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ELASTIC PHASE TRANSITIONS IN PLUTONIUM

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The rich phase diagram of plutonium with a large number of different transitions in a narrow temperature interval has been puzzling scientists for decades. We offer a theoretical proof that most of the structural transformations in plutonium at temperatures exceeding the Debye temperature are the elastic phase transitions. The proof is given in the framework of the Landau theory of phase transitions and space group theory with the anomalously small value of the elastic shear constants related to tetragonal and orthorhombic lattice deformations taking into account.

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1. INTRODUCTION

Recent years have shown an increasing interest in studying properties of Pu [1–11], one of the most unusual elements in Nature. Its structural behavior as a function of temperature is rather unique and involves several phase transitions in a narrow temperature interval. The physical origin of such a behavior is not fully understood and it is a matter of debates. Plutonium has six crystalline phases at ambient pressure and temperatures up to melting. Some of these temperature-driven phase transitions are accompanied by a significant change of volume. In two of these phases, δ and δ', which have the largest specific volumes and respectively have the *fcc* (face-centered cubic) and *bct* (body-centered tetragonal) structures, plutonium has negative and low thermal expansion coefficient, while in the other phases, its thermal expansion coefficient is positive and high. The δ-phase is very unstable, but plutonium can be stabilized in the δ-phase by alloying with a trivalent metal, for example, with several molar percents of gallium. Such an alloy is stable in the temperature range from -75 to 475 °C and has almost zero thermal expansion coefficients.

In the framework of the first-principle density-functional theory [5], the bond strengths have been calculated between 12 nearest neighbors in pure Pu and Pu-3.7 at. % of Ga, and it has been suggested that the bond strengths in δ-Pu are anisotropic and this anisotropy corresponds not to the generally accepted cubic space group $Fm\bar{3}m$ but to the monoclinic Cm space group. Therefore, according to Ref. [5], the tetragonal, orthorhombic, or monoclinic deformation of δ-Pu can lead to the equilibrium (α-Pu, monoclinic space group $P2_1/m$). By this, the authors of Ref. [5] explain the sequence of temperature-driven polymorphic transformations in Pu. Introduction of Ga reduces the anisotropy of bond strengths, thereby stabilizing the δ-Pu *fcc* lattice [5]. These results have been criticized in Ref. [6]: the authors of Ref. [6] have shown that for the calculational setup reported in Ref. [5], the anisotropy of bond strengths between the nearest neighbors in δ-Pu cannot exceed a numerical error associated with the operation of the program algorithm and is actually three orders less than it was obtained in Ref. [5]. It is also impossible to agree with the arguments given in Ref. [5] because they contradict Curie's principle [12]: the symmetry elements of a crystal are also symmetry elements of any of its properties, i. e., the crystal symmetry group either coincides with the symmetry group of a property (for example, bond strengths) or is a subgroup of the property symmetry group (but not conversely). The phase transition $\delta \to \alpha'$ (*fcc* $\to$ monoclinic) in alloys of plutonium with gallium and aluminum was considered in Ref. [10, 11] using the Landau theory. The α' phase has the same space group as the monoclinic α phase of pure plutonium, except that some of the Pu atoms are substituted by alloying element. This transition was consid-

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ered as a martensitic-like phase transformation involving a coherent, continuous motion of many atoms over short distance without diffusion. The transformation mechanism was proposed that combines strains of unit cells and displacements of atoms and which can predict the softening signature or other anomalies seen in phonon dispersion experiments and temperature variation of the elastic moduli. It has been demonstrated that the $\delta \to \alpha'$ transition can be described as a sequence of displacive transformations that require specific intermediate structures (trigonal and hexagonal in particular).

In this article, we show using the Landau theory of phase transitions and space group theory (group–subgroup relations) that the sequence of polymorphic transitions in pure Pu at temperatures exceeding the Debye temperature are elastic phase transitions with order parameters defined by homogeneous deformations.

2. RESULTS AND DISCUSSION

The fact that all polymorphic transitions in Pu occur at temperatures considerably exceeding the Debye temperature ($\theta_D \approx 110$ K) and that the lowest-temperature transition $\alpha \to \beta$ (simple monoclinic → base-centered monoclinic structure) corresponds to $T = 398$ K at ambient pressure leads to the conclusion that the reason behind the phase transitions is the anharmonicity of the crystal lattice. Together with the usual transitions caused by the equality of chemical potentials of two various structures, structural phase transitions of another type, caused by the instability of the crystal lattice under small homogeneous deformations, can occur. For displacive phase transitions, it is generally important to consider correlation effects [13]. But in our case, for three-dimensional systems, these effects are not very essential and the Landau theory of the phase transitions can be used [14–16]. The stability of a lattice under small homogeneous deformations is characterized by a system of inequalities for second-order elastic constants, following from the positive definiteness requirement for the second-order part of the crystal thermodynamic potential. In the case of the cubic crystal, these inequalities are [14] $C_{11} + 2C_{12} > 0$, $C_{11} - C_{12} > 0$, and $C_{44} > 0$, where $C_{\alpha\beta}$ are isothermal second-order elastic constants in the Voigt notation. These inequalities can be violated with a change of thermodynamic parameters such as the pressure and temperature (P, T) defining the crystal state. As a result, the transition into a spontaneously deformed state occurs. The stability of this new state is determined by the anharmonic contribution to the expression for the thermodynamic potential (i. e., by the third and fourth order elastic constants). The deformation tensor components are the order parameters at such transitions. These transitions are called the elastic phase transitions. In the case of plutonium, in favor of such transitions speaks the fact that the elastic shear constant $C' = (C_{11} - C_{12})/2$ of δ-Pu is anomalously small compared with shear constant C_{44} [17].

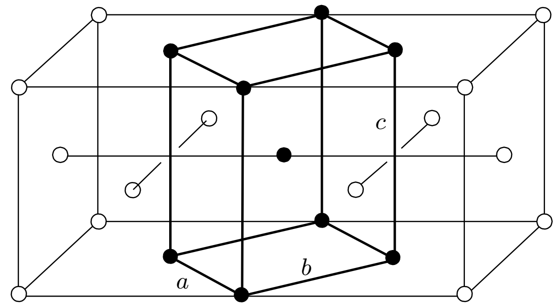
Using the results of the Bravais lattice symmetry analysis [18], it can be shown that from six crystalline structures characteristic of Pu, five structures are related among themselves by a homogeneous deformation. From this standpoint, we consider the sequence of polymorphic transformations in Pu.

1. The high-temperature ε-phase exists at 472–640 °C and has the *bcc* structure, which transforms into a *bct* lattice ($c/a = 1.33$) by a distortion of the cube along one of its 4th-order axes (the so-called δ'-phase). The symmetry analysis shows that the Bravais lattice Γ_c^ν transforms into Γ_q^ν ($\varepsilon \to \delta'$). The reason for this transition is the instability of the *bcc* lattice caused by the softening of the elastic shear constant C' related to the deformation $u_{33} = -2u_{22} = -2u_{11}$.

2. The δ'-phase is rather unstable (the temperature interval of its existence is 450–472 °C at ambient pressure) and under a further decrease in temperature, a transition of the δ'-phase into the δ-phase occurs that has the fcc structure and exists at 310–450 °C. These two phases are related by a homogeneous deformation. Thus the lattice Γ_q^ν transforms into Γ_c^f ($\delta' \to \delta$).

The transitions $\varepsilon \to \delta' \to \delta$ ($bcc \to bct \to fcc$) are a typical Bain transformation. Bain originally described such a transformation by a continuous and coordinated shift of one or more atoms in the unit cell in order to understand the mechanism of the transition from austenite to martensite in iron. Both the cubic Bravais lattices (*bcc* and fcc) are regarded as special cases of the more general *bct* unit cell (see Figure). If the height-to-width ratio of the lattice constants is $c/a = 1$, then the *bct* Bravais lattice coincides with the *bcc* lattice. On the other hand, a *bct* Bravais lattice with $c/a = \sqrt{2}$ fully matches the fcc lattice, as is schematically shown in Figure.

3. The Bravais parallelepiped for a cubic system can be reduced to the Bravais parallelepiped for the orthorhombic system (γ-phase). This means that the γ-phase has the face-centered orthorhombic lattice, fco, by a shear deformation in the parallelepiped base plane. It is caused by the softening of the shear



The centered tetragonal unit cell with lattice parameters a, b, and c at special ratios. Atoms belonging to the conventional unit cell are indicated by solid dots; bcc: $a = b$, $c/a = 1$, bct: $a = b$, $1 < c/a < \sqrt{2}$; fcc: $a = b$, $c/a = \sqrt{2}$; fco: $a \neq b \neq c$

constant C' that is accompanied by the deformation $u_{22} = -u_{11}$; as a result, we obtain the lattice Γ_o^f ($\delta \to \gamma$, which is stable in the temperature range 218–310 °C).

4. From the Bravais orthorhombic system parallelepiped at the base deformation (changing the angle between its edges), we obtain the Bravais monoclinic system parallelepiped (the β-phase, which has a base-centered monoclinic structure (bcm) with the existence interval 119–218 °C). The lattice Γ_o^f transforms into Γ_m^b ($\gamma \to \beta$).

5. The symmetry analysis shows that the transition from the β-phase into the α-phase (which has the simple monoclinic lattice) via a homogeneous deformation is impossible because the lattice Γ_m^b is not related to Γ_m by a homogeneous deformation.

Hence, the phase transitions $\varepsilon(bcc) \to \delta'(bct) \to \delta(fcc) \to \gamma(fco) \to \beta(bcm)$ are elastic phase transitions. They occur owing to lattice instabilities related to shear deformations, which are in turn related to the anomalously small value of the corresponding elastic constants.

The character of an elastic transition and the stability of a new phase are determined by the third-order term in the deformation tensor component expansion of the thermodynamic potential, and by the forth-order term [19]. If the third-order invariant, which involves the corresponding third-order elastic constants, is equal to zero, then the transition is of the second order; otherwise, it is of the first order. The stability requirement for the new phase imposes certain restrictions on the third and fourth-order elastic constants. For the phase transition $\varepsilon \to \delta'$ ($bcc \to bct$), the expansion of the thermodynamic potential F is given by

$$F = \frac{3}{4}(C_{11}-C_{12})u^2+\frac{1}{8}(C_{111}-3C_{112}+2C_{123})u^3+ \\ + \frac{3}{64}(C_{1111} - 4C_{1112} + 3C_{1122})u^4, \quad (1)$$

where $C_{\alpha\beta\gamma}$ and $C_{\alpha\beta\gamma\delta}$ are the third and fourth-order isothermal elastic constants and $u = u_{33} = -2u_{22} = -2u_{11}$. Because the third-order invariant is not equal to zero (due to the crystal symmetry), we have a first-order phase transition. For the stability of the new phase, the fourth-order invariant should be positive.

Under the phase transition $\delta \to \gamma$, the third-order term of the expansion tends to zero owing to specific features of the order parameter components: $u_{22} = -u_{11}$. However, if this relation is not satisfied (we note that such relations are not satisfied due to volume changes under the transition), then the third-order invariant becomes nonzero and the transition is a first-order transition.

In relation to the elastic phase transitions in Pu, we now discuss the temperature behavior of the elastic moduli. In Ref. [7], the elastic moduli for polycrystalline Pu-2.4 at. % of Ga were measured by using the resonance-ultrasound spectroscopy in the temperature range 300–500 K. According to Ref. [7], both the bulk modulus B and the shear modulus G decrease with increasing the temperature with a nearly linear temperature dependence. But in this range of temperatures, the thermal expansion coefficient is close to zero, although the values of B and G sharply decrease with temperature (by 25 % in the interval 300–500 K). The Debye-Grüneisen model is typically used to explain temperature dependences of elastic constants, in which the elastic softening should be related mainly to the increase in volume under thermal expansion. The two-level model was therefore used for the explanation of the observable discrepancy in Refs. [7, 8]. This model was previously used for an invar alloy. The model is based on the addition of the two-level electron energy structure to the Debye model of a lattice. Together with the normal Debye temperature and the Grüneisen lattice constant, the model involves two additional parameters: the difference in energy between two levels of an atom and the Grüneisen electronic constant, which has a negative value depending on the concentration of Ga. With regard to nonmagnetic δ-Pu (there are no experimental proofs of a long-range magnetic order in any phase of plutonium [20]), the above model appears to be insufficiently justified. In what follows, we show that the temperature dependence on elastic constants and thermal expansion can be correctly described in the quasiharmonic approximation.

We express the bulk and shear moduli B and G

through the elastic constants. For the cubic lattice [21], $B = (C_{11}+2C_{12})/3$ and $G = (C_{11}-C_{12}+3C_{44})/5$. The temperature dependence of the elastic constants in the quasiharmonic approximation is determined by the dispersion of the microscopic Grüneisen coefficients [22]. The expressions for the adiabatic and isothermal elastic constants obtained in the quasiharmonic approximation, with the processes of phonon viscosity and the thermo-elasticity taken into account, are [23]

$$C^{ad}_{ijkl} = \frac{1}{V_0}\frac{\partial^2 \Phi_0}{\partial u_{ij}\partial u_{kl}} - \frac{TC(T)}{V_0}\left[\langle \gamma_{ij}\gamma_{kl}\rangle - \langle \gamma_{ij}\rangle\langle \gamma_{kl}\rangle\right], \quad (2)$$

and

$$C^{is}_{ijkl} = \frac{1}{V_0}\frac{\partial^2 \Phi_0}{\partial u_{ij}\partial u_{kl}} - \frac{TC(T)}{V_0}\langle \gamma_{ij}\gamma_{kl}\rangle. \quad (3)$$

Here, V_0 is the volume of the unstrained crystal, Φ_0 is the potential energy of the crystal when the atoms are in equilibrium positions,

$$\gamma_{ij}(\mathbf{k},\lambda) = -\frac{1}{\omega_0(\mathbf{k},\lambda)}\left(\frac{\partial \omega(\mathbf{k},\lambda)}{\partial u_{ij}}\right)_0$$

are the microscopic Gruneisen coefficients, $\omega(\mathbf{k},\lambda)$ and $\omega_0(\mathbf{k},\lambda)$ are the respective frequencies of a phonon with a wave vector $\mathbf{k}$ and polarization λ in the deformed and undeformed crystal, and the averaging symbol $\langle\ \rangle$ means

$$\langle f\rangle = \sum_{\mathbf{k},\lambda} f(\mathbf{k},\lambda)c(\mathbf{k},\lambda) \Big/ \sum_{\mathbf{k},\lambda} c(\mathbf{k},\lambda),$$

where $c(\mathbf{k},\lambda)$ is the contribution to the heat capacity of the mode $(\mathbf{k},\lambda)$, and $C(T) = \sum_{\mathbf{k},\lambda} c(\mathbf{k},\lambda)$ is the heat capacity of the crystal. The temperature changes of these constants are caused by both the phonon viscosity and thermo-elasticity processes (the second term in square brackets in (2) characterizes the change in the elastic constants due to thermo-elastic losses). The first term in (2) and (3) includes the change in the elastic constants due to thermal expansion. The thermal expansion tensor is equal to

$$\alpha_{ij} = \frac{C(T)}{V}\sum_{k,l} C^{-1}_{ijkl}\langle \gamma_{kl}\rangle.$$

The linear expansion coefficient of a cubic crystal is $\alpha = (C(T)/3VB)\gamma$, where $\gamma = \langle \gamma(\mathbf{k},\lambda)\rangle$ is the Grüneisen parameter,

$$\gamma(\mathbf{k},\lambda) = -\frac{\partial \ln(\mathbf{k},\lambda)}{\partial \ln V} = \frac{1}{3}\mathrm{Tr}\,\gamma_{ij}(\mathbf{k},\lambda).$$

The quantities $\langle \gamma_{ij}\gamma_{kl}\rangle$ and γ, which respectively determine the temperature changes of the elastic moduli and thermal expansion coefficient, depend on the Grüneisen coefficients $\gamma_{ij}(\mathbf{k},\lambda)$ in different ways and should differ among themselves. Such behavior leads to essential differences for the average values (taking the change of the sign of $\gamma_{ij}(\mathbf{k},\lambda)$ for various vibration modes into account): in the first case, the average values should be larger than in the second one. Under certain conditions, the value $\gamma = \langle \gamma(\mathbf{k},\lambda)\rangle$ can be very small (for example, due to the compensation of contributions from various vibration modes).

Because the Debye temperature of δ-Pu is $\theta_D \approx \approx 110$ K, the basic contribution to (2) in the temperature range 300–500 K is due to the high-frequency modes: longitudinal and transverse acoustic phonons in the neighborhood of the X point and the longitudinal modes in the neighborhood of the L point [24]. Because the thermal expansion coefficient for δ-Pu is very small in this temperature range, the contribution of the term in the square brackets in (2) to the changes of C^{ad}_{ijkl} with temperature is high. Since the heat capacity at $T > \theta_D$ is practically independent of the temperature, elastic constants (2) change linearly with the temperature, except near the phase transition. The δ-phase is unstable under to the shear deformation related to the elastic constant $C' = (C_{11} - C_{12})/2$. However, both B and G have a practically linear temperature dependence because C' is seven times less than C_{44} [17].

3. CONCLUSION

It is shown based on the group theory analysis that the sequence of temperature phase transitions ($\varepsilon(bcc) \to \delta'(bct) \to \delta(fcc) \to \gamma(fco) \to \beta(bcm)$) observed in pure plutonium represents a sequence of elastic phase transitions, i. e., the transitions resulting from the instability of the crystal lattice with respect to uniform deformations. In this case, it is possible to use the Landau theory, taking components of the deformation tensor as the order parameters. We have also shown that the negative sign of the thermal expansion coefficient of δ-Pu and a strong decrease in the elastic constants of δ-Pu with increasing the temperature can be explained within the quasiharmonic approximation. We believe that this result is important by itself (even with no relation to plutonium) and it is crucial for understanding the connection of thermal expansion and temperature dependence of elastic constants in solid state materials.

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