Phonon Mechanisms and Transformation Paths in Pu

T. Lookman, A. Saxena, and R. C. Albers

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
(Received 21 October 2007; published 10 April 2008)

A long-standing problem in Pu science is the crystallographic mechanism for the $\delta \rightarrow \alpha'$ (fcc $\rightarrow$ monoclinic) transformation. Orientation relations between the two structures impose severe restrictions on the possible mechanisms and require the transition to be reconstructive, which we describe as a sequence of three displacive transitions: fcc $\rightarrow$ trigonal $\rightarrow$ hexagonal $\rightarrow$ monoclinic. We predict instabilities along the Λ and Σ branches in the phonon dispersion of the δ phase and formulate a free energy to describe the displacement of atoms across the transition. We suggest that the $\delta \rightarrow \alpha'$ transition in Pu lies at the threshold of a change in character of the orientation relationship from lighter to heavier actinides, correlating with changes in electron itinerancy, magnetism, and volume.

Plutonium not only is complex in its electronic, vibrational, and nuclear properties but also, after six decades of activity, the nature of its $\delta \rightarrow \alpha'$ (fcc $\rightarrow$ monoclinic) phase transformation remains a puzzle. This transformation is believed to be martensitic, involving a coherent, *continuous* motion of many atoms over short distances without diffusion [1], and is particularly challenging because of a large volume change of $\sim 20\%$. The δ phase is considered to be the most important phase with respect to metallurgical properties as it can easily be retained in a metastable state at room temperature by the addition of Ga or Al. The α' phase is similar to the low-temperature α phase of pure Pu with impurities, which at low concentrations slightly modify the lattice parameters without causing any change of symmetry. It was proposed [2,3] that the large volume change required a particular orientation relationship (OR) between the two structures so that the basal plane of the α' is parallel to the (111) plane of the δ with the a axis of the α' parallel to the $[\bar{1}10]$ direction of the δ (Fig. 1). This OR was later corroborated by Zocco *et al.* with TEM [4].

Although a number of approximate structures, e.g., distorted hexagonal [5], "orthorhombic diamond" [6], and those mechanisms invoking Shockley-type partial dislocations [7] and shifting of fcc planes to create hcp structures [8–10], have been proposed for $\delta \rightarrow \alpha'$, it has not been possible to test these experimentally. Only recently have systematic attempts been made to search for transformation mechanisms in materials [11]. Thus, our *objective* is to seek mechanisms that combine strains of unit cells and displacements of atoms (phonons), and that can predict signatures of softening or other anomalies seen in phonon dispersion experiments and temperature variation of elastic moduli. In this Letter we demonstrate that the $\delta \rightarrow \alpha'$ transformation can be described as a sequence of displacive transformations that require specific intermediate structures, in particular, trigonal and hexagonal. By mapping crystal ORs into reciprocal k space, we predict the signatures of the mechanism in the phonon dispersion curves at specific points and branches in the δ Brillouin zone (BZ), which are consistent with anomalies seen in

experiments [12] and predicted by dynamical mean-field theory (DMFT) [13]. However, no mechanisms have been put forward that can explain these results. We provide such a transformation mechanism that ensures (Wyckoff) site compatibility and propose an effective free energy to describe the shuffles and strains for the $\delta \rightarrow \alpha'$ transformation in Pu.

Symmetry provides strong constraints upon possible pathways so that direct (*one-step*), continuous pathways are only allowed between crystal structures that have a group-subgroup symmetry relationship. This implies that every atom in the starting and ending phases has a one-to-one identification and a continuous path that takes each atom from its initial to its final position. It would therefore be natural to make a direct transformation path between the two crystal structures, since the space group of the α' phase ($P2_1/m$) is a subgroup of the δ phase ($Fm\bar{3}m$). Unfortunately, this violates the experimental OR [4], and hence must be incorrect. Another mechanism must be found that involves intermediate crystal structures that provide a bridge between the beginning and ending crystal structures with each linked to the neighboring structures by group-
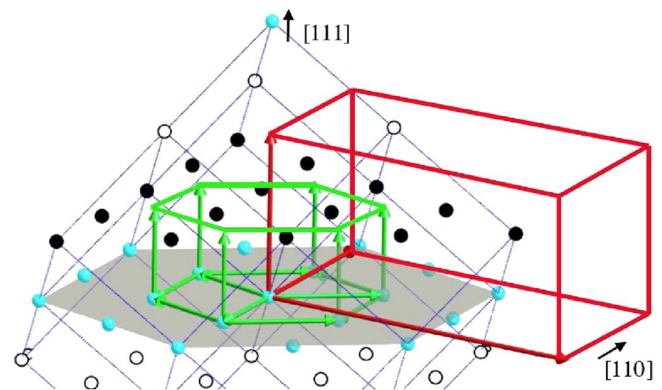

FIG. 1 (color online). Orientation of the α'-Pu monoclinic cell in relation to the δ-fcc parent lattice. Shown are the "intermediate" primitive simple hexagonal (sh) cells and fcc (111) plane; the fcc A, B, C plane atoms are shaded (colored).

P H Y S I C A L   R E V I E W   L E T T E R S

subgroup relationships. We show here that the known OR reduces the number of solutions to only one or two. Recent experimental and theoretical progress also guides the search for the correct mechanism. Inelastic x-ray scattering has allowed the measurement of phonon dispersions along high-symmetry directions in a δ Pu-0.6 wt % Ga alloy [12]. Electronic structure calculations based on DMFT can now describe both the bandlike and localized behavior of the electrons [13]. These indicate softening of the transverse acoustic TA[111] branch near the L point as well as anomalies along the Σ line in the δ BZ. The DMFT also shows an anomaly at the X point.

A *key insight* is that the OR for $\delta \to \alpha'$ in Pu is precisely what occurs in fcc $\to$ sh or fcc $\to$ hcp transformations that obey the Shoji-Nishiyama (SN) mechanism [14] for martensitic transformations. This specifies a transformation path based on continuously distorting from fcc to sh ($P6mm$) or hcp ($P6_3/mmc$) such that the c axis of the latter is parallel to the [111] fcc direction. The alternative mechanism to SN is that in which the [0001] hcp direction is parallel to the [001] fcc direction, and this is obeyed [15] in Fe and Al. We observe that the SN mechanism is a consequence of the requirement that the threefold axis in the fcc becomes a twofold axis in the monoclinic structure. This is exactly the same issue with respect to Pu, since the [111] direction of the fcc structure of δ is a threefold axis and the monoclinic structure of α' has a twofold b axis. The only way this condition can be fulfilled is via a higher symmetry reference sh (or hcp) structure that has a sixfold axis—a multiple of two and three. Hence, the hexagonal is the required intermediate symmetry that is *fundamental* to enabling the $\delta \to \alpha'$ transformation to proceed in Pu. There have been many references to the two-plane structure of the α' monoclinic as being "distorted hexagonal-like" [5,8,9]. However, this is not sufficient because it can arise from a different mechanism, e.g., from a direct, continuous path that is group-subgroup related from fcc to monoclinic, and is mediated by an internal fcc BZ phonon vibration $A1$ of wave vector $\frac{1}{8}(3, 11, 0)$ with appropriate atomic displacements and strains [16]. This path, a lattice correspondence for which it was previously proposed [17], requires an OR in which the b axis of the monoclinic is parallel to the z axis of the fcc and, therefore, *cannot* be the real mechanism for $\delta \to \alpha'$ for which the twofold b axis is parallel to the [111] direction in fcc [4].

Our findings for the transformation, which involve two alternative hexagonal intermediate symmetries (sh, hcp), are summarized in Fig. 2. For illustration, we focus here on the path via sh. Between fcc and sh there is no group-subgroup relationship; in this sense we refer to it as a reconstructive transformation. To convert this into a displacive transformation requires finding a way to connect these two structures through an intermediate crystal structure that has a group-subgroup relationship both with respect to fcc and sh. An extensive search [16] reveals that an intermediate trigonal structure enables this loss of fourfold
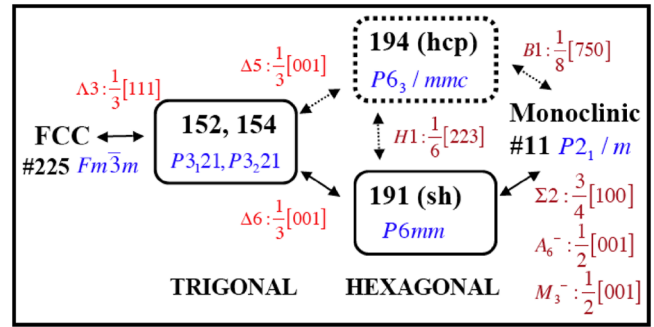

FIG. 2 (color online). Proposed transformation mechanism involving intermediate structures and phonon modes for the $\delta \to \alpha'$ transformation. The two distinct Wyckoff-site-compatible allowed paths are via sh and hcp [21]. The two trigonals, $P3_121$ and $P3_221$, differ only in the atom positions about the screw axis.

symmetry of the fcc in favor of the sixfold hexagonal symmetry. The specific trigonal structure with space group ($P3_121$) and $3a$ Wyckoff site positions is a result of tripling the original fcc primitive cell to yield a 3-atom primitive trigonal cell. The continuous path from fcc to this trigonal structure involves a collective displacement mode shown in Fig. 3, in addition to a C_{44} shear. The breaking of the translation symmetry is accomplished by a $\Lambda3$ phonon with wave vector $\frac{2}{3}(1, 1, 1)$ in the fcc BZ. The same trigonal structure is *also* a subgroup of the sh ($1a$ Wyckoff positions), and Fig. 3 shows that it arises from sh by tripling of the sh primitive unit cell. This is achieved by the action of the $\Delta6$ phonon with wave vector $\frac{2}{3}(0, 0, 1)$ in the hexagonal BZ, the translational symmetry being broken by tiling the lattice with trigonal cells with $3a$ Wcykoff site symmetry from three primitive sh cells. The trigonal is thus a *common subgroup* with atoms lying at $3a$ Wyckoff positions $(x, 0, 1/3)$ in its frame of reference so that the structural parameter x takes the lock-in values $x = 0$ and $x = 1/3$ for fcc and sh, respectively, and for other values of x, the path remains Wyckoff-site-compatible with trigonal symmetry. As Fig. 3 indicates, the atomic displacements in the B, A, C fcc closed-packed layers repeat every three layers.

To complete the mechanism, we show how the sh structure transforms to one of its subgroups, the monoclinic structure. This can occur by combining 16 primitive simple hexagonal cells to form one 16-atom monoclinic cell ($P2_1/m$ with atoms in $2e$ Wyckoff positions) by the simultaneous action of three primary phonons, namely $\Sigma2$, M_3^-, and A_6^- with wave vectors $\frac{3}{4}(1, 0, 0)$, $\frac{1}{2}(1, 0, 0)$, and $\frac{1}{2} \times (0, 0, 1)$, respectively, and other secondary phonons and strains. A total of 16 collective primary and secondary displacement modes yield the monoclinic structure with eight independent atom positions [16]. Because the y positions ($\frac{1}{4}$ or $\frac{3}{4}$ in the b direction) of all the atoms in the monoclinic cell are prescribed by the $2e$ positions, we can obtain an exact match with the experimental x-ray data analysis of
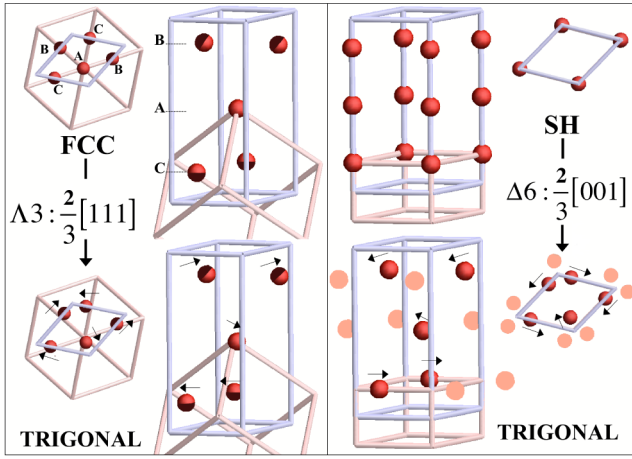
FIG. 3 (color online). Atomic displacements from fcc to sh due to the phonon mechanism with projected views along the [111] fcc (or [0001] sh) directions ($a_h = 3.2$ Å for ~20% volume change for fcc → α'). The 3-atom trigonal unit cell (gray lines, $P3_121$) is a common subgroup that facilitates the transformation from fcc to sh. Left: upper, atom positions in undistorted fcc with A, B, C stacking layers. Structural parameter, $x = 0$ for fcc; lower, atomic displacements within the trigonal cell for $0 < x < \frac{1}{3}$. At $x = \frac{1}{3}$, the atoms would occupy primitive sh positions. Atoms in the B and C planes are shaded differently. Right: upper, atom positions in undistorted sh with $x = \frac{1}{3}$, three primitive sh cells form one trigonal; lower, atomic displacements within trigonal from the sh side. At $x = 0$, the atoms would be at fcc positions. Lighter atoms are outside the gray trigonal cell.

Zachariasen and Ellinger [18]. The direction of the atom displacements within the monoclinic cell, obtained by the action of the dominant phonon modes on the primitive sh cells are shown in Fig. 4. A path to the monoclinic from sh or trigonal is also possible via hcp (Fig. 2). We have thus demonstrated how atoms can move continuously from δ to α' while satisfying site symmetry, ORs, and volume requirements.

Since the reconstructive phase transformation originates from fcc, whereas the sh to trigonal and sh to monoclinic transformations correspond to phonons in the sh BZ, an important question is, what are the phonon signatures in the fcc BZ, i.e., how does one represent the ORs in terms of the two BZs (fcc and sh)? To study this, we utilized the notion of BZ embedding, with specific application to the sh and fcc structures with appropriate scaling of wave vectors. We require that the Γ-A line in sh is parallel to the Γ-L line in fcc, i.e., parallel to the [111] direction. Similarly, the Γ-M line in sh has to be parallel to the Γ-K line in fcc. From these two constraints one can relate other lines and points in the two Brillouin zones (Fig. 5). In particular, the $\Lambda6$: $\frac{2}{3}[111]$ phonon in fcc lies along the same direction as the $\Delta5$: $\frac{2}{3}[001]$ phonon in sh and is predicted to show a softening at $|k| = \frac{2}{3}$ toward the L point (fcc) or A point (sh). Similarly, the $\Sigma2$, M_3^-, and A_6^- phonons in sh BZ that give rise to the monoclinic correspond to the Σ branch (Γ-K line) ($|k| = \frac{2}{3}$), K and L point, respectively, in the fcc BZ.
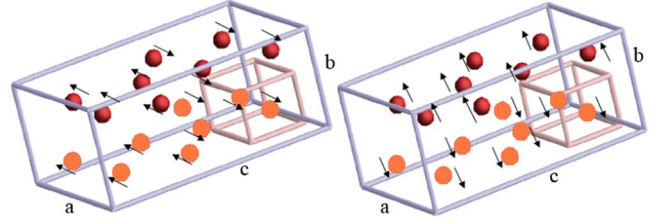

FIG. 4 (color online). The transformation from sh to monoclinic takes place by breaking of translational symmetry with 16 sh primitive cells combining to give one 16-atom primitive monoclinic cell. Shown are the atomic displacements of the largest amplitude modes that distort a 16 cell sh supercell to the known α' monoclinic structure. Left: $\Sigma2$: $\frac{2}{3}[100]$ mode with a maximum amplitude of 0.66 Å. Right: A_6^-: $\frac{1}{2}[001]$ mode with a maximum amplitude (0.1, 0.41). The M_3^- phonon motion is parallel to that of $\Sigma2$; it has a maximum amplitude of 0.5 Å. Atoms in the $b = 1/4$ and $3/4$ planes are shaded differently (fcc $a_o = 4.59$ Å, α' parameters from [18]).

These predictions are *consistent* with the experimental phonon anomalies [12] and some of the results of DMFT [13]. The DMFT also predicts anomalous flattening at the X point in the fcc BZ that has not been observed and is not consistent with our mechanism.

A free energy for fcc → monoclinic with shuffle order parameters (OP) is formed by noting that the $\Lambda3$ phonon that drives the fcc to trigonal transition is a 16-component OP with two nonzero components, ϕ, proportional to each other. From the common sh parent, the $\Delta6$ phonon that drives the transition to trigonal is a four-component vector OP with two nonzero components, ζ, proportional to each other. The hexagonal to monoclinic transition is driven by the dominant $\Sigma2$ phonon with a six-component vector OP with only two equal, nonzero components, η. We thus have symmetry allowed free energy contributions of the form $F(\phi) = a\phi^2 + b\phi^3 + c\phi^4$ for fcc → sh and $F(\zeta, \eta) = a_1\zeta^2 + a_2\zeta^3 + a_3\zeta^4 + b_1\eta^2 + b_2\eta^4 + b_3\eta^6 + d\zeta^2\eta^2$ from sh to trigonal and monoclinic. The trigonal common subgroup of fcc and sh may be represented by (ϕ, ζ) where $\zeta = \frac{1}{3} - \phi$, so that at the lock-in values of $(0, 1/3)$ and $(1/3, 0)$ the symmetry is raised to fcc and sh, respectively. In addition, since trigonal and monoclinic have the same sh parent, η and ζ are coupled, i.e., $\zeta^2\eta^2$, giving rise to couplings between ϕ and η. The effective free energy for fcc → monoclinic becomes $F^{\mathrm{eff}}(\phi) = a'\phi^2 - \frac{\phi^3}{3} + \frac{\phi^4}{4} + d'\phi$, an asymmetric double-well Landau free energy in an external field—a consequence of the intermediate sh structure. At the transition, $d' = \frac{2}{27} - \frac{a'}{3}$ with $a' = 2/9$ and, although all the parameters of this scaled free energy are known at the transition, phonon data below room temperature or a fit to electronic structure data is required to fully parametrize it.

A strain free energy (with triple wells) using known parameters may be formulated in terms of only one shear e_4 [parallel to the (111) plane that takes an undistorted orthorhombic cell with vectors $\frac{2}{3}a_o(1, 1, 1)$, $\frac{a_o}{\sqrt{2}}(-1, 1, 0)$,
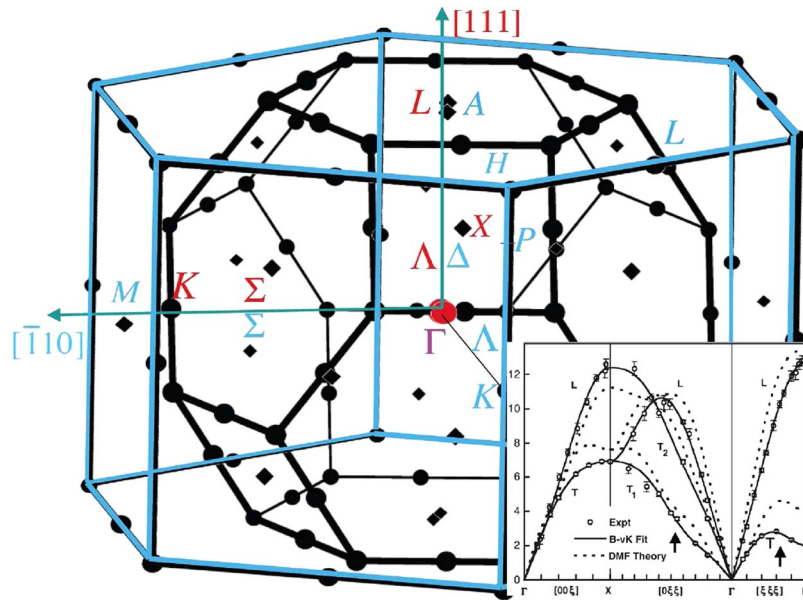
FIG. 5 (color online). Embedding of the fcc and sh BZs with the appropriate OR. The predicted softening is along the $\Lambda: \frac{2}{3}[111]$ and $\Sigma: \frac{2}{3}[001]$ branches and is consistent with the phonon dispersion data (inset from [12] shows energy vs k, and our arrows indicate the amplitude of predicted k vectors with anomalies).

$\frac{a_o}{\sqrt{6}}(1, 1, -2)$, and volume $4a_o^3$ to the monoclinic cell, Fig. 1]. The coefficient G_o in the harmonic part of the free energy $F(e_4) = \frac{G_o(T_o - T)}{2} e_4^2$ has the value [19] 0.157 GPa/K for a Pu/Al alloy, and the transition temperature T_o is 291.4 K. The free energy leads to an entropy jump of 1.4 R at 300 K, consistent with the experimental results for pure Pu and estimates of vibrational entropy for high temperatures [20].

In summary, we have provided a transformation mechanism consistent with available structural and phonon data, which suggests: As the transition starts from the δ phase, one should expect to see in ultrafast time-resolved diffraction the transient emergence of a sixfold axis, which subsequently disappears as the monoclinic phase develops. The anomaly seen along the Λ and Σ branches in the δ phonon dispersion would show temperature dependent softening that would allow a full parametrization of the proposed free energy. Finally, it is well known that δ-phase Pu has a unique position among the actinides in that it sits at a "turning point" between itinerancy and localization of f electrons. Lighter actinides have itinerant f electrons, are nonmagnetic, and have smaller volumes compared to the heavier actinides that have localized f electrons, are magnetic, and have larger volumes [1]. Moreover, lighter actinides have phase transitions from a cubic phase to symmetries such as tetragonal, orthorhombic, and monoclinic, which appear to obey a Wentzcovitch-Lam-type [15] OR. On the other hand, heavier actinides have phase transitions from a cubic phase to sixfold symmetric phases such as hcp, double hcp, etc., which appear to follow the Shoji-Nishiyama-type [14] OR that is valid for Pu. Thus, we propose that the *change in the character of the OR* from lighter to heavier actinides is *directly correlated* with the change in the itinerancy of f electrons, magnetism, and volume, with the $\delta \rightarrow \alpha'$ transition in Pu lying at the

threshold. Other phase transformations, e.g., fcc $\rightarrow$ bcc, could be studied using our approach so that crystal ORs, such as Kurdjimov-Sachs and Nishiyama-Wassermann [14], may be cast in the language of phonon mechanisms.

[1] S. S. Hecker *et al.*, Prog. Mater. Sci. **49**, 429 (2004).
[2] G. B. Olson and P. H. Adler, Scr. Metall. **18**, 401 (1984).
[3] P. H. Adler *et al.*, Acta Metall. **34**, 2053 (1986).
[4] T. G. Zocco *et al.*, Acta Metall. Mater. **38**, 2275 (1990).
[5] A. G. Crocker, J. Nucl. Mater. **41**, 167 (1971).
[6] J. Bouchet *et al.*, Phys. Rev. Lett. **92**, 095503 (2004).
[7] J. P. Hirth *et al.*, Acta Mater. **54**, 1917 (2006).
[8] Y. M. Jin *et al.*, Metall. Mater. Trans. A **36**, 2031 (2005).
[9] J. van Ek *et al.*, Phys. Rev. B **48**, 16280 (1993).
[10] I. Folkins and M. B. Walker, Phys. Rev. Lett. **65**, 127 (1990).
[11] D. R. Trinkle *et al.*, Phys. Rev. Lett. **91**, 025701 (2003).
[12] J. Wong *et al.*, Science **301**, 1078 (2003).
[13] X. Dai *et al.*, Science **300**, 953 (2003).
[14] Z. Nishiyama, *Martensitic Transformations* (Academic, New York, 1978).
[15] R. M. Wentzcovitch and P. K. Lam, Phys. Rev. B **44**, 9155 (1991).
[16] H. T. Stokes *et al.*, ISOTROPY, http://stokes.byu.edu/ isotropy.html (2007); M. I. Aroyo *et al.*, Z. Kristallogr. **221**, 15 (2006).
[17] B. Mettout *et al.*, Phys. Rev. B **48**, 6908 (1993).
[18] W. H. Zachariasen and F. H. Ellinger, Acta Crystallogr. **16**, 777 (1963).
[19] A. Migliori *et al.*, Phys. Rev. B **73**, 052101 (2006).
[20] D. C. Wallace, Phys. Rev. B **58**, 15433 (1998).
[21] The hcp requires cell multiplication of at least 6. Maximum displacement is $\frac{a_h}{3} = 1.07$ Å.