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Packing of ovaloid atoms in actinide structures

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Résumé.

The atomistic mechanisms which result in the structures of eleven actinide elements are deduced from a parent bcc structure. The rich polymorphism and idiosyncratic structures found in uranium, neptunium and plutonium are interpreted in terms of close packings of ovaloid atoms. The incommensurate structure found in α -U is discussed in this framework.

In addition to the standard bcc, fcc and hcp structures which are found all over the Periodic Table, actinide crystals display a number of low symmetry structures which are a prominent feature of this family of elements^{1,2}. Thus, α -neptunium and the β -phases of plutonium and uranium constitute idiosyncratic structures, i.e. they are unique among all known structures. Besides, the incommensurate phase observed in α -U, is the sole case of structural incommensurability reported in crystals of the elements^{3,4}.

The aim of the present work is to propose a unified description of the structures in actinide crystals using a recent theory of reconstructive transitions of the displacive type^{5,6}. More precisely we will show that all the structures, except one, found in crystals of actinide elements can be derived from the same parent bcc structure via a small number of atomistic mechanisms.

The connections of the low-symmetry structures found in actinides with the bcc parent structure is shown in Fig. 1. One can see that three main situations can be distinguished.

1. In the lighter actinides, namely actinium, thorium and protactinium, the more complete sequence of structures $\text{Im}3\text{m}$ ($Z = 1$) $\rightarrow$ $\text{I}4/\text{mmm}$ ($Z = 1$) $\rightarrow$ $\text{Fm}3\text{m}$ ($Z = 1$), which is fully realized in Pa, and only partially in Th and Ac corresponds to the Bain deformation mechanism, as it was reformulated recently at the macroscopic⁵ and atomistic⁶ levels.

2. A large variety of structures are found in the phase diagrams of the heavier actinide elements (americium, curium, berkelium, californium, einsteinium, ...), the more complete set of five distinct structures having been identified in Am, which are denoted AmI ($\text{P}6_3/\text{mmc}$, $Z = 4$), AmII ($\text{Fm}3\text{m}$, $Z = 1$), AmIII ($\text{P}2_1/\text{m}$, $Z = 4$), AmIV (CmCm , $Z = 2$) and AmV ($\text{Im}3\text{m}$, $Z = 1$). The AmV $\rightarrow$ AmII transformation, which takes place with increasing temperature at $T \approx 1352$ K and atmospheric pressure corresponds to the direct Bain deformation. The sequence of phases AmI $\rightarrow$ AmIII $\rightarrow$ AmIV, which is found below 800 K, with increasing pressure⁹, can be understood in the framework of a variant of the Burgers mechanism proposed in ref 6 and represented in Fig. 2.a.

Except the bcc parent structure, the same phases as in Am are observed in Cf [10].

In Cm and Bk three of the Am structures are found¹¹ (fcc, double-hcp, and orthorhombic). In Es only the fcc structure of AmII is presently known.

3. Let us now focus on the complex and puzzling structures which are found in

Fig. 2 : Shifting mechanism from the bcc unit-cell of AmV (small cubes in thick lines) to orthorhombic AmIV (short arrows) and monoclinic AmIII (long arrows). The dashed lines represent the basic translations of the monoclinic unit-cell in direction b_m . (b) to (e) Transformation mechanism from γ -U to β -U structure. (b) schematic change from the $A_1B_1A_2B_2A_3B_3$ to the ABAC sequence of layers. (c), (d) and (e) represent the in plane shifts for the A, B and C β -U layers. Open and solid circles in (c) indicate the atoms ejected from A_1 . Centered circles in (d) and (e) underline the coincidence of the collapsed layers. The dashed lines illustrate the characteristic in-plane motif.

arises just below bcc ϵ -Pu. However, due to its pseudohexagonal character the mechanism of formation can be better viewed by considering an intermediate virtual double hcp structure of the AmI type. Thus, the mechanism generating γ -Pu can be simply described, as shown in Fig.3.b, by an antiparallel $\frac{a}{4}$ shifting of two pairs of alternate planes forming the four layer double hcp structure. One pair of planes is shifted in the $[001]$ bcc direction, whereas the other pair shifts in the perpendicular $[110]$ direction.

As for γ -Pu, the displacive mechanism which leads to the formation of α -Pu, can be more easily represented with respect to the intermediate δ -Pu structure. The shifts which transform the fcc unit-cell of δ -Pu into the sixteen-fold monoclinic α -Pu unit-cell, are represented in Fig. 3.c. Their non-symmetric directions are consistent with the drastic lowering of point-group symmetry between the two structures.

The group-theoretical and macroscopic features associated with the preceding displacive mechanisms are given elsewhere¹³. We were not able to find a realistic mechanism for the formation of the β structure of plutonium from ϵ -Pu.

It remains to clarify the fundamental causes which may be responsible for the complex structures found in intermediate actinides. In this respect let us note that a model of hard sphere packing of atoms does not provide a suitable geometrical description of the actinide structures, as it leads to an interpenetration, or to the absence of contact of the spheres in different crystallographic directions. For example in α -U a packing of spherical atoms yields a distance between the centers of the closest atoms of $2r = 3.06 \text{ \AA}$ and $2r\sqrt{3} = 5.3 \text{ \AA}$ respectively in the x and y orthorhombic directions, r being the spherical atomic radius. In contrast, the corresponding lattice parameters in these directions are respectively $a = 2.85 \text{ \AA}$ and $b = 5.86 \text{ \AA}$ ⁹. Non-coinciding numbers are also found for most of the phases in actinide crystals when assuming a close packing of spheres. Accordingly one is entailed to suggest that non-spherical atoms should give a more coherent

Fig.3 : (a) Formation mechanism of β - and α -N_p. Open, small and large solid circles represent the atomic positions in γ _p, β and α -N_p respectively. Dashed lines show half of the γ -unit-cell. (b) Formation of γ -Pu from a double hcp virtual structure. Open and solid lines indicate the double hcp and γ unit-cells. (c) Formation of α -Pu from δ -Pu in the monoclinic b plane (010). Open and solid circles are the δ and α positions. Small and large circles differ by $\frac{b}{2}$ in the monoclinic [010] direction. Dashed and solid lines are the projections of the cubic and monoclinic unit-cells.

picture of the geometry of the structures. We will now show that an ovaloid form of the atoms is well adapted for the cristallogometrical properties of actinides.

Fig.4.a shows the transformation mechanism from γ -U to α -U using a close packing of hard ovaloids. It consists in a rotation by 90° of the ovaloids, which preserves the close packing structure. In Fig.4.b, the α - β transformation mechanism in N_p is represented in which the ovaloids are turned by about 20° . In Fig.4.c, details of the β -U structure show that it can be understood as a packing of pseudo six-and-three fold distribution of ovaloid atoms, resulting in an intermediate state between the γ -U and α -U distributions.

An experimental confirmation of the assumed ovaloid form for uranium atoms^{3,4} is provided by the incommensurately modulated structure found in α -U below 37 K ⁴, which can be interpreted as an helical distribution of the ovaloids, the pitch of the helix being incommensurate with the α -U translations. One of the two incommensurate wave-vector characterizing the modulated structure is close to $k = \frac{1}{2} a^*$ where a^* is the orthorhombic lattice vector. Rewriting k in bcc coordinates gives $k = \frac{1}{3} (001)$ which is one of the two wave-vectors proposed in our mechanism of the α - β transformation in uranium. In other words, the incommensurate structure reveals traces of the instability which contributes to the structure, i.e. it can be interpreted as a frustrated regime between the α and β ovaloid distributions.

Fig. 4 : Packing of ovaloid atoms in uranium and neptunium. (a) γ - α transformation in U in projection in the bcc (110) plane. Solid and dashed ovals and lines are the projections of the γ and α atoms and unit-cells respectively. (b) γ - β transformations in Np. Solid and dashed lines have the same meaning as in (a). The arrow symbolize the shift of the central atom of the unit-cell. (c) Characteristic motif in β -U, with an hexagonal and triangular packing of ovaloids.

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