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## Anomalous atomic volume of $\alpha$ -Pu

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We have performed full charge-density calculations for the equilibrium atomic volumes of the  $\alpha$ -phase light actinide metals using the local density approximation (LDA) and the generalized gradient approximation (GGA). The average deviation between the experimental and the GGA atomic radii is 1.3%. The comparison between the LDA and GGA results show that the anomalously large atomic volume of  $\alpha$ -Pu relative to  $\alpha$ -Np can be ascribed to exchange-correlation effects connected with the presence of low coordinated sites in the structure where the  $f$  electrons are close to the onset of localization. This effect is correctly described in the GGA but not in the LDA. [S0163-1829(97)01024-2]

Approximately 50 years ago Seaborg moved Th, Pa, and U to their present position in the Periodic Table to form a new "actinide" series which was expected to exhibit properties determined by the progressive filling of the  $5f$  shell. Today it is well established that the unusual ground state properties of the light actinide metals are a reflection of the particular nature of the bonding of the  $5f$  electrons.<sup>1</sup> At the beginning of the series the  $5f$  electrons are itinerant, while the decreasing  $f$ -band width ( $W$ ) and the increasing intra-atomic Coulomb energy integral ( $U$ ) results in a Mott localization between Pu and Am.<sup>2</sup> In fact, the dependence of the equilibrium atomic volumes and other bulk properties on atomic number is in accordance with this picture of itinerant  $5f$  electrons for the lighter elements of the series up to plutonium and localized  $5f$  electrons from Am (Ref. 3) (the atomic volume of americium is some 40% larger than those of the immediately preceding elements). However, theory has not been able to explain why  $\alpha$ -Pu has a somewhat larger atomic volume than that of  $\alpha$ -Np, although in both cases the  $5f$  electrons are assumed to be itinerant. The main difficulty arises from the fact that these elements, especially plutonium, have rather complex low temperature crystal structures. Thus, the  $\alpha$ -Pu structure is monoclinic with 16 atoms per unit cell. In addition, relativistic effects are very important for these heavy elements, and the  $6p$  semicore states contribute significantly to the bonding and should be considered band states. As a result, the calculation of the atomic volumes of the  $\alpha$ -phases constitute a major computational effort.

The possible theoretical explanations for the upturn of the atomic volume of Pu, relative to that of Np, have been that the relativistic spin-orbit splitting of the  $5f$  band gives rise to this behavior,<sup>4</sup> or that Pu lies so close to the onset of  $5f$  localization that correlation effects are not properly described in the local density approximation (LDA).<sup>3,5,6</sup> In the most recent, fully relativistic, full-potential calculations performed concurrently with the present work and applying the generalized gradient approximation<sup>8,9</sup> (GGA) for exchange and correlation Söderlind *et al.*<sup>10</sup> reproduced the experimentally observed trend in the atomic volumes and ascribe the

anomalous Pu volume to the unique monoclinic crystal structure of  $\alpha$ -Pu. These authors also find that the neglect of spin-orbit coupling changes the volume slightly but does not affect the trend. The present authors showed by means of a full charge density scheme that in the LDA there is no upturn in the theoretical atomic volumes of the  $\alpha$  phases between Np and Pu.<sup>6,7</sup> Hence, within the LDA, at least, the crystal structure does not give rise to the anomalous volume of  $\alpha$ -Pu. However, it may be caused by correlation effects not included in the LDA.

It is the aim of the present paper to investigate the anomalous volume of  $\alpha$ -Pu and possibly reach a conclusion as to its cause. We have therefore, in addition to our earlier LDA results,<sup>6,7</sup> calculated the equilibrium volumes of the light actinides from Th to Pu by means of the GGA energy functional in conjunction with our full charge density (FCD) technique<sup>12</sup> based on the output of self-consistent linear muffin-tin orbital calculations performed in the atomic sphere approximation (LMTO-ASA). In the most recent implementation used here we not only used the full charge-density functional but also corrected the kinetic energy for the nonspherical charge density using a gradient expansion. Thereby the accuracy of the method is essentially that of a full-potential method as shown in calculations of bulk ground state properties of the  $4d$  metals, including the shear elastic constants.<sup>11</sup> More importantly, the equilibrium volumes for the actinides presented here, as well as the structural stability not discussed by us, are very similar to those found in the full-potential study by Söderlind *et al.*<sup>10</sup>

The results of our LDA and GGA calculations of the equilibrium atomic radii for the light actinides are shown in Fig. 1 together with the experimental data.<sup>13</sup> The anomalous behavior of  $\alpha$ -Pu is most easily seen in the room temperature experimental data. At 0 K the atomic Wigner-Seitz radius of  $\alpha$ -Pu is only 0.5% larger than that of  $\alpha$ -Np. In the comparison between theory and experiment we note that the GGA results 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

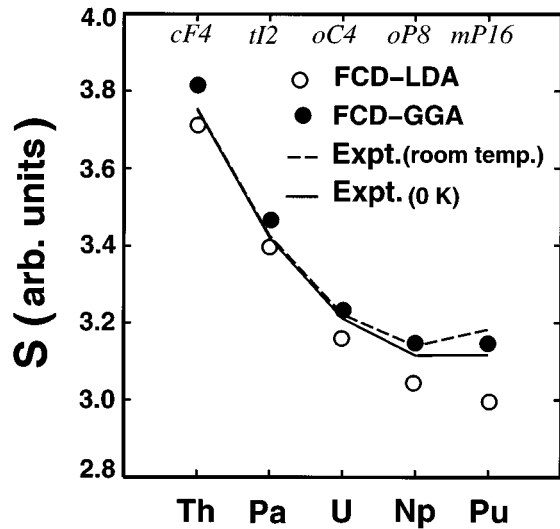


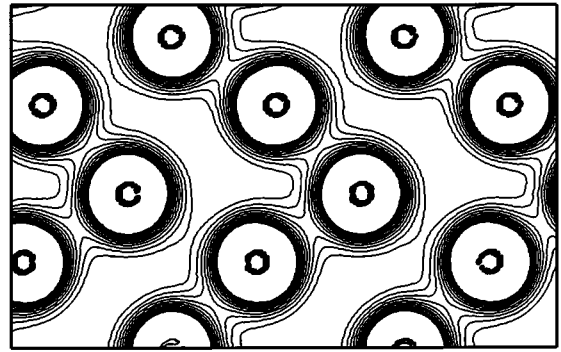
FIG. 1. Full charge density (FCD) results for the equilibrium Wigner-Seitz radii of the light actinide metals. The calculations are performed in the LDA and the GGA for the crystallographic  $\alpha$ -phases indicated in Pearson notation at the top of the figure. The measured room temperature values from Ref. 13 are corrected to  $T=0$  K using the measured mean thermal expansion coefficients.

range from 0.4% to 1.3% above the experimental values.<sup>11</sup> It is furthermore seen that the GGA results give a correct description of the trend including the volume of  $\alpha$ -Pu, as also observed by Söderlind *et al.*<sup>10</sup> Finally, we note that the LDA does not describe the trend and that in fact the difference between the LDA and GGA values is unexpectedly large for  $\alpha$ -Pu. The question arises, why?

We are in possession of the following facts. First, the GGA gives a correct description of the atomic volumes of the  $\alpha$  phases of the light actinides including the upturn at Pu while the LDA does not. Second, the upturn is also absent in calculations for the light actinides in the fcc structure both in the LDA and the GGA, cf. Table I. Third, the neglect of spin-orbit interaction changes the volumes slightly, but does not alter the trend.<sup>10</sup> The conclusion is that the anomalous volume of  $\alpha$ -Pu is caused by correlation effects, which are not captured by the LDA, in conjunction with the  $\alpha$ -Pu crystal structure.

We now discuss this conclusion in detail. In Fig. 2 we

(a)  $\alpha$ -Np (001)



(b)  $\alpha$ -Pu (001)

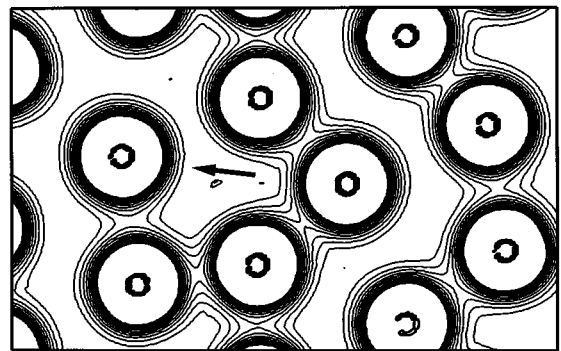


FIG. 2. Charge-density contours (in electron/a.u.<sup>3</sup>) for (a) orthorhombic ( $oP8$ ) Np and (b) monoclinic ( $mP16$ ) Pu cut in the (001) plane. The spacing between the contours lines is 0.02. To facilitate comparison we show approximately two unit cells for Np. The arrow points to the “isolated” atomic site with only a single nearest neighbor in the (001) plane.

show contour plots in the (001) plane of the charge densities used in the calculation for  $\alpha$ -Np and  $\alpha$ -Pu. From the figure it is seen that the main difference between the two structures is the presence of “isolated” sites in  $\alpha$ -Pu which in the (001) plane has only one nearest neighbor. In fact, these low coordinated sites have only three “short bonds,”<sup>5</sup> and when the gradient correction to the LDA, which is large for low but rapidly varying densities, is applied to these sites we expect

TABLE I. Atomic Wigner-Seitz radii in Bohr for the light actinides in their low temperature crystallographic phases, upper panel, and in the fcc structure, lower panel. The experimental values from Ref. 13 (Room temp.) are reduced to  $T=0$  K by means of the mean thermal expansion coefficients.

Structure	Th	Pa	U	Np	Pu
	cF4	tI2	oC4	oP8	mP16
Exp. (Room temp.)	3.756	3.422	3.221	3.142	3.182
Exp. (0 K)	3.744	3.414	3.207	3.116	3.131
FCD-LDA	3.703	3.401	3.154	3.041	2.992
FCD-GGA	3.821	3.475	3.230	3.157	3.154
Structure	cF4	cF4	cF4	cF4	cF4
FCD-LDA	3.703	3.448	3.274	3.201	3.165
FCD-GGA	3.821	3.521	3.347	3.252	3.221

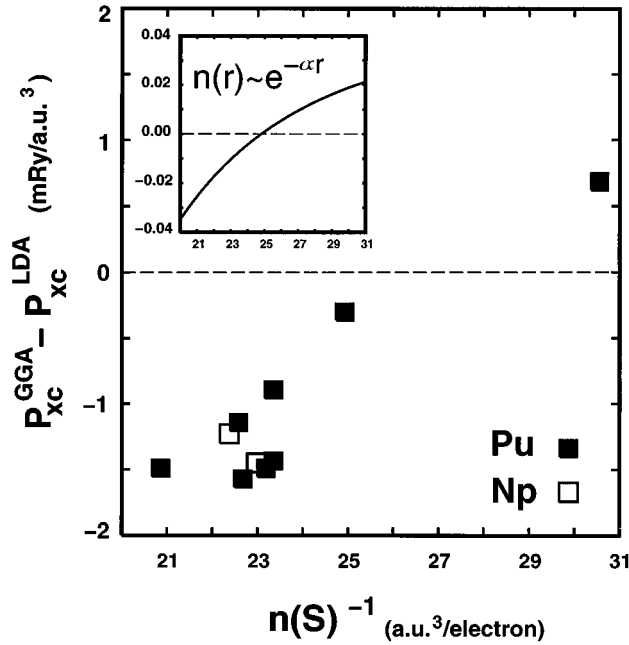


FIG. 3. The difference between the LDA and GGA exchange-correlation pressure contribution  $P_{xc} = n(S)[\mu_{xc}(S) - \epsilon_{xc}(S)]$  from the inequivalent sites in  $\alpha$ -Np and  $\alpha$ -Pu evaluated at the atomic Wigner-Seitz radius  $S$  of  $\alpha$ -Pu plotted as a function of the inverse charge density,  $n(S)^{-1}$ . The inset shows the same quantity (in arbitrary units) for an exponentially decaying model charge density.

a significant change in the volume at which the binding energy versus volume curve has its minimum. This change in the volume of minimum energy, i.e., the equilibrium volume or average bond length, may be analyzed by means of the LMTO-ASA pressure relation<sup>14</sup> where the exchange-correlation contribution to the electronic pressure is given by

$$P_{xc} = n(S)[\mu_{xc}(S) - \epsilon_{xc}(S)]. \quad (1)$$

Here  $n(S)$  is the electronic density at the atomic radius  $S$  and  $\mu_{xc}$  and  $\epsilon_{xc}$  are the exchange-correlation potential and energy

density, respectively. We note that the change in equilibrium volume is directly proportional to the change in the pressure.

In Fig. 3 we show the difference between the LDA and GGA exchange-correlation pressure contributions for the inequivalent sites (2 in Np and 8 in Pu) as a function of the inverse charge density  $n(S)^{-1}$ . In the inset we plot the same pressure difference for an exponentially decaying model charge density illustrating that the trend observed in  $\alpha$ -Pu is a general feature of the GGA energy functional, i.e., below a certain value of the charge density the GGA functional becomes more repulsive than that of the LDA leading to a relative expansion of the system. It is seen that five of the inequivalent sites in  $\alpha$ -Pu have pressure contributions similar to those of the sites in  $\alpha$ -Np, while three sites cause an increase in the electronic pressure relative to the  $\alpha$ -Np value. The isolated site indicated by an arrow in Fig. 2 even shows a positive contribution to the pressure difference. We emphasize that this increase in electronic pressure and the corresponding increase in atomic volume is relative to the LDA value. In other words, the overbinding of the LDA is higher for these isolated sites than for the other sites in the  $\alpha$ -Pu structure and the sites in the  $\alpha$ -Np structure. Hence, the anomalous volume of  $\alpha$ -Pu is caused by exchange-correlation effects related to these sites of low coordination numbers.

In summary, we have shown that the GGA can reproduce the experimentally observed volumes of the light actinides. We find that the anomalously large volume of  $\alpha$ -Pu relative to that of  $\alpha$ -Np is a consequence of the unique, monoclinic crystal structure, in agreement with the results of Söderlind *et al.*<sup>10</sup> 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.

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