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^{69}Ga NMR in $Pu_{1-x}Ga_x$ ($x < 0.01$) alloy

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Abstract

^{69}Ga nuclear magnetic resonance (NMR) experiments have been carried out on the $Pu_{0.995}Ga_{0.005}$ alloy at temperatures between 20 and 420 K at magnetic field of 9.4 T to study the local charge symmetry and magnetic behavior of the Pu atoms surrounding solute Ga. In accordance with optical metallography and X-ray diffraction studies the investigated plates of alloy (20 mm × 3 mm × 0.2 mm) represent at room temperature the single α-phase material without any detectable macroscopic segregation of other phases (the corresponding volume fraction <0.03). It was revealed that the magnetic shift of the ^{69}Ga NMR central line and the electric quadrupole broadening of the Ga NMR spectrum trace temperature dependence of the NMR parameters is observed for the δ-phase plutonium alloy $Pu_{0.95}Ga_{0.05}$. On the basis of ^{69}Ga NMR and X-ray data obtained, it is suggested that specific microscopic areas with a size less than 100 nm exist in the α-phase plutonium alloys $Pu_{0.995}Ga_{0.005}$. The local charge and magnetic environment of the solute Ga in these microscopic areas are similar to the observed in the stabilized δ-Pu alloy.

Keywords: Metals; Electronic states; Nuclear resonances

1. Introduction

It is well known, that alloying of plutonium by elements of the IIIB group (Ga, Al) retains the fcc (face-centered cubic) structure of the δ-Pu phase down to room temperature avoiding transformation to the more metallic monoclinic α-phase [1,2]. However the microscopic mechanism, promoting stabilization of the high-temperature δ-phase, is still an open question. A small amount (∼2 at.%) of Ga is required to reduce greatly an itinerancy of 5f electrons in α-Pu and to affect their coherence state in the conducting band. Many efforts are undertaken to clear up the problem by using different locally sensitive techniques. The EXAFS (extended X-ray absorption fine structure spectroscopy) experiments [3] performed on a fcc Pu alloy stabilized by 1 wt% Ga have showed that, the local structure of plutonium around the Ga atoms is similar to a typical fcc metal. However the local structure of plutonium around Pu atoms was disordered. Inelastic X-ray scattering study [4] results in that δ-Pu is the most anisotropic fcc metal known. Recently, Moore et al. [5] using first-principles density functional theory have calculated the bond strengths between the 12 nearest neighbors in δ plutonium for both pure Pu and a Pu–3.7 at.% Ga alloy. They have found that chemical bonds in pure δ-Pu are highly anisotropic and thus produce a "poor" fcc structure easily transforming to a monoclinic α-phase at low temperature. On the other hand, the bond strengths around the Ga atom become less anisotropic illuminating how Ga plays a stabilizing role for the δ-phase at room temperature. Unfortunately these calculations are not self-consistent, and corresponding feedback effect of the change in local crystal symmetry on the f electron system remains not clear.

The nuclear magnetic resonance of Ga can be considered as an informative local tool for detailed investigation of charge and magnetic environment of the solute atom in Pu–Ga alloys. In particular, it was shown [6,7], that charge symmetry of the neighboring plutonium environment is cubic at the Ga-sites in δ-phase. The nuclear spin of gallium probes local magnetic field arisen at the non-magnetic Ga atom due to transferred hyperfine coupling with the nearest f electron environment of more magnetic Pu. It is of interest to clear up the distribution of the charge and spin density that arisen around Ga in the more diluted Pu–Ga alloys with monoclinic crystal structure of the α-Pu.

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In this paper we present the ^{69}Ga NMR results that investigate the local charge symmetry and magnetic behavior of the Pu atoms surrounding solute Ga in the $Pu_{0.995}Ga_{0.005}$ alloy.

2. Experimental details

The measurements were performed at the sample prepared as the single-sheet stationery packed from isolated plates (20 mm × 3 mm × 0.2 mm) of the alloy. The plates were cut out from an ingot, which is the pure α-phase material after mechanical pressure oblation at room temperature. Then plates were mechanically polished and chemically etched to remove the surface impurities and oxide layer caused by the mechanical treatment. In accordance with optical metallography and X-ray diffraction studies the investigated plates of alloy represent at room temperature the single α-phase material without any detectable macroscopic segregation of other phases (the corresponding volume fraction <0.03).

The ^{69}Ga NMR spectra have been measured at temperatures between 20 and 420 K in magnetic field $H_0 = \upsilon_0/\gamma_{Ga} = 9.4$ T using a phase-coherent pulse spectrometer supplied with the quadrature-detection receiver set-up. The ^{69,71}Ga ($I = 3/2$) spectrum of central transition $m_I = -1/2 \leftrightarrow +1/2$ was obtained by Fourier transformation of the second half of the spin-echo signal following the $(\pi/2)_x$–τ_{del}–$(\pi)_x$ pulse sequence. The duration of $\pi/2$ pulse was about 8 μs, and corresponding frequency band (~100 kHz) excited by the π *rf* pulse was not enough to cover NMR spectrum. The whole spectrum including all of transitions was obtained by summing subsequently several sub-spectra of the echo signal accumulated at different equidistant operating frequencies.

3. Results and discussion

The effects of mechanical treatment on the Ga NMR spectra pattern were separated in the following manner. At the first stage, the NMR spectra were measured in the virginally prepared sample of alloy cooled from room temperature down to $T = 20$ K with its subsequent heating up to a room temperature after NMR measurements performed. At the second stage, the sample was heated up to $T_{anneal} = 150$ °C, the temperature exceeding a little bit more $T_{\alpha-\beta}$, the characteristic temperature of α–β transformation [1]. After annealing at the given temperature within 8 h the sample was slowly cooled together with the furnace down to a room temperature and then to 20 K for NMR. Finally, the alloy has been subjected to the isothermal heat treatment at $T_{anneal} = 200\,^{\circ}C < T_{\beta-\gamma}$ within 20 h, and NMR spectra measurements were repeated at $T = 20$ K for comparison. The performed heat treatments of the sample remove consecutively the rest of elastic strains retained in the sample of $Pu_{0.995}Ga_{0.005}$ after its machining. It is instructive to note that the most part of the self-irradiation damage defects, such as vacancies and interstitials, dissociate completely during the long-time isothermal heat treatment in temperature range of the β-phase [8].

After completing NMR measurements at the $Pu_{0.995}Ga_{0.005}$ sample ($T_{anneal} = 150$ °C), the structural examination of the alloy were performed at room temperature. Some representative results of these optical metallography and X-ray studies are shown in Figs. 1 and 2. According to structural examination the NMR sample represents the α-phase material. An upper limit of the volume fraction for any kind of macroscopic segregations of the more symmetric high-temperature phases is estimated as 0.03.

The ^{69}Ga NMR spectrum of $Pu_{0.995}Ga_{0.005}$ in the external magnetic field of 9.4 T consists of central line (transition $-1/2 \leftrightarrow +1/2$) and a broad pedestal of the satellite lines (transitions $\pm 1/2 \leftrightarrow \pm 3/2$). Such a spectrum is typically observed for a powder of imperfect cubic crystals, where the local deviations of cubic symmetry of charge distribution around Ga-atom take place. The nucleus of Ga has electric quadrupole moment $eQ = 0.17 \times 10^{-24}$ cm^2. Arising electric field gradient (eq_{ii}) causes essential broadening of satellite lines $\Delta\upsilon_Q$ e^2Qq_{zz}. At the same time, the shift (^{69}K) and the line width ($\Delta\upsilon$) of central transition are determined by local fields, which are caused by hyperfine coupling with the nearest electron surrounding of Pu-atoms. In virgin state of the alloy (see Fig. 3a), the line width of central transition exceeds essentially (in 2.5–3 times) the NMR line width observed in the stabilized δ-phase alloys [6,9]. The growth of ($\Delta\upsilon$) is due to the distribution width of the Ga–Pu interatomic distances, which is increased in the mechanically strained state of the α-phase material.

The annealing of alloy at the temperature above the α–β structural transformation (150 °C, 8 h) changes essentially the shape of central line (see Fig. 3b). The fine structure of the cen-

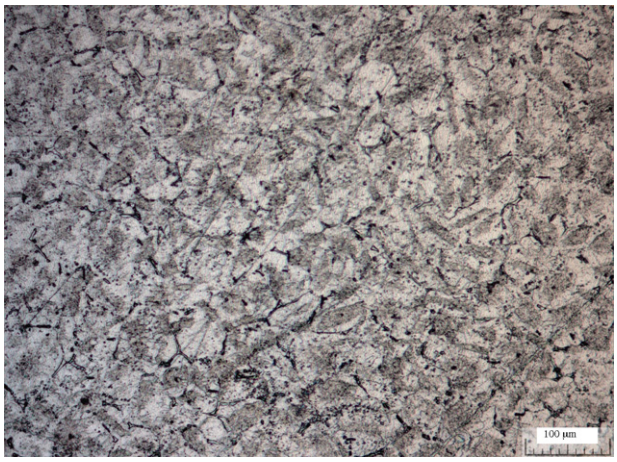

Fig. 1. The microstructure of $Pu_{0.995}Ga_{0.005}$ alloy obtained by the optical metallography.

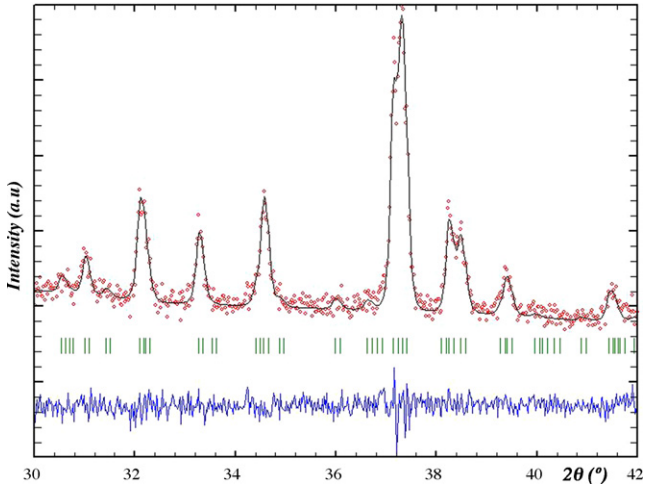

Fig. 2. Room temperature X-ray diffraction pattern of $Pu_{0.995}Ga_{0.005}$ alloy after annealing at $T_{anneal} = 150$ °C during 8 h.

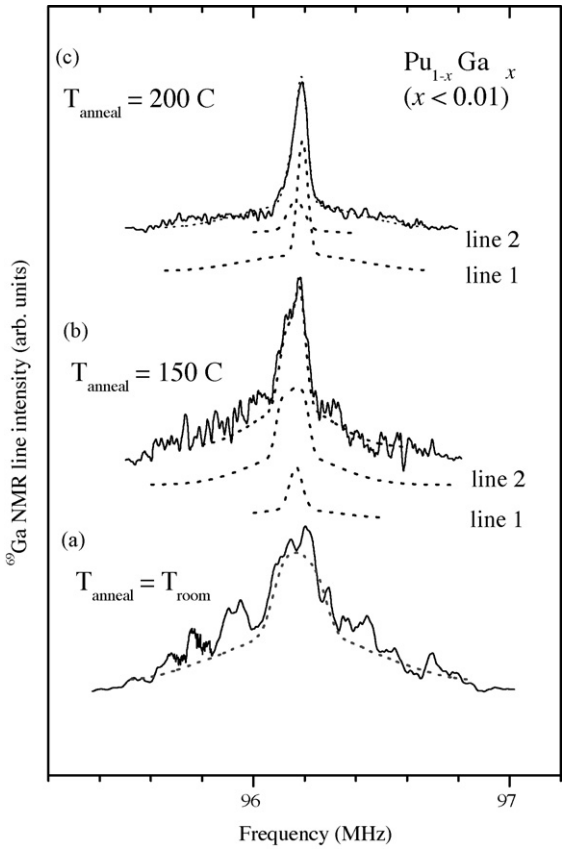

Fig. 3. The ^{69}Ga NMR spectra measured at magnetic field of 9.4 T at 20 K in $Pu_{0.995}Ga_{0.005}$ alloy. (a) The initial α-phase; (b) after annealing at T_{anneal} = 150 °C during 8 h; (c) after annealing at T_{anneal} = 200 °C during 20 h. The doted lines are the result of simulation of the experimental spectrum by two lines with different intensities.

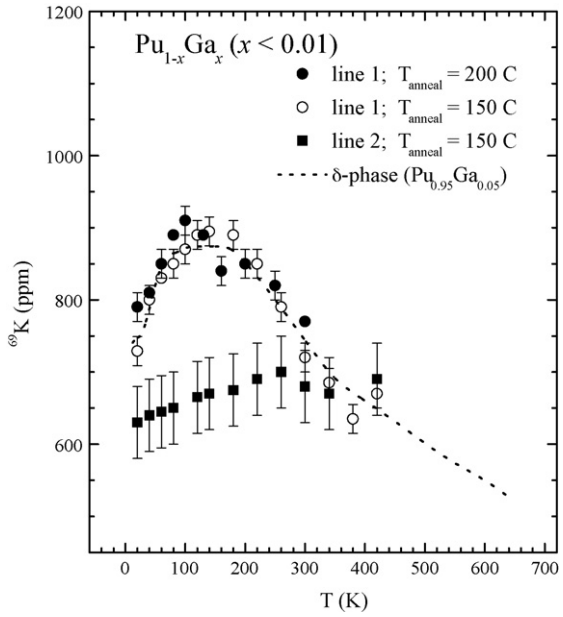

Fig. 4. Temperature dependences of the ^{69}Ga NMR shift for the line-1 and line-2 in the $Pu_{0.995}Ga_{0.005}$ alloy. The corresponding $^{69}K(T)$ dependence for the δ-phase $Pu_{0.95}Ga_{0.05}$ alloy is drawn at the same panel by the doted curve.

tral line can be represented as a superposition of two lines with different Δv and ^{69}K. An additional annealing of the alloy at T_{anneal} = 200 °C during 20 h leads to progressive narrowing of the central line at the expense of the line-1, dominating in intensity, as shown in Fig. 3c. The line width (Δv) of the line-1 is comparable with that is observed in the δ-phase $Pu_{0.95}Ga_{0.05}$ [6,9]. Temperature dependences of the ^{69}Ga NMR shift for the line-1 and line-2 in the $Pu_{0.995}Ga_{0.005}$ alloy obtained before and after annealing of the alloy at T = 200 °C are presented in Fig. 4. The corresponding $^{69}K(T)$ dependence for the δ-phase $Pu_{0.95}Ga_{0.05}$ alloy is drawn at the same panel by the doted curve. Evidently, magnetic shift of the narrow line-1 (Fig. 3c), having relative intensity 0.73(10), changes with temperature like $^{69}K(T)$-dependence in the stabilized δ-Pu alloy $Pu_{0.95}Ga_{0.05}$ [6,9]. The broad line-2 demonstrates a shift being approximately independent on temperature. It is reasonable to assume that the annealing performed above the α–β structural transformation, should take off only the mechanical strains, retained in the initial α-phase [1]. It should remain once more, that the X-ray examination of the annealed at $T \sim 150$ °C sample results in the absence of any traces of the δ-phase macroscopic segregations with characteristic size exceeding 100 nm. The NMR shift of Ga are determined by the static parts of the local magnetic fields arisen at Ga due to transferred hyperfine coupling with the nearest f electron environment of more magnetic Pu. At $T > T^* = 235$ K, the temperature dependent part of the shift $^{69}K(T)$ scales macroscopic magnetic susceptibility $\chi(T)$, following the Curie–Weiss law [8]. The temperature dependence of the ^{69}Ga NMR line shift at $T > T^*$ is typical for nonmagnetic 3D Kondo lattice, where the localized electron spins fluctuate independently each other without any macroscopic coherence. Thus, our results do not exclude the presence of the localized 5f electron states around Ga atoms in the α- and δ-phase of the Pu–Ga alloys. The decrease of the f-electron itinerancy around Ga leading to a local killing the coherence of 5f band states can be suggested as a reason for the transformation of the Ga environment symmetry from monoclinic to cubic.

4. Conclusions

In summary, the results of our investigation indicate that even an isolated Ga atom substituting for Pu in a lattice creates around itself the plutonium environment having a cubic symmetry, with a local decrease of itinerancy for f electrons of actinide. On the basis of ^{69}Ga NMR and X-ray data obtained, it is suggested, that specific microscopic areas with a size less than 100 nm exist in the α-phase plutonium alloys $Pu_{0.995}Ga_{0.005}$. The local charge and magnetic environment of the solute Ga in these microscopic areas are similar to the observed in the stabilized δ-Pu alloy.

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