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Electronic properties of *f*-electron metals using the generalized gradient approximation

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We present a comparison between calculations based upon the local-density approximation (LDA) and the generalized gradient approximation (GGA) of the ground-state properties of the *f*-electron metals Ce, Th, Pa, U, Np, and Pu in their α phase. For α-Ce, Th, Pa, U, and Np the calculations have been performed for the observed crystal structures. Studies for the hypothetical fcc crystal structure have also been done for Pa, U, Np, and Pu. Equilibrium volumes and bulk moduli for these *f*-electron metals have been calculated for both the LDA and GGA formulation of the exchange-correlation energy functional in the full-potential implementation of the linear-muffin-tin-orbital method. The equilibrium volumes, which generally are too low in LDA calculations, are improved considerably by the gradient correction for these elements. Similarly the bulk moduli are decreased substantially when LDA is replaced by GGA and thereby they come closer to the experimentally observed values.

There has been a continuous development of approximations of the exchange-correlation functional since the first local-density approximation (LDA) was proposed by Hohenberg and Kohn[1] and Kohn and Sham.[2] Normally, density-functional theory is applied in connection with the LDA, where the exchange and correlation potential is obtained from a uniform electron gas. Recently a computationally efficient and parameter-free approximation has been presented. It makes use of nonlocal information of the electron density since the exchange and correlation functional generally depends on the density gradient. This generalized gradient approximation, introduced by Perdew and Wang,[3] is in the following referred to as the GGA.

This approximation has already been investigated for a number of atoms, molecules, and solids.[3–7] In the *d* transition series the GGA has proven to be particularly successful when combined with electronic structure methods that treat the potential without a spherical restriction.[7] It has been shown by Körling and Häglund[6] that the overestimation of the binding in a metal, which is characteristic for the LDA, is reduced when the GGA is used for the exchange and correlation functional. Consequently, the errors in the calculated equilibrium volumes of the *d* transition metals have been reduced by about 1/3.[7] This is true for calculations which are not restricted to a spherical potential, i.e., calculations which do not rely on the atomic sphere approximation (ASA). For ASA calculations there seems to be a cancellation of errors introduced by the LDA and ASA, which gives results in better agreement with experiment than the calculations with the combination ASA-GGA.[7] In the *d* transition metals the bulk moduli are also improved when the gradient corrections of the density are taken into account.[7] Here the discrepancy between theory and experiment is halved when the LDA calculation is replaced by a GGA calculation[7] (full potential).

These promising results have encouraged us to study the influence of the gradient-corrected exchange and correlation functional, the GGA, on the atomic equilibrium volumes and bulk moduli for *f*-electron metals. Thus, α-Ce together with the low-temperature phases of the early actinides, Th–Pu, have been calculated with a full-potential linear-muffin-tin-orbital (FP-LMTO) method with both the local-density and the generalized gradient approximations of the exchange and correlation energy.

Itinerant *f* electrons are known to give rise to open and complex crystal structures.[8] For instance, Pa is bct, α-U has an orthorhombic structure with 2 atoms/unit cell, Np has an orthorhombic structure as well but with 8 atoms/unit cell, and Pu has a monoclinic structure with 16 atoms/unit cell. To do a calculation for these elements in their true crystal structure is immensely time consuming. In this report, where the purpose is to study the effect of gradient corrections to the exchange and correlation energy, we have chosen to perform calculations in the fcc crystal structure for all elements and compare the GGA results to the LDA results. For these approximations Pa has been calculated in the observed bct structure ($c/a = 0.825$), and U and Np have been studied in their observed crystal structures, whereas α-Pu has not yet been calculated in its highly complex monoclinic crystal structure.

As already mentioned, the calculations are done with a full-potential LMTO method. In the case of LDA calculations, we have used the Janak, Moruzzi, and Williams parametrization[9] of the von Barth–Hedin[10] exchange and correlation functional, whereas in the GGA calculation the recent recipe proposed by Perdew and Wang[3] has been applied. The gradient terms were evaluated for the full nonspherical charge density in the muffin-tin spheres as well as in the interstitial region.[11] The self-consistent

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calculations were all electron and fully relativistic as described earlier.[12] The basis set, represented by augmented muffin-tin orbitals, contained $5s$, $5p$, $6s$, $6p$, $5d$, and $4f$ partial waves for α-Ce, and $6s$, $6p$, $7s$, $7p$, $6d$, and $5f$ partial waves for Th–Pu. All these orbitals were defined within one energy panel, i.e., they were all allowed to hybridize. Two sets of energy parameters, one with an energy appropriate for the pseudo-core states, and the other with an energy suited for the valence band, were used for the calculation of the basis within the muffin-tin sphere. Summation over the Brillouin zone (BZ) was done using the special **k** point method[13] with 60 **k** points (fcc), 80 **k** points (α-Pa), 54 **k** points (α-U), and 32 **k** points (α-Np) in the irreducible part of the BZ.

In Fig. 1 we show theoretical results for the atomic equilibrium volumes for Th–Pu together with data measured[14] at room temperature. These data, together with Ce data, are also collected in Table I. As can be seen immediately, the treatment of the exchange correlation of the electrons including gradient corrections increases the atomic volumes relative to the local-density results. The increase is relatively independent of the crystal structure, and is of the order of 10%. By studying the detailed behavior of the atomic equilibrium volumes, we draw the conclusion that gradient corrections have approximately the same influence on this quantity for all the early actinides, which show an increase of the equilibrium volumes with a similar magnitude. However, the agreement with experiment shows large variations through the series. For Th we note in Fig. 1 that the LDA gives a volume that is of the order of 20% too small.[15] The gradient-corrected results are considerably improved but these calculations also show a small discrepancy (~ 7%) with experiment for Th. Actually, the least satisfying agreement is found for Th among the presently studied elements. In comparison to experimental data, our calculations give considerably better results for Pa. Here we also observe that the correct crystal structure (bct) actually shows a slightly smaller atomic equilibrium volume than what is obtained from the fcc calculation. This fact is also found for uranium, where the observed orthorhombic (α-U) structure has a somewhat lower volume than the fcc volume. For the actinide with highest density, Np, we again find that calculations with the correct crystal structure yield a slightly lower equilibrium volume than the fcc calculations. We note, however, in Fig. 1 that the small changes in the equilibrium volume due to the various crystal structures are always smaller in magnitude than the difference due to the treatment of the exchange and correlation potential in the calculations. Unfortunately, due to its complexity, we have so far been unable to perform a calculation for α-Pu in its observed monoclinic structure.

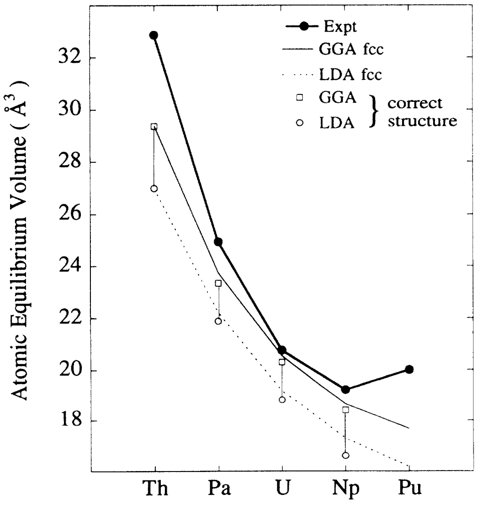

FIG. 1. The equilibrium atomic volumes for the light actinides. Filled symbols refer to room temperature measurements (Ref. 14) and the thin and dotted lines refer to fcc calculations with the LDA and GGA treatment of the exchange correlation, respectively. The theoretical results for the bct (Pa) and orthorhombic (U and Np) crystal structures are shown by open circles (LDA) and open squares (GGA). All volumes presented are in units of Å^3.

TABLE I. Atomic equilibrium volumes in units of Å^3. The theoretical data are obtained with a LDA and a GGA parametrization of the exchange-correlation functional, respectively. These theoretical results are obtained for the fcc crystal structure for all elements, and for Pa, U, and Np results from calculations in their observed (Ref. 14) crystal structure also are shown. The experimental data (Ref. 14) are measured at room temperature.

		Equilibrium volume (Å^3)		
	Crystal structure	LDA	GGA	Expt.
Ce	fcc	22.74	26.05	28.00
Th	fcc	26.98	29.62	32.87
Pa	fcc	22.21	23.74	
Pa	α-Pa	21.88	23.35	24.94
U	fcc	19.18	20.54	
U	α-U	18.33	19.49	20.75
Np	fcc	17.29	18.64	
Np	α-Np	16.60	18.10	19.21
Pu	fcc	16.18	17.67	
Pu	α-Pu			20.00

The parabolic behavior, exhibited by both the theoretical and experimental data in Fig. 1, can be explained from the increasing chemical bonding attributed to the $5f$ electrons as one proceeds towards the heavier elements. Table II shows that the $5f$ occupation increases by approximately one electron for each atomic number in the series (note that the LDA and the GGA give similar d and f occupancies; see below). The $6d$ occupation is, however, essentially constant for Th–Pu and consequently the presence of $6d$ electrons cannot explain the parabolic behavior of the atomic equilibrium volumes. The minimum of the atomic equilibrium volumes is observed to be located at α-Np, whereas theoretically α-Pu (modeled by fcc Pu) has the smallest volume. In our earlier calculation, where a spherical potential and charge density were assumed, this upturn of the atomic equilibrium volume for α-Pu (calculated assuming a fcc crystal structure) was explained as a relativistic effect, namely, due

TABLE II. *d* and *f* occupation numbers for α-Ce and fcc Th–Pu, for calculations that refer to a LDA and a GGA treatment of the exchange-correlation functional.

	LDA		GGA	
	d occupation	*f* occupation	*d* occupation	*f* occupation
Ce	1.63	1.16	1.59	1.10
Th	1.77	0.58	1.79	0.51
Pa	1.72	1.58	1.73	1.54
U	1.60	2.78	1.61	2.75
Np	1.49	3.98	1.49	3.95
Pu	1.41	5.12	1.39	5.11

to the spin-orbit splitting of the 5*f* band.[16,17] Our more accurate full-potential calculations also find that the relativistic effects are important for the atomic equilibrium volume of α-Pu, but that this effect is not large enough in the present calculations to give rise to an upturn in the atomic equilibrium volume for fcc Pu. This effect has already been recognized by Wills and Eriksson.[15] Furthermore, it has recently been proposed that α-Pu cannot be appropriately modeled by either fcc or hexagonal Pu (Ref. 18) since for the close-packed crystal structures (hcp and fcc) interatomic repulsion does not allow the atoms to approach each other closely enough for the formation of strong *f* bonds with a directional dependence. It has earlier been shown,[17] however, that a calculation which treats the *f* electrons as corelike, i.e., electrons that do not participate in the chemical bonding, gives an atomic equilibrium volume of the order of 50% too large in comparison with experiment for Pu. There are other investigations which also show that the 5*f* states are delocalized in the light actinides (Th–Pu) and as an example we mention studies of the cohesive energy.[16] Nevertheless, the upturn in the equilibrium volume of α-Pu (Ref. 14) (Fig. 1) remains unexplained until a proper calculation of α-Pu (in the monoclinic structure) has been performed. Such an investigation is in progress.

In Table I we list the theoretical results for the atomic equilibrium volumes for α-Ce and Th–Pu together with experimental data. Notice that α-Ce is in fact in better agreement with experiment than Th (both these elements are fcc at low temperature). Also, as mentioned above, the agreement between theory and experiment is much better for the GGA than for the LDA calculations. The discrepancy between theory (GGA) and experiment is of the order of a few percent, and this is quite similar to the agreement found for the transition metals.[7] It thus seems that gradient-corrected local-density theory describes α-Ce and Th–Np, assuming delocalized *f* electrons, equally as well as this theory describes the transition metals.

In order to investigate the effect of the gradient corrections on the occupation of the *d* and *f* orbitals, we show in Table II the *d* and *f* occupation numbers. Here it can be seen that the electron distribution on the partial waves is not much influenced by the change from LDA to GGA. It is not likely that this small change of *f* occupation (n_f) will directly affect the atomic volumes and explain the difference between the LDA and the GGA results. The increase of the equilibrium volume when GGA replaces LDA is of the order of 10% which is about the same order of magnitude as the difference between two consecutive light actinides. As regards the 5*f* occupation, the corresponding difference between consecutive actinides is about one electron (see Table II), whereas the shift in n_f caused by the change of exchange and correlation potential is much smaller (a few hundredths of an electron, see Table II). The conclusion must be that it is not this latter fact which explains the improved equilibrium volumes for the GGA calculations.

Next we present our calculated bulk moduli. In Table III we give our theoretical bulk moduli for α-Ce, and for Th–Pu. Here, as in the case of the atomic equilibrium volumes, we present calculations in the fcc structure (all elements), α-Pa, α-U, and α-Np. The results presented in Table III were calculated at the theoretical equilibrium volume, instead of at the experimental volume. This explains the difference between these results and the ones calculated by Wills and Eriksson.[15] Notice from Table III that there is a large difference between the LDA and the GGA bulk modulus, and that the GGA results normally agree better with experiment (except for Pa). The bulk modulus dependence on the crystal structure is also quite large for certain elements. When comparing the experimental and theoretical (GGA) data we observe that for Th and Pa the agreement is fair, whereas for the rest of the actinides the calculations do not even reproduce the experimental trend. Part of this discrepancy is connected to the error made in the calculation of the equilibrium volume. However, the theoretical volume for α-U is very close to the experimental volume, whereas the bulk modulus is ~ 50% too large in the calculations. Clearly other causes for this failure must be found. We speculate that the remaining discrepancy might be due to the fact that all calculations have been done with fixed crystallographic parameters. In principle, those parameters should have been optimized with respect to the total energy, but this would have been extremely time consuming. It is clear that this optimization will always lower the

TABLE III. Theoretical and experimental bulk modulus. The theoretical data are obtained with a LDA and a GGA parametrization of the exchange-correlation functional, respectively. These theoretical results are obtained for the fcc crystal structure for all elements, and for Pa, U, and Np results from calculations in their observed (Ref. 14) crystal structure are also given. The experimental data (Ref. 19) are measured at room temperature.

		Bulk modulus (kbar)		
	Crystal structure	LDA	GGA	Expt.
Ce	fcc	605	487	290
Th	fcc	826	615	580
Pa	fcc	1413	1216	
Pa	α-Pa	1462	1234	1600
U	fcc	1862	1479	
U	α-U	2403	1722	1130
Np	fcc	1993	1605	
Np	α-Np	3000	1700	740
Pu	fcc	2142	1435	
Pu	α-Pu			550

bulk modulus and thus improve our theoretical results in Table III, since the bulk modulus is overestimated.

In conclusion we have implemented the generalized gradient correction (GGA) to density-functional theory in connection with a full-potential energy band method. The theory has been applied to calculate the ground-state properties of Ce and the early actinides (Th–Pu). Generally, without exception, the approach with gradient corrections to the LDA gives results with improved agreement with experiments. The theoretical calculations (GGA) reproduce the experimental volumes within a few percent whereas the theoretical bulk modulus compares worse with experiment. This latter finding is probably due to our assumption of a lattice which is rigid under compression. We argue that by optimizing the crystal structure data, as a function of volume, we should obtain a more accurate bulk modulus.

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