

Simple model for complex structures

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The complex structures of the low-temperature phases of light actinides are analyzed in terms of a simple model involving Pettifor's structural energy difference theorem in combination with an estimate of the structural dependence of the electrostatic interaction in the solid. With this simple model the complex structures of the actinides are contrasted to the simpler ones of the transition metals, and in agreement with observations we find that at ambient conditions the *f*-electron elements favor distorted structures, whereas *d*-electron metals "prefer" cubic or hcp structures. [S0163-1829(98)04003-X]

I. INTRODUCTION

The chemical bonding in light actinides and transition metals are by now known to be similar, in the sense that the Friedel model¹ explains the parabolic trend in the equilibrium volume.²⁻⁴ However, there are a couple of marked differences between the light actinides and the transition metals. The focus of the present paper is on the structural properties, and how these relate to the current understanding of the chemical bonding in these two sets of systems. The transition metals all form in rather close-packed/high-symmetry structures such as hexagonal-close-packed (hcp), face-centered-cubic (fcc), and body-centered-cubic (bcc) (Mn is an exception). In sharp contrast, the light actinides form at low temperatures in low-symmetry/open-packed structures, which indicate a more covalent character of the chemical bonds. For instance, Pa forms in a body-centered-tetragonal (bct) structure, and U and Np in orthorhombic structures with two and eight atoms per cell, respectively. Pu forms at low temperatures in a monoclinic structure with 16 atoms per cell. Since the equilibrium volumes (presumably reflecting the nature of the bonding) of both the transition metals and the light actinides are described equally well by the same model, the Friedel model, one may wonder why there is such a large structural difference. Recently the present authors⁵ elaborated on this issue by means of first-principles theory, where the total energy of any crystal structure may be calculated to great accuracy (~ 1 m Ry/atom). This theory showed a complete success in reproducing the structural properties of the light actinides.

A mechanism for how to understand the unique low-symmetry/open-packed structures of *f* elements was also suggested by us.⁵ The mechanism has a close resemblance to a Peierls/Jahn-Teller-like distortion, and may be viewed as follows. Suppose the energy-band structure of an actinide metal along a high-symmetry line of a hypothetical bcc structure at ambient conditions is like the one shown in Fig. 1. Because this band is along a high-symmetry direction it may have a high degeneracy, say 2 (there will always be such bands along high-symmetry directions of crystals with high symmetry). In Fig. 1 we compare the bcc bands with the

bands of a slightly distorted (say tetragonal or orthorhombic) bcc structure. For the latter the crystal symmetry is lower, and as a consequence the degeneracy may be broken, and one band is found at slightly higher energy and the other band at slightly lower energy. If the bands in Fig. 1 are intersected by the Fermi level (E_F), there will be a part of the Brillouin zone (*k* space) where the contribution from the energy bands of the distorted structure will lower the total energy. The part of the Brillouin zone (or rather section of the symmetry line) where this occurs is shaded in Fig. 1. For all other sections of the symmetry line, the symmetry-split bands are either both above E_F , not affecting the total energy, or both below E_F , in which case the energy from the two split bands is equal to two times the average energy of these two bands, which is exactly the energy of the two degenerate bands of the high-symmetry structure. Thus it is only at *k* points where one of the bands is pushed above E_F and the other remains occupied that gain energy due to the lowering of the crystal symmetry. The shaded area in Fig. 1 will be larger if the bands are narrower, and as a consequence there will be more states contributing to the lowering of the total energy of the distorted structure. Since there are balancing terms which favor the close-packed structure, for instance electrostatic interactions and Born-Mayer repulsion, it is only in systems with narrow bands where the Peierls/Jahn-Teller-like mechanism dominates and a transformation to low symmetry structures occurs.⁵ Thus from Fig. 1 we

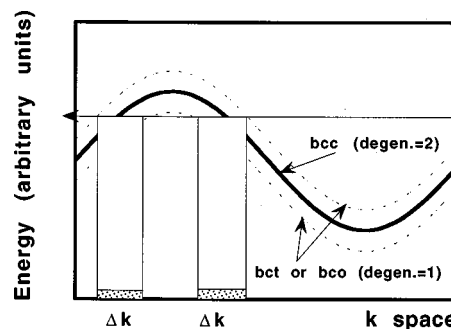


FIG. 1. Model band structure of high- and low-symmetry structures. The Fermi level is marked by a horizontal line.

now observe two important criteria for when distorted structures are expected to be found. First of all, it is necessary that the bands are narrow and, second, it is important that they are intersected by the Fermi level. Both these conditions are fulfilled for the $5f$ bands in the light actinides.

II. MODEL

The Peierls/Jahn-Teller-like model presented above is only qualitative, and a simple quantitative model, to use as a complement to elaborate and time-consuming total-energy calculations based on density-functional theory, has not been available. It is of course highly desirable to have such a simple model, not only because it would presumably be much less labor intensive, but also because extracting a few important terms which reproduce an observation enables a deeper physical understanding. Recently, Pettifor proposed such a simple model which is based only on the eigenvalue spectrum of a crystal (or molecule).⁶ By means of the so-called structural energy difference theorem, highly accurate structural properties were calculated for sp -bonded molecules and solids.⁶ Two terms were isolated as the most important ones: a repulsive term due to the overlap repulsion, and a bonding term due to the filling of bonding states. The two terms are different for different atomic geometries, but, as shown,⁶ it is sufficient to calculate only the latter if the bond lengths are adjusted in the two structures so that the repulsive terms are equal. A further simplification is to set the repulsive contribution in proportion to the second moment of the eigenvalue spectrum.⁶ These simplifications mean that one can use a simplified model for the electronic structure, then make sure that the second moment of the model electronic structure (as given by the density of states) is the same for different atomic geometries (by, for instance, adjusting the bond lengths) and the energy differences between two crystal structures is then obtained from the sum of the occupied states of the resulting electronic structure. We have implemented this method using Andersen's⁷ canonical bands. In our method the model electronic structure is thus set equivalent to the eigenvalue spectrum of the canonical bands. Hence, for the f -electron metals we only consider pure canonical (unhybridized) f bands, and for the transition metals we do the same for the d bands. This approach is of course in itself an approximation, because we neglect the direct influence or hybridization with other bands in the comparison between different crystal structures. However, we shall see below that this approach is valid for both the d -transition metals, as was demonstrated by Duthie and Pettifor⁸ and by Skriver,⁹ as well as for the f metals. The very dominant influence the $5f$ states have on the light actinide crystal structures has been shown before,⁵ and the results shown below confirm this picture nicely.

In our calculations for the canonical bands we made sure that the second moment was the same for all considered crystal structures. In practice we could ensure this simply by multiplying the canonical bands with a prefactor which is chosen to result in a specific second moment. This is somewhat different from adjusting the bond lengths, as done by Pettifor.⁶ Once prefactors were found for all pertinent geometries, we evaluated energy differences between these geometries simply by calculating the sum of the resulting eigen-

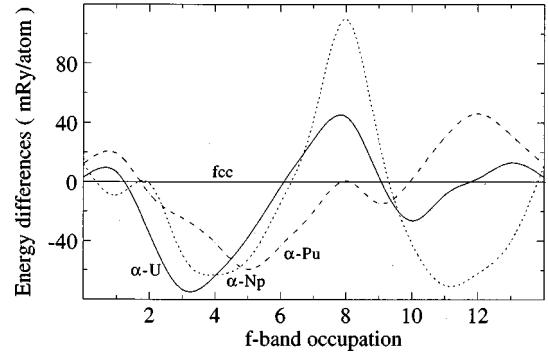


FIG. 2. Structural stability for f occupations between 0 and 14, using a model described in the text.

value spectrum. The energy differences were then converted from canonical units to m Ry, using tabulated values of the band masses for the f electrons.¹⁰

To the one-electron term we added an estimate of the structure-dependent part of the electrostatic interactions in the solid, based on the theorem of Fuchs,¹¹ which states that the electrostatic energy per ion of a lattice of point ions (with charge $+Z|e|$) in a compensating uniform negative charge density is given by

$$E_{\text{electro}} = -\frac{1}{2}(Z|e|)^2 \frac{\alpha_E}{R_{\text{WS}}}, \quad (1)$$

where α_E is the Ewald constant, and R_{WS} is the Wigner-Seitz radius. Esposito *et al.*¹² used this theorem as an argument for correcting their atomic sphere approximation calculations of Cu. In a real solid the electron density is not uniform, but nevertheless one may estimate the structure-dependent part of the electrostatic interaction, treating the charge of the muffin-tin spheres as point ions in a compensating uniform electron gas. From our previous work⁵ on these materials, we know that the interstitial charge corresponds to approximately one electron per atom, and this is the value for Z we used in Eq. (1) above, together with calculated Ewald constants.

III. RESULTS

Before entering into the details of our model calculations, we first point out that it has been proposed that structurally the α -Pu phase may be replaced with a much simpler, two atom per primitive cell, body-centered monoclinic structure,¹³ which in the rest of the paper we will refer to as pseudo- α -Pu. We have compared the total energy of the α -Pu and pseudo- α -Pu structures at ambient conditions, and find that the total energy differs only by a few m Ry/atom. This finding is consistent with the suggestion of Crocker¹³ that the two structures are very similar.

In Fig. 2 we display the calculated energy of our model for different, pertinent structures (d -electron-like; fcc and f -electron-like; α -U, α -Np, and pseudo- α -Pu) and for f -band occupations (n_f) between 0 and 14. The electrostatic contribution is here calculated according to Eq. (1), and the results are given in Table I. Notice that for $n_f \sim 3$ (corresponding to U) the α -U structure is stable, for $n_f \sim 4$ (corresponding to Np) the α -Np structure is stable, and for $n_f \sim 5$

TABLE I. Estimate of the structural dependence of the electrostatic (Madelung) energies (E_{electro}) in m Ry, from Eq. (1).

Structure	Ewald constant	R_{WS}	U		R_{WS}	Np		R_{WS}	Pu	
			Z	E_{electro}		Z	E_{electro}		Z	E_{electro}
fcc	1.79175	3.22	1	3	3.14	1	3	3.18	1	3
α -U	1.78362			6			6			6
α -Np	1.76013			14			14			14
pseudo- α -Pu	1.75831			15			15			15

(corresponding to Pu) the pseudo- α -Pu structure is stable. These model results are in perfect agreement with experiment. Figure 2 suggests further that the α -U, α -Np, and α -Pu structures are quite close in energy for U, Np, and Pu, which motivated us to perform accurate total-energy calculations,¹⁴ based on the generalized gradient approximation (GGA) (Ref. 15) to density-functional theory, of the structural stability of U, Np, and Pu (and also Am, to be discussed below). These results are displayed in Fig. 3. Note that, in agreement with the behavior shown in Fig. 2, the lowest energy is found for the experimentally observed structure for all three elements. The relative ordering of the structural energies in Figs. 2 and 3 are slightly different for Np, but for U and Pu the relative ordering is the same in the two figures. Our simple model thus reproduces perfectly with one exception the full GGA calculations, a rather good test of the model.

In Fig. 4 we compare the structural stability, as given by our model, for the d elements. In this figure we compare a typical transition metal structure (fcc) with typical f -electron structures (α -U, α -Np, and α -Pu). Since f -electron-like structures are not observed for the transition metals (except Mn, to be discussed below), it is gratifying that the model captures this behavior and yields the f structures unstable for all band fillings. However, for d -band occupations close to 4.5, Fig. 4 suggests that actinidelike structures should be very close to the fcc structure. For this reason we compare the GGA energy of paramagnetic Mn (which has a d occupation close to 5) in the fcc and α -Pu structure. In agreement with the results of Fig. 4, we find a relatively small energy difference, with the fcc structure being ~ 8 m Ry lower than the α -Pu structure. Again, GGA calculations and our simple

model are consistent, although our model calculations suggest that the two structures should be even closer in energy. We point out that Fig. 4 implies that distorted structures should have a chance of being stable for band fillings close to 5, exactly the situation in Mn, for which a distorted complex (f -electron-like) structure is observed. However, such a structure is not found in the isoelectronic elements Tc and Re, and the complex structure in Mn is accompanied with magnetism. Clearly other interactions are important, and we will discuss them below.

IV. DISCUSSION

The computational effort of Pettifor's structural energy difference theorem, whether one adds an Ewald correction—as done here—or not, is only a fraction of that of density-functional calculations. In addition, its accuracy shows that it may serve as a useful tool for estimates of structural stability. For instance, Fig. 2 suggests that when the $5f$ shell in Am becomes delocalized (as a function of pressure) this should result in an α -Pu structure. There are of course other structures which we have not tried which may have lower energy, but at least Fig. 2 shows that the α -U structure should not be stable, in contrast to what has been suggested based on experiments.¹⁶ In fact, density-functional calculations treating the $5f$ electrons as nonmagnetic and delocalized (forming band states) for Am at a compressed volume ($V/V_0 \sim 0.6$) predict about 25 m Ry/atom lower total energy for Am in the α -Pu structure compared to the α -U structure. These first-principles results are shown in Fig. 3, which also reveal that the α -Np structure has an intermediate

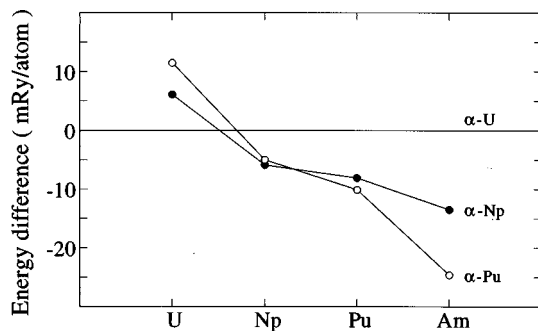


FIG. 3. Calculated total energies (GGA) of selected structures for uranium, neptunium, plutonium, and americium. For U, Np, and Pu, the calculations are performed at their respective (measured) equilibrium volumes, whereas for Am a volume corresponding to its delocalized phase (see text) is chosen.

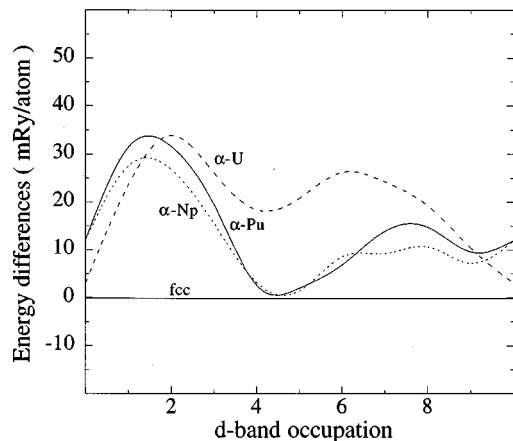


FIG. 4. Structural stability for d occupations between 0 and 10, using a model described in the text.

total energy, in agreement with the trend given by our simple model in Fig. 2. Regarding the experiments, it should be pointed out that the x-ray-diffraction spectra were not consistent with the α -U structure; they were merely the closest fit.¹⁶ Based on our results in Fig. 2, we conclude that the high-pressure structure in Am (at ~ 110 kbar) is either not α -U as suggested, or alternatively that the $5f$ configuration at this pressure is not delocalized and spin degenerate. Many other possibilities are of course possible, such as itinerant magnetism, partial delocalization, and so on. In addition to reproducing the structural properties of U, Np, and Pu Fig. 2 suggests that the fcc structure should be stable for an f occupation of ~ 0.5 , which is consistent with the observed structure in Th.

The results presented here are consistent with the analysis made previously,⁵ since the relative balance between the electrostatic term and the term coming from the structural energy difference theorem depend on volume. For very large volumes, approaching the atomic limit, one can imagine all the charge being inside the muffin tins, and the Ewald energy as given here will be zero, whereas the band term will be small but nonzero. Thus for large volumes the latter term should dominate, and we find that, in line with the analysis of previous investigations,⁵ distorted structures are then found stable in our model, both for the f and d elements. In the limit of small volumes (high pressures), however, the electrostatic terms (Madelung energy) overcome the band energy described above, leading to all actinide metals transforming into high-symmetry structures (Th: hcp; Pa: hcp; U: bcc; Np: bcc; Pu: bcc).¹⁷ This discussion also explains why

Mn attains a complex structure, whereas its isoelectronic elements Tc and Re do not. That is, the width of the $3d$ bands in Mn are considerably narrower compared to the bandwidths of the $4d$ and $5d$ elements.

V. SUMMARY

In summary, we have elaborated on Pettifor's structural energy difference theorem, and added a Ewald correction. The latter term [Eq. (1)] is found to be crucial, since otherwise we would calculate actinidelike structures also to be stable for the d elements. Our model reproduces most of the structural features in the transition metals and light actinides. In addition, we point out problems with the current interpretation of the high-pressure phase of Am as being delocalized, paramagnetic, and in an α -U structure above ~ 110 kbar.^{3,4} At least one of these assignments must be wrong. We have also argued that our model is consistent with the unique structure observed in Mn, although we have not studied this phase in detail, but merely point out the tendency for d electrons to particularly strongly favor distorted structures for d fillings corresponding to Mn and for narrow bands.

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