Theoretical atomic volumes of the light actinides

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(Received 13 November 1998; revised manuscript received 9 June 1999)

The zero-pressure zero-temperature equilibrium volumes and bulk moduli are calculated for the light actinides Th through Pu using two independent all-electron, full-potential, electronic-structure methods: the full-potential linear augmented-plane-wave method and the linear combinations of Gaussian-type orbitals-fitting function method. The results produced by these two distinctly different electronic-structure techniques are in good agreement with each other, but differ significantly from previously published calculations using the full-potential linear muffin-tin-orbital (FP-LMTO) method. The theoretically calculated equilibrium volumes are in some cases nearly 10% larger than the previous FP-LMTO calculations, bringing them much closer to the experimentally observed volumes. We also discuss the anomalous upturn in equilibrium volume seen experimentally for α-Pu.

I. INTRODUCTION

The light-actinide metals, from Th to Pu, pose a severe challenge to modern electronic-structure theory due in part to the existence of highly directional and high density-of-states *f*-electron bonding, which promotes the formation of a large number of exceptionally complicated crystal structures. In fact, the light actinide metals (excluding Ac) together with Ce are the only elemental solids known to exhibit *f* bonding under ambient conditions. In addition, the heavy nuclei of the light-actinide metals induce large relativistic effects on their valence-band structures, and usually require inclusion of spin-orbit-coupling effects. Despite these difficulties, many all-electron electronic-structure calculations have been carried out for the light-actinide metals.[1–5] To the best of our knowledge, only one full-potential technique, the full-potential linear muffin-tin-orbital (FP-LMTO) method has thus far been applied,[4] but taken all together, the cumulative theoretical results for the bulk properties (such as the equilibrium volume and bulk modulus) are at best ambiguous, even for the simplest of these materials, fcc Th.

Local-density approximation[6] (LDA) calculations of the ambient properties of fcc Th using the linear muffin-tin-orbital (LMTO) method within the atomic-sphere approximation (ASA) produced zero-pressure volumes that range from slightly compressed relative to experiment to slightly expanded, depending on the inclusion or neglect of spin-orbit corrections and combined-correction terms.[1–3] When those calculations were repeated using a full-potential (FP-LMTO) method,[4] the presumably more accurate FP-LMTO method yielded a volume nearly 20% smaller than the best LMTO-ASA result and experiment. If this FP-LMTO result is correct, fcc Th exhibits the largest LDA-induced contraction for any elemental solid other than fcc Pu (and the other heavy fermion systems), which will be discussed later, and the largest volume discrepancy between FP-LMTO and LMTO-ASA calculations found to date. Additional FP-LMTO calculations using the generalized-gradient-approximation[7] (GGA) produced a zero-pressure volume 10% larger than the FP-LMTO LDA result, but still nearly 10% smaller than the measured value, which is another rather anomalous result. In fact, FP-LMTO GGA calculations have consistently yielded volumes that are significantly smaller than experiment for all of the light-actinide metals, with the size of the error ranging from just under 6% for Np up to about 10% for Th.[4] Recent full-charge-density-LMTO calculations on Th found an LDA lattice constant that lies between the LDA values found in the earlier LMTO-ASA and FP-LMTO calculations and a GGA lattice constant that is significantly larger than the FP-LMTO GGA result. Taken together, these inconsistent results raise serious doubts about the reliability of the existing theoretical calculations for the light-actinide metals.

To resolve these issues, we have carried out electronic-structure calculations on the light actinides using two independent methods: the linear combinations of Gaussian-type orbitals-fitting function (LCGTO-FF) method,[8] as implemented in the program GTOFF (Ref. 9) and the full-potential linearized augmented plane-wave (FLAPW) method.[10] Although both methods are all-electron, full-potential techniques capable of producing high-precision total energies within the LDA and GGA approximations, they employ radically different numerical approximations and basis sets. Application of both methods to a single system thus provides assurance that the final results obtained are free of numerical artifacts. For this paper, LDA and GGA calculations were carried out scalar-relativistically and fully relativistically (i.e., with spin-orbit effects included). The FLAPW method includes spin-orbit coupling as a perturbation,[10] while the LCGTO-FF performs a non-perturbative treatment of spin-orbit effects, which has only recently been implemented.[11] It is of particular interest to compare the scalar and fully relativistic results across the light actinides; not only does this comparison justify the perturbative approach to spin-orbit coupling, it also illustrates the effects of spin-orbit coupling on the bulk properties.

Section II briefly recapitulates the FLAPW and

LCGTO-FF methods, which have been discussed extensively elsewhere,[8–10] along with the details of the present calculations. Section III then discusses the results for equilibrium volumes and bulk moduli for Th through Pu, both in the fcc (Th→Pu) and α (Pa→Pu) crystal phases (when different from fcc). We have included the fcc phase for Pa→Pu as it has often been used as a surrogate for the much more complex α structures. Section IV presents our concluding remarks.

II. METHODS

The LCGTO-FF technique is distinguished from other electronic structure methods by its use of three independent GTO basis sets to expand the orbitals, charge density, and exchange-correlation (XC) integral kernels; here using either the Hedin-Lundqvist[6] LDA model or the Perdew-Wang 91 GGA model.[7] The charge-fitting functions are used to reduce the total number of Coulomb integrals required by replacing the usual four-center integrals in the total energy and one-electron equations with three-center integrals. The charge-fitting function coefficients are determined by minimizing the error in the Coulomb energy due to the fit;[12] thereby allowing high-precision calculations with relatively small basis sets. The least squares XC fit used here acts as a sophisticated numerical quadrature scheme capable of producing accurate results on a rather coarse numerical integration mesh. Scalar-relativity was recently implemented and tested in GTOFF (Ref. 13) using the nuclear-only, Douglas-Kroll-Hess (DKH) transformation,[14,15] neglecting terms involving cross products of the momentum operator.[16] For this paper, scalar-relativistic cross-product terms and spin-orbit coupling terms have also been implemented within the nuclear-only approximation,[11] allowing a fully relativistic treatment.

The precision of any LCGTO-FF calculation will, of course, be largely determined by the selection of the three GTO basis sets. In this work, $23s20p15d11f$ uncontracted orbital-basis sets were derived for the light actinides from atomic basis sets tabulated by Minami and Matsuoka.[17] These basis sets were reduced to $17s14p11d7f$ contracted basis sets using coefficients from atomic calculations that used the same density-functional model as the crystal calculations. The charge density and XC integral kernels were fitted with 25*s* and 21*s* basis sets, respectively, selected on the basis of prior experience with LCGTO-FF calculations. All of these basis sets can be obtained from the authors.

All Brillouin zone (BZ) integrations required for the LCGTO-FF calculations were carried out on a uniform mesh with 72 irreducible *k* points in the fcc Brillouin zone (163 for α-Pa and 63 for α-U), using a Gaussian-broadened, histogram, integration technique, with a broadening factor ranging from 4 mRy for Np to 10 mRy for Th. The SCF cycle was iterated until the total energy varied by less than 0.02 mRy/atom.

The all-electron FLAPW method that we have used has been described by Singh;[10] here we discuss only the essential features relevant for comparison with the other full-potential techniques. Energy parameters for the FLAPW basis functions were set near the centers of their respective bands by monitoring the eigenvalues of the calculation whose volume lay closest to equilibrium. Local orbitals[10] were added to enhance the variational freedom and allow the semicore $5d$, $6s$, and $6p$ orbitals to be treated along with the valence electrons, with the added energy parameter used to simultaneously treat the residual *s* and *p* character of the valence electrons. Local orbitals with *f* character were also used to maximize valence-band accuracy and ensure orthogonality with the core $4f$ states. The results that we obtained were found to be insensitive to small changes in all energy parameters. Spin-orbit coupling was incorporated for the valence electrons at the second-variational level,[10] in which the effects of spin-orbit coupling are treated perturbatively in a set of scalar-relativistic orbitals found within an energy window of specified width. The results obtained here were found to be stable with respect to the size of this window.

The size of the FLAPW basis is determined by a plane-wave cutoff, K_{max}, whose value was given by the relation $R_{MT}K_{max}=9.0$, which was found to be satisfactory in determining the bulk properties. For BZ integrations, 60 irreducible points in the fcc Brillouin zone (80 points in α-Pa, 126 in α-U, 8 in α-Np, and 16 in α-Pu) were sampled according to the scheme of Monkhorst and Pack,[18] and all BZ integrations were reduced to simple sums of a Fermi-Dirac-function temperature-broadened integrand, with an effective temperature of 2.0 mRy. Increasing the number of points sampled in the BZ changed the total energies by less than 0.25 mRy/atom for the α phases, and 0.75 mRy/atom for the fcc structures. The values thus obtained for the equilibrium volumes and bulk moduli were found to be converged with respect to the number of BZ points sampled. All self-consistent calculations were iterated until the total energy changed by less than 0.01 mRy/atom. The same LDA and GGA models were used as in the LCGTO-FF calculations.

As is evident from the preceding discussion, the FLAPW and LCGTO-FF methods differ significantly. First, the FLAPW method utilizes a diffuse orbital-basis set that can be systematically enriched by simply adding more plane waves. This is in sharp contrast to the local basis set used in the LCGTO-FF method, which tends to be somewhat more difficult to improve systematically. On the other hand, the FLAPW basis functions have discontinuities in their second derivatives at the muffin-tin sphere boundaries that do not exist in the LCGTO-FF basis sets.

The implementations of relativity used by the LCGTO-FF and FLAPW methods also differ dramatically. The FLAPW method avoids the well-known variational collapse problem by using a basis set that is formed from pure electronic solutions to the muffin-tin Dirac-Kohn-Sham equations inside the muffin-tin spheres. (In the interstitial region, nonrelativistic solutions are used.) The non-muffin-tin corrections to the potential are then accounted for perturbatively at each iteration. This approach to solving the full-potential Dirac-Kohn-Sham equations should be accurate provided the muffin-tin solutions do not differ greatly from the fully relativistic orbitals and the effects of relativity are small in the interstitial region. This second-variational treatment can be expected to slightly underestimate the effect of spin-orbit coupling. On the other hand, the LCGTO-FF method decouples the electron and positron degrees of freedom of the full-potential Dirac-Kohn-Sham equations to second order in the ratio of the effective potential to the combined kinetic and rest mass energies, with the effective potential being

replaced here by the bare nuclear potential to reduce the computational resources required. Although this nuclear-only approximation is very reliable for scalar-relativistic calculations, it will produce a systematic overestimate of spin-orbit coupling effects.[11]

We wish to emphasize that that the LCGTO-FF and FLAPW techniques may be viewed as complementary methods, to the extent that they utilize different numerical approximations. Thus, if one of the two methods were to encounter difficulties due to inadequacies in its basis set or implementation of relativity, it is unlikely that the second method would exhibit the same problem. This makes a joint study of the type carried out here especially valuable for investigating systems, like the light actinides, that have previously exhibited a significant sensitivity to computational details. In addition, the results of LCGTO-FF and FLAPW calculations should provide approximate upper and lower bounds for the spin-orbit coupling effects that are expected to play a crucial role in the light actinide metals.

III. RESULTS

For each choice of system (Th→Pu), method (LCGTO-FF or FLAPW), model (LDA or GGA), and level of relativity (scalar or full), total energies were calculated for five or six volumes lying near the energy minimum. The calculated energies for each combination were then fitted with either a cubic function of the volume or a second-order Birch fit,[19] to obtain the zero-pressure volume (V_0) and bulk modulus (B_0). The fitted results are compared with previous calculations[3–5] and experiment[20–31] in Tables I and II. We have performed these calculations in both the fcc (Pearson cF4) and experimentally determined α structures, in order to determine to what extent the cubic close-packed structure can serve as a surrogate for the more complex (and much more computationally demanding) α structures. No attempt was made to relax the structural parameters of the α phases in this study. Indeed, the α-Np and α-Pu phases were already too demanding for the current implementation of the LCGTO-FF method.

Inspection of the results for the equilibrium volumes listed in Table I reveals several interesting features. First, the LCGTO-FF and FLAPW methods give nearly identical scalar-relativistic results for Th→Pu and fully relativistic results for Th→U. For Np and Pu the spin-orbit induced shifts produced by the LCGTO-FF method are notably larger than those produced by the FLAPW method; an unsurprising result since the two methods are expected to provide upper and lower bounds to spin-orbit coupling effects. This level of agreement between such disparate methods provides a high degree of confidence in the quality of the results produced by both methods. In contrast, the fully-relativistic FLAPW and FP-LMTO results[4] differ substantially for both the LDA and GGA models, with the volumes differing by roughly 3–10 % in each case, with the notable exception of $\alpha-$Pu. This is an exceptionally large disagreement for two full-potential methods. The good agreement between the LCGTO-FF and FLAPW results lends confidence to the FLAPW calculations. In addition, the fully-relativistic FP-LMTO GGA volume for Th is anomalously small compared to experiment. Taken together, these features strongly suggest that the source of the disagreement between the present results and the FP-LMTO results is some error in the earlier calculations.[4]

The FLAPW GGA results are compared with experiment (in most cases only room temperature experimental data is available) in Fig. 1 for the α phases. The agreement between theory and experiment is quite good. A similar plot is shown in Fig. 2 for the fcc crystal structures, in which we see that the fcc have significant errors when compared to the α phase experimental volumes. The fcc phases do, however, obey the same general trend with regard to spin-orbit contributions; spin-orbit effects have negligible impact on the equilibrium volumes for Th→U, and cause an expansion of the lattice for Np and Pu. Similarly, GGA results are always expanded relative to LDA.

The upturn in equilibrium volume for Pu seen in Fig. 1 has been a subject of some contention. Based on LMTO-ASA studies, this upturn was originally ascribed to spin-orbit effects on the valence electrons.[2,3] FP-LMTO studies by Wills and Eriksson,[4] however, not only did not find an upturn, but found a contraction with the inclusion of spin-orbit coupling, leading them to hypothesize that the LMTO-ASA calculations reached the wrong conclusion about the effects of spin-orbit coupling due to their treating the $6p$ semicore states as core states. Recently, however, Pénicaud[32] has performed a fully relativistic LMTO-ASA calculation for the light actinides in which the $6p$ states were treated as valence states (in a relativistic j,κ basis), and found no such contraction. Indeed, the LMTO-ASA studies show a systematic trend towards an expansion in volumes when spin-orbit effects are treated perturbatively[3] and nonperturbatively.[32] Our present studies are consistent with the LMTO-ASA results, and Fig. 1 shows that spin-orbit effects on the valence electrons are responsible for a gradual increase of the equilibrium volume as one proceeds along the sequence of the light actinides, but it does not appear to account for the anomalous upturn in volume for α-Pu.

Another possibility for the upturn is that it represents a finite-temperature effect (since experimental volumes are measured at room temperature). While it is true that thermal expansion increases for Np and Pu, however, if the measured thermal expansion coefficients[34] (resulting in an increase for the volume of 2.4% for Np, and 4.8% for Pu) are used to correct the zero-temperature calculations, the two atomic volumes will be the same at room temperature (about 130 in atomic units) and not have the expected upturn. It is quite interesting that our density-functional calculations predict the atomic volumes so well until we reach Pu. For fcc δ-phase Pu, the theoretical volume is too small by about 20%. Although this is an exceptionally large error for a GGA calculation, it has been known for many years that δ-Pu is anomalous due to its position on the boundary between the light actinides that have itinerant $5f$-electrons and the heavy actinides that have localized $5f$-electrons (which form a second rare-earth-like series). Although the volume found here for δ-Pu is 10% larger than that found with FP-LMTO method,[4] that increase is not large enough to remove the discrepancy between theory and experiment. However, the large experimental difference in volume between the low-temperature α and much higher temperature δ phases suggest that new physics (beyond LDA or GGA) is responsible

TABLE I. The equilibrium volume (atomic units) obtained here for the light actinides with LCGTO-FF and FLAPW calculations using the LDA and GGA models, with and without spin-orbit (SO) effects included, are compared to results from LMTO-ASA calculations with combined correction terms and calculated temperature expansion corrections (Ref. 3), FCD-LMTO calculations (Ref. 5), and FP-LMTO calculations (Ref. 4).

	cF4 (fcc)				α-phase			
Method	LDA	+SO	GGA	+SO	LDA	+SO	GGA	+SO
					Th			
	cF4							
LMTO-ASA	232.1	229.4						
FCD-LMTO	212.7		233.7					
FP-LMTO		182.1		199.9				
LCGTO-FF	200.5	199.3	216.9	214.8				
FLAPW	199.7	204.1	219.3	218.1				
Experiment		221.7(298 K)[a]						
					Pa			
	cF4				tI2			
LMTO-ASA					178.8	177.5		
FCD-LMTO	171.7		182.8		164.8		175.8	
FP-LMTO		149.9		160.2		147.7		157.6
LCGTO-FF	159.6	160.6	171.5	173.9	155.9	156.3	168.7	169.9
FLAPW	160.2	160.7	172.3	172.8	156.8	155.8	169.3	168.4
Experiment					168.30(298 K)[b]			
					U			
	cF4				oC4			
LMTO-ASA					144.4	147.1		
FCD-LMTO	147.0		157.1		131.4		141.2	
FP-LMTO		129.4		138.6		123.7		131.5
LCGTO-FF	136.1	140.0	146.1	151.5	129.0	130.5	138.5	141.8
FLAPW	136.5	136.9	147.5	148.7	127.9	128.5	137.7	140.1
Experiment					138.89(4.2 K)[c]			
					Np			
	cF4				oP8			
LMTO-ASA					125.5	128.2		
FCD-LMTO	137.4		144.1		117.8		131.8	
FP-LMTO		116.7		125.8	112.0		122.1, 124.2[d]	
LCGTO-FF	121.1	128.8	131.6	142.2				
FLAPW	120.8	126.9	131.4	137.9	116.4	118.3	124.6	127.7
Experiment					129.9(293 K)[e]			
					Pu			
	cF4				mP16			
LMTO-ASA	114.7	130.9			114.7	130.9		
FCD-LMTO	132.8		140.0		112.2		131.4	
FP-LMTO		109.2		119.2			124.2[d]	
LCGTO-FF	111.5	125.7	121.2	141.4				
FLAPW	111.9	120.2	122.3	133.4	109.7	114.2	117.2	124.4
Experiment		168.0(653 K)[f]				134.95(294 K)[g]		

[a]Ref. 20.
[b]Ref. 21.
[c]Ref. 22.
[d]Ref. 33.
[e]Ref. 23.
[f]Ref. 24.
[g]Ref. 25.

TABLE II. The bulk modulus (GPa) obtained here for Th→Pu with LCGTO-FF and FLAPW calculations using the LDA and GGA models, with and without spin-orbit (SO) effects included, are compared to results from FP-LMTO calculations (Ref. 4) and room temperature data.

	cF4 (fcc)				α-phase			
Method	LDA	+SO	GGA	+SO	LDA	+SO	GGA	+SO
					Th			
	cF4							
FP-LMTO		82.6		61.5				
LCGTO-FF	64.8	71.7	58.8	63.4				
FLAPW	61.0	78.6	56.7	73.1				
Experiment		58(1)[a]						
					Pa			
	cF4				tI2			
FP-LMTO		141		122		146		123
LCGTO-FF	121	119	102	94	119	110	95	97
FLAPW	123	104	100	96	111	110	105	105
Experiment					157(5)[b]			
					U			
	cF4				oC4			
FP-LMTO		186		148		240		172
LCGTO-FF	160	142	101	110	179	166	135	116
FLAPW	148	228	125	99	176	144	149	124
Experiment					135.5[c]			
					Np			
	cF4				oP8			
FP-LMTO		199		161		300		170
LCGTO-FF	185	141	142	112				
FLAPW	190	136	137	140	260	234	196	158
Experiment					73.5[d]			
					Pu			
	cF4				mP16			
FP-LMTO		214		143				130[e]
LCGTO-FF	218	124	170	97				
FLAPW	194	143	153	121	307	244	232	153
Experiment					47.2(7)[f], 54.6[g]			

[a]References 26.
[b]References 27.
[c]References 28.
[d]References 29.
[e]References 33.
[f]References 30.
[g]References 31.

for the large expansion of the δ phase (the enormous difference cannot be explained by any known thermal expansion mechanism). It is likely that large intra-atomic electron-electron Coulomb correlations (a large effective Hubbard U) are responsible for the anomalous properties of δ-Pu. It may even be possible that some localization is already apparent in the α phase for Pu, thus accounting for the slight (around 5%) discrepancy between the computed and measured atomic volume, and causing the upturn. In heavy fermionsystems, it has been argued[35] that the effects of strong electron-electron correlations (which is responsible for the huge specific-heat enhancements) leads to heavier band masses (renormalized bands with a reduced effective band width). In terms of a Friedel model description of bonding,[36] such an effect (a narrower f-band width) would reduce the strength of the f bonding, which should expand the lattice.

Table II lists our results for the bulk modulus for the light actinides Th→Pu, in both the fcc and α phases. Since the FP-LMTO calculations found a substantial decrease in the equilibrium volumes, it not very surprising that they predict a correspondingly larger bulk modulus. Comparison with the experimentally determined bulk moduli, however, which is shown in Fig. 3 (see Fig. 4 for the fcc bulk moduli), show that our most accurate fully relativistic GGA FLAPW results are in somewhat strong disagreement, particularly for the heavier actinides, Np and Pu. We do not recover the turnover

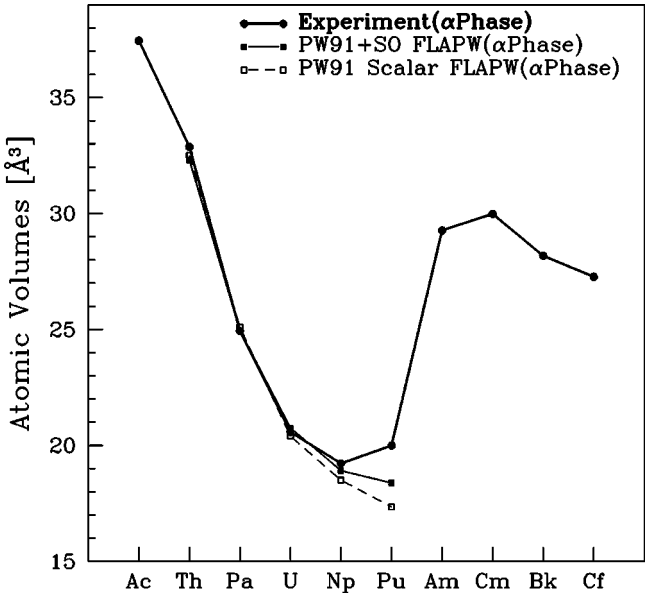

FIG. 1. The equilibrium volume of the light actinides in the α-phases as calculated by FLAPW, both in the scalar-relativistic (open squares) and fully relativistic (solid squares) treatments. These numerical results were obtained using the GGA form of exchange and correlation. Experimental results are also shown (solid circles).

seen experimentally past Pa. There are several possible reasons for this discrepancy. One is that the bulk modulus is more sensitive than the equilibrium volume to numerical errors in our calculations. Another explanation is that temperature effects (all of the available experimental data is at room temperature or above) may play an increasingly important role, softening the bulk modulus, especially for Np and Pu.

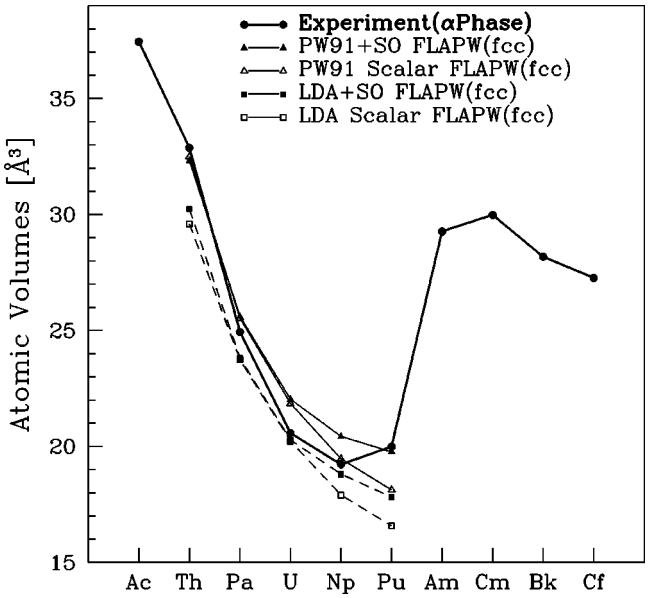

FIG. 2. The equilibrium volume of the light actinides in the fcc phase as calculated by FLAPW, both in the scalar-relativistic (open squares) and fully relativistic (solid squares) treatments. These numerical results were obtained using the GGA form of exchange and correlation. Experimental results are also shown (solid circles), but for the respective α phases.

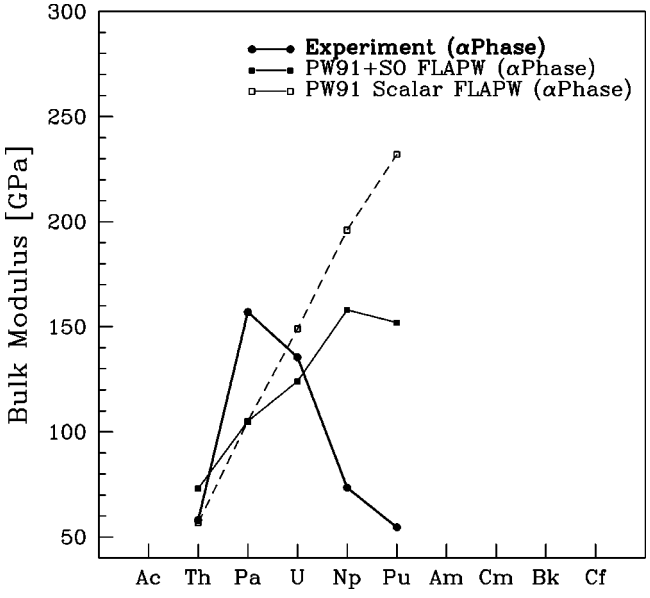

FIG. 3. The bulk moduli of the light actinides in the α phases, as calculated by FLAPW, both in the scalar-relativistic (open squares) and fully relativistic (solid squares) treatments within the GGA, compared to experiment (solid circles).

Strong anharmonic effects have been found recently in the Debye-Waller temperatures for U, Np, and Pu.[37]

IV. CONCLUSIONS

In summary, it has been demonstrated that the LCGTO-FF and FLAPW electronic-structure methods produce a zero-pressure volume and bulk modulus for the light actinides Th→Pu that are in good agreement with each other but differ significantly from previous full-potential results

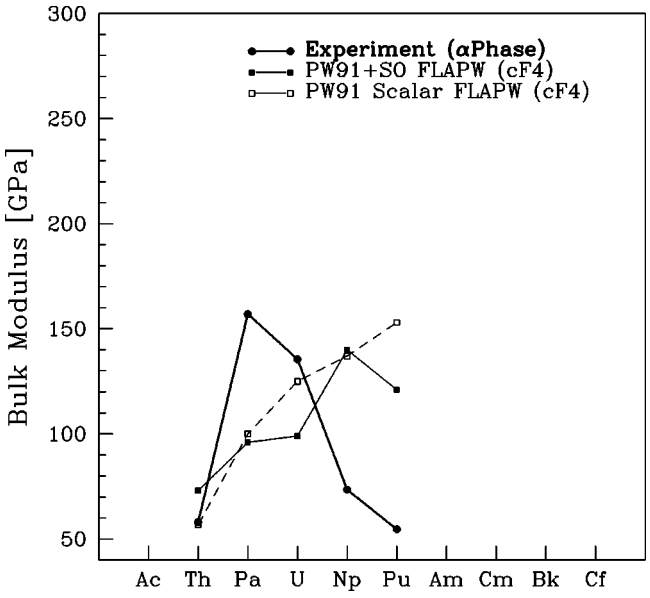

FIG. 4. The bulk moduli of the light actinides in the fcc phase, as calculated by FLAPW, both in the scalar-relativistic (open squares) and fully relativistic (solid squares) treatments within the GGA. For comparison, these values are compared to experiment (solid circles) in the respective α phases.

obtained from the FP-LMTO method,[4] with the present volumes being roughly 3–10 % larger. Given the good agreement between the LCGTO-FF and FLAPW methods, it seems likely that the earlier FP-LMTO results were in error. If so, this might account for the 3 to 10 % underestimate of the volumes found for all of the light-actinide crystals with the FP-LMTO method using the GGA exchange-correlation potentials. The present results do not affect the long standing problem of the anomalous volume of δ-Pu, which presumably is due to correlation effects that are not adequately accounted for in either the LDA or the GGA.

ACKNOWLEDGMENTS

J.C.B. thanks J. P. Perdew for providing the subroutines used to implement the PW91 GGA in GTOFF. This research was supported by the Department of Energy under Contract No. W-7405-ENG-36. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Energy Research of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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