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Semi-empirical models describing thermodynamic properties of f-metals

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Abstract

The unusual thermodynamic properties (abnormal elastic and thermophysical features and complex phase diagrams) of a number of metals with unfilled f-shells (4f and 5f) are caused by the proximity of close energies of different electron configurations. According to the modern concepts, electron states differ either in the degree of screening of the localized f-electron spins (Kondo volume-collapse model) or in localization and delocalization of f-electrons (Mott transition). At finite temperatures, a thermodynamically stable state of a mixture of atoms with different electron configuration becomes feasible due to the configuration entropy contribution, with concentrations of atoms of different sort being determined from thermodynamic potential minimum. A successful semi-empirical model capable of describing behavior of material in this state is the Aptekar–Ponyatovsky (AP) model, which treats a system of atoms of different sort as a substitution solid solution with component-to-component ratio varying as a function of temperature and pressure. The terminal component concentrations correspond to the states of material in adjacent polymorphous modifications. This paper discusses the capabilities of the AP model to describe thermodynamic properties of unalloyed cerium (4f-metal) as well as unalloyed δ-plutonium and δ-Pu-based alloys (5f-metals). The paper shows that the results obtained within a single model provide an adequate description of abnormal behavior of these metals at varying external conditions, this proves the common nature of these anomalies associated with the evolution of the f-electron subsystem.

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Keywords: Semi-empirical models; f-Metals; Thermodynamic properties

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1. Introduction

The electronic structure of metals with unfilled f-shells is characterized by narrow f-bands and closely spaced value energies of different electron states. Due to this fact, even minor changes in the external conditions (temperature, pressure, alloying, etc.) cause electron reconfiguration and, therefore, change of the crystalline structure. This makes the implementation of a great number of polymorphous modifications possible as well as coexistence of atoms in different states but with close energies within one polymorphous modification. To describe this state of a material, Aptekar and Ponyatovsky [1] proposed a model of pseudo-binary solid solution whose components are atoms in different electron states. Concentrations of atoms of different sorts are determined from the thermodynamic potential minimum and are functions of temperature and pressure. Thus, the material can be treated as a substitutional alloy composition constantly varying with varying external conditions, such as temperature and pressure. Within a wide range of temperatures and pressures, symmetry of the crystalline lattice does not change though continuous electron phase transition takes place in the material, which causes the unusual material behavior and properties at varying temperatures and pressures.

2. Basic equations for the model of ternary solid pseudo-solution

Consider a ternary alloy containing atoms of three kinds: X, Y and Z. Assume that components X and Y are atoms of an f-metal in different electron states, and component Z consists of alloying atoms. The following equation is valid for the concentrations of all atoms: $X+Y+Z=1$. States $X=1-\mathrm{Z}$ ($Y=0$) and $Y=1-\mathrm{Z}$ ($X=0$) correspond to different polymorphous modifications of the alloy.

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Write down molar thermodynamic Gibbs potential for the ternary alloy in the following form:

$$G = G_x X + G_y Y + G_z Z + G_{xy} XY + G_{xz} XZ + G_{yz} YZ - TS_{\mathrm{conf}} \qquad (1)$$

Here G_x, G_y and G_z are the thermodynamic potentials of components X, Y and Z, G_{xy}, G_{xz}, G_{yz} are the thermodynamic potentials of mixing of the solid solution components, T the temperature and S_{conf} is the configuration entropy associated with a number of possible locations of atoms of three kinds in the lattice sites: $S_{\mathrm{conf}} = -R\,(X \ln X + Y \ln Y + Z \ln Z)$, where R is the universal gas constant. All thermodynamic potentials are functions of pressure P and temperature T. Concentration of the alloying component Z is a fixed parameter while concentrations X and Y are the internal parameters of the system and can vary with the variation of the external conditions. Concentration X is assumed as an independent variable. At given T, P and Z, equilibrium concentration X is determined from the minimum of the thermodynamic potential $(\partial G/\partial X)_{P,T,Z} = 0$; $(\partial^2 G/\partial X^2)_{P,T,Z} > 0$:

$$\Delta G + G_{xy}(1 - Z - 2X) + \mathrm{RT} \ln \left[\frac{X}{1 - X - Z}\right] = 0,$$

$$-2G_{xy} + \mathrm{RT}\left[\frac{1}{X} + \frac{1}{1 - X - Z}\right] > 0. \qquad (2)$$

where $\Delta G = G_x - G_y + Z(G_{xz} - G_{yz})$. The first equation of (2) can have either one or three solutions, in the latter case the thermodynamic potential (1) has two minima and one maximum. A detailed analysis of solutions of system (2) for the case of $Z = 0$ is done in [2], therefore it is not discussed in the paper. Thermodynamic potential minima corresponding to some values of concentrations X_1 and X_2 can be either of the same or different depths. Physically, minima of different depths mean that metastable states can exist. At two minima of the same depth, phase equilibrium is reached: $G(X_1) = G(X_2)$. In this case it can be proved that $X_1 = 1 - X_2 - Z$ and $\Delta G = 0$ [2].

In the (P,T)-plane, areas corresponding to thermodynamic potential minima of different depths are the areas of meta-stable state of the phases corresponding to the less deep minimum. Lines along which one minimum disappears are determined by $(\partial G/\partial X)_{P,T,Z} = 0$; $(\partial^2 G/\partial X^2)_{P,T,Z} = 0$:

$$\Delta G + G_{xy}(1 - Z - 2X) + \mathrm{RT} \ln \left[\frac{X}{1 - X - Z}\right] = 0,$$

$$-2G_{xy} + \mathrm{RT}\left[\frac{1}{X} + \frac{1}{1 - X - Z}\right] > 0. \qquad (3)$$

and limit the areas where meta-stable states of the phase exist.

The Helmholtz free energy for of individual phases is written as a sum of three terms: static lattice potential, quasiharmonic phonon free energy and the free energy arising due to thermal excitation of electrons. The static lattice potential was taken in the form of Vinet–Ferrante–Ross–Smith [3]; the quasiharmonic free energy of phonons is written in the Debye approximation; the contribution to free energy, conditioned by thermally excited electrons, is written in the traditional temperature-squared approximation.

Potentials of mixing are $G_{ij} = U_{ij} + PV_{ij} - TS_{ij}$ (at $ij = xy$, xz, yz), where U_{ij}, V_{ij}, S_{ij} are energy, volume and entropy of mixing, respectively. For them, simple empirical relations are used with parameters selected to fit the experimental data. A satisfactory agreement with the experimental data is reached even at constant values $U_{ij} = \mathrm{const}$, $V_{ij} = \mathrm{const}$, and $S_{ij} = \mathrm{const}$.

All thermodynamic functions of the solid solution can be derived from the thermodynamic potential (1) by taking into account that the concentration X is a function of temperature and pressure.

3. Application of solid pseudo-solution model to the description of the unusual features of f-metals

3.1. Non-alloyed cerium in the γ-α-transformation range

Cerium is the first lanthanide, in which electrons start filling the 4f-shell. The unique features of cerium include an intricate phase diagram with a large number of polymorphous modifications; an isomorphic γ-α-transition with a critical point in the solid state and significant anomalies of thermodynamic properties in the vicinity of this transition. They are directly associated with the reconfiguration of the 4f-shell subsystem and change of its contribution to the binding energy. Application of the AP model to the description of the abnormal behavior of unalloyed ($Z = 0$) cerium in the vicinity of the γ-α-transition is discussed in detail in Ref. [2]. Note that the AP model directly includes the existence of the critical point. The critical point on the line of phase equilibrium corresponds to the merging of the both thermodynamic potential minima into a single minimum at $X_1 = X_2 = 0.5$, with equality $(\partial^2 G/\partial X^2)_{P,T,} = 0$ holding; this gives an equation determining the critical temperature $2RT_{\mathrm{cr}} = G_{xy}(P,T_{\mathrm{cr}})$.

Applicability of the AP model can be illustrated through the comparison of the calculated and experimental thermodynamic functions. Figs. 1–5 compare the calculated and experimental data on the pressure dependencies of the isentropic bulk compression modulus $B_S(P)$ [4] and heat capacity $C_P(P)$ [5] (Fig. 1), and isothermal compressibility $\chi_T(P)$ at different temperatures [6] (Fig. 2), as well as data on the abnormal behavior of the thermal expansion coefficient near the γ-α-transition at different

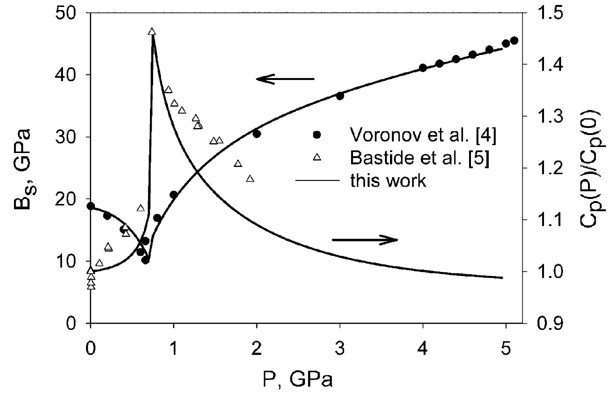

Fig. 1. Adiabatic compression modulus B_S vs. pressure at $T = 293$ K and pressure dependent specific heat C_P at $T = 300$ K.

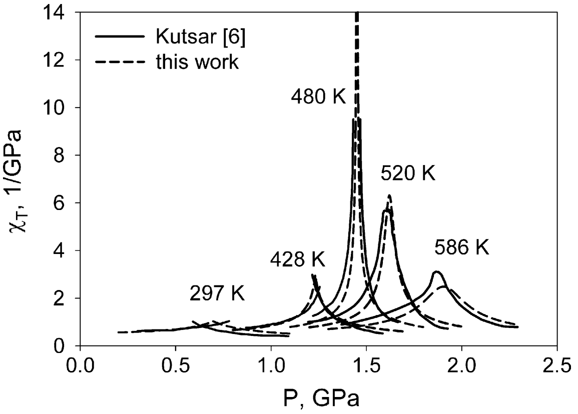

Fig. 2. Variation of isothermal compressibility coefficient χ_T with pressure at different temperatures.

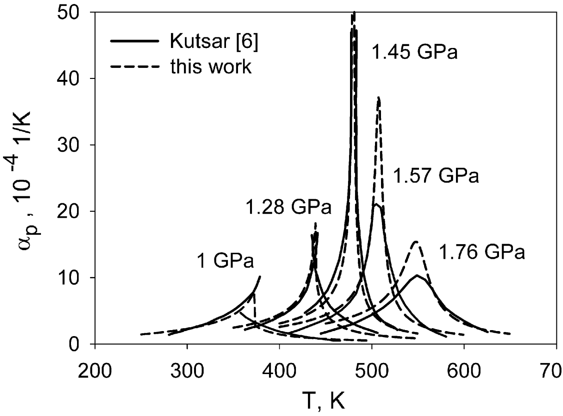

Fig. 3. Variation of the thermal expansion coefficient α_p with temperatures at different pressures.

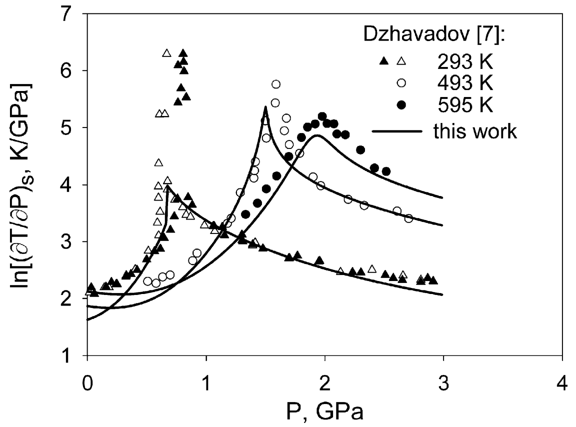

Fig. 4. Pressure dependence of $\ln(\partial T/\partial P)_s$ (with T and P in K and GPa, respectively).

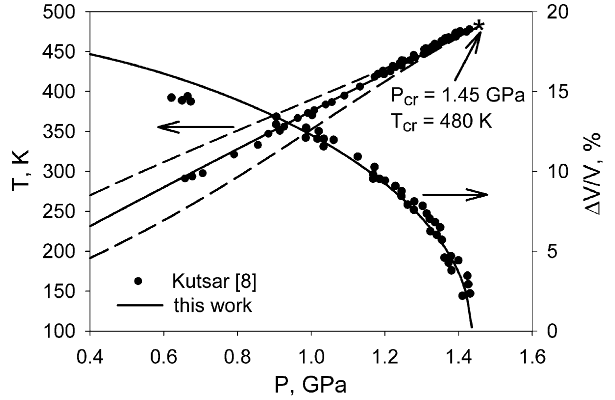

Fig. 5. Pressure dependence of the (γ-α) phase transition temperature and volume jump. Dotted lines correspond to the loss of stability metastable phase states.

pressures and temperatures (Fig. 3), temperature response of the material to adiabatic pressure variation $(\partial T/\partial P)_S$ [7] as a function of pressure at different temperatures (Fig. 4), the curve of γ-α phase equilibrium and the bulk effect of transformation $\Delta V/V$ along that curve (Fig. 5) [8]. In addition to the (α-γ)-equilibrium curve, Fig. 5 shows dashed curves of stability loss for metastable phases, calculated from Eq. (3). Graphical comparison of the calculated and experimental data shows that the two-phase equation of state based on the AP model properly describes the abnormal behavior of cerium. The difference obtained for the phase energies is $\Delta E_{\gamma\alpha}/R \sim 250$ K and for the mixing energy is $U_{\gamma\alpha}/R \sim 960$ K.

3.2. δ-Plutonium alloys

Plutonium is a 5f element, and among actinides it occupies a borderline state. In plutonium contribution of 5f-electrons to the binding energy changes significantly, and this change displays in a sharp (∼25%) difference of the atomic volumes of its α- and δ-polymorphous modifications. Like cerium, plutonium is characterized with a complex phase diagram and abnormal thermodynamic properties, in particular, a negative coefficient of thermal expansion for δ-plutonium. Application of the AP model to describe the abnormal properties of plutonium associated with the δ-α-transition is more complicated since α-Pu and δ-Pu are not always the adjacent phases. Unalloyed and slightly alloyed plutonium demonstrates existence of β- and γ-phases between α- and δ-phases. Therefore, some fictitious phase was considered in our calculations as a phase adjacent to δ-phase. The parameters of the fictitious phase turned out to be close to those of α-plutonium, and this gives grounds with minor reservations to render the fictitious phase as α-plutonium.

This paper describes thermal expansion of δ-plutonium alloys with aluminum and gallium in the model of the pseudo-ternary solid solution. One of undoubted advantages of this model is its capability to describe material behavior in the area of metastable states (states with less deep minimum of thermodynamic potential). This appears to be very important since the majority of experimental data correspond to the metastable state of δ-phase. Figs. 6 and 7 compare calculated and experimental [9,10] data on temperature dependence of the lattice parameters at different concentrations of alloying elements. For pictorial view of the comparison, the true design curves are displaced along the axis of ordinates by amount Δa, indicated in the title of the figure (the sign "−" corresponds to downward displacement. Fig. 8 compares experimental [11,12] and calculated data on the lattice parameters versus alloying element concentration at the room temperature in Pu–Ga and Pu–Al systems. These plots prove

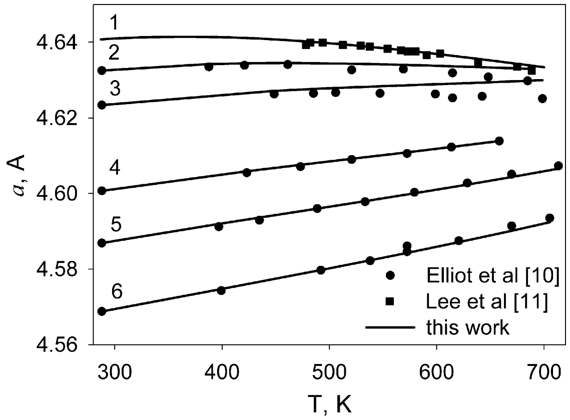

Fig. 6. Lattice parameters vs. temperature for Pu–Al. (1) $Z=0$ at.%; (2) $Z=1.2$ at.%; (3) $Z=2.5$ at.%; (4) $Z=5$ at.%; (5) $Z=7$ at.%; (6) $Z=10$ at.%; $\Delta a=-10^{-3}$, -5×10^{-4}, 3×10^{-4}, -3×10^{-3}, -2×10^{-3} and 3×10^{-3} Å, respectively.

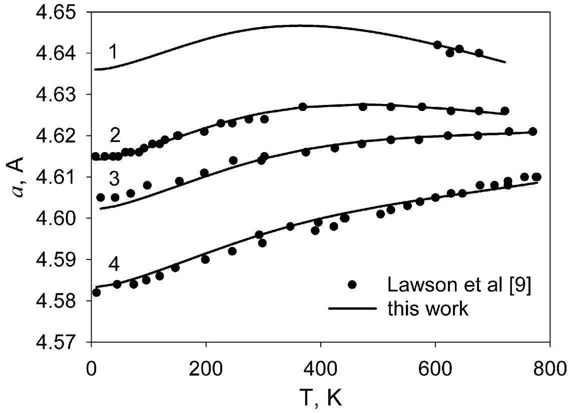

Fig. 7. Temperature dependence of lattice parameters for Pu–Ga alloys: (1) $Z=0$ at.%; (2) $Z=2$ at.%; (3) $Z=4$ at.%; (4) $Z=6$ at.%; $\Delta a=4\times10^{-3}$, 2×10^{-3}, 9×10^{-3} and 9×10^{-3} Å, respectively.

that the AP model adequately describes the thermal expansion (compression) of δ-plutonium alloys within the whole range of their existence. The obtained agreement of the calculated and experimental data gives the promise of high confidence in the calculated thermal expansion coefficient versus temperature in Pu–Ga and Pu–Al alloys presented in Fig. 9. In addition to the thermal expansion, this model adequately describes also the compressibility, the heat capacity and the (α-δ)-phase diagram. These results will be presented elsewhere.

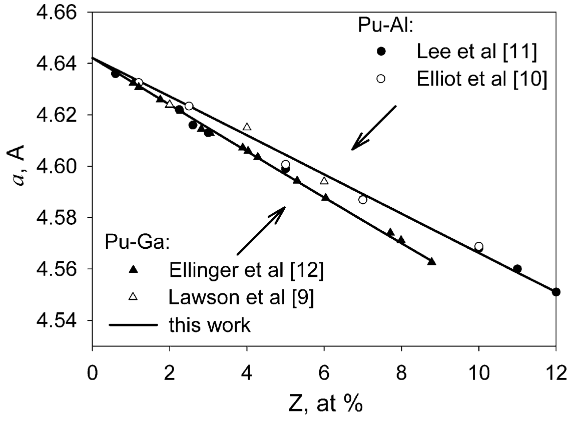

Fig. 8. Lattice parameters vs. alloying element concentration.

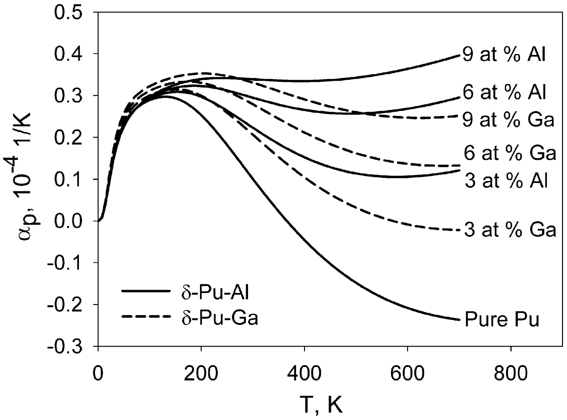

Fig. 9. Temperature dependence of the thermal (volume) expansion coefficient for Pu–Al and Pu–Ga systems.

Note that the temperature dependence of the lattice parameters of Pu–Ga alloys is also well described with the use of two-level Weiss invar model [9]. Our previous paper [13] considers thermal expansion (compression) of a number of δ-plutonium alloys with Al, Ce, Zn Zr with the help of the Strässler–Kittel model [14] which also shows a good agreement with the experimental data. However, the Aptekar–Ponyatovsky model is preferable since it directly links anomalies of material properties with the proximity to phase transition and properties of the adjacent phases. The difference in energy between δ-Pu and α-Pu, according to the AP model, is $\Delta E_{\alpha\delta}/R\sim330$ K at the energy of mixing equal to $U_{\alpha\delta}/R\sim1500$ K that is rather more than the appropriate values for Ce. Note that the Weiss and Strässler–Kittel models used $U/R\sim1400$ K as the excited atom energy [9,13].

4. Conclusion

The consideration of the abnormal properties of the two most exotic f metals with the single model presented in this paper shows that these anomalies are of the same nature and proves the adequacy of the Aptekar–Ponyatovsky model. The nature of the anomaly is first of all associated with f-electron subsystem reconfiguration, which varies the binding role of f-electrons. It is important that this reconfiguration goes smoothly within one element and is characterized with significant hysteresis effects caused by high mixing energy for atoms by different electron configurations. The high energy of mixing considerably exceeds the energy difference between the atoms with different electron configurations and results in strong interaction between them, due to which the material is no longer just a mechanical mixture of atoms of different sort.

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