

Equilibrium properties of δ -Pu: LDA + U calculations (LDA \equiv local density approximation)

J Bouchet^{†‡}, B Siberchicot[†], F Jollet[†] and A Pasturel[‡]

[†] Centre d'Etudes de Bruyères-Le-Châtel, 91680 Bruyères-Le-Châtel, France

[‡] Laboratoire de Physique Numérique, CNRS, 25 Avenue des Martyrs, BP 166,
F-38042 Grenoble Cédex 9, France

Received 11 October 1999

Abstract. Equilibrium properties for the δ -phase of Pu have been calculated. Taking into account strong electron correlations in the 5f shell, we show how the equilibrium volume and the bulk modulus are improved in comparison to previous results using the local density approximation (LDA) or the generalized gradient approximation (GGA). In addition, an augmentation of the orbital moment is observed following Hund's rules, reducing the total magnetic moment. The stability of the δ -phase is explored and for the first time a positive value for the tetragonal shear constant is found.

1. Introduction

Among the actinides, plutonium is one of the most intriguing metals because of its spectacular and unusual properties. In the actinide series the competition between the itinerant and local character of the f electrons is responsible for its unique properties. The series can be divided into two sub-series: the light (${}_{90}\text{Th}$ – ${}_{94}\text{Pu}$) and the heavy (${}_{95}\text{Am}$ and beyond) actinides, with very different characteristics. The volume behaviour of the light actinides is very similar to that found for the transition metals, with a parabolic decrease of the volume as a function of atomic number. This trend can be explained by the itinerant character of the 5f electrons which participate in the chemical bonding, and thus the light actinides are considered to form a 5f transition series. The density functional theory in the local density approximation (LDA) gives a good description of the ground state of the light actinides in agreement with experiment (except for Th) and a simple Friedel model can explain the parabolic decrease of the volumes. However, neptunium and plutonium deviate from this theoretical estimation, since Pu has a larger volume than Np. Furthermore, in contrast to the transition metals which adopt close-packed structures, such as body-centred cubic, face-centred cubic and hexagonal close packed, the light actinides have very distorted and open structures. With the filling of the f shell, the complexity increases to reach a maximum with the ground-state crystal structure of Pu (α -Pu) which is monoclinic with 16 atoms/cell and is the most distorted structure of the light actinides. Structural differences between light actinides and transition metals—in spite of their exhibiting the same electronic behaviour—have their roots in the bandwidth of the dominant electrons for bonding (d electrons in transition metals, f electrons in light actinides). In fact, Söderlind *et al* [1] have shown that the 5f bandwidth is sufficiently narrow at the equilibrium volume of the light actinides (~ 1 – 3 eV) to favour a Peierls distortion [2], in contrast to the case for the transition metals (d bandwidth: ~ 3 – 10 eV). Their calculations led them to the conclusion

that for the same bandwidth, metals crystallize in the same structure. For heavy actinides, the pattern is reversed: 5f electrons are localized, the crystal structures are more compact like fcc or hcp and this sub-series may be described as a second rare-earth series. This picture places plutonium as the link between the two series, at the transition from delocalized to localized states, and thus it adopts some characteristics of the two series.

Plutonium has no fewer than seven different crystalline forms—more than any other metal—and so shows the most complicated phase diagram in the periodic table. Owing to its position in the actinides' series, it is difficult to say whether Pu is a pure light actinide. It is very interesting to note that the phase diagram reproduces the same aspects as for the actinide series. In fact the α -, β - (monoclinic with 34 atoms/cell) and γ - (orthorhombic with 8 atoms/cell) phases contrast with the high-temperature simple structures δ (fcc) and ϵ (bcc) which are traditional close-packed structures. In addition there are large volume changes between phases, the δ -phase assuming the lowest density (including the liquid), and from δ -Pu to α -Pu there is a 17% volume decrease. Similar collapses are only observed in a few cases, like Ce ($\gamma \rightarrow \alpha$ phase transition) and Sm compounds where this transition can be understood in terms of a Mott transition from localized to itinerant 4f states [3]. The situation for the plutonium element is certainly connected with some of its unusual properties [4] like: the electrical resistivity, the thermal conductivity—which is the lowest reported for any pure metal [4]—or the negative thermal dilatation coefficient of the δ - and δ' -phases, for instance.

Recent developments in the theoretical understanding of the electronic structure of Pu seem to show that the anomalously large volume of α -Pu relative to that of α -Np is the result of the proximity to the onset of 5f localization and a sign of electron correlation. Kollar *et al* [5] compare the LDA and GGA results and show that the upturn between Pu and Np is due to correlation effects not included in the LDA but described in the GGA. Their calculations also show that the spin-orbit coupling improves the volume but that it is not responsible for the upturn. Söderlind and co-workers [6] conclude for α -Pu that the 5f band dominates the bonding and the 6d band is less important for the crystal structure, contrary to previous results of van Ek *et al* [7]. So we can assume that the large volume of the δ -phase arises from localized 5f states and predominantly 6d bonding, whereas 5f bonding dominates for the more open structures. However, we must modify this explanation, since the δ -Pu volume is located between the α -phase (delocalized electrons for the most part) and americium (localized electrons) and is probably intermediate between these extremes. To understand the $\alpha \rightarrow \delta$ phase transition, it seems essential to appreciate the gain in energy arising from the Hund's rules for localized 5f states and f-band cohesion for itinerant 5f states. Experimental results confirm this picture [4, 8, 9]: the XP spectra of α -Pu show a strong signal at the Fermi level corresponding to the 5f states, whereas for the δ -Pu this signal is shifted to higher binding energies. At the same time the bandwidth is broadened by 15% from α -Pu to δ -Pu and the spectral weight at E_F is reduced.

The LDA, which is sufficient to describe light actinides, with however the largest disagreement for α -Pu, underpredicts the δ -phase volume by of the order of 35% for the LDA and 28% for the GGA [10]. δ -Pu is not the only material for which the LDA fails to reproduce the ground-state properties; Mott insulators, like 3d transition metal oxides, or some transition metal perovskites [11], and a great variety of materials whose the electronic structure contains partially filled valence d or f shells complete the list. It is well established that this deficiency of the LDA is linked to the strong on-site repulsion U between electrons in the localized d or f states. In fact, correlation effects arise when U exceeds or equals the mean conduction bandwidth W . In this contribution we used the LDA + U method to include the f-f correlation energy in the LDA band-structure calculation. This method has been widely tested for metal oxides [12] and high- T_c superconductors [13] with good results. It is still a one-electron theory

but the one-electron potentials are orbital dependent and allow an orbital polarization [14].

The purpose of the present paper is to perform a study of the f–f interactions in plutonium. With an appropriate treatment of the correlations we will show how the bulk properties of the δ -phase can be found. In section 2 we describe the LDA + U theory to show how the LDA functional is modified to take into account the correlation between f electrons, in section 3 the details of calculations are presented and in section 4 we present our results, and our point of view regarding the situation in plutonium.

2. The LDA + U method

We give here a short description of the LDA + U method; for a review, see reference [15]. The electrons are separated into two subsystems: delocalized s, p and d electrons which are described by an orbital-independent one-electron potential (LSDA); and localized 5f electrons for which we take into account the orbital degeneracy and a Coulomb interaction of the form $\frac{1}{2}U \sum_{\sigma \neq \sigma'} n_{\sigma} n_{\sigma'}$, where n_{σ} are f-orbital occupancies. In a spin- and orbitally degenerate system, we can consider an Hamiltonian of the form

$$\hat{H} = \sum_{i,j} \sum_{m,m'} \sum_{\sigma} t_{ij}^{mm'} \hat{c}_{im\sigma}^{\dagger} \hat{c}_{jm'\sigma} + \frac{(U-J)}{2} \sum_i \sum_{m \neq m'} \sum_{\sigma} \hat{n}_{im\sigma} \hat{n}_{im'\sigma} + \frac{U}{2} \sum_{i,m,m'} \sum_{\sigma} \hat{n}_{im\sigma} \hat{n}_{im'-\sigma} \quad (1)$$

where $\hat{c}_{jm'\sigma}$ is an annihilation operator of an electron with orbital index m and spin σ ($=\uparrow, \downarrow$) at the lattice site i , $t_{ij}^{mm'}$ are the hopping integrals and $\hat{n}_{im'-\sigma}$ is the number operator of the f electron at site i , orbital m with spin σ . Thus the first term of (1) describes hopping of electrons between lattices sites i and j ; interactions between localized electrons are described by the second and third terms, where U and J represent the on-site Coulomb and exchange interactions respectively. Thus, with the Hamiltonian (1), it is possible to achieve the filling of incomplete f (or d) shells in the atomic limit according to Hund's rules, whereas in a simple LSDA approach, all orbitals have the same occupancy.

If we want to correct the LSDA functional for localized electrons we must first extract the LSDA treatment to avoid double counting of the interaction. The spin-density functional theory assumes a local exchange–correlation potential which is a function of the local charge and spin densities; it is a weak-coupling mean-field theory [16], so fluctuations around the average occupancies are neglected. In the mean-field approximation we can write

$$\hat{n}_{m\sigma} \hat{n}_{m'\sigma'} = \hat{n}_{m\sigma} n_{m'\sigma'} + \hat{n}_{m'\sigma'} n_{m\sigma} - n_{m\sigma} n_{m'\sigma'} \quad (2)$$

where $n_{m\sigma}$ is the mean value of $\hat{n}_{m\sigma}$ and $n_{\sigma} = \sum_m n_{m\sigma}$. If we insert this approximation in equation (1), we obtain for the potential energy in the mean-field approximation E^{MF}

$$E^{MF} = \frac{U-J}{2} \sum_i \sum_{\sigma} n_{i\sigma} (n_{i\sigma} - n_{im\sigma}) + \frac{U}{2} \sum_i \sum_{\sigma} n_{i\sigma} n_{i-\sigma}. \quad (3)$$

What is the role of the LSDA in this energy? Solovyev *et al* [17] have discussed this 'removed energy' intensively; they proposed extracting an energy-only function of the total number of electrons per spin $n_{i\sigma}$ —this expression can be obtained from (1) in an atomic limit where the single-particle occupancies $n_{im\sigma}$ are close to 0 or 1:

$$E_{cor}^{LSDA} = \frac{U-J}{2} \sum_{i\sigma} n_{i\sigma} (n_{i\sigma} - 1) + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \quad (4)$$

This energy is now subtracted from E^{MF} to obtain the total-energy correction for the localized states:

$$\Delta E = \frac{U-J}{2} \sum_{i\sigma} n_{i\sigma} (1 - n_{im\sigma}) = \frac{U-J}{2} \sum_{im\sigma} (n_{im\sigma} - n_{im\sigma}^2). \quad (5)$$

Then, the correction to the potential acting on the localized orbital ($m\sigma$) is found by taking the derivative of (5) with respect to the occupation number $n_{im\sigma}$:

$$\Delta V_{im\sigma} = (U - J) \left(\frac{1}{2} - n_{im\sigma} \right). \quad (6)$$

Thus, we have obtained an orbital-dependent one-electron potential. In our calculations, we used for U and J the Coulomb and exchange matrices $U_{mm'}$ and $J_{mm'}$ defined from Slater integrals [18].

3. Computational approach

We have used a full-potential linear muffin-tin orbital (FP-LMTO) [12, 19] method with three approximations for the exchange–correlation potential: the local spin-density approximation (LSDA) with the von Barth–Hedin density functional, the generalized gradient approximation (GGA) introduced by Perdew and Wang [20] and the LSDA + U following (5) and (6). In most cases the generalized gradient correction, more particularly in actinides [21], improves the results for the volumes and bulk moduli compared with the LDA. In the FP-LMTO method the crystal is divided into non-overlapping muffin-tin spheres and the remaining interstitial region. The potential is expanded in spherical harmonics inside the spheres—in our calculations we have worked with a cut-off $l_{max} = 6$ —and is Fourier transformed in the interstitial region. We have treated three kinds of state: deep-core states, which are found by solving Dirac’s equation for free atoms with the potential taken as the spherical part of the crystalline potential inside the MT sphere and zero outside, valence states which are described with three energy panels and semicore states which are treated in a separate energy panel since they have little hybridization with valence states. We have chosen a ‘standard’ actinide basis set [6] with 7s, 6p, 6d, 5f in the valence band and 6s as the semicore orbital; the 6p states are semicore-like but are treated as bands in the main valence panel. The self-consistent, all-electron calculations were performed with a fully relativistic treatment of the core states and a scalar-relativistic treatment with spin–orbit coupling for the valence states. The total and partial densities of states were calculated using 144 k -points in the fcc phase. For the elastic constant calculations this number is increased to 376 for the tetragonal shear calculation and to 744 for the orthorhombic shear owing to the very small energy difference between different strains. For the Coulomb interaction strengths we have used the value 0.23 Ryd calculated by Bandyopadhyay and Sarma [22] from Hartree–Fock–Slater atomic calculations.

4. Results and discussion

We present in figure 1 the equilibrium volume V_0 for our exchange–correlation potentials. The curves are obtained by a Birch–Murnaghan fit of the total energy versus volume points. We have derived from these fits the value of the bulk modulus B_0 for the different approximations (see table 1). Our results for δ -Pu show that the FP LDA and GGA calculations underestimate V_0 and overestimate B_0 ; these trends are in agreement with the work of Söderlind *et al* [21]. The GGA volume, although better than the LDA value, shows a discrepancy of about 27% from the experimental value. As we expected, the volume is improved in a localized f-state treatment (figure 1) and for $U = 0.23$ Ryd we found an equilibrium volume of 25.21 \AA^3 in agreement with the experimental value of 25.156 \AA^3 . We have corrected the high-temperature value of 24.9 \AA^3 by the negative thermal expansion coefficient ($-0.26 \times 10^{-4} \text{ K}^{-1}$) since our calculations are made for zero temperature. In addition to the volume results, we found a better bulk modulus, with a value of 60 GPa for $U = 0.23$ Ryd compared to the GGA result of 153 GPa. This

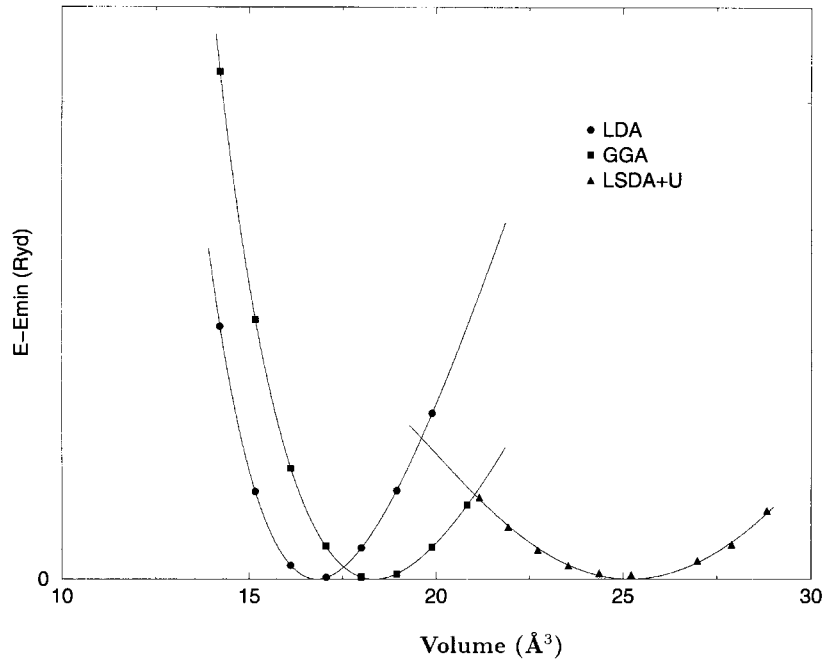


Figure 1. The total energy of δ -Pu versus the volume calculated using the LDA, the GGA and the LSDA + U method.

Table 1. Equilibrium volumes, bulk moduli and elastic constants for δ -Pu obtained with a FP-LMTO method, calculated including generalized gradient corrections of Perdew–Wang type or Hubbard corrections. Comparison with experimental values and other calculations. The value of C' for α -Ce is a result from reference [30].

		V_{eq} (\AA^3)	B_0 (GPa)	C' (GPa)	C_{44} (GPa)	C_{11} (GPa)	C_{12} (GPa)
FPLMTO ^a	LDA	16.18	214.2	−48			
	GGA	17.67	143.5				
FCD ^b	LDA	19.66					
	GGA	20.72					
Present calculation	GGA	18.37	136	−35			
	LDA + U	25.21	61	12	75	69	53
Experiments ^c		24.91	29.91	4.78	33.59	36.28	26.73
Th (experiment)		32.1	57.7	13.2	47.8		
α -Ce (experiment)		28.1	29	11.9 (theory)			

^a Reference [21].

^b Reference [5].

^c Reference [24].

improvement is obviously bound up with the volume's increase. Experimentally, with a δ -stabilized Pu–1 wt% Ga sample, Calder, Draney and Wilcox [23] found $B_0 = 32.4$ GPa in agreement with the ultrasonic measurement $B_0 = 29.9$ GPa of Ledbetter and Moment [24]. Pénicaud [25], with a relativistic orbital method and by neglecting the interatomic hybridization and overlap of the 5f orbitals, has obtained $B = 70$ GPa.

We have also investigated the possibility of a magnetic moment for δ -Pu but this problem is very controversial. All spin-polarized density functional calculations give a non-zero magnetic moment for the δ -phase volume [26,27]. Experimentally [4], it seems that the δ -phase is non-magnetic, but recently Méot-Reymond and Fournier [28] have performed low-temperature magnetic susceptibility measurements on stabilized alloys in the δ -phase and on pure plutonium (α -phase). They found magnetic moments μ_{eff} of $1.7 \mu_B$ and $1.2 \mu_B$ for Pu-6 at.% Ce and Pu-6 at.% Ga respectively. It is impossible to reach a conclusion regarding the pure δ -phase because, as it is not stable at low temperature, all the experimental results have been obtained on δ -stabilized alloys. The atomic Pu configuration is $7s^25f^6$ whereas for the solid we found generally $7s^26d^15f^5$, so if f electrons are fully polarized in the 5f shell and the first and second Hund's rules respected, we expect a spin moment of $5 \mu_B$ and an orbital moment of $5 \mu_B$, coupled antiparallel to the spin, yielding a total magnetic moment of $0 \mu_B$. This filling of the 5f shell is the only one among those for the actinides which gives this remarkable result. Solovyev *et al* [27] obtained values of $M_S = 4.5 \mu_B$, $M_L = -2.4 \mu_B$ and $M_J = 2.1 \mu_B$ at the experimental δ -phase volume. These calculations were performed in the atomic sphere approximation (ASA) with spin-orbit coupling. In the full-potential approximation and with the LSDA we found similar values: $M_S = 4.23 \mu_B$, $M_L = -1.94 \mu_B$ and $M_J = 2.29 \mu_B$. In a LSDA + U treatment and at the δ -phase volume, M_J takes values of $1.55 \mu_B$ and $1.3 \mu_B$ for $U = 0.23$ Ryd and $U = 0.33$ Ryd. So the localization of f electrons reduces the total magnetic moment in comparison with a delocalized treatment, and this agrees well with a non-magnetic δ -Pu. In fact the spin contribution to the total magnetic moment is compensated by the orbital contribution but not enough to cancel it: $M_S = 5 \mu_B$ and $M_L = -3.45 \mu_B$ for $U = 0.23$ Ryd. However, according to Hund's rules a stronger localization increases the orbital moment and we reach the value of $M_L = -3.7 \mu_B$ for $U = 0.33$ Ryd. M_S reaches a limit value of $5 \mu_B$ which corresponds to a total polarization of the 5f electrons in the spin-up channel. So the localization is a redistribution within the f shell with respect of Hund's rules: an *orbital polarization* [14].

We present in figure 2 the calculated density of states (DOS) for the volumes corresponding to the theoretical (figure 2(a)) and experimental (figure 2(b)) δ -values in the GGA functional. The 5f and 6d partial DOS are also represented and it is obvious that the 5f contribution dominates for all volumes. We can see, as expected, a decrease in the 5f bandwidth when the volume increases, since the 5f overlap becomes less and less important. For the two volumes the Fermi energy is located between the $5f_{5/2}$ and the $5f_{7/2}$ bands in a minimum of the density of states.

The DOS for the magnetic LDA solution are shown in figure 3(a). First, we can see that in the spin-polarized case, the band is strongly broadened, particularly for energy above E_F . In addition, the DOS value at the Fermi level is also considerably increased, and the separation between the $5f_{5/2}$ and the $5f_{7/2}$ peaks has disappeared. This is consistent with ASA calculations [27].

We can see in the LDA + U DOS (figure 3(b)) that the 5f are no longer pinned to the Fermi level, but are below, centred around -2 eV. The 5f-state localization is of course at the origin of this withdrawal of the 5f electrons from the Fermi level. There is a large reduction of the density of states at the Fermi level with an LDA + U value of $N(E_F) = 56$ states Ryd $^{-1}$ compared to the spin-polarized solution of about 190 states Ryd $^{-1}$. Recently Joyce's experiments [29] have shown a broader peak centred 1.7 eV below E_F and dominated by 5f-orbital character, and we can associate this with the region centred around 2 eV in our LDA + U DOS. The γ -term of the electronic specific heat for δ -Pu is very large (53 mJ mol $^{-1}$ K $^{-2}$) and twice as high as for α -Pu (22 mJ mol $^{-1}$ K $^{-2}$), suggesting a narrow resonant state pinned at the Fermi energy, similar to the situation found in the heavy-fermion systems of uranium. In our DOS we do

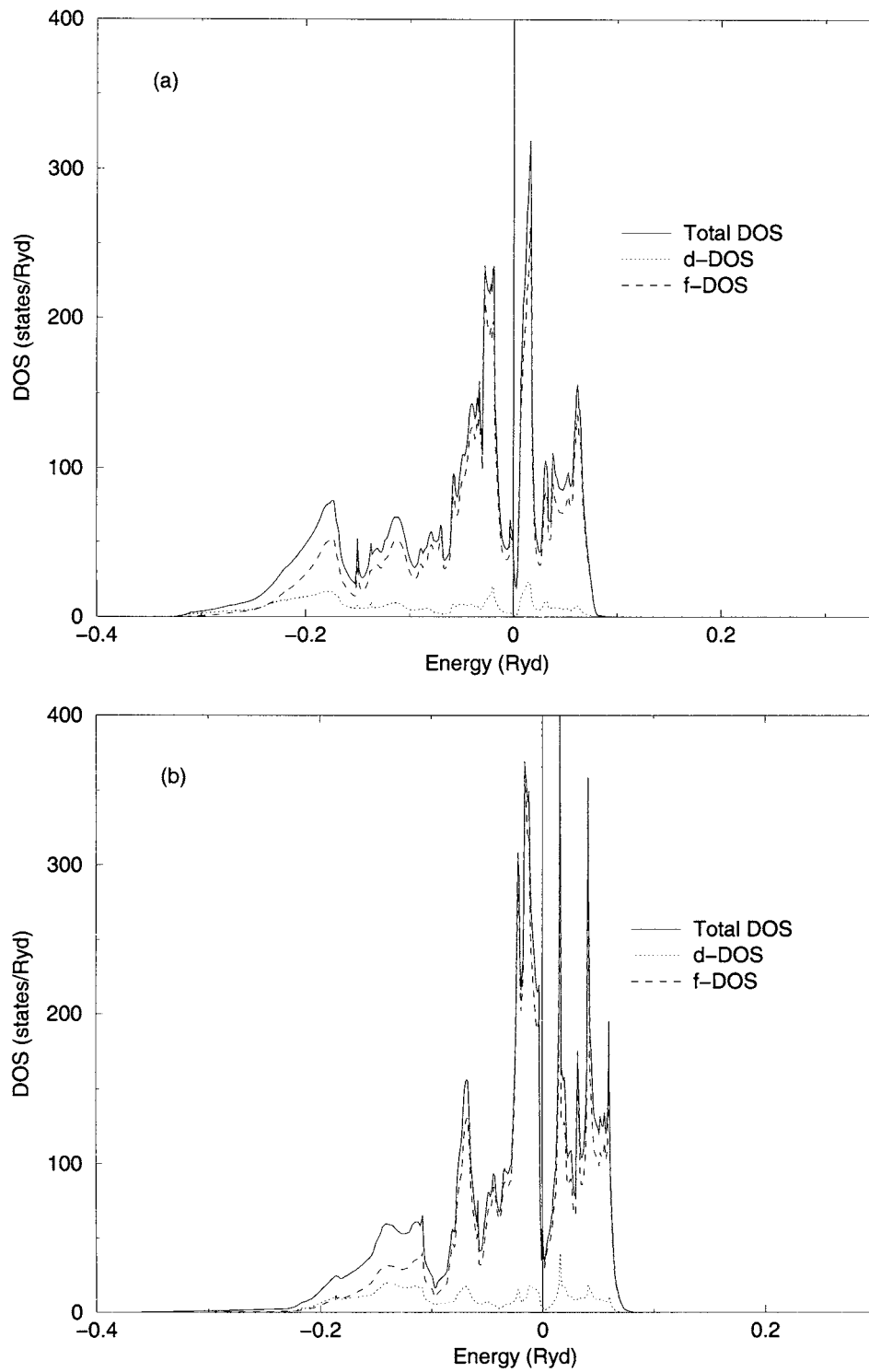


Figure 2. Electron densities of states (DOS) for the theoretical (a) and experimental (b) volumes of δ -Pu obtained using the GGA.

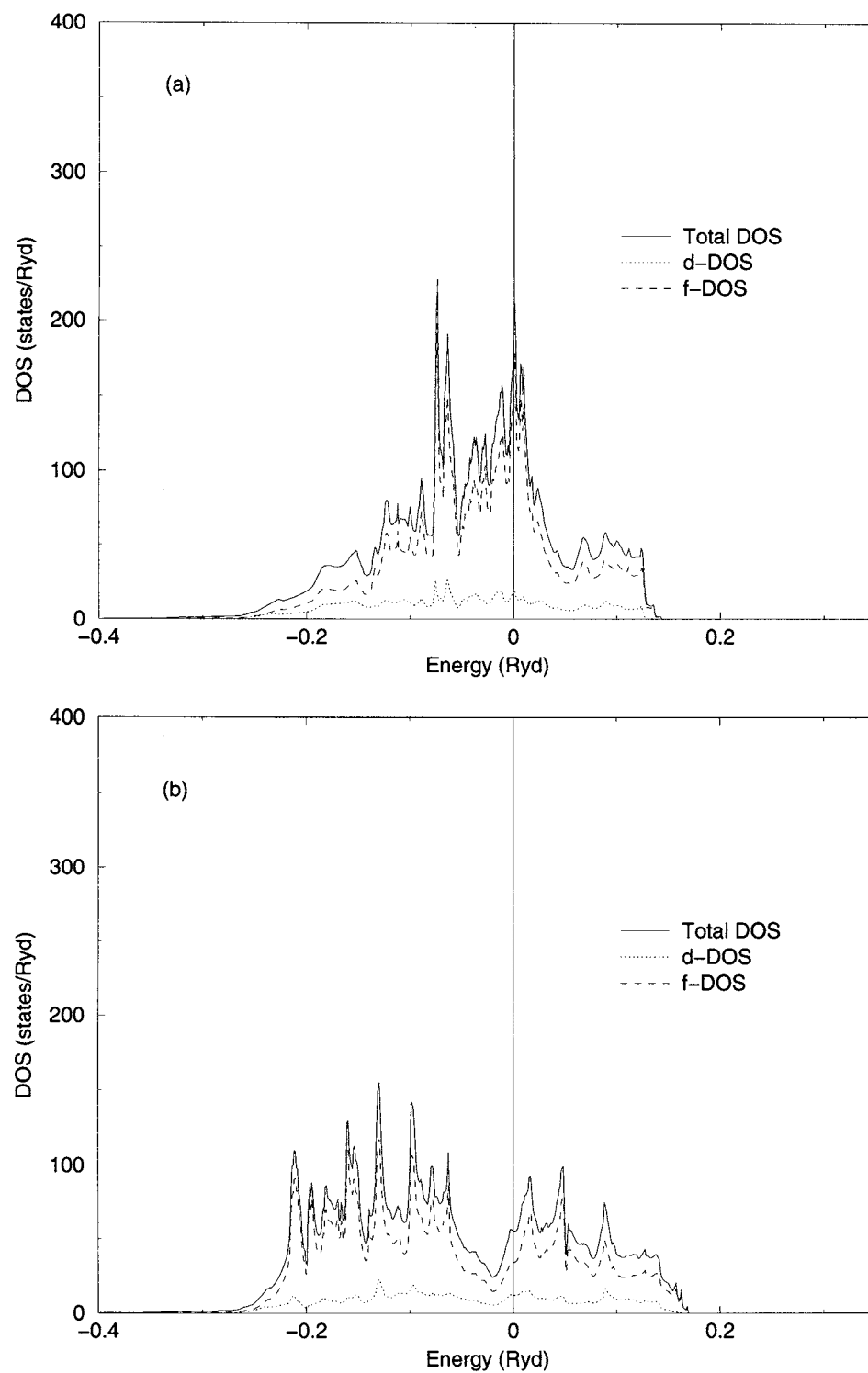


Figure 3. Electron densities of states (DOS) at the experimental volume of δ -Pu obtained using the LSDA (a) and the LSDA + U method (b).

not reproduce this peak, and it seems necessary to introduce many-body effects to retrieve it. More experience must be gained before we can explain the origin of this peak at the Fermi level.

To illustrate the predominant role played by the f-electron behaviour, we have explored the Bain path of Pu. In plutonium an intermediate phase (δ') occurs in the δ - ϵ (fcc-bcc) transition. The δ' -phase has a bct structure with $c/a = 1.33$. As for the bcc and fcc structures, they can be described as peculiar bct structures with $c/a = 1$ and $c/a = \sqrt{2}$ respectively. So the transition $\delta \rightarrow \delta' \rightarrow \epsilon$ is just a deformation of the tetragonal parameter c/a via the values $1.41 \rightarrow 1.33 \rightarrow 1.0$ —a Bain deformation. We have performed a study of the energy variation as a function of the c/a ratio for the bct structure: the Bain path. The results are shown in figure 4 for an itinerant and a localized treatment of the f electrons. We can see that the localized configuration stabilizes the fcc structure whereas the itinerant configuration favours a more distorted structure: bct with c/a near 1.2. An interesting result is the presence of another minimum in the localized picture. It corresponds to a $c/a = 1.3$, close to the value 1.33 for the δ' -structure. The slight change in the volume which followed the δ - δ' transition ($<1\%$) and the fact that the δ' -phase value of c/a is slightly lower than $\sqrt{2}$ indicate that the δ' -structure is a distorted fcc structure, obtained by a weak tetragonal distortion. However, the bcc structure is located in a maximum and so it is not stabilized in our LDA + U treatment, like in the LDA. The theoretical volume of bcc-Pu at 0 K may be responsible for this result; indeed, the linear thermal expansion coefficient of the bcc structure is positive whereas it is negative for δ - and δ' -structures. We have also calculated the elastic constant C' which is a

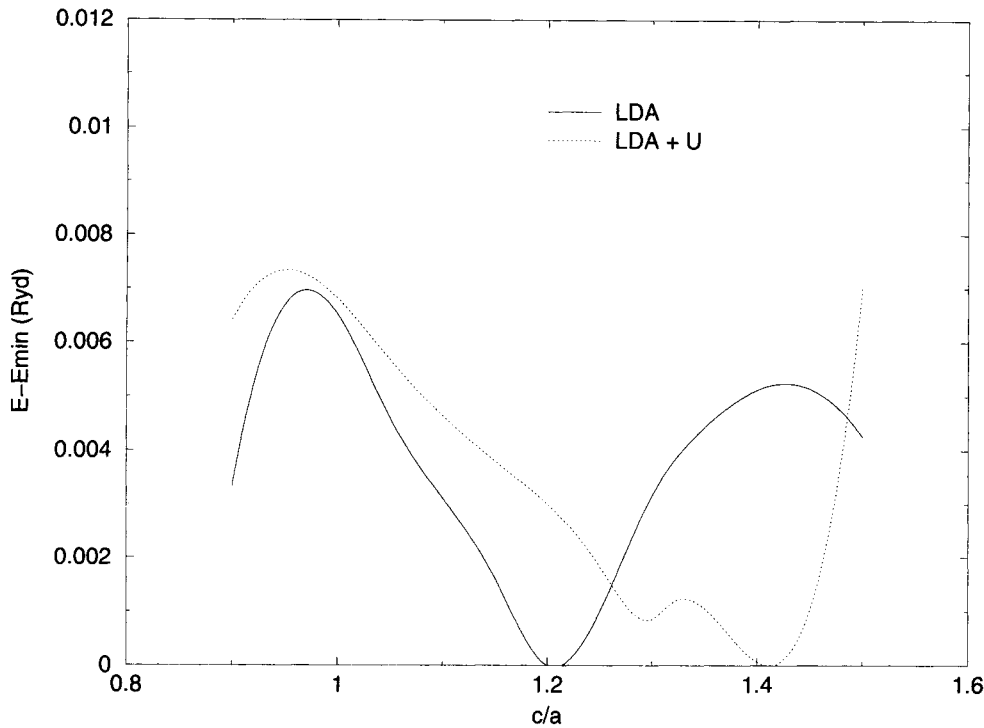


Figure 4. The Bain path for Pu. $c/a = \sqrt{2}$ and $c/a = 1$ correspond to fcc and bcc structures respectively.

direct measurement of the phase stability under a tetragonal deformation. It is obtained with a volume-conserving tetragonal strain:

$$\begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1/(1 + \delta)^2 \end{pmatrix} \quad (7)$$

where δ is an infinitesimal strain (<0.01). The calculations were done at the experimental δ -phase volume. As expected from the Bain path, the value of C' is highly negative in a LDA [30] or a GGA calculation (see table 1). With the LDA + U method we obtained a positive value of 12 GPa, compared to the experimental value of 4.75 GPa [24]. We have also reported in table 1 the values of the other cubic elastic constants. The existence of the δ' -phase is closely connected to the extremely small value of C' , since in this case a fcc \rightarrow bct transition requires a slight change in energy. This is confirmed by the energy difference between the fcc and bct structures in figure 4 (~ 1 mRyd).

To understand the stabilization of the δ -phase in Pu it is important to note that, in the actinides, the phase stability is driven by 5f electrons. An itinerant character of these electrons yields a distorted structure (light actinides) whereas a localized character yields symmetric structures (heavier actinides). The principal effect of the Hubbard correction is to prevent 5f participation in the bonding: the 5f electrons are removed from the Fermi level to higher binding energies. The consequence is the stabilization of the fcc structure. Following this idea, it is worth making a connection between δ -Pu, when the strong on-site repulsion is taken into account, and two other materials: α -Ce and Th, which adopt the fcc structure. The situation in these two metals is very similar; they each have one f electron in the atomic configuration and in the solid its influence on the bonding is negligible. We can see that our results for C' , V_{eq} and B_0 bear strong similarities to the experimental and theoretical values for α -Ce and Th (table 1), suggesting the same electronic behaviour.

In summary, by means of a treatment of the strong correlations between 5f electrons we have obtained a major improvement in comparison to the standard band result. Indeed, an accumulating body of results suggests, as previously expected, that the localization of the f electrons is crucial for describing δ -Pu. The anomalous experimental volume of the δ -phase is restored, with a good trend for the bulk modulus. The localization of the electrons in the 5f shell according to Hund's rules produces a decrease of the total magnetic moment in agreement with experiment. For the first time we have shown that the fcc phase is stabilized ($C' > 0$), contrary to LDA or previous calculation results, as a direct consequence of the correlations. All elastic constants have been calculated and good orders of magnitude have been obtained.

Acknowledgments

We wish to thank G Zerah, S L Dudarev and J P Julien for useful discussions.

References

- [1] Söderlind P, Eriksson O, Johansson B, Wills J M and Boring A M 1995 *Nature* **374** 524
- [2] Söderlind P, Wills J M and Eriksson O 1998 *Phys. Rev. B* **57** 1320
- [3] Eriksson O, Brooks M S S and Johansson B 1990 *Phys. Rev. B* **41** 7311
- [4] Fournier J-M and Troć R 1984 *Handbook on the Physics and Chemistry of the Actinides* vol 1, ed A J Freeman and G H Lander (Amsterdam: North-Holland) pp 29–173
- [5] Kollar J, Vitos L and Skriver H L 1997 *Phys. Rev. B* **55** 15 353
- [6] Söderlind P, Wills J M, Johansson B and Eriksson O 1997 *Phys. Rev. B* **55** 1997
- [7] van Ek J, Sterne P A and Gonis A 1993 *Phys. Rev. B* **48** 16 280

- [8] Cox L E, Eriksson O and Cooper B R 1992 *Phys. Rev. B* **46** 13 571
- [9] Eriksson O, Cox L E, Cooper B R, Wills J M, Fernando G W, Hao Y G and Boring A M 1992 *Phys. Rev. B* **46** 13 576
- [10] Becker J D, Wills J M, Cox L and Cooper B R 1996 *Phys. Rev. B* **54** 17 265
- [11] Solovyev I, Hamada N and Terakura K 1996 *Phys. Rev. B* **53** 7158
- [12] Dudarev S L, Botton G A, Savrasov S Y, Szotek Z, Temmerman W M and Sutton A P 1998 *Phys. Status Solidi a* **166** 429
- [13] Gunnarsson O, Andersen O K, Jepsen O and Zaanen J 1989 *Phys. Rev. B* **39** 1708
- [14] Sandalov I S, Hjortstam O, Johansson B and Eriksson O 1995 *Phys. Rev. B* **51** 13 987
- [15] Anisimov V I, Aryasetiawan F and Liechtenstein A I 1997 *J. Phys.: Condens. Matter* **9** 767
- [16] Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev. B* **44** 943
- [17] Solovyev I, Dederichs P H and Anisimov V I 1994 *Phys. Rev. B* **50** 16 861
- [18] Anisimov V I, Solovyev I V, Korotin M A, Czyżyk M T and Sawatzky G A 1993 *Phys. Rev. B* **48** 943
- [19] Savrasov S Y 1996 *Phys. Rev. B* **54** 16 470
- [20] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R and Singh D J 1992 *Phys. Rev. B* **46** 6671
- [21] Söderlind P, Eriksson O, Johansson B and Wills J M 1994 *Phys. Rev. B* **50** 7291
- [22] Bandyopadhyay T and Sarma D D 1989 *Phys. Rev. B* **39** 3517
- [23] Calder C A, Draney E C and Wilcox W W 1981 *J. Nucl. Mater.* **97** 126
- [24] Ledbetter H M and Moment R L 1976 *Acta Metall.* **24** 891
- [25] Pénicaud M 1997 *J. Phys.: Condens. Matter* **9** 6341
- [26] Schadler G, Alberts R C, Boring A M and Weinberger P 1987 *Phys. Rev. B* **35** 4324
- [27] Solovyev I, Liechtenstein A I, Gubanov V A, Antropov V P and Andersen O K 1991 *Phys. Rev. B* **43** 14 414
- [28] Méot-Reymond S and Fournier J M 1996 *J. Alloys Compounds* **232** 119
- [29] Joyce J, Arko A, Cox L E and Czuchlewski S 1998 *J. Alloys Compounds* **271** 826
- [30] Söderlind P, Eriksson O, Wills J M and Boring A M 1993 *Phys. Rev. B* **48** 9306