

Ground-state electronic structure of actinide monocarbides and mononitrides

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The self-interaction corrected local spin-density approximation is used to investigate the ground-state valency configuration of the actinide ions in the actinide monocarbides, AC (A=U,Np,Pu,Am,Cm), and the actinide mononitrides, AN. The electronic structure is characterized by a gradually increasing degree of f electron localization from U to Cm, with the tendency toward localization being slightly stronger in the (more ionic) nitrides compared to the (more covalent) carbides. The itinerant band picture is found to be adequate for UC and acceptable for UN, while a more complex manifold of competing localized and delocalized f -electron configurations underlies the ground states of NpC, PuC, AmC, NpN, and PuN. The fully localized $5f$ -electron configuration is realized in CmC (f^7), CmN (f^7), and AmN (f^6). The observed sudden increase in lattice parameter from PuN to AmN is found to be related to the localization transition. The calculated valence electron densities of states are in good agreement with photoemission data.

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I. INTRODUCTION

Among the six generation IV reactor technologies that have been chosen to address the future nuclear energy requirements, three are so-called fast neutron reactors.¹ Given their efficient use of existing uranium-ore (fast breeders) and the possibility of burning the higher actinides, i.e., disposing of the nuclear waste produced by existing thermal nuclear reactors, these reactors address a number of concerns surrounding the issue of nuclear energy. As there are no moderators, the fission reactions depend on fast neutrons, requiring a small core with a high power density and very efficient heat transfer. The ongoing research and development is therefore considering possible alternatives to the predominantly oxide based fuels. Both carbide and nitride fuels are being investigated for this purpose given their superior thermophysical properties² such as high melting point, high heavy atom density, and high thermal conductivity, and, with respect to Na cooled fast reactors, good compatibility with the coolant. Compared to the well established oxide fuels, relatively few studies exist regarding the physics and chemistry of these materials. Thus, modeling of the structural and dynamical properties under ambient or operating conditions can provide valuable information concerning fuel performance and stability. In this paper the focus is on ground-state properties where we use density-functional-based total energy calculations to study the electronic structure of the actinide monocarbides and mononitrides.

Due to the onset of $5f$ -electron localization phenomena, the theoretical description of the actinide compounds presents a considerable challenge. While band structure calculations, based on the local spin-density approximation (LSDA) to density-functional theory, are very successful in describing the cohesive properties of itinerant electron systems they have serious problems when dealing with more strongly correlated electron systems. The reason for this is that the exchange and correlation effects underpinning the standard LSDA approaches are those of the homogeneous electron

gas, which cannot account for the strong electron-electron interactions that are inherent to f -electron systems.

In the actinide metals for example, the localization transition that occurs from Pu to Am is not correctly reproduced.³ In the early actinide metals the overlap between f orbitals on neighboring sites results in f -electron delocalization and band formation. However, with increasing nuclear charge the f -orbitals contract with the result that, in the late actinides, the then strongly correlated electrons prefer to remain localized on site. Thus, whereas LSDA based methods give a good description of U and Np, from Pu onward additional assumptions or parameters derived from experiment need to be invoked,⁴⁻⁹ diminishing the predictive power of the approach.

The above *localization/delocalization* crossover greatly influences the phase diagrams of actinide materials. For example, the electronic and magnetic properties of U compounds are very different from those of the corresponding Bk compounds.¹⁰ Even for a given actinide element, its various alloys and compounds can display a wide spectrum of behavior, from localized to itinerant, due to the large effect that small changes in external or chemical pressure have on the f -electron contribution to the chemical bonding. Indeed, Hill¹¹ suggested that, in actinide compounds, the actinide-actinide distance determines the degree of magnetic order through control of the f - f overlap. However, many actinide compounds do not follow the systematics based solely on f -band formation and it has since become clear that f - d and f - p hybridizations are equally important in explaining the electronic and magnetic properties of these compounds.

Experimentally, a large number of actinide compounds crystallizes in the NaCl structure. The monochalcogenides AX (X=O,S,Se,Te,Po) and mononitrides (X=N,P,As,Sb,Bi), as well as the actinide monocarbides, belong to this class of materials. Experimental studies indicate a trend toward f -electron localization with increasing actinide atomic number and increasing anion size. For the actinide carbides and nitrides, the large orbital overlap resulting from small anion size competes with the trend toward

more localized f orbitals as the actinide nuclear charge is increased. The resulting competition between band formation and correlation places these compounds at the borderline of the localization/delocalization transition. Thus, whether a localized or itinerant f -electron model is more adequate to describe these compounds depends on the details of the underlying electronic structure.

To describe the strongly correlated electrons in the actinide carbides and nitrides, we use the self-interaction corrected (SIC) local spin-density (LSD) method.^{12,13} The SIC-LSD method is an *ab initio* approach that corrects for an unphysical self-interaction of atomiclike localized states in the LSD total energy functional.¹⁴ The method has previously been applied successfully to the description of actinide metals and compounds. Because it is based on total energy considerations, the SIC-LSD methodology enables us to predict the ground-state valency configuration of the actinide ion and to describe the localization-delocalization transition that occurs in the carbides and nitrides as the actinide series is traversed.

The balance of this paper is organized as follows. In Sec. II we give a short description of the SIC-LSD methodology (Sec. II A) followed by presentation of results for the Uranium compounds (UN and UC) (Sec. II B), the remaining transuranium compounds (Sec. II C), and for the localization-delocalization transition (Sec. II D). In Sec. III we present a general discussion of our results in the context of other experimental and theoretical work. Finally, in Sec. IV, we present some concluding remarks.

II. ELECTRONIC STRUCTURE OF ACTINIDE CARBIDES AND NITRIDES

A. SIC-LSD

The SIC-LSD energy functional, E^{SIC} , is obtained from the LSD energy functional, E^{LSD} , by subtracting from it an unphysical self-interaction, $\delta_{\alpha}^{\text{SIC}}$, orbital by orbital, for all the occupied orbitals, namely,

$$E^{\text{SIC}} = E^{\text{LSD}} - \sum_{\alpha} \delta_{\alpha}^{\text{SIC}}. \quad (1)$$

Since, for the itinerant (delocalized) electrons the self-interaction vanishes, in practice the above sum runs only over localized orbitals. In the SIC-LSD method both localized and delocalized states are expanded in the same set of basis functions, and are thus treated on an equal footing. Different localized/delocalized configurations are realized by assuming different numbers and combinations of localized states—here f states on actinide-atom (A) sites. Since the different localization scenarios constitute distinct local minima of the same energy functional, E^{SIC} , their total energies may be compared and the global energy minimum then defines the ground-state total energy *and* the valence configuration of the A ion. This latter is defined as the integer number of electrons available for band formation, namely $N_{\text{val}} = Z - N_{\text{core}} - N_{\text{SIC}}$ where Z is the atomic number, N_{core} is the number of core (and semicore) electrons, and N_{SIC} is the number of localized, i.e., self-interaction corrected, states.

We will use either the f^n or the A^{m+} nomenclature to describe the actinide-ion configuration, implying $n = N_{\text{SIC}}$ and $m = N_{\text{val}}$, respectively. Note that the number of f electrons on a given ion may be larger than n , since, in addition to the localized f states, the band states contribute to the total f -electron count.

The SIC-LSD approach has been implemented using the tight-binding linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA).¹⁵ The spin-orbit interaction has been explicitly added to the scalar-relativistic one-particle Hamiltonian, and included in the self-consistency cycle. All the calculations in the present paper have been done for the NaCl structure (observed experimentally), and assuming a ferromagnetic arrangement of the spins. In order to improve the packing, empty spheres have been introduced on high-symmetry interstitial sites. Two uncoupled energy panels have been considered when constructing the LMTO's, with s , p , d , and f orbitals on all spheres. The valence panel includes the $7s$, $6d$, and $5f$ orbitals on the actinide atom, and the $2s$ and $2p$ orbitals on the N and C atoms, with the remaining orbitals downfolded.¹⁶ The semicore panel comprises the actinide $6p$ states, all other channels being downfolded.

B. UN and UC

Given the large extent of the U $5f$ -orbitals, combined with the small radii of the carbide and nitride atoms, UC and UN have always been assumed to qualify for a standard band structure description, with the f -electrons treated as itinerant. Correspondingly, the electronic structure of these compounds has been studied using various band structure approaches.¹⁷⁻²⁴ The resulting values for the lattice parameters of both UC and UN, as well as the elastic constants for UC (Ref. 23) have been found to be in good agreement with experiment.

In the SIC-LSD approach, the LSDA band picture is reproduced when all the f electrons are treated as delocalized [$U(f^0) \equiv U^{6+}$ configuration]. The densities of states (DOSs) corresponding to this configuration are shown in Figs. 1(a) and 1(b) for UC and UN, respectively. The two DOSs are overall very similar, and in agreement with earlier LSDA based calculations, for example by Trygg *et al.* for UC,²³ and by Samsel-Czekala *et al.* for UN,²⁵ where the different features are explained in detail. Thus, we find the electronic structure to be characterized by the overlap of the U- f states with the C/N p -states and dominated by the large narrow U- $5f$ peak situated at the Fermi level. The $2p$ states are situated at slightly lower energy in UN compared to UC, centered respectively around -0.3 Ry in the former, and -0.2 Ry in the latter, relative to the Fermi level, and indicating a relatively larger degree of f - p hybridization in UC.

The results of our total energy minimization as a function of lattice parameter and different localized/delocalized f -electron configurations (including the fully delocalized f^0 configuration) are shown in Figs. 2(a) and 2(b). For UC, in Fig. 2(a), we find the f^0 configuration to be energetically most favorable, confirming that the LSDA based DOS in Fig. 1(a) adequately represents the corresponding electronic

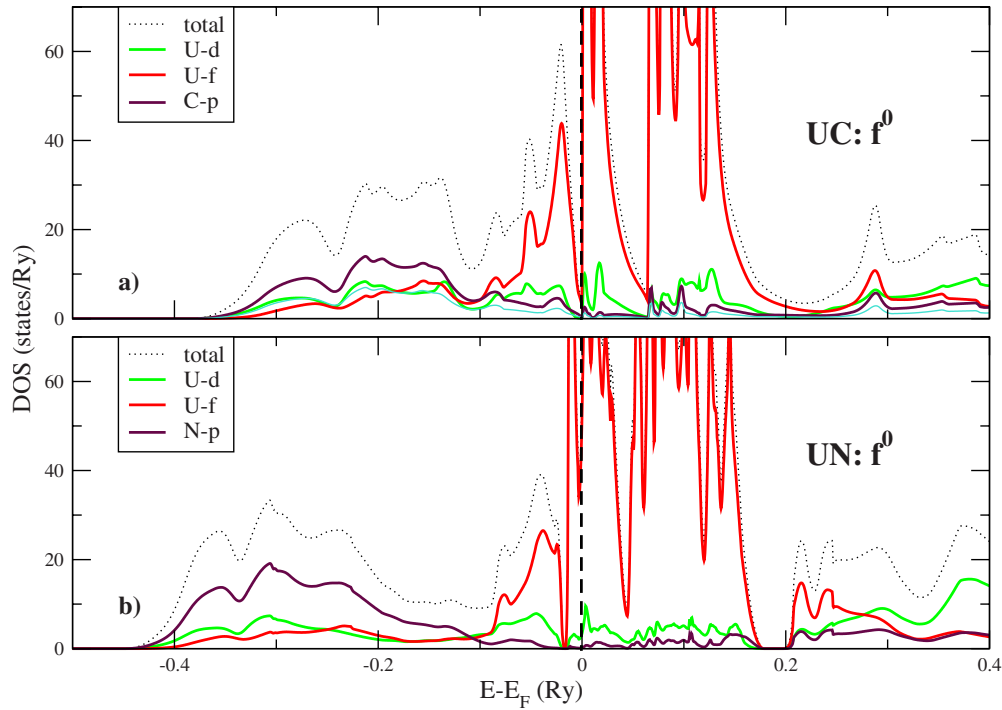


FIG. 1. (Color online) Density of states of (a) UC, and (b) UN in the LSD approximation.

structure. For UN, we find the global energy minimum to occur in the f^1 configuration, as can be seen in Fig. 2(b), indicating that the LSD picture of Fig. 1(b) might not be a good representation of the UN ground state as f -electron localization is starting to set in. The reason for the difference in localization behavior can be traced to the fact that the nitride is more electronegative than the carbide. In the DOS (Fig. 1), compared to the rather considerable p - f overlap in UC, we observe that for UN the p band is situated lower in energy with respect to the Fermi level and a valley develops between the p and f states. With the reduced p - f overlap in UN, hybridization becomes less predominant, the gain in band formation energy is reduced, and the gain in localization energy becomes relatively more important.

There is experimental evidence that supports the picture of increased localization in UN compared to UC. For UC, the calculated Fermi surface in the LSDA agrees well with the measured de Haas-van Alphen frequencies,²² indicating that the $5f$ electrons are indeed delocalized. The XPS and BIS measurements on UC (Ref. 26) confirm this itinerant behavior, but the observation of $4f$ satellites in the spectra indicates that correlations among the $5f$ electrons already have a noticeable effect. The interpretation of experimental results is less straightforward for UN, where it remains unclear whether a localized, delocalized, or dual localized/delocalized picture can best account for the observed properties.^{25,27,28} ARPES studies on UN seem to reveal some degree of localization of the Uf states, with two nondispersive bands detected in the vicinity of the Fermi level,²⁹ compared to a single dispersive band at the Fermi level in UC.³⁰ Specific heat measurements of, respectively, $\gamma = 18.7$ mJ/K² mol for UC, and $\gamma = 49.6$ mJ/K² mol for UN, are a clear indication of considerable renormalization of the f bands by the electron-electron interactions not accounted for

in the LSDA. Results from neutron scattering experiments on UN (Refs. 31 and 32) have similarly been interpreted in terms of highly correlated itinerant f electrons.

Overall, experiment clearly indicates a growing impact of correlations from UC to UN, but it is less obvious whether, combined with a narrowing of the f -peak at the Fermi level, an actual f -electron localization transition will occur. For UN the SIC-LSD calculations do indicate such a transition, however it should be noted that the calculated energy difference, $E_{f^0} - E_{f^1}$, between the f^0 and f^1 configurations is very small. Indeed, this is true both for UC and UN where the respective energy differences are -2 and $+12$ mRy. This approximate degeneracy of configurations implies that the gain in energy from band formation and the gain in SIC energy from localization are of similar magnitude indicating an electronic structure at the border of the localization-delocalization transition. Rather than a fully developed itinerant- f ground state for UC and a localized f^1 ground state for UN, the electronic structure is intermediate between f^0 and f^1 , with the former

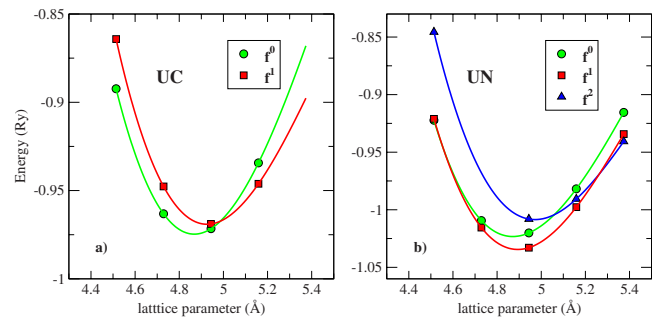


FIG. 2. (Color online) Total energy as a function of lattice parameter for (a) UC, and (b) UN for different localization/delocalization configurations.

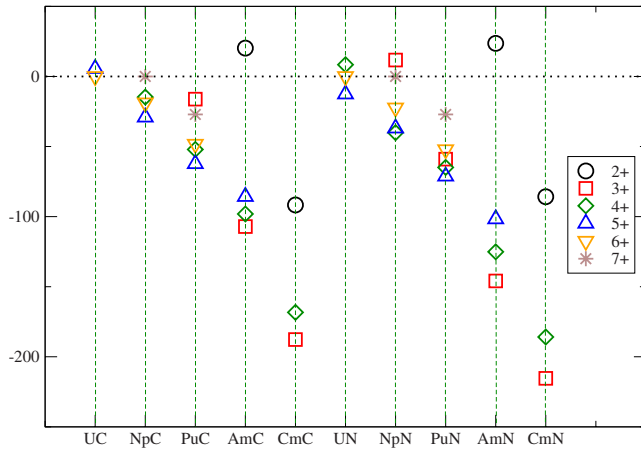


FIG. 3. (Color online) SIC-LSD total energies for the actinide nitrides and carbides from U to Cm. For each compound the energies for a number of different valency configurations are given (in mRy/f.u.) relative to the LSDA total energy.

configuration having relatively more weight in UC and the latter configuration having relatively more weight in UN. In both the f^0 and f^1 cases, a significant amount of itinerant f electrons is found (the total f -electron count is ~ 3.0 for UN and ~ 2.8 for UC) and the LSD description is acceptable. The observed difference in total energies correctly reproduces the increasing influence of electron-electron correlations from UC to UN. However the actual electronic structure of these compounds is more complex than can be reproduced by either the localized or itinerant f limit of the SIC-LSD single Slater determinant wave function, and would need to be addressed by more sophisticated approaches.^{33,34}

C. Transuranium nitrides and carbides

Applying SIC-LSD to the carbides and nitrides beyond U, we observe a trend toward increasing localization with increasing actinide atomic number. The results of our total energy calculations are summarized in Fig. 3. Here, for each of the actinide compounds AC (A=U, Np, Pu, Am, and Cm) and AN, the calculated total energies for a number of configurations are given relative to the LSD total energy. Positive and negative energies, respectively, indicate configurations that are less or more favorable than the fully delocalized scenario. Only for UC is the LSD configuration the ground state, as was discussed earlier. From NpC to CmC, the ground-state valency configuration gradually changes from A^{5+} to A^{3+} . This trend repeats itself from UN to CmN. As expected the increase in nuclear charge leads to the contraction of the $5f$ orbitals, and thereby a decrease in overlap with neighboring sites. The localization energy becomes relatively more important than the band formation energy, leading gradually to the localization of an increasing number of f electrons. A detailed look at the total energies in Fig. 3 reveals that, on average, for a given actinide ion, the nitride displays a lower ground-state valency than the corresponding carbide. Most importantly, a clearly preferred ground-state configuration (a configuration that has a sub-

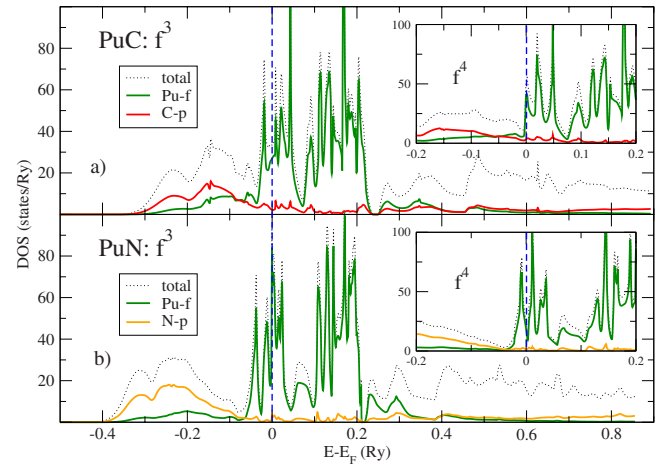


FIG. 4. (Color online) Density of states for (a) PuC in the f^3 configuration, and f^4 configuration (inset), (b) PuN in the f^3 configuration, and f^4 configuration (inset).

stantially lower energy than the rest) emerges in the nitride series for AmN and CmN, for the carbide series such a configuration emerges only for CmC. The electronic structure of the early actinide compounds beyond UN and UC thus remains a complex manifold of different valency configurations, closely separated in energy, with the contribution from the more localized configurations becoming gradually more important relative to the less localized configurations as we move through the actinide series.

We can try to understand this configuration degeneracy on the basis of the DOS for PuC and PuN in Fig. 4. Notice that, in these plots, only the band states are displayed, i.e., the itinerant valence states including the delocalized f states. Specifically, the localized f 's are not shown since the SIC-LSD approach, which, after all, is a one-electron ground-state theory, does not give accurate removal energies of localized states due to electron-electron interaction (multiplet) effects,³⁵ and the neglect of screening and relaxation effects.³⁶ In the SIC-LSD, if a given f state hybridizes strongly with the broad p bands the gain in band formation energy can overcome the gain in localization energy. If, on the other hand, the f states are restricted to a narrow band the gain in band formation energy is small and localization is energetically more favorable. In the f^3 configuration of Fig. 4, for both PuC and PuN, the itinerant f states fill a narrow peak below the Fermi level which is, however, still strongly hybridized with the broad p band. Localizing an additional f state leads to the f^4 configuration depicted in the respective insets to Fig. 4, with an associated gain in localization (i.e., self-interaction correction) energy. However, the Fermi level has also moved closer to the p band resulting in a depopulation of Fermi energy f states and a considerable loss of hybridization energy. While the gain in energy from localizing a given f state is approximately the same for both PuC and PuN, the corresponding loss in band formation energy differs. In PuC f - p hybridization is slightly more pronounced than in PuN where the p states are further separated from the f states due to the increased electronegativity. In PuN, with a calculated total energy difference $E_{\beta^3} - E_{\beta^4} = -5$ mRy, both configurations contribute almost equally to the ground-state

TABLE I. Actinide carbide/nitride data: column 2, ground-state configuration. Column 3, calculated lattice parameter in the LSD approximation. Column 4, calculated lattice parameter in the ground-state configuration. Column 5, experimental lattice parameter (Refs. 10, 37, and 38). Column 6, calculated bulk moduli.

	Ground state	alat _{LSD}	alat _{calc} (Å)	alat _{exp} (Å)	<i>B</i> (GPa)
UC	f^0 (U ⁶⁺)	4.84	4.84	4.960	229
NpC	f^2 (Np ⁵⁺)	4.85	4.90	4.999	179
PuC	f^3 (Pu ⁵⁺)	4.86	4.91	4.965	172
AmC	f^6 Am ³⁺)	4.87	5.02		149
CmC	f^7 (Cm ³⁺)	4.86	4.98		151
UN	f^1 (U ⁵⁺)	4.87	4.89	4.890	238
NpN	f^2/f^3 (Np ⁵⁺ /Np ⁴⁺)	4.87	4.91/4.96	4.897	201/228
PuN	f^3 (Pu ⁵⁺)	4.89	4.93	4.905	188
AmN	f^6 (Am ³⁺)	4.92	5.02	4.995	153
CmN	f^7 (Cm ³⁺)	4.90	4.99	5.041	154

electronic structure. In PuC, the f^3 configuration, is slightly more favorable ($E_{f^3}-E_{f^4}=-9$ mRy) due to the increased hybridization. The total (localized+itinerant) f -electron count for the different scenarios shown in Fig. 4 is PuC(f^3)=5.17, PuC(f^4)=5.15, PuN(f^3)=5.38, and PuN(f^4)=5.35. Clearly, for both compounds the total number of f electrons changes only marginally through the $f^3 \rightarrow f^4$ transition, however there are overall 0.2 f -electrons less in PuC than in PuN due to the increased orbital overlap.

Overall then, the bonding in PuN is more ionic in nature compared to the more covalent bonding in PuC. This difference is even more noticeable if we try to localize a fifth f -electron. In this case, we find the resulting Pu³⁺ configuration to be almost degenerate with both the Pu⁴⁺(f^4), and the Pu⁵⁺(f^3) configurations in PuN, whereas in PuC it is energetically unfavorable by ~ 40 mRy. From the inset of Fig. 4(a), we see in the f^4 configuration of PuN a narrow f peak just below the Fermi level, a level that can then be localized with a moderate loss in band formation energy. On the other hand, in the f^4 configuration of PuC [inset of Fig. 4(b)] the Fermi level is below the first peak in the f states. As a consequence localizing an additional f state would imply depopulating the C p band which would then result in charge transfer. Clearly, the associated loss in Madelung and hybridization energy would then be considerably larger than the gain in localization energy and is, therefore, unfavorable.

Again, we are driven to assume that the actual electronic ground-state configuration of these early actinide carbides and nitrides is more complex than any of the limiting configurations in the almost degenerate manifold can describe. If the true ground-state is fluctuating between a given set of configurations, as is the case for PuC (where the f^3 and f^4 configurations are close to being energetically equivalent), one would expect some intermediate degree of localization. With the fully delocalized LSD (f^0) configuration and the fully localized f^5 configuration being energetically rather unfavorable compared to the f^3 configuration, by, respectively, 60 and 40 mRy, these configurations should not contribute significantly to the electronic structure. Thus it is reasonable to assume that the electronic structure of PuC consists of a

manifold of coexisting localized and delocalized f states, similar to the two main components f^3 and f^4 . The fact that f^3 gives the global energy minimum, and that localizing an additional f electron is only slightly less favorable, might also indicate an intermediate scenario with three localized f electrons and a strongly renormalized itinerant f peak.

It is interesting to note that for compounds at the end of the actinide series, the trivalent ground-state configuration becomes noticeably more favorable than both the tetravalent and pentavalent configurations. In the carbide series this clearly preferred ground-state configuration emerges only for CmC, whereas in the nitride series the multiconfiguration degeneracy is already lifted for AmN. These observations can then be taken as a clear indication that the trend toward localization is more pronounced for the nitride compounds than for the carbides, and is in agreement with earlier suggestions of a primarily ionic character of the AN chemical bonds.²⁴

In Table I the calculated lattice parameters in the ground-state configuration of the actinide carbides and nitrides (column 4) are compared to the corresponding experimentally observed values (column 5). The agreement is generally very good, with a deviation from experiment of around 1.5% for the carbides and 0.5% for the nitrides. However, at odds with experiment, the calculations predict the lattice parameters of a particular actinide carbide and nitride to be approximately equal. In fact the measured lattice parameters of the carbides (UC, NpC, and PuC) tend to be larger than those of their nitride counterparts by almost 2% (see Table I). Given the more covalent nature of bonding in the carbides, one would actually expect the opposite to happen, i.e., that the nitride lattice parameters would be relatively larger; although this effect may be somewhat counterbalanced by the increased overlap due to the slightly smaller nitride anion.

On the experimental side it turns out that actinide monocarbides exist as defect structures, AC_{1-x}.³⁹ Furthermore, the fraction of randomly distributed C vacancies affects the measured lattice parameters. For PuC_{1-x} a range of different lattice parameters is found depending on x as well as temperature (the value quoted in Table I is for $x \sim 0.2$ and T

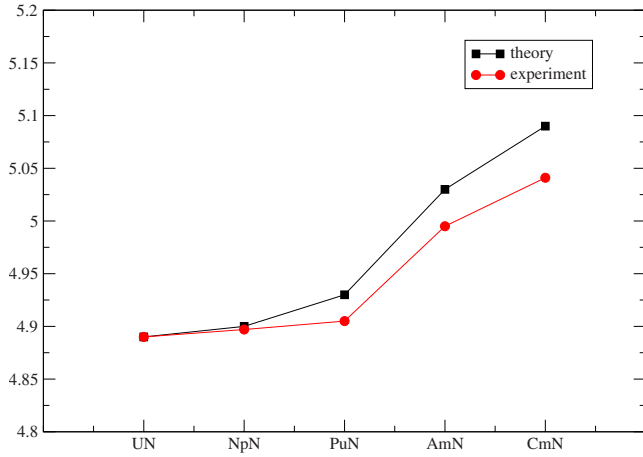


FIG. 5. (Color online) Lattice parameters (in Å) of the actinide nitrides: experiment versus theory.

~100 K).³⁸ Using a supercell consisting of four PuC formula units with one single carbon atom removed, we studied the effect of C vacancies on the total energy and lattice parameter. We find the ground state of PuC_{0.75} to remain Pu⁵⁺ with 3*f* electrons localized on each Pu site as in PuC, but the equilibrium lattice parameter is now increased to 4.99 Å. Thus, it appears that the relatively large lattice parameters of the actinide carbides, compared to the nitrides, are related to the presence of C vacancies in the actual compounds, rather than to differences in the electronic structure between PuC and PuN. No experimental values for AmC and CmC seem to exist.

The bulk moduli obtained in the respective ground-state configuration are given in column 6 of Table I. Both in the carbide and the nitrides series the bulk modulus decreases from U to Cm. Compared to the experimental value, $B = 194$ GPa, as well as band structure results, we overestimate the value for UN.^{24,40,41} For NpN to AmN, we find our values to be in relatively good agreement with the values calculated by Brooks *et al.*,⁴⁰ but somewhat larger (except for AmN) than the values obtained by Atta-Fynn *et al.*²⁴ A cohesive energy of 14.15 eV is found for the f^1 scenario of UN, which is within the range of values found by Kotomin *et al.*,⁴¹ using two different density functional codes.

D. Localization-delocalization transition in actinide nitrides

From the total energies in Fig. 3 we observe that in the nitride series a preferred ground-state configuration only emerges at AmN and CmN. This sudden localization that occurs between PuN and AmN is reflected in the jump in the corresponding lattice parameters that is seen in Fig. 5. The abrupt increase in the measured lattice parameters is well reproduced by our calculated values; in the SIC-LSD calculations it is clearly associated with the fact that the localized *f* states no longer participate in bonding. An increasing lattice parameter from UN to AmN is also observed in our LSD calculations (column 3 of Table I), as well as in earlier LSDA or GGA based calculations, which can be interpreted as a sign of increased localization.^{24,40} However, in the case of standard LSD and GGA calculations, the change in lattice

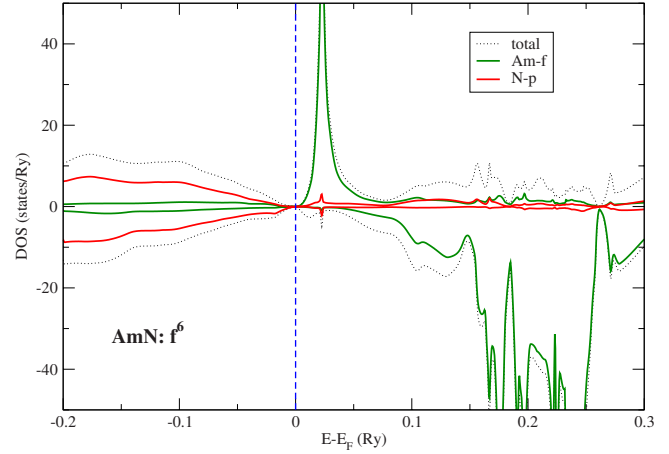


FIG. 6. (Color online) DOS of AmN in the f^6 ground-state configuration.

parameter is gradual and a result of gradual narrowing of *f* bands with increasing actinide atomic number; as distinct from a localization transition as in SIC-LSD. The jump between PuN and AmN has not been observed in previous LSD and GGA calculations. A further indication of localization is the observed noticeable decrease in bulk modulus from PuN to AmN that can be seen from the corresponding values in Table I.

From our SIC-LSD calculations we thus predict a delocalization-localization transition to occur between PuN and AmN and that the resulting ground-state configuration for AmN is Am³⁺ with six localized *f* electrons, the DOS of which is shown in Fig. 6.

With the *N-p* band capable of accepting three valence electrons through charge transfer and hybridization, in the trivalent ground state the *p* band is completely filled, and the Fermi level is situated below the empty *f* peak. AmN is apparently close to being a semiconductor. As we noted in an earlier publication on the Americium pnictides,⁴² the vanishingly small DOS at the Fermi level of AmN is not in agreement with the rather high values for the observed temperature independent paramagnetic susceptibility.⁴³ However, a subsequent photoemission study by Gouder *et al.*⁴⁴ seems to have confirmed both the predicted $5f^6$ ground state as well as the semiconducting character of AmN. In a separate publication, the experimentally observed high value for the susceptibility was explained by a Van Vleck mechanism.⁴⁵

III. GENERAL DISCUSSION

The strength of the SIC-LSD is that it is a parameter free theory of the ground state which allows one to determine the valence state by comparing energies. Furthermore, it casts light on the systematics of localization-delocalization transitions in that the self-interaction is nonzero for localized states but vanishes for band states; the latter being the reason why the LSDA remains valid for the itinerant *f* states. Given that SIC-LSD is a ground-state theory it relates mainly to occupied states. Accordingly in the calculated DOS, the delocalized *f* states tend to be situated at too low binding en-

ergies due to the fact that the correlations among the electrons occupying these states are not fully accounted for. Thus, for the DOS in Fig. 6, even though it correctly reproduces the pseudogap, the DOS cannot straightforwardly be mapped onto the main features of the XPS and BIS measurements. Indeed, as calculated, the positions of both the localized and delocalized f states are not well defined. In the LDA+U approximation, guided by experiment, an effective U parameter is introduced that separates the f manifold into the lower and upper Hubbard bands and removes the f degrees of freedom from the Fermi level.⁴⁶ In a study of AmN, assuming localized f states, and using a U parameter of 2.5 eV, Ghosh *et al.*⁴⁵ were able to reproduce the $5f$ binding positions of the photoemission measurements (~ 2.5 eV). As indicated above, in the fully first-principles SIC-LSD no parameter for modeling the strong correlations is introduced. However, we can attempt to estimate the position of the $5f$ states from our calculated values for, respectively, the SIC corrected f states and the band f states by using a transition state argument.^{47,48} For AmN, this gives a binding energy of 3.3 eV, which is about 30% larger than the value of 2.5 eV determined from experiment.

The LDA+U approach has similarly been applied to PuN (Ref. 7) and PuC.⁴⁹ In both cases the localized f manifold consists of five f electrons, as a result of which no itinerant f states appear at the Fermi level of the corresponding DOS. This is in contradiction to the results from photoelectron emission studies where a triplet of $5f$ related features is observed, including a strong peak at the Fermi level.^{49,50} The SIC-LSD calculations predict an f^3 ground-state configuration, albeit with strong contributions from the f^4 , and in the case of PuN, also the f^5 initial state configurations. Both the f^3 and the f^4 configurations are characterized by coexisting localized and delocalized f states, which, as can be seen from Fig. 4, results in a large DOS at the Fermi level, in agreement with photoemission experiments. For completeness, we should mention that the photoelectron measurements by Havela *et al.*⁵⁰ at the time were interpreted in terms of a $5f^3$ ground state for PuN, in good agreement with our predicted ground-state configuration.⁵¹

Finally, with respect to the high temperature behavior of the actinide nitrides and carbides, it has been observed that for the nitrides the thermal conductivity decreases from UN to PuN and it was suggested that this decrease is caused by a decrease in the electronic contribution to the thermal conductivity.⁵² This explanation would thus agree with the observed tendency toward a decreasing number of itinerant

electrons with increasing actinide atomic number. An interesting feature in this context is the variation of the lattice parameter with temperature observed experimentally; a dependency that has been previously modeled by molecular dynamics simulations.⁵³ In our SIC-LSD calculations, an increasing lattice parameter would result in the more localized scenarios becoming gradually more favorable. This would imply, that as far as the f -electron contribution is concerned, the thermal conductivity for a given compound would decrease with increasing temperature. The measured data⁵² do seem to show such a trend at least for UN and NpN. Here however, it should be noted that SIC-LSD is a ground-state theory that does not take into account all possible fluctuation effects that are associated with increasing temperature. An extension of the present work to include finite temperature effects is currently being pursued based on the local self-interaction correction implemented in the multiple scattering theory.³⁴ In combination with the coherent potential approximation and the disordered local moments theory, this approach allows one to study possible spin and valence fluctuations as a function of temperature. The utility of this methodology has already been demonstrated for Ce (Ref. 34) and Gd.⁵⁴

IV. CONCLUSION

We have studied the ground-state electronic structure of the actinide mononitrides and monocarbides. A trend toward increased f -electron localization as a function of actinide atomic number has been observed, which is slightly more predominant in the nitrides than in the carbides. With the exception of UC, the light actinide compounds are best described in terms of a manifold of several coexisting localized/delocalized configurations. A localization transition occurs in the late actinides which results in a jump in lattice parameter from PuN to AmN. The valence electron manifold of all these compounds reproduces the main features of the photoemission experiments, including the band gap (pseudogap) that is observed in AmN.

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