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MD simulations of phase stability of PuGa alloys: effects of primary radiation defects and helium bubbles

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Abstract

The present paper is dedicated to classical molecular dynamics study of the polymorphous transitions in Plutonium Gallium alloys in cooling-heating cycles at ambient pressure. It is demonstrated in a series of MD simulations with Modified Embedded Atom Model (MEAM) that initially fcc samples of the model PuGa alloy (3 $at.\%$ Ga) undergo polymorphous transition when cooling, and crystal structure of the resulting phase has lower symmetry than the initial fcc structure and the resulting phase may be considered as an analog of α'-phase that is confirmed by the analysis of its microstructure and by numerical simulations of X-ray diffraction. In the paper we present the results of virtual MD experiments with defect-free model PuGa samples and model PuGa samples containing 0.3 $at.\%$ of primary radiation defects in the form of randomly distributed in the bulk of the samples vacancies or 0.6 $at.\%$ of radiogenic He in the form of nano-sized bubbles. The samples equilibrated at ambient conditions were subjects to cooling-heating cycles in which they were initially cooled down to $100K$ and then heated up to 500K at ambient pressure. The rate of change of the temperature of the samples in the cycles was $10K/ns$. All the samples undergo direct and reverse polymorphous transitions in the cooling-heating cycles. Obtained hysteresis loops of the direct and reverse phase transition showed that for the samples containing vacancies both transitions were shifted to lower temperatures relative to the samples without defects. This computational result directly agrees with experimental data on unconventional stabilization mechanism of PuGa alloys. Analysis of the data for the samples containing helium shows much less effect on the phase stability if compared to that of primary radiation defects (despite of the fact that helium concentration is twice of that for the primary radiation defects).

Key words: Plutonium Gallium alloys, Classical Molecular Dynamics, Modified Embedded Atom Model (MEAM), Phase Stability, Aging

1 Introduction

According to the phase diagram of plutonium-gallium binary system (see Fig.1) at ambient conditions PuGa alloys are metastable being in δ-phase. Since the boundaries of the stability of δ-phase are very sensitive to doping of Pu with a small amount of Ga one may suppose that the phenomena associated with the ageing and leading to changes in thermodynamic and mechanical properties of the material will affect the phase stability properties as well.

It is known experimentally that δ-phase PuGa alloys containing $\lesssim 3at.\%Ga$ partially transform martensitically to the monoclinic α' structure starting at temperatures of about $150K$ [1]. In [2,3] it was shown that at fixed Ga concentration the kinetics of the transition, the amount of resulting phase, and the temperatures of the direct and reverse transition onsets are strongly affected by the age as well as by the history of thermal treatment (heating, quenching, conditioning *etc.*) of samples. The phenomenon of enhanced stabilization of the low-temperature δ-phase due to 1) thermal cycling through the δ to α' forward and reverse transformations and, 2) due to samples aging is presently known as unconventional stabilization. Thus, according to [1] thermal cycling experiments with 22-year old Pu samples showed that aged material do not undergo transformation when cooling down to $-165^{O}C$. However, after heating up to $200^{O}C$ and subsequent cooling the transformation was observed. Obvious explanation is that at $200^{O}C$ the most of radiation defects accumulated in the material during its aging is annealed.

During the last decade classical molecular dynamics approach with Modified Embedded Atom Model (MEAM) as a model of interatomic interactions was applied to simulations of radiation damage of Pu and its alloys due to self-irradiation and investigation into associated phenomena such as behavior of Helium bubbles in the bulk of the material, properties of primary radiation defects (PRD), and effects of PRD on thermodynamic and mechanical properties of the material [4–12]. In this paper we use atomistic simulation to investigate the role of PRD and radiogenic helium as factors affecting the phase stability of PuGa alloys and possibly responsible for the unconventional stabilization.

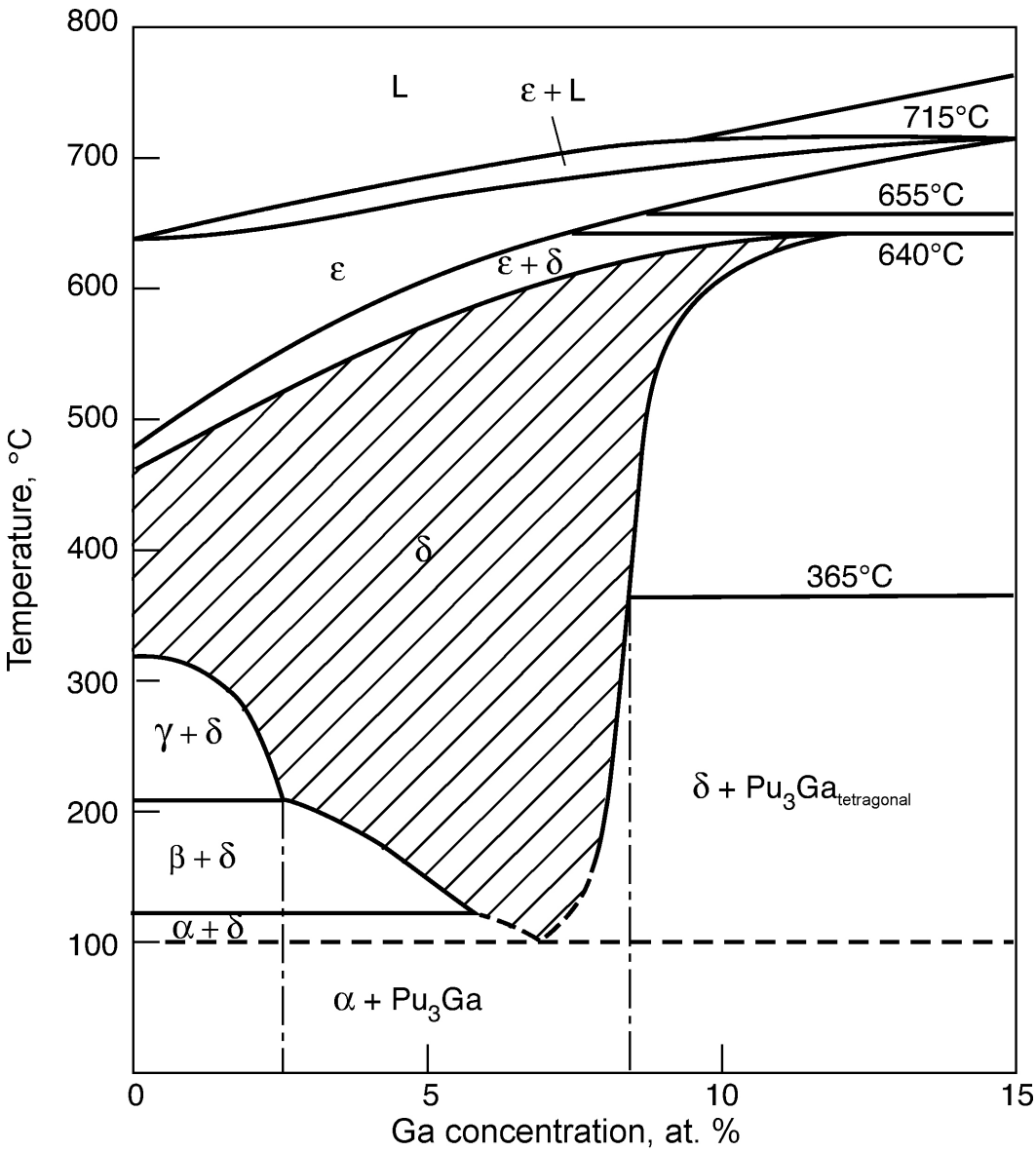

Fig. 1. Phase diagram of PuGa alloys [13] (Adopted from [19])

2 MD modeling of $\delta \rightarrow \alpha'$ transition

Prior to carry out MD simulations of the effects of primary radiation defects and radiogenic helium on the phase stability of the PuGa alloys one has to verify that the used MD model of interatomic interactions reproduces basic properties of δ-phase PuGa alloys from the point of view of its phase stability. In [11] it was demonstrated that current version of MEAM potential adequately reproduces mechanical properties of PuGa alloys as dependent on Ga concentration. Early the role of gallium as a factor stabilizing fcc structure of Pu at ambient conditions was also investigated using MD-MEAM simulations in [14]. Here we report the results of MD-MEAM (with MEAM parameteriza-

tion from [11]) calculations of PuGa alloy (3 $at.\%$ Ga) samples cooling from ambient temperature down to $100K$. In this MD calculations we used samples ($30X30X30$ unit cells, $108,000$ atoms) with randomly distributed gallium atoms. Calculation were carried out for NPT ensembles at ambient pressure and flexible supercell to provide zero non-diagonal elements of stress tensor. The cooling was performed with the temperature step of $5K$, and the system was relaxed at each temperature point during $0.05ns$. Figure 2 shows typical dependence of density on temperature in MD simulation of cooling of PuGa alloy sample from $300K$ down to $100K$. A sudden increase in sample density takes place at temperature $\sim 150K$ that corresponds to the transition of the sample to more dense phase. Analysis of the crystal structure of the sample after the transition showed that the amount of new structure upon the transition is 100%. The new phase has density about 17 g/cm^3 that is less than that of real α'. In fact we face here the shortcoming of the MEAM model which does not provide stable α' monoclinic structure of PuGa alloys at finite temperatures. Nevertheless, an analysis of the new structure obtained showed that its properties are close to those of α'. Hereafter, the low temperature phase obtained in our MD-MEAM simulations we call α^*.

Indeed, as one can see in Fig. 2 the high density α^*-phase has much greater thermal expansion coefficient than the parent δ-phase. In Fig. 3 the calculated dependence of density on temperature at zero pressure for α^*-phase is presented in comparison with experimental data on the thermal expansion for α-Pu, and one can see that the results of MD simulations and experimental data agree quite well. Structural changes that take place during $\delta \rightarrow \alpha^*$ transition are shown in Fig. 4. From the comparison of δ, α^*, and α' local structures it is seen that α^* structure is on the transformation path from δ to α'. We also calculated virtual X-ray powder diffraction patterns for δ, α^*, and α' structures for the wavelength 1.5406 nm that are presented in Fig. 5. In Figs. 5(a),(c) X-ray powder diffraction reflexes of δ[18] and α[17] phases are presented as well. One can see that the pattern for α^* (Fig. 5(b)) reveals new peaks if compared to that of δ-phase (Fig. 5(a)) indicating lowering of the symmetry of the crystal and rearrangements of atoms toward the monoclinic α' crystal structure.

Thus, one may conclude that the current MD-MEAM model reproduces basic characteristics of polymorphous transition taking place when cooling down δ-stabilized Pu-Ga alloys, and the temperature of the transition to high-density low-symmetry α^* phase is close to the experimental value. The product phase in MD simulations has much higher density than the initial fcc (the density increase is about 7%) and its structure and thermal expansion are quite similar to those of experimentally observed α'-phase. The amount of resulting α^* structure in MD simulations of cooling of PuGa alloys upon the transition is close to 100%, while experimentally determined maximum amount of newly formed α'-phase does not exceed $15 - 20\%$. The current work hypothesis of

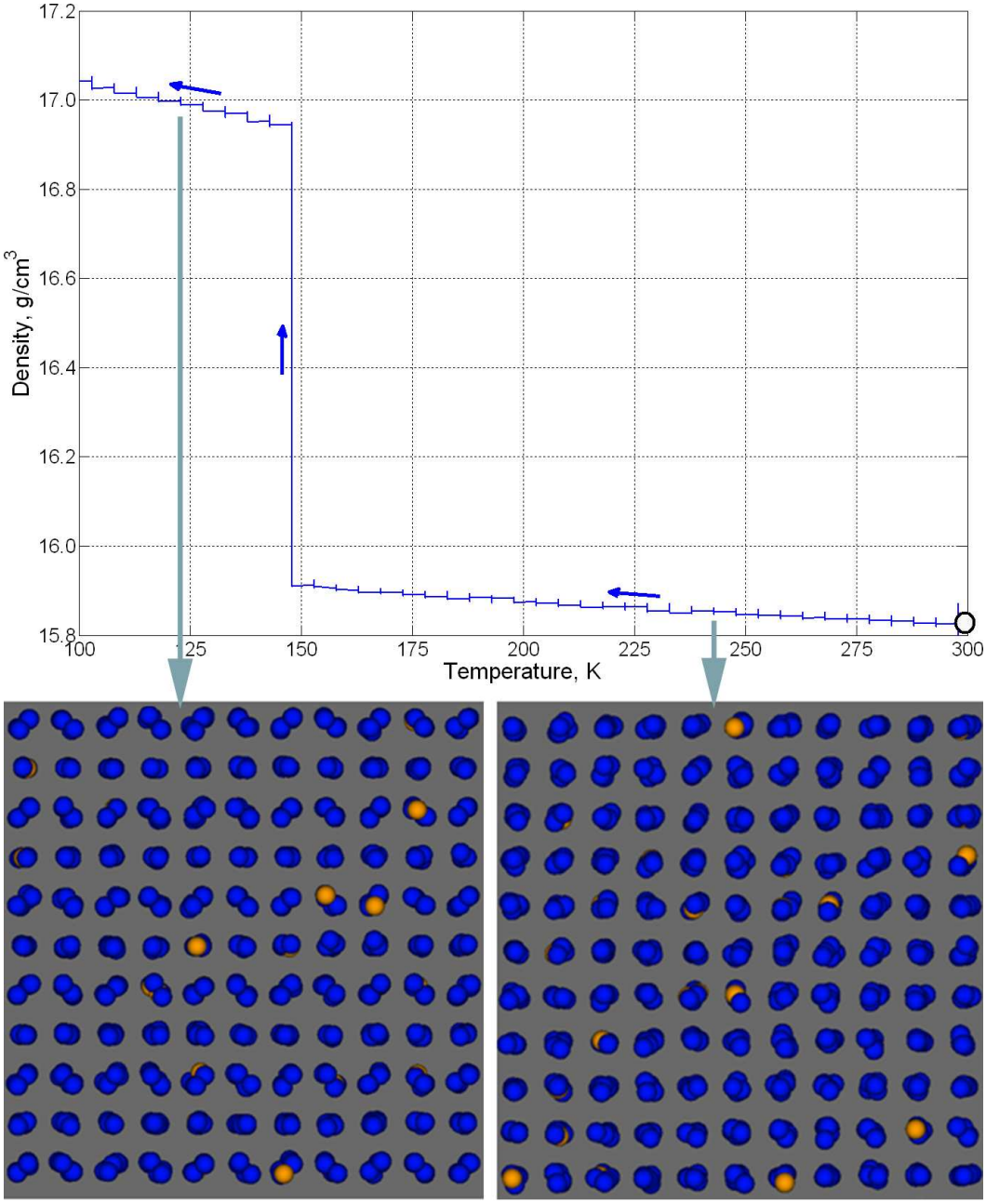

Fig. 2. (Color online) Typical dependence of density on temperature in MD simulation of cooling of PuGa alloy form 300 K down to 100 K at zero pressure (above) and structures of original fcc (bottom right) and product high density phase (bottom left) at corresponding temperatures.

α'-phase growth stopping in the experiments is that the decrease in specific volume (about 25%) at $\delta \rightarrow \alpha'$ transition results in strong stresses around α'-nuclei, while in MD simulations the decrease in specific volume is only $\sim 30\%$ of that for real experiments and the stresses around the new phase nuclei are not sufficient to stop the transition and allows the entire sample to transform.

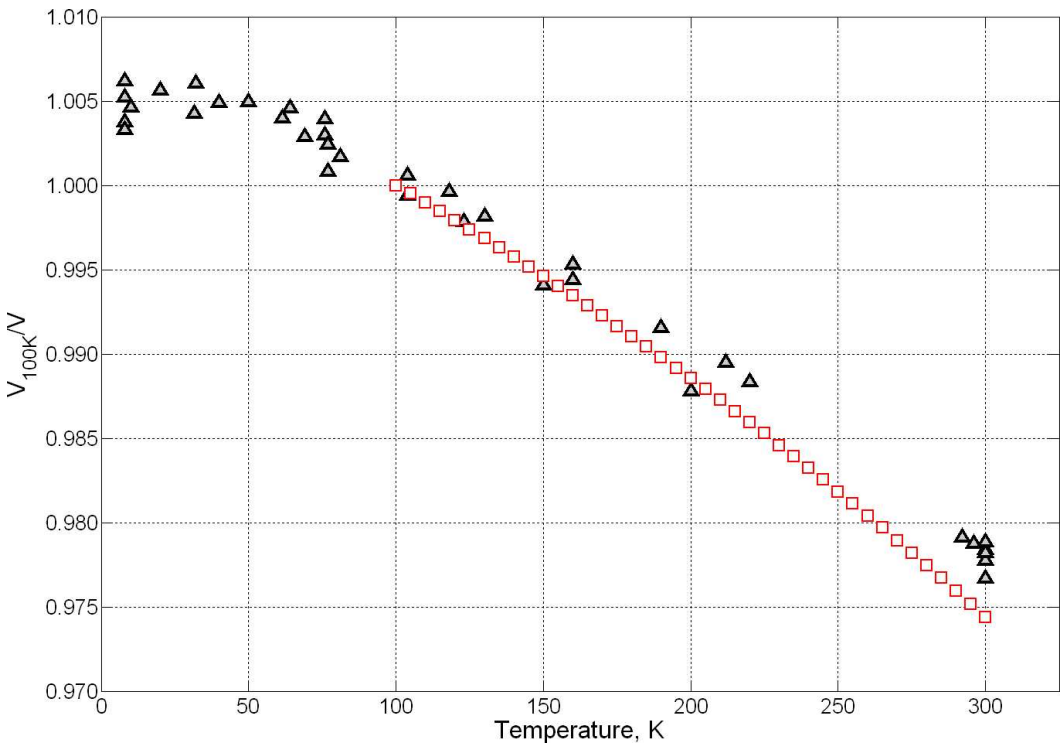

Fig. 3. Experimental data on thermal expansion of α-Pu [16] (triangles) and thermal expansion of high density α^* phase obtained in MD-MEAM simulations (squares).

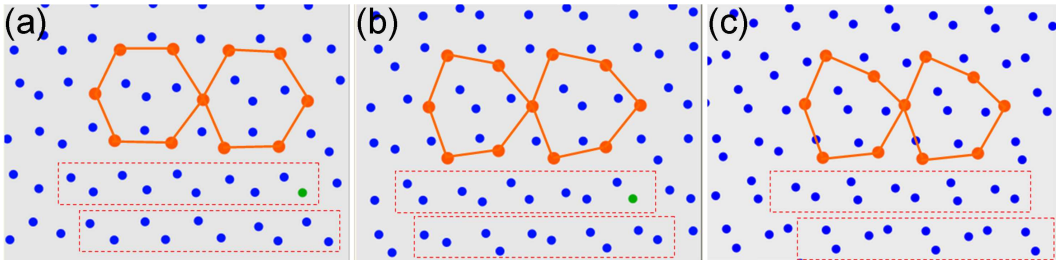

Fig. 4. Initial fcc structure of model PuGa sample (a), structure of model PuGa sample upon transformation at -150^oC (b), and structure of monoclinic α'-phase at -150^oC (c). Comparison of relative positioning of atoms laying in different atomic planes (marked by dashed rectangulars) makes evidence of structural changes leading to the crystallite similar to that of monoclinic α'-phase.

3 MD modeling of PRD and radiogenic helium effects on phase stability of PuGa alloys

In the present section we discuss the results of MD simulations of aging factors, namely, PRD and radiogenic helium, on the phase stability of δ-stabilized PuGa alloys. As it was shown in [8] single vacancies dominate as PRD. Hence, at first we investigated the effects of presence of randomly distributed single vacancies in the bulk of PuGa samples. The concentration of vacancies was set to 0.3%. Since in MD simulations we limited to deal with relatively small systems

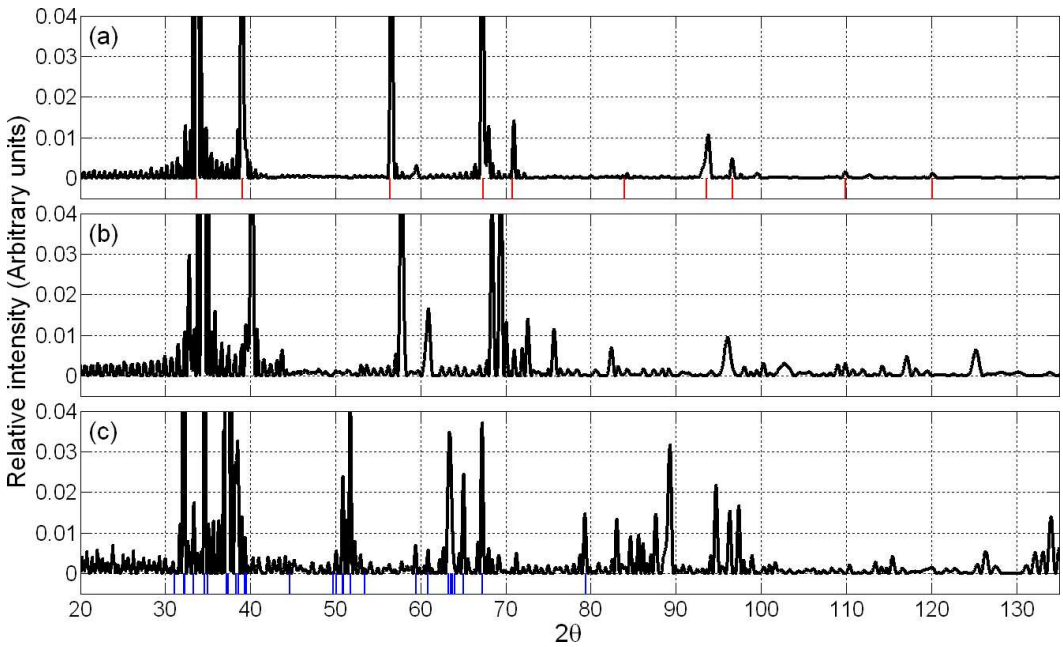

Fig. 5. Virtual X-ray powder diffraction patterns: fcc δ-phase (a), α^*-phase (b), monoclinic α'-phase (c). Vertical lines in figures (a) and (c) represent theoretical X-ray powder diffraction reflexes of δ[18] and α[17] phases respectively.

and short physical times, and the process of new phase nucleation is of random character, varied macroscopically identical (containing the same amount of Ga and defects) but microscopically different samples undergo transitions at different temperatures. To determine average temperature for the direct and reverse transitions we performed 50 independent cooling-heating numerical experiments for 50 microscopically different samples containing PRD. The same number of simulations were performed for macroscopically identical defect-free samples. All the samples were cooled down to $100K$ and then heated up to $500K$ with the same rate of change of sample temperatures as in Section 2. Results of MD simulations of cooling-heating cycles of the defect-free samples and the samples containing 0.3% PRD in the form of single vacancies are presented in Fig. 6 and Fig. 7 respectively. As one can see in Figs. 6,7 the obtained hysteresis loops for the direct and reverse transitions showed that for the samples containing vacancies both transitions were shifted to the lower temperatures if compared to the samples without defects. The average shift of the transition temperatures is $\sim 35K$.

The next series of calculations was carried out for the samples containing radiogenic helium. Helium accumulates in PuGa alloys in the form of nano-sized bubbles with the average size 1.4 nm [15]. The model for MD simulations of He and He bubbles behaviour in Pu was constructed in [10]. To study the effects of He bubbles on the phase stability of PuGa alloys we constructed 50 macroscopically identical samples of Pu3 $at.$%Ga, and than in each of them we randomly built in four bubbles containing ~ 180 He atoms each. Thereby,

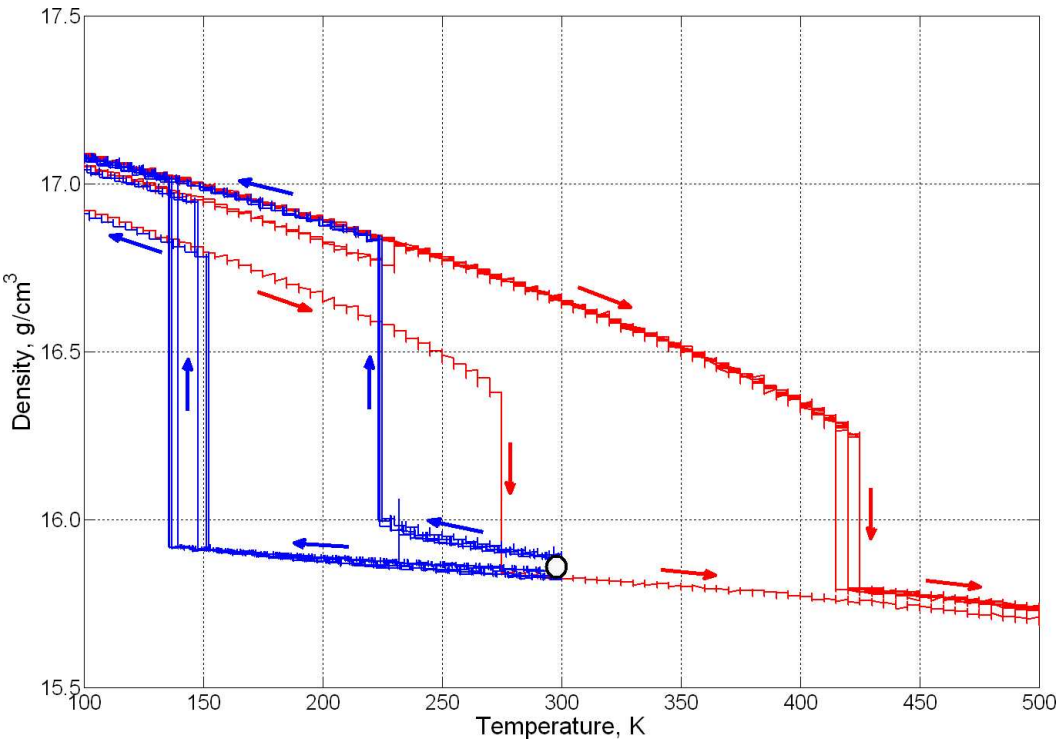

Fig. 6. (Color online) Cooling (blue) and heating (red) trajectories in density-temperature plane obtained in MD simulations for defect-free Pu-Ga samples (3 $at.\%Ga$).

the overall He concentration was 0.66 $at.\%$ that corresponds to $\sim$ 160 years of self-irradiation of ^{239}Pu. Results of MD simulations of the cooling-heating cycles for the samples containing radiogenic He in the form of bubbles are presented in Fig. 8.

Analysis of the data for the defect-free samples containing PRD and the samples containing helium bubbles shows much less helium effect on the phase stability as compared to that of primary radiation defects (despite of the fact that helium concentration was twice of that for PRD). Indeed, all but one of heating trajectories of the samples with He bubbles show the reverse $\alpha^* \rightarrow \delta$ transitions at temperatures $> 400K$ (see Fig. 8) as in the case of the defect-free samples (see Fig. 6), whereas for the samples containing PRD all the heating trajectories show the reverse $\alpha^* \rightarrow \delta$ transitions at the temperatures $< 400K$ (see Fig. 7). On the other hand cooling trajectories for the samples containing helium are very close to those for PRD samples. Nevertheless looking at the whole hysteresis loops and keeping in mind huge helium concentration one may conclude that helium has less stabilization effect than single vacancies.

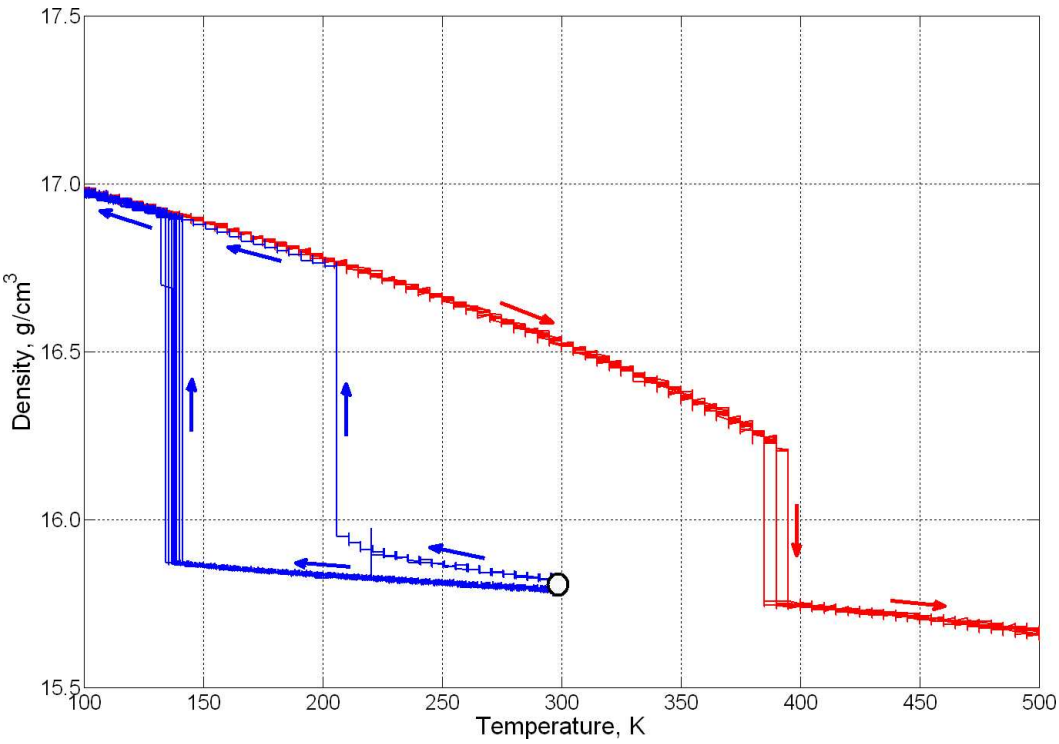

Fig. 7. (Color online) Cooling (blue) and heating (red) trajectories in density-temperature plane obtained in MD simulations for Pu-Ga samples (3 $at.\%Ga$), containing 0.3 $at.\%$ of PRD in the form of single vacancies.

4 Summary

In this paper the MD-MEAM model of PuGa alloys has been used for simulations of the effects of primary radiation defects and nano-sized helium bubbles on the phase stability of the fcc-phase. It was shown that the MD-MEAM model used reflects properly the phenomena associated with the phase transition taking place when samples of δ-phase PuGa are cooled down.

Comparative analysis of the results of a series of numerical MD experiments with defect-free model PuGa samples (3 $at.\%Ga$) and model PuGa samples containing 0.3 $at.\%$ of primary radiation defects in the form of single vacancies or 0.66 $at.\%$ of He in the form of nano-sized bubbles is presented. All the samples were cooled down to 100 K and then heated up to 500 K at ambient pressure. Obtained hysteresis loops for the direct and reverse phase transitions showed that for the samples containing single vacancies both transitions were shifted to the lower temperature relative to that of the samples without defects. The presented MD simulation result is the first one that directly agrees with the experimental data on the unconventional stabilization [1]. Analysis of the data for the samples containing helium shows much less effect of He on the phase stability if compared to that of primary radiation defects in the form of single vacancies (despite of the fact that helium concentration was twice of

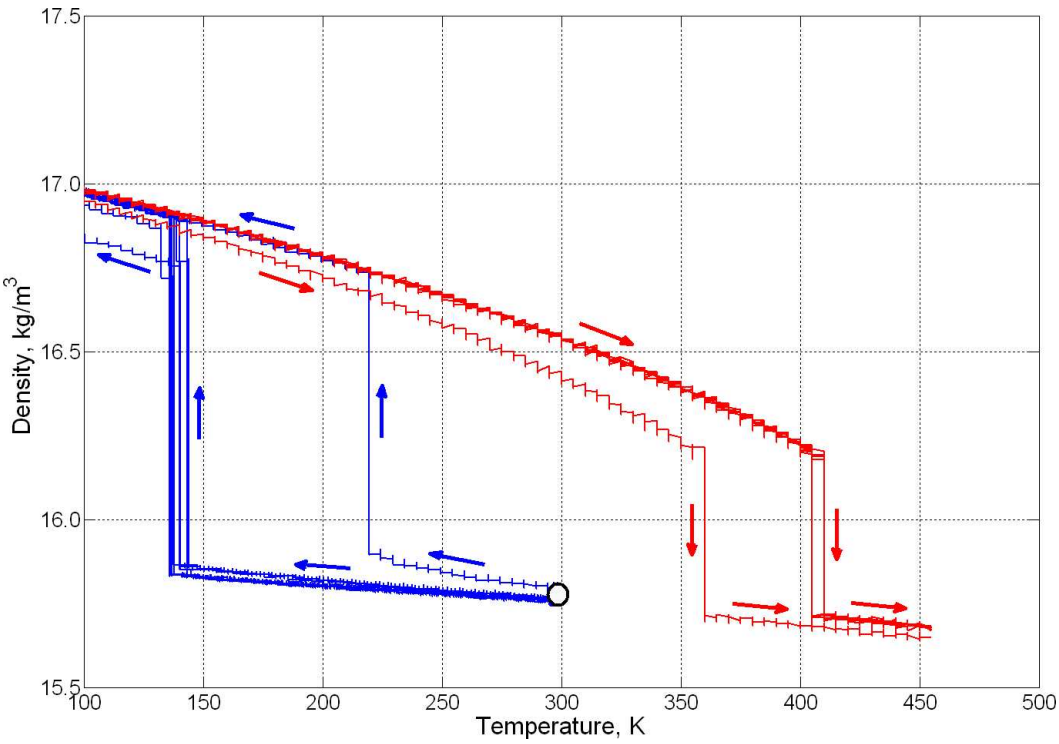

Fig. 8. (Color online) Cooling (blue) and heating (red) trajectories in density-temperature plane obtained in MD simulations for Pu-Ga samples (3 $at.\%Ga$), containing 0.66 $at.\%$ of He in the form of nano-sized bubbles. Color online.

that for primary radiation defects).

To answer the questions about the role of stresses in stopping $\delta \rightarrow \alpha'$ phase transformation when the amount of newly formed phase is about $15 - 20\%$ one needs to significantly improve the model interatomic interactions in order to reproduce properties of high-density monoclinic α'-phase more adequately.

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