Journal of Alloys and Compounds, 213/214 (1994) 410–413
JALCOM 4089

New muffin tin orbital band calculations of equilibrium properties and electronic structure of actinide metals

M. Pénicaud

Centre d'études de Limeil-Valenton, F-94195 Villeneuve St. Georges Cedex (France)

Abstract

We test the fully relativistic muffin tin orbital (MTO) method of band calculations by obtaining at the experimental equilibrium densities of actinide metals (Ra–Cf) the pressure, which should be zero. We also compare with experiment the calculated equilibrium atomic radii and bulk moduli. An f.c.c. structure is used, with an atomic volume in some cases equivalent to that of a more complex structure. Our calculations are in agreement with previous studies if we expand the wavefunctions in angular momenta up to $l_{\max}=3$ (f-states), but we show that we do not have converged results and that it is necessary to make the expansion up to $l_{\max}=8$. The character of f-electrons in the actinide series is well shown by examination of the f-electron partial densities of states (DOSs) relative to the total DOS.

1. Introduction

The first relativistic and self-consistent band calculations on actinide metals (Ra–Cf) were done with the linear muffin tin orbital (LMTO) method [1, 2]. Good results were obtained for theoretical prediction of the experimental equilibrium volume. We examine the approximation of stopping the wavefunction expansion in angular momenta at $l_{\max}=3$ (f-states) and we calculate the participation of f-electrons in the metallic bonding in the actinide series.

2. Relativistic muffin tin orbital (MTO) method [3]

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

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

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

$$\kappa<0, \qquad l=-(\kappa+1), \qquad j=l+\tfrac{1}{2}$$

$$\kappa>0, \qquad l=\kappa, \qquad j=l-\tfrac{1}{2}$$

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

The energies $E_n(\vec{k})$ and coefficients $B_{n\kappa\mu}(\vec{k})$ are solutions of a linear homogeneous system involving logarithmic derivatives of wavefunctions $\phi_{\kappa\mu}$ on the atomic sphere and "structure constants" $SR_{\kappa'\mu',\kappa\mu}(\vec{k})$ that depend only on the type of crystal lattice considered. With the wavefunctions we can obtain a new electronic density and a new potential by using the local density approximation. For the exchange correlation terms we take the Kohn–Sham parametrization [4] as in ref. 5 instead of the Von Barth–Hedin parametrization [6] used in refs. 1 and 2 which gives a lower value for the pressure.

The expansion (1) of wavefunction is infinite, but for practical reasons it is stopped at a maximum value of l, $l_{\max}$; the order of matrices is then $2(l_{\max}+1)^2$.

3. Equilibrium properties

In previous studies [1, 2] $l_{\max}=3$ was taken, corresponding to effectively occupied states (s, p, d, f) in actinide metals. In Fig. 1(a) our calculations show that convergence is only obtained with $l_{\max}=8$. We can see in Figs. 1(b) and 1(c) the differences in calculated atomic radii and bulk moduli. We have poor agreement between experiment and "$l_{\max}$-converged" MTO band calculations for the f.c.c. structure from Th to the last actinide metals. For Pa, U, Np and Pu we have anisotropic structures quite different from f.c.c., but recent calculations for the real crystal lattices of Pa and U do not show better agreement [7]. For the series Am, Cm, Bk and Cf it is necessary to perform relativistic

0925-8388/94/$07.00
SSDI 0925-8388(94)04089-M

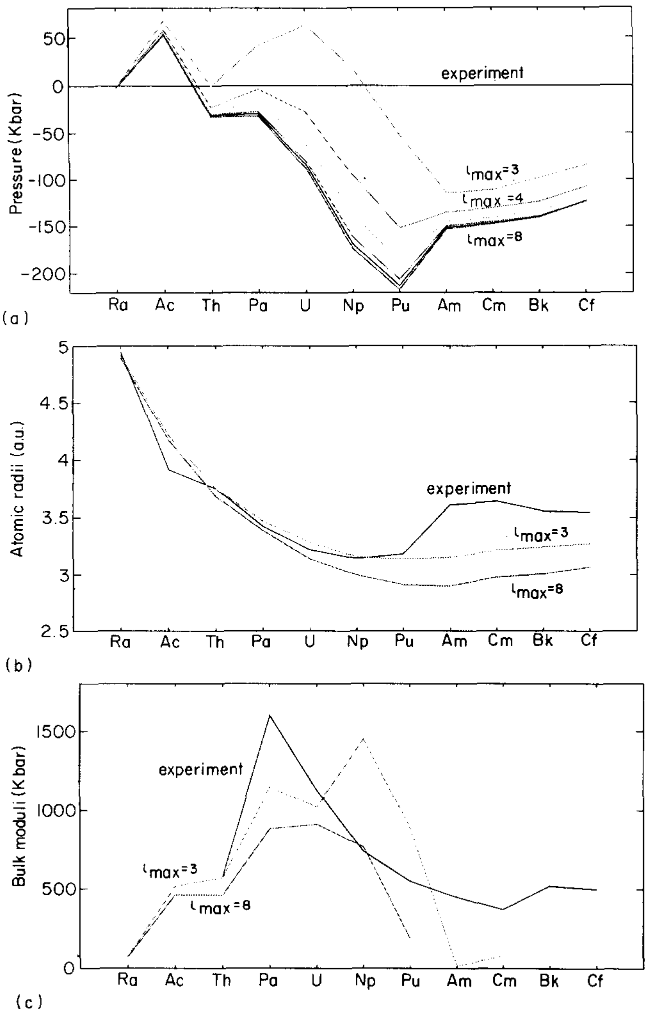

Fig. 1. Comparisons for actinide metals between experiment and MTO calculations for f.c.c. structure with various cuts (l_{max}) in expansions of wavefunctions in angular momenta: (a) pressure at normal densities; (b) equilibrium atomic radii; (c) bulk moduli at normal densities.

and spin-polarized [8] calculations for the d.h.c.p. structure, but this has not yet been done.

4. Electronic structure

We calculate the participation of f-electrons in the metallic bonding in actinide metals. In Table 1 we see the contribution of 5f orbitals increasing in the actinide series. Looking at Fig. 2, where energies are relative to the Fermi energy, no f-contribution for Ra and Ac is seen. For Th the two peaks of the $5f_{5/2}$ and $5f_{7/2}$ states appear but are well above the Fermi level. The $5f_{5/2}$ and $5f_{7/2}$ partial densities of states (DOSs) for Th are extended in energy, with two maxima which coincide. Going from Th to the heavier actinides, the $5f_{5/2}$ and $5f_{7/2}$ partial DOSs penetrate progressively below the Fermi level, but at the same time their bandwidth becomes still narrower and their second maximum decreases. The f-electrons have an itinerant behaviour and participate in the bonding from Pa to Pu, the crystallographic structures being anisotropic: tetragonal for Pa, orthorhombic for U and Np, monoclinic for Pu. If possible, a calculation for these structures would show increased bonding character of f-electrons, as was shown in the calculation of the tetragonal β phase of Np [9]. Localization of 5f electrons occurs with Am. The bandwidths of the 5f partial DOSs decrease suddenly and these DOSs no longer hybridize with 6d states, but instead the 5f states behave like atomic states. The 5f electrons from Am to Cf are localized like the 4f electrons of lanthanides.

TABLE 1. Occupation numbers in conduction band obtained from MTO calculations for f.c.c. structure (Z_c is the number of valence electrons)

Metal	Z_c	Occupation number						
		7s	$7p_{1/2}$	$7p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$	$5f_{5/2}$	$5f_{7/2}$
Ra	2	0.927	0.163	0.182	0.250	0.439	0.015	0.018
Ac	3	0.662	0.139	0.140	0.735	1.133	0.073	0.093
Th	4	0.663	0.186	0.164	1.018	1.452	0.205	0.270
Pa	5	0.619	0.141	0.154	1.035	1.443	0.757	0.797
U	6	0.524	0.106	0.116	0.959	1.353	1.580	1.289
Np	7	0.489	0.099	0.111	0.881	1.264	2.495	1.584
α-Pu	8	0.540	0.099	0.124	0.819	1.160	3.648	1.534
Am	9	0.756	0.171	0.185	0.679	0.996	5.354	0.819
Cm	10	0.789	0.209	0.181	0.645	0.872	5.701	1.567
Bk	11	0.780	0.204	0.167	0.618	0.797	5.794	2.606
Cf	12	0.796	0.208	0.207	0.551	0.722	5.883	3.65
δ-Pu	8	0.662	0.119	0.152	0.761	1.126	4.067	1.059

4.1. Comparison of α-Pu and δ-Pu DOSs

It has been claimed that δ-Pu represents already the case of 5f electron localization [10]. In Fig. 2 the bandwidths of the 5f partial DOSs decrease from α-Pu to δ-Pu showing a relative localization, and the ratio of the occupation numbers (Table 1) of $5f_{5/2}$ to $5f_{7/2}$ increases from α-Pu to δ-Pu but by less than from α-Pu to Am. In conclusion, δ-Pu does not represent the predominantly localized 5f case.

5. Conclusions

From our MTO band calculations for the f.c.c. structure of actinide metals we can see the character of 5f electrons in the series. However, we have poor agreement with experiment for the bulk properties for Am, Cm, Bk and Cf because our calculations are not spin polarized, while for U, Np and Pu some new method must be found.

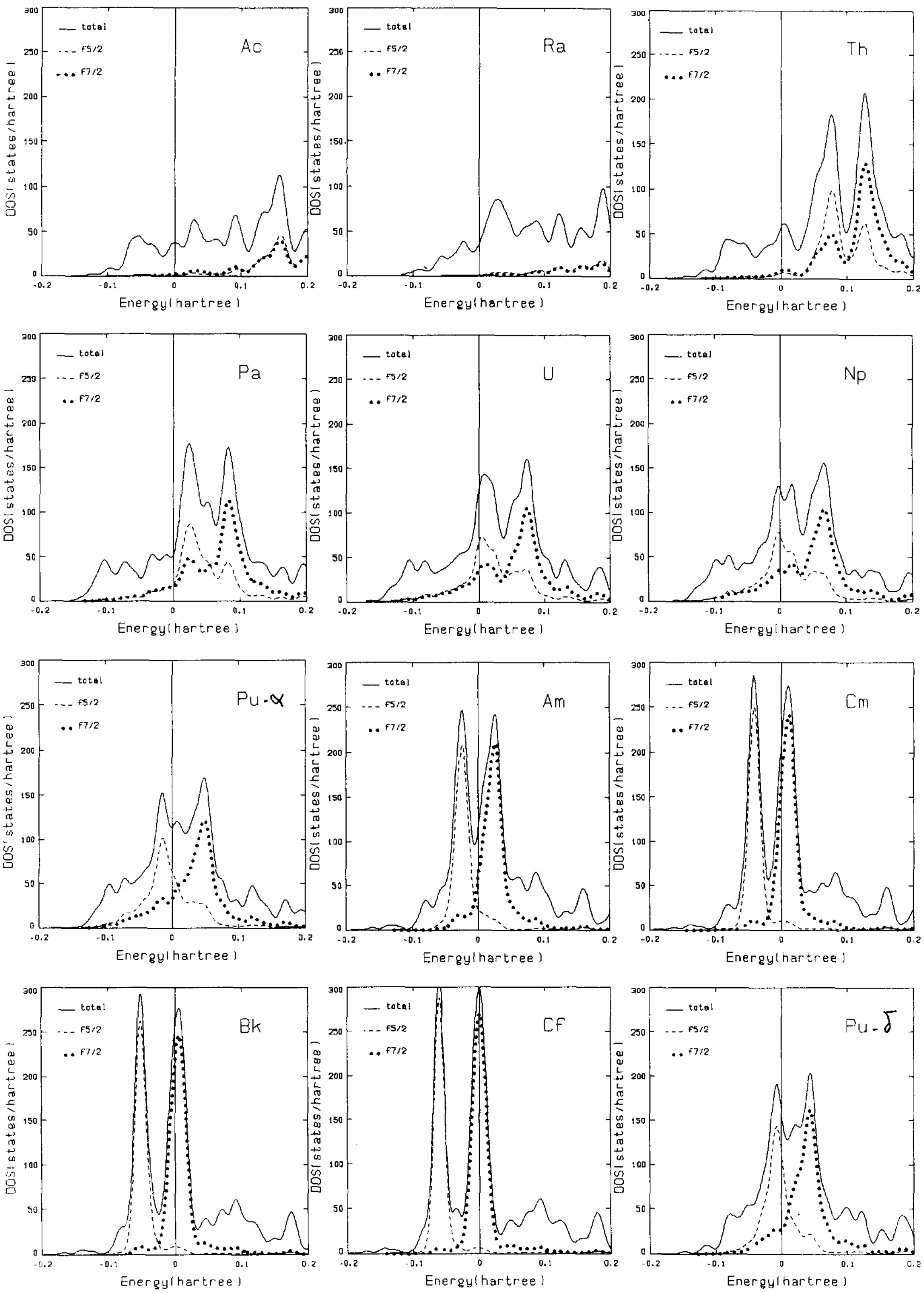

Fig. 2. Densities of states for actinide metals calculated for f.c.c. structure. Energies are relative to the Fermi energy.

References

1 H.L. Skriver, O.K. Andersen and B. Johansson, *Phys. Rev. Lett.*, *41* (1978) 42.

2 M.S.S. Brooks, *J. Phys. F: Met. Phys.*, *13* (1983) 103.

3 M. Pénicaud, in J.R. Asay, R.A. Graham and G.K. Staub (eds.), *Shock Waves in Condensed Matter 1983,* Elsevier, Amsterdam, 1984, p. 61.

4 W. Kohn and L.J. Sham, *Phys. Rev.*, *140* (1965) A1133.

5 A.M. Boring, R.C. Albers, G.R. Steward and D.D. Koelling, *Phys. Rev. B, 31* (1985) 3251.

6 U. Von Barth and L. Hedin, *J. Phys. C: Solid State Phys., 5* (1972) 1629.

7 J.M. Wills and O. Eriksson, *Phys. Rev. B, 45* (1992) 13879.

8 I.V. Solovyev, A.I. Liechtenstein, V.A. Gubanov, V.P. Antropov and O.K. Andersen, *Phys. Rev. B, 43* (1991) 14414.

9 A.M. Boring, G.H. Schadler and R.C. Albers, *J. Less-Common Met., 144* (1988) 71.

10 J.L. Smith and E.A. Kmetko, *J. Less-Common Met., 90* (1983) 83.