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Theory of reconstructive transformations in actinide elements: Packing of nonspherical atoms and macroscopic symmetries

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Atomistic and macroscopic mechanisms explaining the formation of the structures in crystals of eleven actinide elements are given, and shown to correspond to a small number of irreducible degrees of freedom of the parent bcc structure. The causes of the rich polymorphism and idiosyncratic structures found in U, Np, and Pu are assigned to a close packing of ovaloid atoms. The incommensurate structure found in α-U is interpreted in this framework.

The polymorphism found in crystals of the actinide group[1,2] is unquestionably the richest among all the elements: in addition to the standard bcc, fcc, and hcp structures, which are found all over the Periodic Table, actinides display a number of low-symmetry structures (e.g., tetragonal, orthorhombic, monoclinic) that are prominent features of this family of elements. Thus, the α phase of neptunium and the β phase of plutonium constitute model examples of *idiosyncratic* structures,[3] i.e., they are unique among all known structures, and the understanding of their formation still constitutes an unsolved problem. Besides, the incommensurate phase observed in α uranium[4,5] is the sole case of structural modulation reported for crystals of the elements.

Although the pressure-temperature phase diagrams of a large number of actinide elements were thoroughly investigated,[6] there have been only recently[7,8] attempts to describe theoretically the corresponding phase transformation mechanisms, as these mechanisms are assumed to be of the reconstructive type and thus to be unconveniently interpreted in the framework of the traditional approaches to phase transitions. 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.[9,10] 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. Furthermore, we will illustrate, on the examples of uranium and neptunium, the property that *the structures can be understood on the basis of the shape of the electronic shell of the individual atoms.*

The connections of the different low-symmetry structures found in crystals of actinide elements with the bcc structure are shown in Fig. 1. One can see that three main situations can be distinguished.

In the lighter actinides, namely actinium, thorium, and protactinium, the more complete sequence of structures $Im3m\,(z=1)\rightarrow I4/mm\,(z=1)\rightarrow Fm3m\,(z=1)$, 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 macroscopic[9] and atomistic[10] levels. Thus, the bcc lattice transforms into an fcc lattice via a deformation which compresses the cubic cell along the 4^z axis and stretches it by the same extent along the two other fourfold axes. The spontaneous strain tensor components expressing the preceding deformation are

$$\eta_1=\frac{1}{\sqrt{6}}(e_{xx}+e_{yy}-2e_{zz})\ ,$$

and

$$\eta_2=\frac{1}{\sqrt{2}}(e_{xx}-e_{yy})\ .$$

They form the basis of a two-dimensional irreducible representation (IR) at the center of the bcc Brillouin zone (Γ point), which is denoted τ_3 in Kovalev's tables.[11] The tetragonal structure is obtained when $\eta_1\neq 0$, $\eta_2=0$, and when the ratio a/c is smaller than one. For the specific value $a/c=1/\sqrt{2}$, the tetragonal structure becomes the fcc structure, i.e., the angle between the diagonals in the (110) bcc plane becomes 90°. The associated atomistic mechanism, which was exposed in detail in Ref. 10, consists in a shifting of three successive layers of the bcc structure in the [011] bcc direction. For general displacements of the successive layers by $a\sqrt{2}/6$, $a\sqrt{2}/3$, and $a\sqrt{2}/2$, the fcc phase is formed.

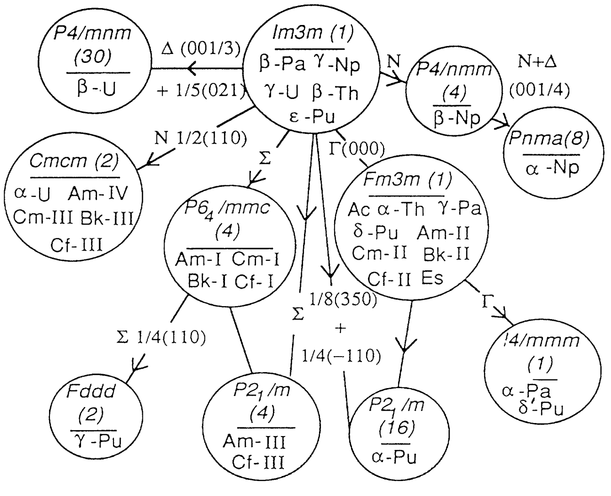

FIG. 1. Symmetry relationship between the structures in actinide elements.

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In Pa, the β-bcc structure transforms into tetragonal α-Pa at about 1450 K.[12,13] The values of the lattice constants in the two phases[12] give the following numbers at room temperature: $\eta_1 \simeq 0.15$ and $a/c = 0.825$. The fcc phase of Pa is obtained by quenching the high-temperature form[14] and corresponds to the value $\eta_1 \simeq 0.31$. In Th, one observes a strongly first-order transformation between the bcc (β-Th) and fcc (α-Th) phases at 1678 K.[15] At room temperature the deformation is $\eta_1 \simeq 0.02$. The pressure-temperature diagram of Ac was not investigated and only the fcc structure was observed in this element at room temperature (RT) and atmospheric pressure[1] (AP).

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,[16] which are denoted AmI ($P6_3/mmc, z=4$), AmII ($Fm3m, z=1$), AmIII ($P2_1/m, z=4$), AmIV ($Cmcm, z=2$), and AmV ($Im3m, z=1$). The AmV→AmII transformation, which takes place[17] with increasing temperature and AP at $T_c = 1352$ K, corresponds to the direct Bain deformation mechanism previously discussed for light actinides.

The sequence of phases AmI→AmIII→AmIV, which is found below 800 K, with increasing pressure,[18] can be understood in the framework of a variant of the Burgers mechanism proposed in Ref. 10. Thus, the three corresponding structures are obtained from the bcc structure, as shown in Fig. 2(a), by an antiparallel shifting of the atoms in the (110) bcc planes, along the $[\bar{1}10]$ and $[1\bar{1}0]$ bcc directions. This primary mechanism induces, as a secondary (improper) effect, a compression of the cubic unit cell along one of the fourfold axes [001] and a simultaneous decompression along the two other fourfold axes: For *arbitrary* shifts along $[\bar{1}10]$ and $[1\bar{1}0]$ one gets the orthorhombic (AmIV) and monoclinic (AmIII) phases for two different instabilities of the bcc lattice. The two instabilities are respectively associated with two different points of the bcc Brillouin zone, both located on the Σ line: The N point $[k_9 = (\frac{1}{2}\frac{1}{2}0)]$ leads to the orthorhombic structure AmIV, the unit cell of which is doubled with respect to the bcc unit cell along the cubic direction [110], whereas at the middle of the Σ line $[k_4 = (\frac{1}{4}\frac{1}{4}0)]$, one obtains the monoclinic structure of AmIII, the unit cell of which is quadrupled in the same direction. For the *specific* atomic shifts $a\sqrt{2}/12$ in the same preceding directions, where a is the cubic lattice constant, the monoclinic structure *becomes the double hcp structure of AmI,* i.e., the β-monoclinic angle which is 106.1° (Ref. 18) becomes 120°.

Except for the bcc parent structure, the same phases as in Am are observed in Cf.[19] In Cm and Bk three of the Am structures have been found[20] (fcc, double hcp, and orthorhombic). In Es only the fcc structure of AmII is presently known.[19]

Let us now focus on the complex and puzzling structures which are found in intermediate actinides: uranium, neptunium, and plutonium. In their pressure-temperature phase diagrams[6] the bcc structure, denoted γ-U, γ-Np, and ε-Pu, is stable below the melting line and thus appears as the natural parent structure for the three elements as was assumed in our approach for all actinide elements. Two sequences of phases will not be discussed further, namely, ε-Pu→δ'-Pu($I4/mm, z=1$)→δ-Pu(fcc, $z=1$), which takes place on cooling at AP,[1] and γ-U($Im3m, z=1$)→α-U(Cmcm, $z=2$), which occurs on cooling at high pressures,[1] as they can respectively be interpreted in the framework of the Bain deformation and Burgers mechanisms invoked above. All the remaining structures found in U, Np, and Pu require specific mechanisms and will now be described separately.

The crystallographic description of the β phase of uranium ($P4_2/mnm, z=30$), which is found between 941 and 1048 K at AP, has been the subject of thorough discussions over the past decades.[1] The connection between

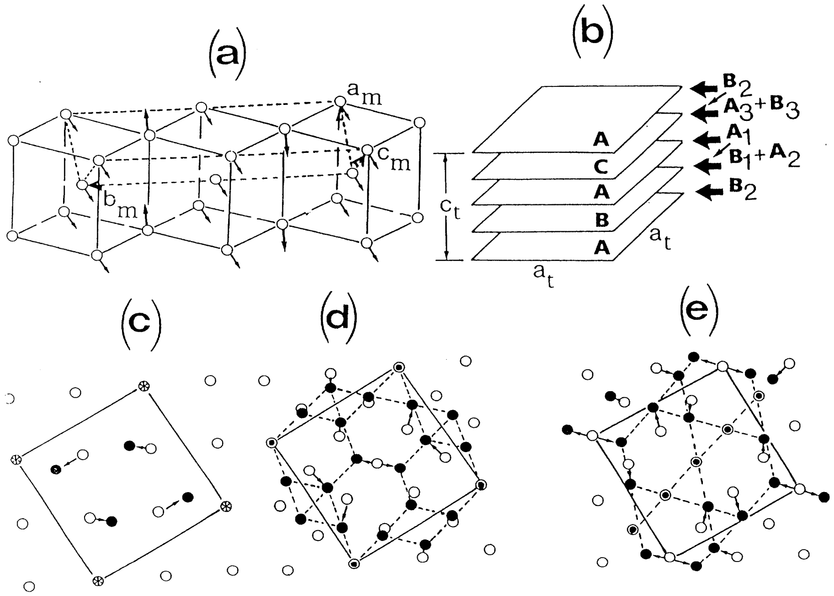

FIG. 2. (a) Shifting mechanism from the bcc unit cell of AmV (small cubes in thick lines) to orthorhombic AmIV (short arrows) and monoclinic AmIII (long arrows). The dashed lines represent the basic translations of the monoclinic unit cell in direction $\mathbf{b}_m$. (b)–(e) Transformation mechanism 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)–(e) represent the in-plane shifts for the A, B, and C β-U layers. Open and solid circles are the γ and β positions. Crossed 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.

the γ-U and β-U structures and the displacive mechanism proposed by us for the transformation of one structure into the other is illustrated in Figs. 2(b)–2(e) and can be summarized as follows: Six successive layers of the (100) type, of the bcc bilayer structure $A_1B_1A_2B_2A_3B_3$, generate the four-layer $ABAC$ β-U structure[1] in two correlated steps [Fig. 2(b)]: (i) Each couple of bcc layers (B_1+A_2) and (A_3+B_3) *collapse* and form respectively the B and C β-U layers; (ii) one atom of each of the A_1 and B_2 bcc layers are ejected and complete the B and C layers, the remaining atoms of A_1 and B_2 constituting the two A layers of β-U, which are shifted one with respect to the other by $(a/2,a/2,0)$. Figures 2(c)–2(e) decompose the corresponding displacements of the uranium atoms from their bcc to their β-U positions.

Macroscopically, the entire transformation mechanism can be understood as a drastic compression of the bcc planes along the z axis and a simultaneous large decompression within the collapsed planes. The numbers found for the spontaneous strain components induced by the transformation, calculated from the numerical values of the lattice constants in the two phases,[21] are $e_{zz}=+0.365$ and $e_{xx}=e_{yy}=-0.465$. They are indicative of the huge magnitude of the displacements in the assumed mechanisms. Two different IR's, six and twenty-four dimensional of the $Im3m$ space group, associated with the two wave vectors $k_1=\frac{1}{3}(001)$ and $k_2=(0\frac{2}{5}\frac{1}{5})$ located inside the bcc Brillouin zone, express the symmetry properties of the two preceding mechanisms.

The formation of the two low-symmetry phases of neptunium,[22] namely β-Np ($P4/nmm,z=4$) and α-Np ($Pnma,z=8$) which appear consecutively on cooling at all pressures below bcc γ-Np, can be understood on the basis of standard symmetry considerations, as they are related by a group-subgroup relationship to the bcc structure. Thus, the γ-Np$\rightarrow$$\beta$-Np transformation is induced by a six-dimensional IR of the $Im3m$ space group, denoted $\tau_8(k_9)$, at the N point of the bcc Brillouin-zone boundary. One can show that the equilibrium values of the corresponding six-dimensional order parameter ($\eta_1=\eta_4\neq0$, $\eta_2=\eta_3=\eta_5=\eta_6=0$) involves only two of the six branches of the star of the wave vector k_9: $k_9^1=\frac{1}{2}(112)$ and $k_9^4=\frac{1}{2}(110)$. The connection between the β and γ unit cells is shown in Fig. 3(a). The lowering of symmetry which leads to the orthorhombic α-Np is associated to an additional six-dimensional IR, denoted $\tau_1(k_8)$, where the wave vector $k_8=\frac{1}{4}(001)$ is located on the Δ line of the bcc Brillouin zone. The coupling of $\tau_4(k_9)$ and $\tau_1(k_8)$ results in the eightfold orthorhombic unit cell represented in Fig. 3(a). In the same figure are indicated the displacements of the Np atoms which transform successively γ-Np in β- and α-Np. One can see that the tetragonal structure corresponds to an antiparallel shifting along the z axis of two among the four Np atoms contained in each tetragonal unit cell. The magnitude of the displacements, deduced from the lattice parameters of γ- and β-Np,[22] is $\pm\Delta z=0.42$ Å$\simeq\frac{1}{8}a$. The formation of the orthorhombic structure requires an additional antiparallel shifting of all the eight atoms contained in each orthorhombic cell, simultaneously along the c-tetragonal and b-orthorhombic axes. For four atoms that were immobile in the tetragonal structure, the magnitude of the shifts at the γ-α transformation is about 0.3 Å, whereas for the four remaining atoms it is 0.6 Å. The calculated relative jump in volume is $\Delta V/V\simeq-2.6\%$ for the γ-β transformation and $\Delta V/V\simeq-2.9\%$ at the β-α transformation. With respect to the bcc structure the calculated spontaneous strains are $\Delta a/a=-0.038$, $\Delta c/c=-0.017$ for the β phase and $\Delta a/a=-0.05$, $\Delta b/b=-0.018$, $\Delta c/c=-0.017$ for the α phase. All these numbers show that the β and α structures of neptunium are the result of a moderate compression of the γ structure and are in agreement with the preservation of the group-subgroup relationship between the phases.

At last, we will consider the three idiosyncratic structures[3] of plutonium, namely γ-Pu ($Fddd,z=2$), β-Pu ($I2/m,z=17$), and α-Pu ($P2_1/m,z=16$), which appear in the preceding order on cooling over a wide range of pressures.[6] As for β-U, these structures have been the subject of intensive discussion over the past years.[1]

In the pressure-temperature phase diagram of Pu, the four-layered orthorhombic γ-Pu arises just below bcc ε-Pu.[23] 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, which was shown here above to form from a bcc structure. Then, the mechanism generating γ-Pu can be simply described, as shown in Fig. 3(b), by an antiparallel shifting of two pairs of alternate planes forming the four-layer double hcp virtual structure, by $a/4$. One pair of planes is shifted in the [001] bcc direction, whereas the other pair shifts in the perpendicular [1$\bar{1}$0] bcc direction.

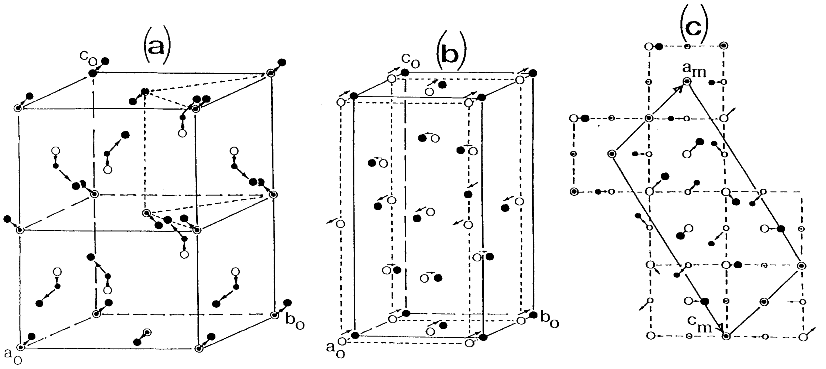

FIG. 3. (a) Formation mechanism of β- and α-Np. Open, small, and large solid circles represent the atomic positions in γ-, β-, and α-Np, respectively. Dashed lines show half of the γ unit cell. (b) Formation of γ-Pu from a double hcp virtual structure. Open and solid lines indicate the double hcp and 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 $b/2$ in the monoclinic [010] direction. Dashed and solid lines are the projections of the cubic and monoclinic unit cells.

The displacement of the Pu atoms in three directions forming angles of 120° in the (110) plane produces at the macroscopic level a shear deformation corresponding to a compression along the a and c orthorhombic directions and a decompression along b. In other words, the angles between the diagonals in the (110) bcc plane, which are 70.5° and 109.5° in ε-Pu, become respectively 60° and 120° in γ-Pu. The numbers obtained from the lattice parameters of the two phases ($\Delta a/a=-0.15$, $\Delta b/b=+0.12$, $\Delta c/c=-0.01$) show that the decompression along c is one order of magnitude smaller than along a or b.

According to the preceding description, it should be underlined that the double hcp AmI structure and γ-Pu are induced by the same twelve-dimensional IR of the $Im3m$ space group at $k_4=(\frac{1}{4}\frac{1}{4}0)$. The two structures differ only by the magnitude of the atomic displacements from the bcc positions.

As for γ-Pu, the displacive mechanism that 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 sixteenfold monoclinic α-Pu unit cell[23] are represented in Fig. 3(c). Their nonsymmetric directions are consistent with the drastic lowering of point-group symmetry between the two structures. Macroscopically, the ε-Pu$\rightarrow\alpha$-Pu transformation is induced by two, 24- and 12-dimensional IR's, of the $Im3m$ space group, respectively associated with the wave vectors $k_1=\frac{1}{8}(350)$ and $k_2=\frac{1}{4}(-110)$ located inside the bcc Brillouin zone. With respect to the δ-Pu fcc structure, it corresponds to a compression along the x and y cubic axes ($\Delta a/a=-0.16$, $\Delta b/b=-0.06$) and a decompression along z ($\Delta c/c=0.04$), the monoclinic angle *increasing* from 102° to 104°.

We were not able to find a realistic mechanism for the formation of the β structure of plutonium[24] from ε-Pu. A number of authors stressed the resemblance between β-Pu and β-U,[1] but in β-Pu the structure cannot be simply described in terms of stacking of atomic planes, as its monoclinic structure consists in a stacking of *seventeen* tetragonal layers. Such a structure can be formally generated from ε-Pu using a mechanism analogous to the one proposed for the formation of β-U (i.e., a collapsing of successive sequences of *three* ε-Pu planes), but it should imply too large a compression of the bcc lattice to be physically sound.

In summary, except for β-Pu, we have proposed within a unified model a set of mechanisms which lead to the formation of all the structures in actinide crystals. At the microscopic level these mechanisms are described in terms of atomic displacements from a parent bcc structure, and at the macroscopic level, as large deformations of the bcc lattice, which transform following a reduced number of IR's of the $Im3m$ space group.

It remains to clear up the fundamental causes which may be responsible for the rich polymorphism and complex structures found more particularly 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 $2r=3.06$ Å and $2r\sqrt{3}=5.3$ Å, 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 $a=2.85$ Å and $b=5.86$ Å.[17] Noncoinciding 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 *nonspherical* atoms should give a more coherent picture of the geometry of the structures. We will now show that an *ovaloid* form of the atoms, the so-called *Cassini ovaloids,* is well adapted for a description of the crystallogeometrical properties of actinides. A physical justification of this assumption lies in the fact that in actinides, although the f orbitals play an essential part in the determination of the density of electron distribution, which in turn determines the minimal interatomic distance in the crystal, the shape of the atoms in the crystal structure results from the hybridization of s, p, d, and f shells, as was recently stressed in Refs. 7 and 8. Consequently the ovaloid form, which coincides with the angular distribution corresponding to the spherical harmonics Y_{20}, provides the more suitable first approximation for a nonspherical atomic close packing.

Figure 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 γ-β transformation mechanism in Np is represented, in which the ovaloids are turned by about 20°. In Fig. 4(c), details of the β-U-structure, as given in Fig. 2, show that this structure can be understood as a packing of pseudo six- and threefold distribution of ovaliod 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 is provided by the incommensurately modulated structure found in α-U below 37 K,[4,5]

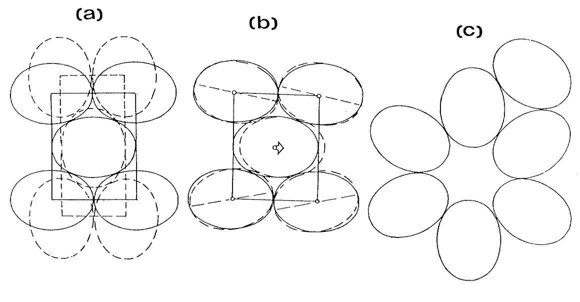

FIG. 4. Packing of ovaloid atoms in uranium and neptunium. (a) γ-α transformation in U in projection in the bcc (110) plane. Solid and dashed ovals and lines are the projections of the γ and α atoms and unit cells, respectively. (b) γ-β transformations in Np. Solid and dashed lines have the same meaning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

which can be interpreted[25] as a helical distribution of the ovaloids, the pitch of the helix being incommensurate with the α-U translations. One of the two incommensurate wave vectors characterizing the modulated structure[5] is close to $\mathbf{k}=\frac{1}{2}\mathbf{a}^*$, where $\mathbf{a}^*$ is the orthorhombic reciprocal lattice vector. Rewriting $\mathbf{k}$ in bcc coordinates gives $\mathbf{k}=\frac{1}{3}(001)$, *which is one of the two wave vectors proposed in our mechanism of the γ-β transformation in uranium.* In other words the incommensurate structure reveals traces of the instability which contribute to the β structure, i.e., it can be interpreted as a frustrated regime between the α and β ovaloid distributions. A more detailed discussion of the charge-density wave in α-U will be given elsewhere.[25]

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