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ANOMALY OF CRYSTAL LATTICE THERMAL EXPANSION AND BULK MODULUS BEHAVIOR OF δ-PLUTONIUM

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Anomalous behavior of thermal expansion and bulk modulus for the face centered cubic phase of metallic plutonium is considered proceeding from the valence-fluctuating nature of the Pu $5f$ electrons. It is shown that the approach based on the fundamental properties of the systems the ground state of which is a quantum-mechanical superposition of the localized and itinerant electron configurations allows to quantitatively describe temperature dependence of the crystal lattice parameters and bulk moduli for both gallium-stabilized Pu-Ga alloy with fcc structure and unalloyed δ-Pu within the fcc phase existence region.

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1. INTRODUCTION

According to inelastic neutron scattering experiments performed a few years ago by the US research team the ground state of plutonium metal is governed by valence fluctuations [1]. By other words, the fcc δ-Pu is a mixed-valence (sometimes called intermediate valence) system with Kondo temperature $T_K = 975\,\mathrm{K}$ [1]. Thus, it could be considered that this result resolves the long-standing controversy between the experiment and theory concerning magnetism of the Pu metal. Evidences in favor of possible effect of magnetism on negative thermal expansion and low temperature electrical resistivity was suggested already in early publications by Lallement [2] and Arko et al. [3]. Later it was shown that the agreement between the results of density functional theory (DFT) calculations of Pu electronic structure and experimental data requires formation of magnetic moments on plutonium [4]. An extensive bibliography concerning this subject is presented in publications by Söderlind et al. [5–7]. However, efforts to detect magnetic moments on plutonium experimentally have not been successful [8]. To resolve this collision at least for δ-Pu it was suggested to consider this plutonium phase as a system with fluctuating (intermediate) valence [9,10]. Inelastic neutron scattering experiments [1] provided strong arguments in favor of this physical scenario. Neutron spectroscopy measures magnetic excitations (dynamic magnetic susceptibility) in a material, i. e., it probes directly magnetic fluctuations. In our case these fluctuations, usually called spin fluctuations, develop from interconfigurational excitations of the Pu ion from the magnetic f^5 ($J = 5/2$) to the nonmagnetic f^6 ($J = 0$) state. The physics of spin fluctuations driven via valence fluctuations can be elucidate by the Anderson impurity model (AIM) that describes the interaction of magnetic impurity with clouds of conduction electrons [11]. Further, the magnetic form factor $F(Q)$ (here Q is the absolute value of scattering vector) determined in [1] coincides with its tabulated behavior for the mixture of $5f^4 + 5f^5$ electronic configurations in the intermediate coupling regime. Moreover, dynamical mean field theory (DMFT) calculation of the inelastic magnetic scattering intensity $F^2(Q)\,\chi''(\omega)$ (here $\chi''(\omega)$ is the imaginary part of dynamic magnetic susceptibility) is in excellent agreement with the measurements. Also, quantitative estimates of the static magnetic susceptibility of δ-Pu reproduce the measured value rather well [1]. Let us emphasize, the general features of the δ-Pu dynamic magnetic response are not qualitatively different from those for typical intermediate-valence materials, e. g., the Ce based systems [12, 13].

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However, in spite of significant progress achieved over decades, not only magnetism, but also many other unusual physical aspects of plutonium metal remain to be widely debated. Particularly, the problem of plutonium elastic properties is of special interest. It has long been known that the unalloyed plutonium shrinks upon heating within the existence region of δ-phase, and δ-phase Pu-Ga alloys possess zero or weak positive thermal expansion coefficient [14, 15]. This effect is usually explained in terms of the so-called «invar» mechanism [15,16], which assumes the presence of some two-level system, with Pu atoms located on the upper level being smaller in size then on the lower one. Energy splitting between the levels is approximately 1400 K ($\sim$ 112 meV), and level's population depends both on temperature and gallium concentration [15]. However, the physical nature of the two level system of «invar» model is not entirely clear (see, e. g., Ref. [16]). Unusual bulk modulus softening with increasing temperature is also challenging since this effect exists in the fcc plutonium phases within the same temperature intervals where their crystal lattice either shrinks or possess almost zero thermal expansion coefficient [14]. Lawson performed detailed thermodynamic analysis of the bulk modulus and thermal expansion behavior of δ-Pu and concluded that, perhaps, different mechanisms are responsible for temperature dependence of these two properties [17]. Harrison [18] came to a similar conclusion (about the independence of the thermal behavior of crystal lattice and bulk modulus) based on an idea of multiplicity of the plutonium electron configurations and the thermally activated nature of their filling. At the same time, Harrison specially noted that the nature of the electronic states under consideration remains an open question, and the magnetic properties are not affected.

Migliori et al. consider the bulk modulus anomalous behavior as a result of magnetic excitations in the system [19], but their specific interpretation in terms of the so-called disordered local moment (DLM) model causes serious questions (see, e. g., Ref. [20]), related primarily to the predicted behavior of the magnetic form factor, which contradicts experimental data obtained in [1]. As said above, according to the neutron spectroscopy data $F(Q)$ behaves in agreement with the expectations for mixture of $5f^4$ and $5f^5$ electronic configurations with the maximum at $Q/(4\pi) \sim 0.3\,\text{Å}^{-1}$ and a finite value at $Q \to 0$. Migliori et al. [19] state that according to their DLM model $F(Q)$ also has the maximum near $Q/(4\pi) \sim 0.3\,\text{Å}^{-1}$, but vanishes at $Q = 0$.

But the contradictions between the conclusions of the authors [1] and [19] are deeper. The discussions concern the fundamental nature of the pure Pu δ-phase and Pu-Ga alloys with the fcc structure. Söderlind et al. developed the theoretical description of plutonium in terms of a metal with itinerant (band) $5f$ electrons [5–7]. Using the first-principal, parameters-free DFT calculations they are able to describe most of anomalous plutonium properties, including negative thermal expansion and bulk modulus softening of δ-Pu with increasing temperature. Their approach extended the DFT to include orbital-orbital interactions (often referred to as orbital polarization). Söderlind *at al.* [6] proposed a magnetic-cancellation model for plutonium where the magnitudes of the spin and orbital moment are exactly the same. The resulting net magnetic moment is thus zero in this model. From the band-structure computation they obtained spin and orbital moment densities and the form factor as a Fourier transform of the magnetization density. According to this calculation the form factor is expected to be due to the orbital component only and thus to vanish at $Q = 0$. Unfortunately, neutron spectroscopy has certain limitations for measurements within the small Q region. As a result $F(Q)$ experimental values for $Q <\sim 0.13\,\text{Å}^{-1}$ are absent preventing thus to obtain «true» behavior of the δ-Pu form factor. The most important conclusion of [5–7] is that strong electron correlations, responsible for the valence fluctuating ground state [1], is inconsistent with the experimental phase diagram of plutonium. Nevertheless, Söderlind *at al.* are to take into account the dynamic magnetism, though of different nature than in [1], to develop a consistent *ab initio* free energy model derived from a fully relativistic density functional theory for δ-Pu [7].

In the present paper we suggest an alternative scenario to explain anomalous thermal and elastic properties of the fcc phases of plutonium metal.

2. CALCULATION ALGORITHM

Based on the results of inelastic neutron scattering experiments [1], we consider the fcc δ-Pu as a valence fluctuating system in order to describe temperature dependence of the atomic volume and bulk modulus. As known [21], in such systems the effective ionic magnetic moment $\mu_{eff} = 3T\chi(T)$ vanishes for $T \to 0$ (here $\chi(T)$ is the magnetic susceptibility). This means that μ_{eff} turns out to be completely screened due to the interaction with conducting electrons forming the nonmagnetic ground state (the many-particle Kondo singlet).

At high temperatures μ_{eff} tends to its free ion value $\mu_{ion}^2 = J(J+1)\left(g\mu_B\right)^2$, where J is the total ionic magnetic moment (here we consider an f electronic shell). Therefore, the effective f shell valence decreases with increasing temperature in the case of nearly empty f electronic configuration, fluctuating between 3+ and empty 4+ states, as it occurs in the case of Ce metal. In the case of such valence-unstable ions as Sm and Yb, fluctuating between nearly filled 3+ and half- or completely occupied 2+ states, the effective valence increases with increasing temperature [22–25]. Atomic volume behaves in the opposite way, increasing with temperature in the first case while deceasing in the second one, as, e. g., in some Yb-based compounds [22,25]. Since the electronic configuration of the metallic plutonium is close to $5f^5$ [1, 26], it should be considered as an almost half-filled, regardless of whether the case of week LS ($L = 5$, $S = 5/2$, $2J + 1 = 6$), intermediate or strong (electronic configuration $5f_{5/2}$) spin-orbit coupling is realized in Pu [27]. Therefore, the effective plutonium valence ν is expected to increase with increasing temperature due to valence fluctuations while atomic volume decreases.

According to Ref. [21], the effective occupation of the basic f electron configuration $n_f(T)$ of a valence fluctuating system may be written as

$$n_f(T) = \tilde{n}_f - \Delta nf(T) = \tilde{n}_f(T) - f(T)\,\Delta n_f(0), \quad (1)$$

where $\tilde{n}_f$ characterizes a fraction of electrons that passes from the basic f configuration to the conduction band or fraction of electrons that passes from the conduction band to the basic f configuration at high enough temperatures $T \gg T_K$, $\Delta n_f(0)$ is the total n_f variation due to the Kondo effect at $T \to 0$, and $f(T) = \Delta n_f(T)/\Delta n_f(0)$ is the universal function, which scales quite well with T/T_K and becomes vanishingly small for temperatures of order of $10 \times T_K$. Relation (1) derived in [21] in terms of non-crossing approximation is applicable for both cases of nearly empty and nearly filled basic f electron configuration (see, e. g., Ref. [22]). Assuming that at high temperatures the Pu valence tends to its free ion value $\nu = 3$, the respective temperature variation of ν is

$$\nu(T) = 3 - \Delta n_f(0)\, f(T). \quad (2)$$

As soon as we guess the plutonium atomic volume $V(T) = a^3(T)/4$ to depend on the effective $5f$ shell occupation, $V(T)$ is expected to decrease with temperature since the fluctuation driven electronic configuration smoothly changes towards the basic $5f^5$ configuration (here a is the crystal lattice parameter of fcc Pu). Respectively, temperature dependence of fluctuating contribution $a_f(T)$ to the variation of the crystal lattice parameter for fcc Pu is as follows:

$$a_f(T) = a_0\left[\tilde{n}_f(T) + f(T)\,\Delta n_f(0)\right]/\Delta n_f(0). \quad (3)$$

Here a_0 is the fcc lattice parameter at $T \to 0$. For a comparison with the experimental data it is necessary to calculate total dependence of the lattice parameter $a(T)$ on temperature which is the sum of $a_f(T)$ and the phonon contribution $a_{ph}(T)$:

$$a(T) = a_f(T) + a_{ph}(T). \quad (4)$$

The value of $a_{ph}(T)$ can be calculated using standard Grüneisen relation:

$$\beta = V\left(\frac{\partial V}{\partial T}\right)_P = \gamma_{ph}\frac{C_V^{ph}}{B_T^{ph}}. \quad (5)$$

where β is the thermal expansion coefficient, γ_{ph} is the lattice Grüneisen constant, and C_V^{ph} is the phonon specific heat at constant volume. B_T^{ph} and B_T^f are the phonon and spin-fluctuation contributions, respectively, to the isothermal bulk modulus $B_T = B_T^{ph} + B_T^f$ [1)].

Temperature dependence of B_T^f can be calculated using the thermodynamic relations via the spin-fluctuation contribution to the specific heat at the constant volume $C_V^f(T)$ [2)]

$$B_T^f(T) = V\left(\frac{\partial^2 F}{\partial V^2}\right)_T = \\ = V\frac{\partial^2}{\partial V^2}\left\{\int_0^T C_V^f(T')\,dT' - T\int_0^T \frac{C_V^f(T')}{T'}dT'\right\}, \quad (6)$$

where F is the Helmholtz free energy, and $C_V^f(T)$ can be quantitatively estimated using the Rajan formula [30]:

$$C_V^f(T) = A\int_{-\infty}^{\infty} \frac{g_f(V,E)\left(\frac{E}{2k_BT}\right)^2}{\cosh^2\left(\frac{E}{2k_BT}\right)}dE. \quad (7)$$

Here A is a normalization factor. It is customary to take $g_f(E)$ to be Lorentzian centered at the energy E_0 and having half-width (FWHM) $\Gamma/2$:

$$g_f(V,E) = \frac{\Gamma/2}{(\Gamma/2)^2 + (E - E_0)^2}. \quad (8)$$

[1)] Actually, here and below we deal with spin-fluctuation contribution since all the thermodynamic functions are calculated using spin-fluctuation characteristics provided by neutron spectroscopy. We omit notation «spin-fluctuations» to avoid misunderstanding with relations (1)–(3).

[2)] Previously, such relations were used successfully by Allen and Liu [28] and Manley et al. [29] to consider similar problems.

3. RESULTS AND DISCUSSION

To calculate the phonon contribution $a_{ph}(T)$ to the temperature variation of $a(T)$ with equation (5), we assume for simplicity that C_V^{ph} is described by the Debye relation with Debye temperature Θ_D, and both Θ_D and B_T^{ph} being temperature independent. Therefore, there are three free parameters to calculate $a_{ph}(T)$, i. e., Θ_D, B_T^{ph}, and γ_{ph}. Also three parameters are required to calculate $a_f(T)$, namely, T_K, $\tilde{n}_f$, and $\Delta n_f(0)$.However, as soon as the expectation value of the high-temperature Pu valence is 3+ ($5f^5$ configuration), then $\tilde{n}_f = 1$, and we are left with only two fitting parameters, T_K and $\Delta n_f(0)$. Initial value of T_K is given by the results of the inelastic neutron scattering experiments [1], while $a_0 = 4.605$ Åcorresponds to the experimentally observed crystal lattice parameter for δ-phase Pu-4 at. % Ga alloy at low temperature [14, 15].

Calculation result of $a(T)$ for δ-phase Pu-4 at. % Ga alloy is shown in Fig. 1 *a*. Parameters for calculations are given in the Table. The best agreement with the experiment was found with the value of $E_0 = k_B T_K = 146$ meV which corresponds to the high-energy feature of the δ-Pu inelastic neutron scattering spectrum [1], but not the spin fluctuation energy $E_0 = 84$ meV characterizing a clear resonance-like feature of the spectrum. This circumstance will be discussed below. Note, that description of the experimentally observed $a(T)$ temperature dependence requires rather small valence variation. From equation (2) it follows, that the value of ν changes from $\nu = 2.9863$ at $T \to 0$ to $\nu = 2.9905$ at $T = 800$ K, i. e. $\Delta\nu = 0.0042$ within this temperature interval.

Similar calculation of $a(T)$ was performed also for pure δ-Pu, which exhibits even more pronounced effect of the crystal lattice compression. Parameters required to fit $a(T)$ for this material are given in the Table and the result is shown in Fig. 1 *b*. $a_0 = 4.637$ Å is the expectation value of the crystal lattice parameter of unalloyed δ-Pu at $T \to 0$ (see Fig. 4 in Ref. [15]). Since the volume of pure δ-Pu is higher than that of Pu-4 at. % Ga, $5f - 6d$ hybridization is weaker, i. e. $5f$ electrons are more localized in the pure material, the characteristic energy $E_0 = k_B T_K$ is expected to be less as compared to the fcc Pu-Ga alloy. Our calculations confirm this expectation. In fact, $E_0 = 137$ meV is required to obtain the best fit of calculated curve to the experimentally measured $a(T)$ within the δ-phase existence temperature range. For calculation we used the same parameters θ_D and B_T^{ph} as for the alloy, while the lattice Grüneisen constant γ_{ph}. was slightly increased. Because the lattice compression is rather

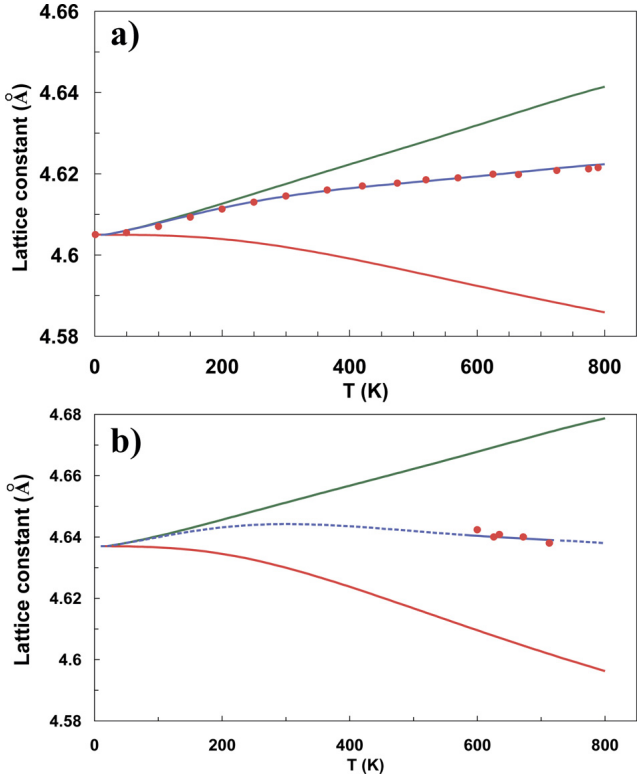

Fig. 1. Temperature dependence of the crystal lattice parameters of δ-Pu-4 at. % Ga alloy (*a*) and unalloyed δ-Pu (*b*). Circles correspond to the experimental data (within the δ-phase existence region for the unalloyed material [14, 15]). Solid lines show the results of calculations according to relations (3)–(5): green and red solid lines show phonon and fluctuation contributions, respectively, while blue solid line is their sum. Dotted line in b) indicates the hypothetical crystal lattice behavior of pure δ-Pu outside of the δ-phase existence region

strong within the temperature interval of pure δ-phase existence, $\Delta n_f(0)$ is approximately twice than in the case of Pu-4 at. % Ga. The valence variation between the extrapolated to zero temperature value $\nu = 2.9729$ and $\nu = 2.9819$ at $T = 800$ K is found to be also higher, namely, $\Delta\nu = 0.0090$. Note, that parameters Θ_D and γ_{ph} (see the Table) for both compositions turn out to be quite comparable to the analogous parameters of the «invar» model [15].

Having obtained the description of lattice volume as a function of temperature, we can calculate specific heat $C_V^f(T)$ and then bulk modulus for both compositions under consideration. The normalization factor A in Eq. (7) is chosen in order to provide the value of fluctuation (electronic) contribution to the specific heat $C_T^f(T \to 0)/T = 45\,\text{mJ}/(\text{mol}\cdot\text{K}^2)$ for δ-Pu-4 at. % Ga, the most correct experimental value [31]. Furthermore, since the system tends to paramagnetic regime ($5f^5$

Table. Parameters for calculations temperature behavior of atomic volume and bulk moduli for δ-phase of Pu-4 at. % Ga alloy and unalloyed δ-Pu (Figs. 1–4). Parameters' definitions are described in the text. The valence values of $5f$ states are also given for $T \to 0$, $T = 800$ K, and $T \to \infty$

Parameter	δ-Pu-4 at.% Ga	Pure δ-Pu
Θ_D, K	120	120
a_0, Å	4.605	4.637
B_T^{ph}, GPa	38	38
γ_{ph}	0.7	0.8
$\tilde{n}_f$	1	1
$\Delta n_f\,(0)$	0.01366	0.0271
$E_0 = k_B T_K$, meV	146	137
$\Gamma/2 = 0.8E_0$, meV	116.8	109.6
γ_f	2.8	2.8
$\nu\,(T \to 0)$	2.9863	2.9729
$\nu\,(T = 800$ K)	2.9905	2.9819
$\nu\,(T \gg T_K)$	3	3

configuration) at high temperature $T \gg T_K$, the dynamic magnetic response shifts towards the lower energy with increasing T and transforms to a quasielastic line in the high temperature limit. To take into account this feature, the following Grüneisen-like relation can be used[3]:

$$E_0\,(V) = E_0 \left(\frac{V\,(T)}{V_0}\right)^{-\gamma_f}, \qquad (9)$$

where $E_0 = 146$ meV and 137 meV for δ-Pu-Ga and pure δ-Pu, respectively (see the Table), $V\,(T) = a^3\,(T)\,/4$, and $a\,(T)$ are the resulting curves calculated with Eq. (4) and shown by solid lines in Figs. 1 *a* and 1 *b*. Now only two fitting parameters remain in order to calculate T-dependence of the fluctuation contribution to bulk modulus, namely, $\Gamma/2$ and γ_f. The calculated bulk moduli for δ-Pu-4 at. % Ga alloy and pure δ-Pu are shown in Fig. 2. Best agreement between calculated and experimental B_T *vs* T curves was achieved at $\gamma_f = 2.8$ for both compositions. The ratio $\Gamma/2\,(V) = 0.8E_0\,(V)$ between

[3] Similar relation was used to calculate the energy of two-level system in terms of the «invar» model [15].

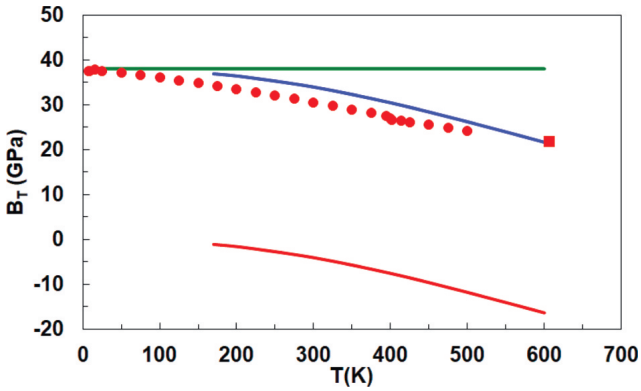

Fig. 2. Temperature dependence of bulk moduli for δ-Pu-4 at.% Ga alloy and pure δ-Pu. Red circles correspond to the experimental data for δ-Pu-3.6 at. % Ga alloy [14], and the red square shows the available experimental value for practically pure δ-Pu (0.2 at.% Ga) [32]. Solid lines demonstrate calculated phonon B_T^{ph} (green) and fluctuation B_T^f (red) contributions, while blue line show resulting $B_T = B_T^{ph} + B_T^f$ curve

the peak energy and the half-width was kept constant throughout the calculation process regardless of the change in volume V/V_0 (see the Table).

Figure 3 *a* demonstrates the variation of characteristic energy E_0 as a function of volume for the δ-Pu-Ga alloy. As seen, only about 3 % change in E_0 is sufficient to correctly describe the bulk modulus of δ-Pu-Ga alloy (experimental data correspond to the composition with 2.36 at. % Ga [14]). Specific heat at constant volume of this composition exhibits also rather small variation by order of 5 % due to variation of the volume and, therefore, E_0 (see Fig. 4).

Actually, the δ-Pu-4 at. % Ga crystal lattice still expands, although very weakly, with temperature. If so, then a corresponding softening of the bulk modulus is not surprising. However, our approach predicts similar bulk modulus behavior also for the δ-phase of pure Pu, in agreement with the available (existent) experimental data [14] (see Fig. 2). Note, that in this case the characteristic energy E_0 exhibits hypothetical non-monotonic behavior as a function of volume (Fig. 3 *b*). Initially, E_0 decreases until the volume reaches its value corresponding approximately $T = 300$ K, i. e. the inflection point of the $a\,(T)$ curve (Fig. 1 *b*). Within this temperature interval the fluctuation contribution turns out to be too small as compared to the phonon contribution. However at $T > 300$ K the lattice begins to compress, E_0 increases and at $T \sim 600$ K practically returns to its initial value 137 meV (Fig. 3 *b*). Maximum change in specific heat of unalloyed δ-Pu does not exceed 3 % when

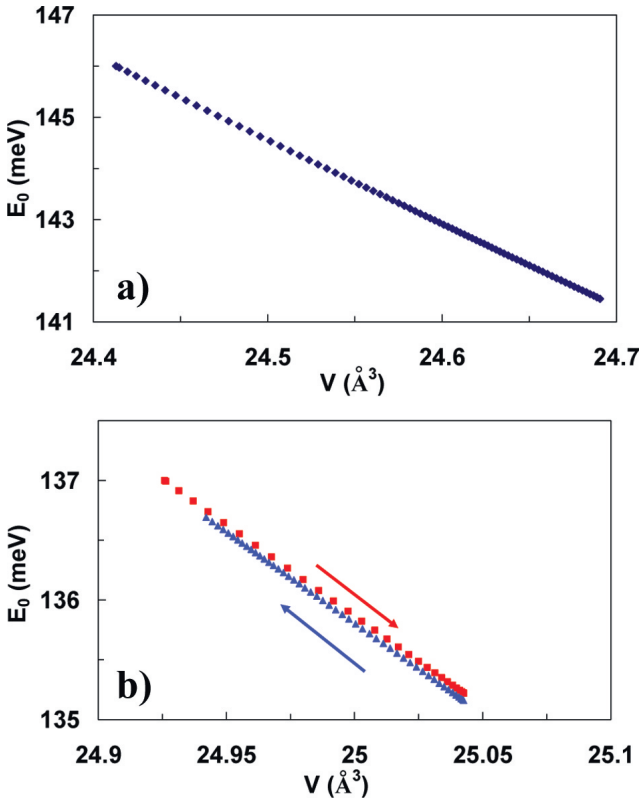

Fig. 3. Characteristic energy E_0 as a function of plutonium atomic volume $V(T) = a^3(T)/4$ calculated with the relation (9) for Pu-4 at.% Ga alloy (upper panel) and unalloyed δ-Pu (bottom panel). Red squares indicate E_0 variation at temperature below ~ 300 K, where the lattice hypothetically expands. Blue triangles show the E_0 increase as a result of fluctuation domination effect which leads to the crystal lattice compression (see Fig. 1 *b*). Blue line is shifted down by 0.06 meV for clarity. Arrows indicate the direction of E_0 change

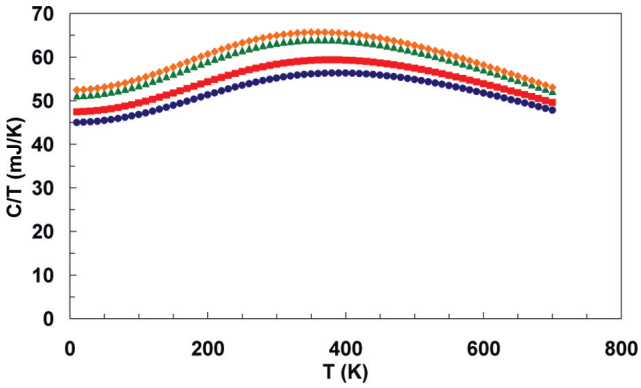

Fig. 4. Fluctuation contribution to the specific heat at constant volume $C_V^f(T)$ (relation (7)) for Pu-4 at. % Ga and pure δ-Pu. The curves correspond to the values of volume, and, therefore, the values of E_0 at $T = 10$ K (blue circles) and $T = 600$ K (red squares) for alloy, and $T = 10$ K (green triangles) and $T = 300$ K (orange rhombs) for unalloyed material. Curves at 600 and 300 K correspond to the maximal $C_V^f(T)$ variation as a function of $V(T)$, and, thus, E_0 for two composition, respectively

E_0 varies between 137 and 135.2 meV (Fig. 4). Hence, using the universal function $f(T) = \Delta n_f(T)/\Delta n_f(0)$, our approach is able to explain the behavior of crystal lattice and bulk modulus not only for the fcc phase of Pu-Ga alloy, but also for unalloyed plutonium with the δ-phase existence range.

Despite obvious agreement with experimental data, our calculations do not claim to provide an exact quantitative description of the thermal expansion and elastic properties of the metallic plutonium fcc phases due to a number of more or less arbitrary assumptions we have made.

First, no doubts, that in mixed-valence systems with $5f^5$ or $5f^{13}$ electron configuration increase in temperature results in increasing effective valence, decreasing ionic volume, and downwards shift of the characteristic energy E_0. However, the fact that the change in volume obeys the same universal function $f(T) = \Delta n_f(T)/\Delta n_f(0)$ as valence is our basic assumption. Besides, this universal function is derived for the case of fluctuation between two electron configurations. Meanwhile, at least three configurations are involved into fluctuation in metallic δ-Pu [1, 31, 33, 34]. Therefore, an application of the same universal function for Pu is also our assumption.

The second assumption is the functional dependence of E_0 on volume, given by relation (9). Generally speaking, it requires justification.

Third, we used Rajan's expression (7) to calculate fluctuation contribution to the specific heat, so that our specific heat calculations are actually more or less reliable estimates of this thermodynamic function.

And, finally, the last note. As mentioned above, we used the initial value $E_0 = 146$ meV in our calculations for δ-Pu-4 at. % Ga alloy. This energy corresponds to the high-energy feature of the δ-Pu inelastic neutron scattering spectrum arising because of the Kondo lattice effects [1]. It cannot be excluded that that namely these effects govern the δ-Pu properties of our interest.

4. CONCLUSION

In our opinion, the above assumptions do not cancel out the main advantage of our scenario based on

the clear physical arguments without involvement artificial physical mechanisms. Inelastic neutron scattering experiments demonstrate δ-Pu to be the mixed-valence system. Therefore, under increase in temperature the valence of a system tends to its value for the free ion whereas the atomic volume behaves accordingly depending on the number of electrons in $5f$ shell, i. e., on whether the $5f$ shell is «almost empty» or «almost filled». Further, using the thermodynamic relations we showed that our approach, considering δ-Pu as a valence-fluctuating system, allows us to describe in a uniform way not only thermal expansion, but also bulk moduli of δ-Pu-Ga alloy and δ-phase of unalloyed Pu, including their temperature dependence and absolute values. We would like to add that Lawson specially emphasize the key role of valence fluctuations to stabilize the δ-phase both at high and low temperature in his recent publication [33].

As already mentioned in Introduction, there exist other versions to explain thermal behavior of the plutonium metal fcc phases. Besides the «invar» model by Lawson et al. [15] it is worth noting the work by Solontsov and Antropov [35]. They argue that most likely mechanism of negative thermal expansion of δ-Pu and its alloys is the result of magneto-volume effect induced by overdamped paramagnetic spin fluctuations of itinerant electrons. The most consistent computational-theoretical approach to describe the physics of all plutonium phases is developed by Söderlind, Landa, Sadigh, Migliori et al. [5–7]. The last two theories must involve magnetic fluctuation as a necessary ingredient to explain the thermal behavior of the δ-Pu crystal lattice [5, 35] and the bulk modulus softening [5–7]. In the present paper we show that the anomalous thermal behavior of crystal lattice and bulk modulus can be explained by considering fcc metallic plutonium as a strongly correlated system with valence fluctuations. In this scenario magnetic fluctuations are mediated by valence fluctuations[4)].

Obviously, the existence of a few approaches to describe properties of this amazing material in itself suggests that the physics of metallic plutonium still holds many mysterious. In recent publication on the experimental results of x-ray magnetic circular dichroism authors claim that neither spin nor orbital magnetic moments exist in Ga-stabilized δ-Pu [36]. So that further experimental and theoretical efforts are required to achieve deep understanding of metallic plutonium physics.

[4)] Note that figure 31 in Ref. [5] and our figure 1b look very similar.

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