampling of the Brillouin zone was done using the special *k*-point method[22] and the number of *k* points we used was 175 (fcc and bcc), 75 (α''), 52 (α-U), 72 (α-Np), and 16 (α-Pu). Hence, the calculation for Am in the α-Pu structure was identical to the calculation we performed for plutonium recently,[23] with the exception of the atomic number (95 instead of 94). Total energy calculations were carried out for each crystal structure as a function of volume. These energies were then fitted to a Murnaghan equation of state (EOS) which enabled us to calculate the Gibbs free energy

$$G=E+PV-TS=H-TS \tag{1}$$

for the considered structures of Am. Here *H*, *S*, and *E* are the enthalpy, entropy, and internal energy of the system. In our calculations $T=0$ and *E* is the total (electronic) energy. A phase transition between the two phases occurs if their Gibbs free energy coincides for a given pressure. Using the EOS (pressure as a function of volume) for the two phases, we are able to calculate the volume collapse associated with the transition.

III. RESULTS

Our main results are shown in Fig. 1. Face-centered cubic Am is calculated allowing for both spin and orbital polarization (GGA+OP) whereas the calculation of the other structures assumes spin degeneracy. As can be seen immediately, the experimentally suggested α-U phase is considerably higher in energy than the α-Pu phase, and even the bcc structure is lower in energy. This indicates that this structure is incompatible with the calculated electronic structure of Am and it seems to be a very unlikely candidate for a delocalized phase in Am. This conclusion is supported by calculations aimed at optimizing the b/a, c/a, and y parameters of this orthorhombic structure. This optimization lowers the minimum energy by about 7.5 mRy/atom (not shown) and introduces a large distortion of the cell. New optimized values for the parameters are $b/a=1.75$, $c/a=1.75$, and $y=0.10$. This large distortion suggests that the α-U structure is mechanically very unstable for Am and therefore not a candidate as a stable phase. The relaxation brings the orthorhombic (now very different from α-U) structure close to the bcc structure, but nowhere near the α-Pu structure. The transition to the lowest energy structure, the monoclinic (α-Pu) structure, is calculated to occur at about 80 kbar (8 GPa) and the volumes are 21.8 Å^3 and 16.3 Å^3 for the fcc and the monoclinic phase, respectively. The transition pressure is somewhat lower than the values (150–175 kbar) previously suggested by experimental work.[11] The calculated 25% volume collapse is somewhat lower than what has been calculated previously[15] (34%), where the α-U structure was assumed to be the high pressure structure, but considerably larger than the experimentally observed volume collapse between Am II and Am III.[11] In Fig. 2 we show the corresponding EOS for our total energy calculations as obtained from our Murnaghan fits. Together with these results we also plot some experimental data.[8,11] The theoretical curves are fcc and monoclinic (α-Pu), respectively, whereas the experimental data represent Am I (dhcp), Am II (fcc), and Am III (α''). The pressure is plotted as a function of V/V_0 for all data. The theoretical V_0 depends upon which phase is considered, but here we decided to chose $V_0=26.85$ Å^3, which is rather close to our (fcc in core) calculation (see below). This is also the theoretical equilibrium volume obtained from spin polarized GGA calculations (not shown) of dhcp Am and therefore seems to be an appropriate choice. The quantitative behavior is very similar between theoretical and experimental data. Close to the theoretical transition pressure, 80 kbar, the fcc calculations agree very well with experimental Am II (fcc) data as does our α-Pu calculation with experimental Am IV (α') data. At lower pressure (close to zero) there is a discrepancy between theory and experiment that is rather serious. The equilibrium volumes, bulk moduli, and pressure

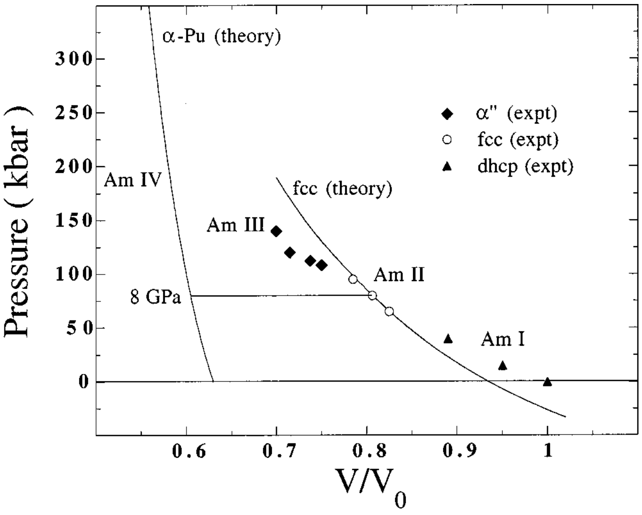

FIG. 2. Equation of state as obtained from Murnaghan fits to the total energies for fcc and monoclinic (α-Pu) structures. Results indicate a volume collapse of 25% at 80 kbar (8 GPa) pressure from the fcc to the monoclinic phase.

derivative of the bulk modulus are give in Table I. The fcc (GGA+OP) calculation gives an equilibrium volume too low compared to the experimental dhcp equilibrium volume. For comparison, we corrected for this discrepancy in the equilibrium volume by shifting the total energy curve so that B and B' were unchanged but the equilibrium volume was identical to the experimental value 29.3 Å^3 (not shown). In this case, the Mott transition already occurs at about 44 kbar and the volume collapse increases to about 40%. Hence, correction for this discrepancy does not improve our theoretical agreement with experiment. It is unclear how to compare our theoretical transition pressure (80 kbar) with experimental data because there is a large hysteresis in the experiments. It may be interpreted that our transition occurs too early at 80 kbar. This might be due to an underestimated total energy gain associated with the localization of the $5f$ electrons in our calculations. Therefore, in another comparison, we artificially lowered the total energy curve for the (GGA+OP) calculation by 14 mRy (0.2 eV) and this resulted in a transition pressure close to 150 kbar (15 GPa) with, still, a considerable 20% volume collapse. The calculated (GGA) zero-temperature equilibrium volumes of Ce and light actinides[24,25] (Th–Pu) are on average about 7% smaller than measured room temperature data. It therefore seems likely that the itinerant monoclinic phase (α-Pu) of Am also has too low a calculated equilibrium volume in the present calculations. The equilibrium volume is calculated to be 16.9 Å^3. If we introduce a correction so that the monoclinic phase obtains a 7% larger equilibrium volume, we instead obtain a transition pressure of about 100 kbar (10 GPa) and a volume collapse of about 18%. This correction gives a somewhat better agreement with experiment for the transition pressure, whereas the calculated volume collapse is rather insensitive to this correction.

Experimentally[8,11] an orthorhombic (α-U) structure at about 150 kbar (15 GPa) was proposed in Am. In our calculation this orthorhombic structure (with $b/a, c/a$, and atomic coordinate y set equal to their equilibrium values for uranium) is substantially higher in energy than the monoclinic phase, and provided our description of the electronic structure is accurate, we therefore rule out the orthorhombic phase in the high pressure/low temperature phase diagram of Am. If, hypothetically, a transition to the α-U phase took place, completely neglecting the monoclinic (α-Pu) phase, the transition is calculated to occur at about 200 kbar (20 GPa) accompanied by a volume collapse of about 21%.

In Table I we summarize our EOS data for the calculated crystal structures. The Murnaghan fit of fcc Am gave a bulk modulus (B) of about 430 kbar (43 GPa) and a B' equal to 2.9. The equilibrium volume is too low, only 25.1 Å^3 compared to the observed volume of 29.3 Å^3, but the bulk modulus is in rather good agreement with experiment. Our calculations underestimate the equilibrium volume by about 14%, which may indicate that the $5f$ contribution to the chemical bond is overestimated in our GGA+OP scheme at lower pressures. The large discrepancy for the equilibrium volume is a serious failure of the theory, but is consistent with the results found for Pr recently,[18] where the difference between theory and experiment for the equilibrium volume was about 14%. It is possible to remove most of the $5f$ bonding by putting these electrons *ad hoc* as core electrons. In Fig. 3 we compare calculations for fcc Am (GGA+OP) with nonpolarized (GGA) calculations with the $5f$ electrons treated as core electrons ($5f$ in core). The ($5f$ in core) calculation is shifted down an amount 0.17 Ry (2.3 eV) to allow a clearer comparison between the two energy curves. The equilibrium volume for the ($5f$ in core) calculation is in somewhat better agreement, 26.6 Å^3, but still almost 10% too low compared to experiment. The corresponding bulk modulus is about 460 kbar (46 GPa), in rather close agreement with our (GGA+OP) calculation. B' is also in good agreement with the (GGA+OP) theory, 3.4 compared to 3.0. From Fig. 3 we conclude that for the volume range close to equilibrium the two theoretical treatments (GGA+OP) and ($5f$ in core) are in relatively good agreement, with a small discrepancy of about 4% in their respective equilibrium volumes. Notice, however, that for compressed volumes the total energy curves begin to separate between the two calculations. This is certainly expected because the ($5f$ in core) treatment should become less satisfactory at higher pressures. We anticipate an increased overlap at smaller volumes between the $5f$ orbitals, which eventually will form band states. At this point, it would of course be grossly inaccurate to treat them as core states. This effect is inherent in the (GGA+OP) theory where a suppression of the magnetic moments signals delocalization.

In Fig. 4 we show the spin, orbital, and total magnetic moments as a function of atomic volume for fcc Am calculated using the (GGA+OP) approach. The symbols represent the calculations, the full line here is a guide for the eye only. The orbital moment is enhanced by the orbital polarization of the $5f$ orbitals and at the equilibrium volume it is about -0.85 Bohr magnetons. The majority contribution to the orbital moment is traced to the $5f$ spin-down states (-0.93) with a small contribution also from the $6d$ spin-down (0.13) and spin-up (-0.05) states. With the orbital polarization switched off the orbital moment is smaller in magnitude (-0.65 Bohr magnetons). The $5f$ band is less than half full and therefore the sign of the spin-orbit coupling (corresponding to Hund's third rule of an open-shell atom)

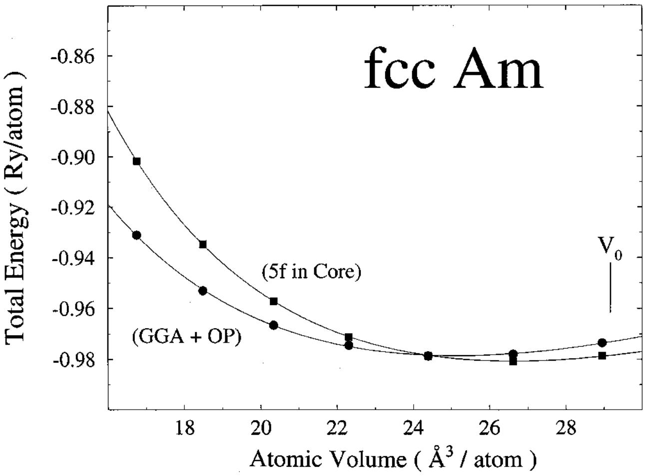

FIG. 3. Two different treatments of the localized fcc phase of Am. The (GGA+OP) treatment, used in the present calculations, compared to a calculation where the $5f$ electrons are treated as core electrons. The latter calculation is shifted down an amount of 0.17 Ry (2.3 eV) to enable a more visual comparison.

turns the orbital moment antiparallel to the spin moment. The total and spin magnetic moments slowly decrease in magnitude with volume, whereas the orbital moment is almost constant until about 17 Å^3 where both spin and orbital moments collapse to zero. This signals a complete $5f$ delocalization in Am, and $5f$ band states that contribute to the chemical bonding between atoms. At this volume the $5f$ states in Am are itinerant, as in the lighter actinides, Th–Pu. Magnetic calculations for Am in the α-Pu structure collapse to nearly zero magnetic moment (not shown), confirming this picture. Consequently, in this paramagnetic regime (Fig. 1), fcc Am is the most unfavorable structure and instead the monoclinic (α-Pu) structure has the lowest energy. This result confirms the simple model calculations carried out by Söderlind *et al.*[12] who showed that for a $5f$ band occupation of about six, the α-Pu structure should be lower in energy than both the α-U and fcc structures.

The orbital polarization energy, the $1/2E_{\sigma}^{3}L_{\sigma}^{2}$ term, was of the order of 2–7 mRy throughout the volume range studied. The Racah parameter E_{σ}^{3} is a linear combination of Slater integrals and was in our calculations for Am of the order of 4–6 mRy. Calculations without orbital polarization gave a somewhat lower transition pressure (65 kbar) and a somewhat larger volume collapse (28%).

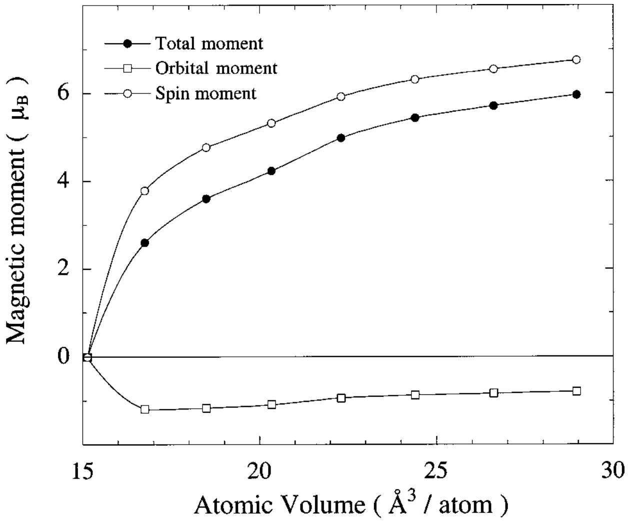

FIG. 4. Spin, orbital, and total magnetic moments (Bohr magnetons) as obtained from the (GGA+OP) calculation of fcc Am.

IV. DISCUSSION

We have studied six crystal structures of Am with a first-principles method using the (GGA+OP) scheme. The total energy for five of these structures (bcc, bcm, α-U, α-Np, and α-Pu) was calculated assuming spin degeneracy whereas for the fcc structure, this requirement was lifted. At 80 kbar we calculate a transition from fcc Am to monoclinic Am and a volume collapse of 25%. We interpret this transition as a Mott transition; the onset of a low symmetry crystal structure is prompted by delocalization of the $5f$ electrons in Am. The low density fcc phase is also modeled by a calculation with the $5f$ electrons occupying core states. For low pressures this rather *ad hoc* approximation is in relatively good agreement with the (GGA+OP) calculations, with a very similar B and B' but a 4% larger equilibrium volume. With increasing pressure the treatment with $5f$ electrons in the core becomes gradually inappropriate, with an inaccurate total energy as a result.

Calculations of the transition pressure between fcc and monoclinic Am are sensitive to the accuracy of the total energy for both the localized and the itinerant phase. The transition pressure would be considerably higher and the volume collapse smaller if the equilibrium volume for the monoclinic phase was 5–10 % larger. This is certainly within the usual error associated with a GGA calculation for an f-electron metal. The transition pressure would also increase considerably upon a small downward shift (0.1–0.2 eV) of the energy curve for the low density fcc phase. Thus, inaccuracies in the calculations could easily explain the fact that we calculate a transition pressure somewhat lower than the values reported for this transition. A large volume collapse, however, seems relatively insensitive to possible inaccuracies in the total energy calculations and we therefore have confidence in this result. We appreciate the difficulties involved in determine the correct crystal structure from high pressure experiments and the necessary fitting that has to be done. Also, the hysteresis in the experimental results make it hard to directly compare our results with experiment. We believe, however, that Fig. 2 is clear evidence that our technique is able to describe the correct physics of the high pressure transitions in Am. To get a more accurate description overall the exchange/correlation functional needs to be improved.

In the present paper we have investigated the total energy of two different configurations: delocalized $5f$ states and localized, chemically inert $5f$ states. Provided there are no complications involving other electronic configurations, such as mixed valence, Kondo behavior, and so on, we rule out the α-U structure as the high pressure phase of Am. Calculations of the type presented here seldom give the wrong structural stability and in our case we find that the α-U structure is ~20 mRy higher in energy than the lowest energy structure, α-Pu. This is a rather large energy difference. Also the α'' structure, although not relaxed with respect to its internal parameters, shows very high energies compared to the α-Pu structure. As regards the stability of the α-Pu structure, we mention that there are other structure types, not investigated here, which may be lower in energy. However, a blind search for these structures without experimental input is beyond current computational capabilities.

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