

Electron localization in the series of actinide metals. The cases of δ -Pu and Es

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 6341

(<http://iopscience.iop.org/0953-8984/9/30/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 09:13

Please note that [terms and conditions apply](#).

Electron localization in the series of actinide metals. The cases of δ -Pu and Es

M Pénicaud

Commissariat à l'Energie Atomique, Centre d'Etudes de Limeil-Valenton, 94195 Villeneuve St Georges Cédex, France

Received 28 January 1997, in final form 21 April 1997

Abstract. Ground-state properties of the whole series of actinide metals available to make bulk measurements, i.e. from Ra to Es, are investigated by means of total-energy calculations in the local density approximation (LDA) using a fully relativistic muffin-tin orbital band structure method. With experimental equilibrium volumes, quite good agreement is obtained from Ra to α -Pu with the usual LDA scheme and from Am to Cf with unhybridized 5f electron states calculations; an excellent agreement is found for Es with unhybridized 5f and 6d electron states calculations and for the δ -Pu phase with unhybridized $5f_{7/2}$ electron states calculations. Therefore it has been possible to take account of the partial localizations of electrons which yield the gap between the densities of α -Pu, δ -Pu, Am and Es.

1. Introduction

The occupation of electron bands of different angular momenta (s, p, d, f, ...) and their degree of broadening contribute to the properties that differentiate between different metals.

It is known [1, 2] that the series of actinide metals, corresponding to the progressive filling up of the 5f electronic subshell, must be split in two. In the first sub-series, from Pa to Pu, the 5f electrons bind in the manner of d electrons in transition metals. In the other sub-series, starting with Am, the 5f electrons are localized, similarly to electrons in deep atomic layers, and like the 4f electrons of lanthanides do not take part in metallic bonding.

Previous calculations of the equilibrium volumes of actinide metals were performed with semi-relativistic [3] and relativistic [4] linear muffin-tin orbital (LMTO) methods in a face centred cubic (fcc) crystal structure. The agreement with experiment was satisfactory up to U, but too small values were obtained for Np and Pu. The relativistic calculations, however, improve the results significantly. More recently, full-potential LMTO calculations with variational treatment of spin-orbit coupling has been performed in the real crystalline structures; for Np [5] and α -Pu [6] the agreement was not yet complete but the upturn of the values of the equilibrium volume between them is reproduced.

The localization of 5f electrons in Am was obtained [3] by semi-relativistic and spin-polarized calculations. In our opinion, however, this is not definitive as a final theory should treat spin polarization simultaneously with spin-orbit coupling [7] and correct the local density approximation (LDA) for the localization effect.

Here are results obtained with our fully relativistic muffin-tin orbital (MTO) band calculation method [8]. We present a theoretical calculation of the equilibrium volumes of the whole series of actinide metals available to make bulk measurements, i.e. from Ra to Es. Completely localizing the 5f electrons or not, we have tried to reproduce the transitions in

volume between α -Pu (19.86 g cm^{-3}), δ -Pu (15.92 g cm^{-3}) and Am (13.67 g cm^{-3}). Special attention has been focused on finding the electronic structure of Es metal in accordance with its low density (8.84 g cm^{-3}).

An fcc structure is used for all the calculations instead of the, in some cases, much more complex crystal structure: Ra is body centred cubic (bcc), Ac and Th are fcc, Pa is body centred tetragonal, U and Np are orthorhombic, α -Pu is monoclinic, δ -Pu is fcc, Am, Cm, Bk and Cf are double hexagonal close packed and Es is fcc. To obtain reliable theoretical equilibrium volumes in open structures such as orthorhombic or monoclinic it is necessary to perform ‘full-potential’ calculations [5,6]; this has not yet been done in a fully relativistic treatment when the wave functions are solutions of the Dirac equation and are expressed with the corresponding quantum numbers.

2. The relativistic MTO method. Treatment of localized electrons

The one-electron MTO wave functions ψ in each unit cell are given by

$$\psi(\mathbf{k}, E_n, \mathbf{r}) = \sum_{\kappa\mu} i^l B_{n\kappa\mu}(\mathbf{k}) \phi_{\kappa\mu}(E_n, \mathbf{r}). \quad (1)$$

Here, $\phi_{\kappa\mu}(E_n, \mathbf{r})$ are the solutions of the Dirac equation for a spherical potential, \mathbf{k} is the Brillouin zone wave vector, $E_n(\mathbf{k})$ is the energy and κ is the Dirac quantum number such that

$$\begin{array}{lll} \kappa < 0 & l = -(\kappa + 1) & j = l + \frac{1}{2} \\ \kappa > 0 & l = \kappa & j = l - \frac{1}{2} \end{array}$$

where j and μ are the quantum numbers for the total angular momentum and l for the orbital angular momentum.

The energies $E_n(\mathbf{k})$ and coefficients $B_{n\kappa\mu}(\mathbf{k})$ are solutions of a linear homogeneous system involving logarithmic derivatives of wave functions $\phi_{\kappa\mu}$ on the atomic sphere and ‘structure constants’ $SR_{\kappa'\mu',\kappa\mu}(\mathbf{k})$ that only depend on the type of crystal lattice considered. The MTO method [8] is therefore applied, and a relativistic generalization of the LMTO method [9,10] is only used to obtain approximate values for the one-electron energies $E_n(\mathbf{k})$ in the region of fixed energy E_v . These approximate values are incorporated in the MTO secular determinant to obtain the correct ones which are, then, totally independent of the choice of E_v , and at the same time the unphysical ‘ghost bands’ [10] are reliably eliminated. A new electronic density can be obtained from wave functions and a new potential is provided by using the LDA.

We have obtained quite good agreement between MTO calculations and experimental equilibrium volume from Ra to α -Pu [11]. We do have bonding 5f electrons up to α -Pu and the band theory may be applied. In these calculations, 6s, 6p_{1/2} and 6p_{3/2} were treated as band states and for the exchange–correlation terms the Kohn–Sham (KS) parametrization [12] was taken. The expansion (1) of the wave function is infinite but best agreement was obtained in [11] when it was stopped at a maximum value of l , $l_{max} = 3$ (f states).

From Am, 5f electrons become localized. It is well known that the LDA fails to describe properties of systems with localized d and f electrons. In this case, LDA overestimates the band character of electronic states.

Several different attempts (SIC–LDA [13–16], LDA + U [17,18], SRC [19], ...) were made to overcome these limitations and repair LDA by introducing some corrections for localized states, but they proved not completely satisfactory and are difficult to use, specially in the fully relativistic case. Moreover, we should point out that α -Pu, δ -Pu and Am are

all found experimentally to be non-magnetic and in the case of a paramagnetic regular crystal the LDA + U method ground-state energy should coincide with that in the LDA approach [19]. The SIC-LDA method reproduces quite well the localized nature of the d (or f) electrons in transition (or rare-earth) metal compounds, but SIC one-electron energies are usually in strong disagreement with spectroscopy data (for example for transition metal oxides occupied d bands are ≈ 1 Ryd below the oxygen valence band) [18].

Here, we have chosen a simpler procedure which gave good results for the equilibrium volume of the lanthanide metals [20]. Since LDA is known to overestimate the extent of the localized orbitals and hence the effects of interatomic hybridization and overlap, we neglect these terms in the matrix elements. We reproduce the localized character of electrons by removing the coupling between their states and other angular momenta. To do this using the MTO method, we only have to cancel the corresponding matrix elements in our ‘structure constants’.

A more empirical approach has been previously used for the lanthanide metals, where the 4f electrons were treated as part of the core and only s, p and d partial waves were considered in the conduction band [21]: the results were not very different from [20]. Similarly the same treatment has been used for the 5f electrons in the calculation of the equilibrium volumes of the last actinide metals Am, Cm, Bk and Cf [22]: the theoretical atomic radii were respectively 1.1 and 3.2% higher than the experimental ones for Am and for Cf.

3. Equilibrium properties

In figure 1, our calculated equilibrium Wigner–Seitz atomic radii are compared with the experimental values obtained from the equilibrium density of the common isotope quoted in [23, 24] and in [25] for Ra and [26] for δ -Pu. The agreement is good for MTO calculation with delocalized 5f to α -Pu. The treatment with fully unhybridized 5f is obtained by cancelling the matrix elements between f and angular momenta s, p and d and those between the $5f_{5/2}$ and $5f_{7/2}$ states. When bonding begins to be caused by 5f electrons with Th, this treatment fails.

Best agreement for Am, Cm, Bk and Cf is obtained by unhybridized 5f, where we cancel the coupling of 5f states with the s, p and d but allow the coupling between $5f_{5/2}$ and $5f_{7/2}$ states. We also use the Hedin–Lundqvist (HL) [27] exchange–correlation instead of KS [12]. For a given atomic radius the pressure is always lower with HL parametrization, so the theoretical equilibrium volume is also lower with HL. For example, for the equilibrium atomic radius of Ra, HL gives 4.60 au, KS 4.92 au; the experimental value is 4.95 au. For Am, HL gives 3.62 au, KS 3.75 au and the experiment 3.61 au. This is why we have taken KS for our calculations with delocalized 5f and HL for the calculations with localized states (δ -Pu and from Am to Es): this way we have the best agreement with experiment.

To obtain the theoretical value for δ -Pu the coupling of the $5f_{5/2}$ states with s, p and d states is allowed; the coupling of $5f_{7/2}$ with s, p and d is still forbidden. This yields the exact experimental value of the equilibrium atomic radius. This is in accordance with the recent x-ray and high-resolution UV photoemission study which found the localization of δ -Pu 5f electrons half-way between Am and α -Pu [28].

For Es we obtain excellent agreement with the experimental equilibrium volume if we cancel the coupling of the 5f states with the s, p and d and the coupling of 6d states with the s and p. In this case also the HL exchange–correlation was used.

In figure 2, the pressure is split on angular momenta. We see that metallic bonding is due to d and f electrons and from Pa to α -Pu the effect of f electrons dominates.

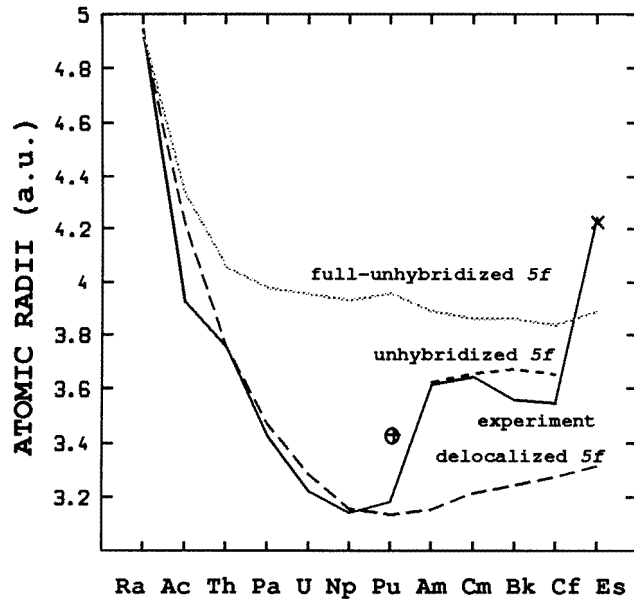


Figure 1. A comparison of experimental and calculated (in fcc structure) equilibrium atomic radii. +, experimental and \circ , calculated, with unhybridized $5f_{7/2}$ electron states, values for δ -Pu; \times , calculated value for Es with unhybridized 5f and 6d electron states.

Also when we have large partial pressures, a small volume change can alter the total pressure significantly, which results in a higher value of the theoretical bulk modulus,

$$B = -V \frac{dP}{dV} \quad (2)$$

as shown in figure 4 below.

In figure 2, in the partial pressures we have the contributions from the valence band and the 6s, $6p_{1/2}$ and $6p_{3/2}$ semicore bands; in figure 3 we show their relative importances. If the contribution of the 6s is always small, the contributions of the $6p_{1/2}$ and $6p_{3/2}$ bands are greater than that of the valence band for U, Np and α -Pu. In addition, the semicore bands contribute significantly to the partial pressures of all angular momenta and not only to that of their angular momentum character.

When comparing theoretical and experimental [24] (and for δ -Pu unpublished results obtained as in [29]) bulk moduli in figure 4, we observe excellent agreement for Th, U and Am and moderate agreement for Cm, Bk and Cf; however a noticeable discrepancy is observed for Pa, Np, α -Pu and δ -Pu. These differences can be explained because sometimes our calculations were not performed within the real crystalline structures, or because theoretical and experimental volumes are different. This is not the case for δ -Pu, which has an fcc structure and for which we have found the exact equilibrium volume, but we should point out that the fcc phase can only exist at ambient temperature when stabilized with a small amount of Ga (or Al, ...); we have not taken account of this effect in the electronic structure.

It is also important to point out that the theoretical calculations of the bulk modulus performed, by full-potential LMTO, in the real crystalline structure of Pa, U and Np [5] are in strong disagreement with the experimental values too, specially for Np where 1700 kbar was found in comparison with 740 kbar for the experiment [24].

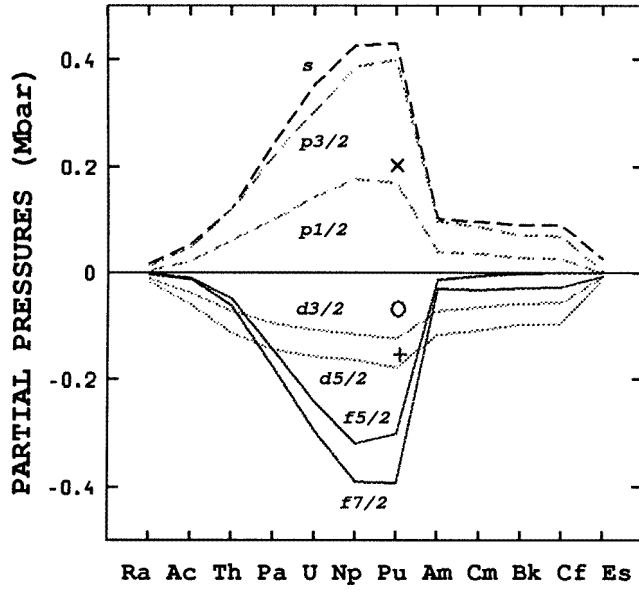


Figure 2. The splitting of pressure on angular momenta for the values of theoretical equilibrium volumes. Delocalized treatment of 5f electron states from Ra to α -Pu; unhybridized 5f from Am to Cf; unhybridized 5f and 6d for Es. \times , s, +, $5f_{5/2}$ and \circ , $5f_{7/2}$ partial pressures for δ -Pu obtained with unhybridized $5f_{7/2}$ electron states.

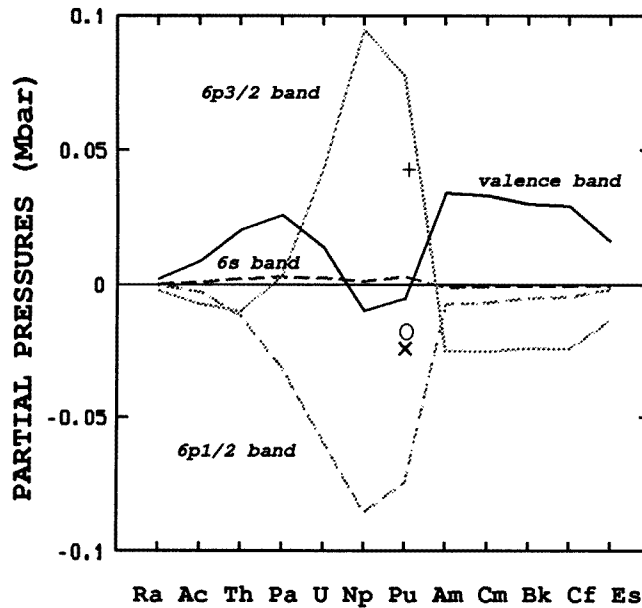


Figure 3. A comparison of the contributions of the valence band and the semicore bands to the pressure for the values of theoretical equilibrium volumes. Delocalized treatment of 5f electron states from Ra to α -Pu; unhybridized 5f from Am to Cf; unhybridized 5f and 6d for Es. +, 6s band, \times , $6p_{1/2}$ and \circ , $6p_{3/2}$ bands partial pressures for δ -Pu obtained with unhybridized $5f_{7/2}$ electron states.

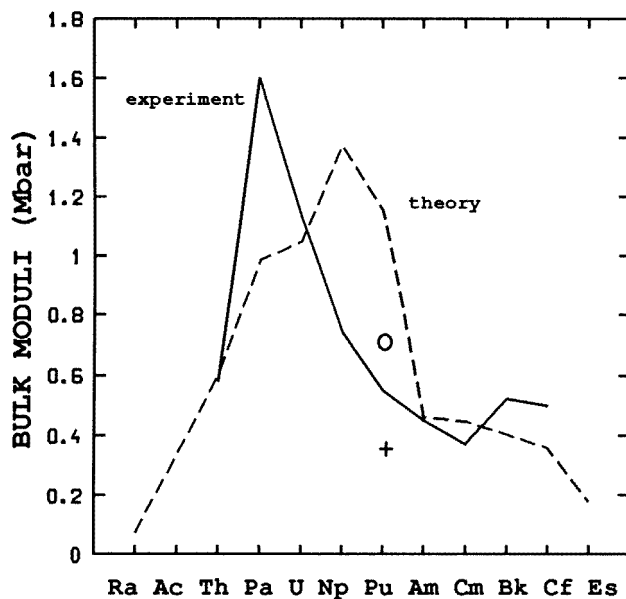


Figure 4. Experimental and theoretical bulk moduli at the values of the respective equilibrium volumes. Delocalized treatment of 5f electron states from Ra to α -Pu; unhybridized 5f from Am to Cf; unhybridized 5f and 6d for Es. +, experimental and O, theoretical values for δ -Pu obtained with unhybridized 5f_{7/2} electron states.

Our model of δ -Pu is not definitive; we can only say that the 5f electrons are partially localized [28]. Our model with unhybridized 5f_{7/2} states and HL exchange–correlation gives an equilibrium atomic radius (3.426 au) in perfect agreement with the experimental one (3.425 au) but a bulk modulus (711 kbar) twice the experimental value (350 kbar). With an alternative model, with unhybridized 5f_{5/2} states and KS exchange–correlation, we have obtained a theoretical equilibrium radius of 3.397 au and a bulk modulus of 577 kbar.

The description of the electronic structure of δ -Pu is maybe beyond the scope of band structure calculations as suggested in [30], where it has been proposed that δ -Pu is a concentrated Kondo system: on each plutonium site a Kondo interaction tends to orient the spin of valence electrons (7s, 6d) in a direction opposite to that of 5f localized electrons. Nevertheless we plan to try some improvements of our models for δ -Pu.

4. Electronic structure

In figure 5, we see the filling of the 5f shell in the actinide metal series. For Ra, there are no 5f electrons yet. In figure 1, its theoretical equilibrium volume is the same with all 5f electron treatments. More exactly for Ra the very small occupation number of 5f states, 0.03 electrons, gives a 0.22% equilibrium radius difference between different treatments of 5f electrons; for Ac, 0.12 electrons in 5f states gives a 2.8% equilibrium radius difference; for Th, 0.52 electrons in 5f states gives an 8.1% equilibrium radius difference; there is no simple relation between the number of electrons in 5f states and the equilibrium radius differences.

The filling of the 5f_{5/2} shell is progressive and is almost complete (approximately six electrons) at Am. From U, the 5f_{5/2} and 5f_{7/2} shells evolve differently. The decrease in the

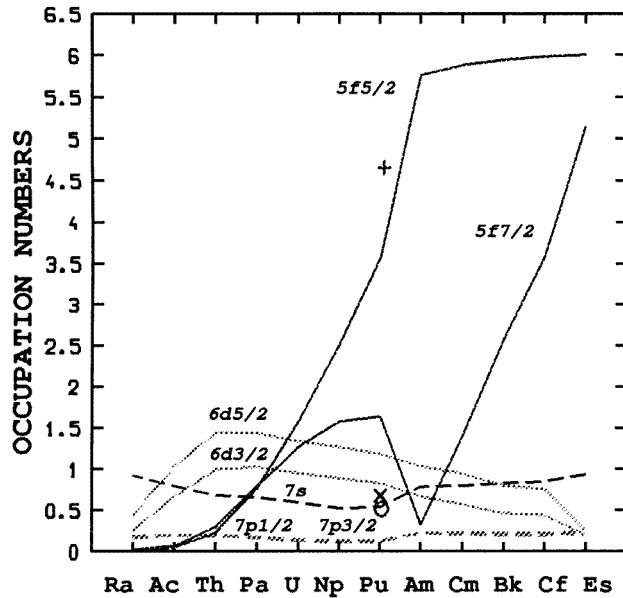


Figure 5. Calculated occupation numbers for the values of theoretical equilibrium volumes. Delocalized treatment of 5f electron states from Ra to α -Pu; unhybridized 5f from Am to Cf; unhybridized 5f and 6d for Es. \times , s, +, $5f_{5/2}$ and \circ , $5f_{7/2}$ occupation numbers for δ -Pu obtained with unhybridized $5f_{7/2}$ electron states.

number of $5f_{7/2}$ electrons between α -Pu and Am is due to their localization. All this can be explained by examination of the position of the $5f_{5/2}$ and $5f_{7/2}$ partial densities of states relative to the Fermi energy in figure 6.

To obtain densities of states (DOS) with a small sampling of the Brillouin zone (19 points in the irreducible wedge of the fcc Brillouin zone), we use Gaussian-smoothed DOS [31].

With Th, the two peaks of the $5f_{5/2}$ and $5f_{7/2}$ partial DOS appear but they are well above the Fermi level. Therefore, the metallic bonding for Ra, Ac and Th is due to 6d electrons, but for Th a small part of the bonding is caused by 5f electrons; this is enough to yield, in figure 1, a very noticeable difference in the values of equilibrium volumes obtained with different treatments of 5f electrons. In [32] it is proposed that the 5f contribution to bonding in Th is the cause of its fcc crystalline structure and, without it, Th would be bcc.

Going from Th to heavier actinides, the $5f_{5/2}$ and $5f_{7/2}$ partial DOS move progressively below the Fermi level. The 5f electrons have an itinerant behaviour and participate in the bonding from Pa to α -Pu. 5f DOSs are broad when 5f are delocalized.

The bandwidths of the 5f partial DOS decrease with δ -Pu, where the coupling of the $5f_{7/2}$ states with the s, p and d is cancelled.

The narrowness of the 5f partial DOS becomes more pronounced with Am, where the $5f_{5/2}$ and $5f_{7/2}$ are uncoupled from the s, p and d. The 5f electrons no longer participate in metallic bonding.

5. Conclusions

We have tried to explain the gap in densities between α -Pu (19.86 g cm^{-3}), δ -Pu (15.92 g cm^{-3}), Am (13.67 g cm^{-3}) and Es (8.84 g cm^{-3}). Using our fully relativistic MTO

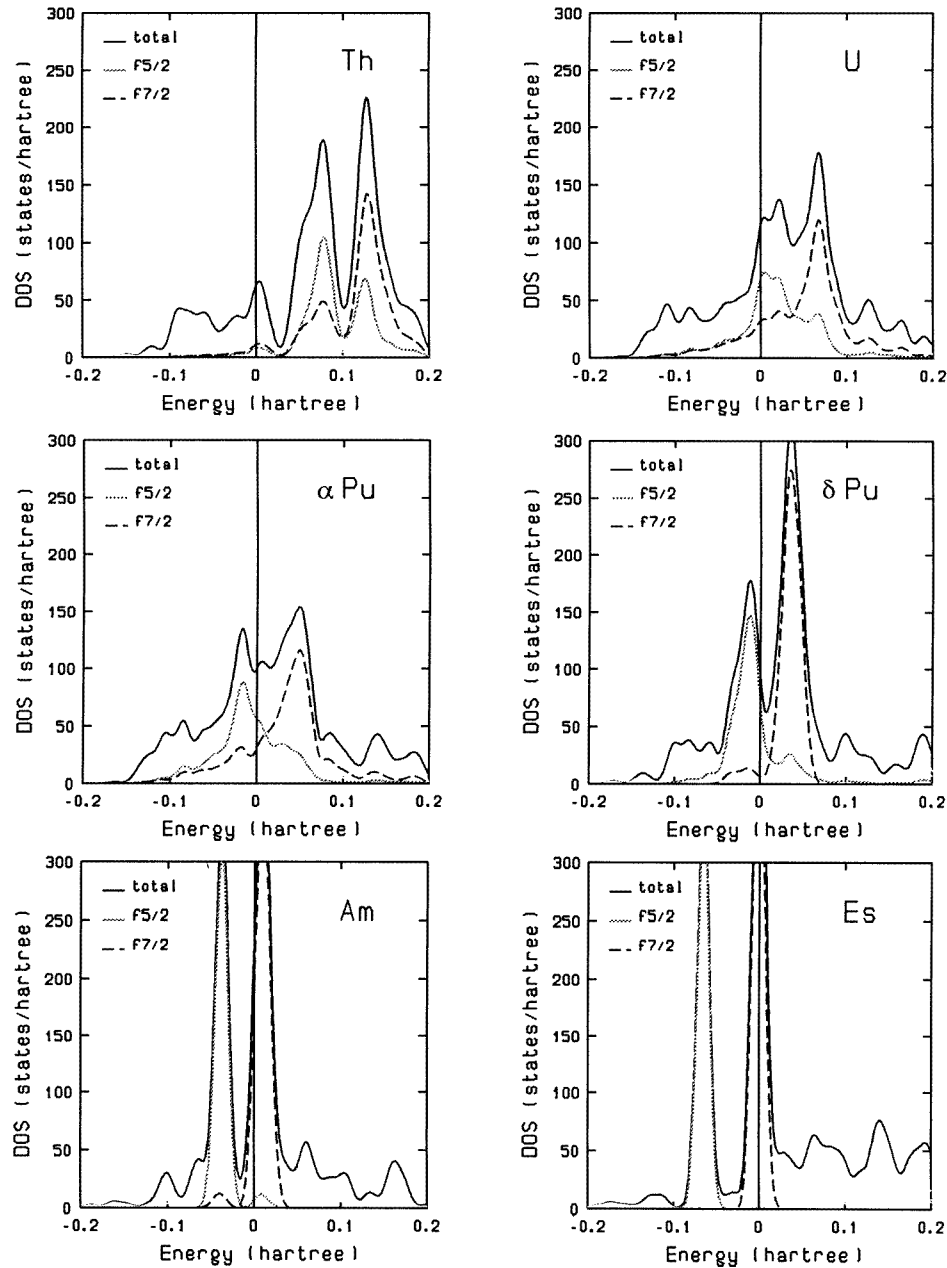


Figure 6. DOSs for the values of theoretical equilibrium volumes. Delocalized treatment of 5f electron states from Ra to α -Pu; unhybridized 5f from Am to Cf; unhybridized 5f and 6d for Es; for δ -Pu unhybridized 5f_{7/2} electron states. Energies are relative to the Fermi energy.

with unhybridized electron states, it was possible to take account of the partial localizations of electrons in δ -Pu, Am and Es which yield the differences in the equilibrium densities. This is a first approach to correct the LDA for localized states in the case of non-magnetic, highly relativistic metals.

References

- [1] Kmetko E A and Hill H H 1970 *Plutonium 1970 and Other Actinides* ed W N Miner (New York: Metallurgical Society of AIME) p 233
- [2] Freeman A J and Koelling D D 1974 *The Actinides: Electronic Structure and Related Properties* vol 1, ed A J Freeman and J E Darby (New York: Academic) p 51
- [3] Skriver H L, Andersen O K and Johansson B 1978 *Phys. Rev. Lett.* **41** 42
- [4] Brooks M S S 1983 *J. Phys. F: Met. Phys.* **13** 103
- [5] Söderlind P, Eriksson O, Johansson B and Wills J M 1994 *Phys. Rev. B* **50** 7291
Söderlind P, Johansson B and Eriksson O 1995 *Phys. Rev. B* **52** 1631
- [6] Söderlind P, Wills J M, Johansson B and Eriksson O 1997 *Phys. Rev. B* **55** 1997
- [7] Solovyev I V, Lichtenstein A I, Gubanov V A, Antropov V P and Andersen O K 1991 *Phys. Rev. B* **43** 14414
- [8] Pénicaud M 1984 *Shock Waves in Condensed Matter 1983* ed J R Asay, R A Graham and G K Straub (Amsterdam: Elsevier) p 61
- [9] Andersen O K and Jepsen O 1977 *Physica B* **91** 317
- [10] Skriver H L 1984 *The LMTO Method* (Berlin: Springer)
- [11] Pénicaud M 1994 *J. Alloys Compounds* **213/214** 410
- [12] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [13] Svane A and Gunnarsson O 1990 *Phys. Rev. Lett.* **65** 1148
- [14] Temmerman W M, Szotek Z and Winter H 1993 *Phys. Rev. B* **47** 1184
- [15] Szotek Z, Temmerman W M and Winter H 1994 *Phys. Rev. Lett.* **72** 1244
- [16] Svane A 1994 *Phys. Rev. Lett.* **72** 1248
- [17] Solovyev I V, Dederichs P H and Anisimov V I 1994 *Phys. Rev. B* **50** 16861
- [18] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 *J. Phys.: Condens. Matter* **9** 767
- [19] Zein N E 1995 *Phys. Rev. B* **52** 11 813
- [20] Min B I, Jansen H J F, Oguchi T and Freeman A J 1986 *J. Magn. Magn. Mater.* **61** 139
- [21] Skriver H L 1983 *Systematics and the Properties of the Lanthanides* ed S P Sinha (Dordrecht: Reidel) p 213
- [22] Eriksson O, Brooks M S S and Johansson B 1990 *J. Less-Common Met.* **158** 207
- [23] Brooks M S S, Johansson B and Skriver H L 1984 *Handbook on the Physics and Chemistry of the Actinides* vol 1, ed A J Freeman and G H Lander (Amsterdam: North-Holland) p 153
- [24] Benedict U 1987 *Handbook on the Physics and Chemistry of the Actinides* vol 5, ed A J Freeman and G H Lander (Amsterdam: North-Holland) p 227
- [25] 1979 *Periodic Table of the Elements* (Chicago: Sargent–Welch)
- [26] Jette E R 1955 *J. Chem. Phys.* **23** 365
- [27] Hedin L and Lundqvist B I 1971 *J. Phys. C: Solid State Phys.* **4** 2064
- [28] Naegele J R, Cox L E and Ward J M 1993 *Proc. 23rd Journées des Actinides (Schwarzwald, 1993)*
- [29] Merz M D, Hammer J H and Kjarmo H E 1976 *Plutonium and Other Actinides* ed H Blank and R Lindner (Amsterdam: North-Holland) p 567
- [30] Méot-Reymond S and Fournier J M 1996 *J. Alloys Compounds* **232** 119
- [31] Fu C L and Ho K M 1983 *Phys. Rev. B* **28** 5480
- [32] Johansson B, Ahuja R, Eriksson O and Wills J M 1995 *Phys. Rev. Lett.* **75** 280