ELSEVIER

Journal of Alloys and Compounds 271–273 (1998) 339–341

Journal of ALLOYS AND COMPOUNDS

# Local density approximation versus generalized gradient approximation: full charge density study of the atomic volume of the light actinides

L. Vitos[a,b,*], J. Kollár[b], H.L. Skriver[a]

[a]Center for Atomic-scale Materials Physics and Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark
[b]Research Institute for Solid State Physics, P.O.Box 49, H-1525 Budapest, Hungary

**Abstract**

We have used a full charge-density technique based on the density functional theory to calculate the atomic volumes of the light actinides including Fr, Ra and Ac in their low-temperature crystallographic phases using the local density approximation (LDA) and the generalized gradient approximation (GGA) for the exchange-correlation energy. The good agreement between the theoretical and experimental values along the series support the picture of itinerant 5f electronic states from Th to Pu. The comparison between the LDA and the GGA results shows that the anomalously large atomic volume of α-Pu relative to α-Np can be ascribed to the presence of low coordinated sites in the monoclinic α-Pu structure, where the f-electrons are more localized and the charge density is very low in the interstitial region. In this system the exchange-correlation effects can be correctly described using the GGA but not within the LDA. © 1998 Elsevier Science S.A.

*Keywords:* Density functional theory; Exchange and correlation energy; Light actinides; Atomic volumes

## 1. Introduction

The unusual ground state properties of the light actinide metals have served a continuous challenge for the theory since they were first discovered. In the pioneering self-consistent, scalar relativistic calculation by Skriver et al. [1] it was shown that the atomic number dependence of the equilibrium atomic volumes and other bulk properties supports the picture of itinerant 5f electrons for the lighter elements of the series (plutonium or lighter), and a Mott localization takes place between Pu and Am [2] (the atomic volume of americium is about 50% larger than those of the earlier elements). However, the theory was not able to explain why Pu has a somewhat larger atomic volume than that of Np, although in both cases the f electrons are assumed to be of itinerant nature. The main difficulty arises from the fact that these elements, especially plutonium, have rather complex zero temperature crystal structures; the α-Pu structure is monoclinic with 16 atoms per unit cell. In addition, the relativistic effects are very important for these heavy elements, and the 6s, 6p semicore states contribute to the bonding essentially and should be considered as band states (which, in the case of a linear method, doubles the number of diagonalizations to be performed in total energy calculations).

The possible theoretical explanations for the upturn of the atomic volume for Pu, relative to that of Np, have been that the relativistic spin–orbit splitting of the 5f band gives rise to this behavior [3], or that Pu lies so close to the onset of localization that correlation effects are not properly described in the local density approximation (LDA) [1,4,5]. In order to decide which mechanism is responsible for the anomalously large Pu volume, several calculations have been carried out [3–8]. Wills and Eriksson [6] in their relativistic, full potential calculation for fcc structures showed that the spin–orbit splitting does not play an important role in this case, although its effect is still unclear for the α-Pu structure [8]. For the observed α-structures using our full charge density scheme we have shown that there is no upturn in the theoretical atomic volumes between Np and Pu using an LDA exchange-correlation functional [5]. At present the most elaborate relativistic, full potential calculations using the generalized gradient approximation (GGA) for the exchange correlation functional [9] managed to reproduce the observed trend in the atomic volumes [8] and the authors ascribe the anomalous Pu volume to the unique monoclinic crystal structure of α-Pu rather than to a strong electron correlation or quasilocalization of the 5f states.

---

[*] Corresponding author. Tel.: 4545 882488/3208; fax: 4545 932399; e-mail: levente@fysik.dtu.dk

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
*PII* S0925-8388(98)00084-X

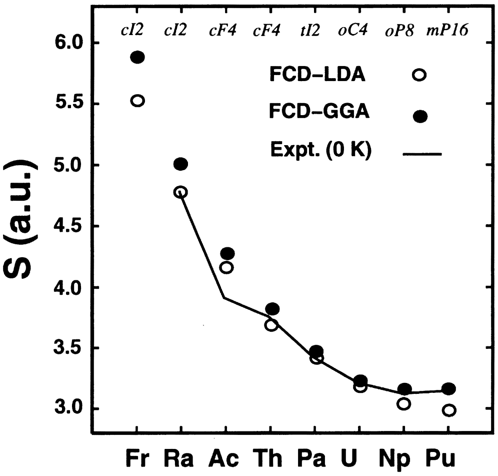

Fig. 1. Calculated and experimental equilibrium atomic volumes for the light actinide metals including Fr, Ra and Ac. The calculations are performed in the LDA and the GGA for the crystallographic α-phases indicated in Pearson notation at the top of the figure. The measured room temperature values from Ref. [13] are corrected to $T=0$ K using the thermal expansion coefficients from Ref. [16].

The principal aim of the present study is to confirm or to rule out our earlier assumption that this anomalous behavior is a sign of strong electron correlation which is not properly described by the LDA energy functional. Therefore, besides our earlier LDA results [5], we have calculated the equilibrium volumes of Fr through Pu using the GGA energy functional, hoping that this improved functional is able to describe the correlation effect more accurately even near the onset of localization. In the calculation we used a full charge density technique based on a full charge density energy functional [10], where the charge density is derived from the output of a self-consistent LMTO–ASA (linear muffin-tin orbital method using the atomic sphere approximation) calculation. The kinetic energy was corrected due to the nonspherical charge density using the gradient expansion; the method is described elsewhere [11]. This technique was successfully applied for several cases for the surface [12] and bulk properties of metals, including the shear elastic constants as well [11].

## 2. Results and discussion

The results of our LDA and GGA calculations of the equilibrium atomic radii for the light actinides including Fr, Ra and Ac in their low temperature crystallographic phases are shown in Fig. 1 and Table 1 together with the experimental data [13]. The anomalous behavior of α-Pu is most easily seen in the room temperature experimental data. At 0 K the atomic Wigner–Seitz radius of α-Pu is only 0.5% larger than that of α-Np. In the comparison between theory and experiment we note that the GGA results for the light actinides are on the average only 1.3% larger than the zero temperature experimental values. This accuracy is similar to the one found in our FCD–GGA calculations for the entire 4d series where the atomic radii oscillates slightly in the range from 0.4 to 1.3% above the experimental values [11].

From Fig. 1 and Table 1 it is seen that the GGA results give a correct description of the trend including the volume of α-Pu, as also observed by Söderlind et al. [8]. The LDA does not describe the experimental trend and in fact the difference between the LDA and GGA values is unexpectedly large for α-Pu. We note that the upturn is also absent both in the LDA and the GGA results obtained for the fcc structure [7,14]. Because of that and because of the fact that the neglect of spin–orbit interaction changes the volumes only slightly, but does not alter the trend [8], we conclude that the anomalous volume of α-Pu is caused by correlation effects, which are not captured by the LDA, in conjunction with the α-Pu crystal structure.

We now discuss this conclusion in detail by examining the pressure contributions coming from different sites of the α-Np and α-Pu structures. The main difference between the two structures lies in the fact that in α-Pu there are several very low coordinated sites where the 5f band width parameters are considerably smaller than those of the others [4] and the detailed analysis shows that the main difference between the LDA and GGA pressure contributions arises from these sites. To demonstrate this effect, in Fig. 2 we plot the difference between the LDA and GGA exchange-correlation ASA pressure contributions for different inequivalent sites in Np and Pu as a function of the inverse charge density $n(S)^{-1}$ at the atomic sphere radius $S$. For this demonstration we simply used the relation [15]

Table 1
Atomic Wigner–Seitz radii in Bohr for the light actinides in their low temperature crystallographic phases

| | Fr | Ra | Ac | Th | Pa | U | Np | Pu |
|---|---|---|---|---|---|---|---|---|
| Structure | cI2 | cI2 | cF4 | cF4 | tI2 | oC4 | oP8 | mP16 |
| Exp. (room temp.) | | 4.790 | 3.922 | 3.756 | 3.422 | 3.221 | 3.142 | 3.182 |
| Exp. (0 K) | | 4.762 | 3.905 | 3.744 | 3.414 | 3.207 | 3.116 | 3.131 |
| FCD–LDA | 5.531 | 4.779 | 4.179 | 3.703 | 3.401 | 3.154 | 3.041 | 2.992 |
| FCD–GGA | 5.880 | 4.998 | 4.273 | 3.821 | 3.475 | 3.230 | 3.157 | 3.154 |

The experimental values from Ref. [13] (room temp.) are reduced to $T=0$ K by means of the thermal expansion coefficients from Ref. [16].

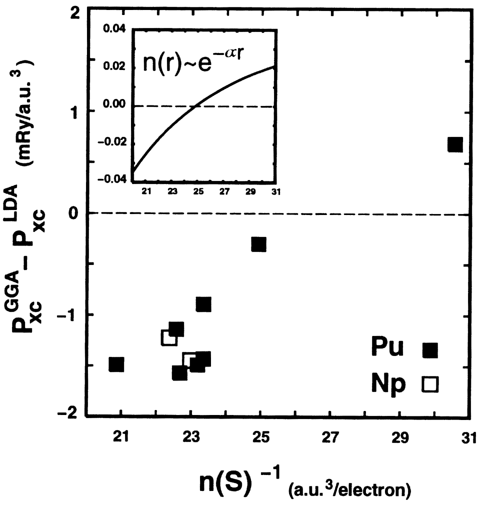

Fig. 2. Differences between the LDA and GGA exchange-correlation pressure contributions $P_{xc}=n(S)[\mu_{xc}(S)-\epsilon_{xc}(S)]$ as a function of the inverse charge density, $n(S)^{-1}$ at the atomic sphere radius $S$ for different inequivalent sites in the α-Np and α-Pu structures (here $\mu_{xc}$ and $\epsilon_{xc}$ stand for the exchange correlation potential and energy density). In the insert of the figure we plot the same quantity for an exponentially decaying model charge density.

$P_{xc}=n(S)[\mu_{xc}(S)-\epsilon_{xc}(S)]$ (here $\mu_{xc}$ and $\epsilon_{xc}$ stand for the exchange correlation potential and energy density). In the insert of the figure we plot the same quantity for an exponentially decaying model charge density illustrating that the observed trend is a general feature of the GGA energy functional: below a certain value of the charge density the GGA functional becomes more repulsive than that of the LDA. Therefore the system will expand compared to the LDA equilibrium volume (and lower the density further).

## 3. Summary

To summarize, we can say that the anomalously large α-Pu volume is a consequence of the unique, monoclinic crystal structure, in agreement with the results of Söderlind et al. [8]. We show that the physical reason for the anomaly is the presence of sites of low coordination numbers in conjunction with exchange-correlation effects only included in the GGA. The effect may be viewed as the result of the near onset of 5f localization.

## Acknowledgements

This work was supported by the research project OTKA 016740 and 23390 of the Hungarian Scientific Research Fund. The Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Foundation.

## References

[1] H.L. Skriver, O.K. Andersen, B. Johansson, Phys. Rev. Lett. 41 (1978) 42.
[2] B. Johansson, Phys. Rev. 11 (1975) 2740.
[3] M.S.S. Brooks, J. Phys. F: Met. Phys. 13 (1983) 103.
[4] J. van Ek, P.A. Sterne, A. Gonis, Phys. Rev. B 48 (1993) 16280.
[5] L. Vitos, J. Kollár, H.L. Skriver, Phys. Rev. B 55 (1997) 4947.
[6] J.M. Wills, O. Eriksson, Phys. Rev. B 45 (1992) 13879.
[7] P. Söderlind, O. Eriksson, B. Johansson, J.M. Wills, Phys. Rev. B 50 (1994) 7291.
[8] P. Söderlind, J.M. Wills, B. Johansson, O. Eriksson, Phys. Rev. B 55 (1997) 1997.
[9] J.D. Perdew, in: P. Ziesche, H. Eschrig (Eds.), Electronic Structure of Solids, Academic Verlag, Berlin, 1991, p. 11.
[10] L. Vitos, J. Kollár, H.L. Skriver, Phys. Rev. B 49 (1994) 16694.
[11] L. Vitos, J. Kollár, H.L. Skriver, Phys. Rev. B 55 (1997) 13521.
[12] L. Vitos, A. Ruban, H. L. Skriver, J. Kollár, (unpublished).
[13] D.A. Young, Phase Diagrams of the Elements, University of California Press, Berkeley, 1991.
[14] J. Kollár, L. Vitos, H.L. Skriver, Phys. Rev. B 55 (1997) 15353.
[15] O.K. Andersen, O. Jepsen, D. Glötzel, in: F. Bassani, F. Fumi, M.P. Tosi (Eds.), Highlights of Condensed Matter Theory, North-Holland, 1985, p. 59.
[16] K.A. Gschneidner Jr., Solid State Physics, Academic, New York, Vol. 16, 1964, p. 275.