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^{69}Ga NMR and magnetic susceptibility in δ-phase of $Pu_{1-x}Ga_x$ ($x = 0.05$, $x = 0.08$) alloys

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A B S T R A C T

^{69}Ga nuclear magnetic resonance spectra, line shifts (^{69}K) and nuclear spin-lattice relaxation rate $^{69}T_1^{-1}$ have been measured in the 20 years aged $Pu_{0.95}Ga_{0.05}$ and in fresh prepared $Pu_{0.92}Ga_{0.08}$ alloys, stabilized δ-phase, at magnetic field of 9.4 T in the temperature range (10–500) K. The line shift and $^{69}T_1^{-1}$ are determined correspondingly by the static and fluctuating-in-time parts of the local magnetic field that originates in transferred hyperfine coupling the Ga nuclear spin with the nearest f-electron environment of more magnetic Pu.

Temperature behavior of the resonance properties is found the same in fresh $Pu_{0.92}Ga_{0.08}$ and aged $Pu_{0.95}Ga_{0.05}$ alloy. The NMR results are in favor that δ-phase of $Pu_{1-x}Ga_x$ alloys represents at $T > 200$ K the Kondo lattice, in which the localized electronic spins fluctuate independently from each other without any macroscopic coherence. The coherent state like in heavy-fermion liquids emerges in $Pu_{0.95}Ga_{0.05}$ below $T^* = 200$ K. A little bit higher estimate of crossover temperature $T^* = 250$ K was founded for $Pu_{0.92}Ga_{0.08}$.

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 and does this alloy very important to engineering applications [1]. However, the electronic structure of the gallium stabilized δ-phase plutonium, its magnetic and transport properties are still now mysterious and unclear, in many aspects, and are the subject of intensive studies and discussions. Unusual properties of plutonium and its alloys come from the dominant role of its narrow 5f band. The large electron contribution to the specific heat [2], the high resistivity $\rho(T)$, and its non-monotonic temperature dependence with a maximum below 200 K [3], abnormal temperature dependence of the static spin susceptibility, χ_s, displayed by ^{69}Ga nuclear magnetic resonance (NMR) shift [4–6], magnetic instability, arisen due to self-damage in δ-Pu alloy at low temperature [7] are the characteristic macro-properties of δ-Pu that make this material close to heavy-fermion systems with a strong localization of f-electrons [8]. At the same time a general conclusion of many experimental researches of a Pu–Ga alloy magnetic state is the following: electronic correlations in δ-Pu are of a dynamic character and their evolution never ends in static magnetic order at low T.

The NMR technique is very informative local tool for studying electron instability in the stabilized δ-phase plutonium alloys. It was shown [4–6,9] that NMR line shift (K) and the nuclear spin-lattice relaxation rate $(T_1)^{-1}$ of Ga are determined by local magnetic field that arise at the NMR probe nucleus due to the spin polarization transferred from the f-electron shells of the actinide neighbor. Thus, the temperature variation of the gallium NMR line shift K traces thermal behavior of the spin contribution χ_s to the magnetic susceptibility. In particular, for the $Pu_{0.95}Ga_{0.05}$ alloy, the temperature dependence $^{69}K(T)$ was found to be nonmonotonic with a maximum at 150 K [4]. Its temperature-reversible behavior indicates that below 150 K the electron spectrum of the δ-phase develops an instability resulting in a decrease of the spin contributions to magnetic susceptibility of the alloy.

In this report, the ^{69}Ga NMR line shift (^{69}K) and nuclear spin-lattice relaxation rate $^{69}T_1^{-1}$ measurement results are presented for aged $Pu_{0.95}Ga_{0.05}$ (Ga05) and fresh prepared $Pu_{0.92}Ga_{0.08}$ (Ga08) alloys, both stabilized in δ-phase. The comparative analysis of the NMR parameters as a function of temperature and Ga content was performed. The specimens were polycrystalline samples, prepared as a sandwich of the alloy plates ($10 \times 2.5 \times 0.2$ mm) separated each other with a mice layer. The plates have been cut out from the central part of an ingot. Finally the specimen was sealed inside glass container filled with spectroscopically pure argon.

The ^{69}Ga NMR spectra have been measured in the temperature range 10–470 K at magnetic field $H_0 = \nu_0/\gamma_{Ga} = 9.4$ T using a phase-coherent pulse spectrometer with a quadrature system of signal detection. To measure the ^{69}Ga NMR spectrum which far exceeded

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the bandwidth of frequencies excited by the radio pulse, we used the summation of the Fourier signal data array gathered on different equally spaced frequencies of the spectrometer. The line shifts for the samples were determined with respect to the position of the peak of the ^{69}Ga NMR line in $GaCl_3$.

The ^{69}Ga NMR spectra in Pu–Ga alloys presented in Fig. 1 consist of central line (transition $m_I = -1/2 \leftrightarrow +1/2$) and a broad pedestal of the satellite lines (transitions $m_I = \pm 1/2 \leftrightarrow \pm 3/2$). Such a spectrum is typical for a powder of imperfect cubic crystals, where the local deviations of cubic symmetry of charge distribution around resonance nucleus take place. Arising electric field gradient (EFG) eV_{ii} causes essential broadening of the satellite lines $\Delta\nu_Q(m_I = \pm 1/2 \leftrightarrow \pm 3/2) \sim e^2QV_{zz}$, where $eQ = 0.17 \times 10^{-24}$ cm^2 is the Ga nucleus quadrupole moment. At the same time, the effect of quadrupole broadening on the width of the central line $\Delta\nu_Q(m_I = -1/2 \leftrightarrow +1/2) \sim (e^2QV_{zz})^2/\nu_0$ is greatly reduced in high magnetic field and its contribution to the width of ^{69}Ga line does not exceed 10 kHz. As is seen in Fig. 1, the full width at half maximum of the central transition line ($\Delta\nu_{1/2}$), and of the satellites ($\Delta\nu_Q$), for Ga08 is, respectively, in two and four times larger than those for Ga05. This is evidence of broader distribution in Ga08 both the local magnetic fields and EFG at gallium sites.

Temperature dependences of the magnetic NMR line shift $^{69}K(T)$ measured in $Pu_{0.95}Ga_{0.05}$ and $Pu_{0.92}Ga_{0.08}$ alloys are shown in Fig. 2. At the temperature higher than 200 K for Ga05 and 250 K for Ga08, the $^{69}K(T)$ data are well fitted with an expression of the Curie–Weiss law form: $K(T) = K_0 + C/(T + \Theta_K)$ with $K_0 = 170(20)$ ppm and $\Theta_K = 280(20)$ K (dotted line in Fig. 2) and $K_0 = 215(30)$ ppm, $\Theta_K = 315(40)$ K (solid line in Fig. 2). As it was pointed out before [5,6], a similar temperature dependence is observed for the NMR line shift of nonmagnetic ions in heavy-fermion systems above the region where the coherent state of the heavy-fermion fluid is

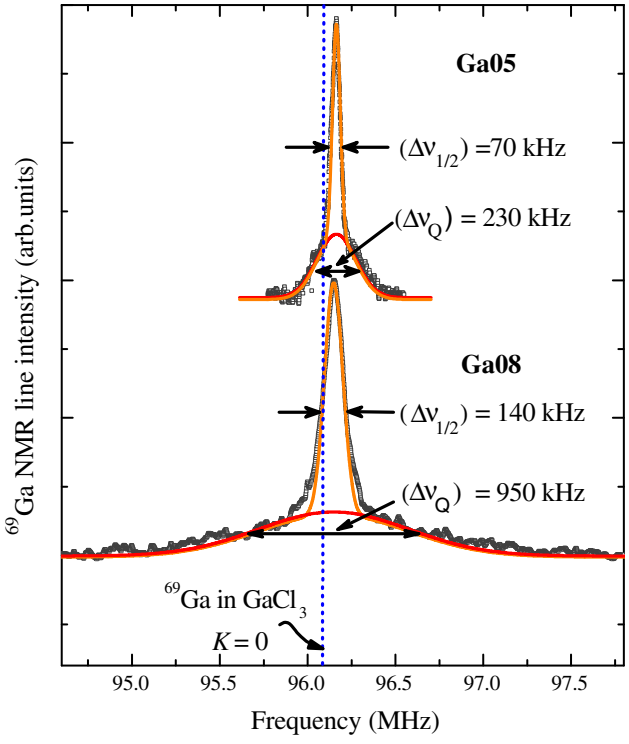

Fig. 1. ^{69}Ga NMR spectra in $Pu_{0.95}Ga_{0.05}$ and $Pu_{0.92}Ga_{0.08}$ alloys at $T = 20$ K. The calculated powder patterns for total spectrum and, separately, only for the satellite lines are shown, respectively, with orange and red curves. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

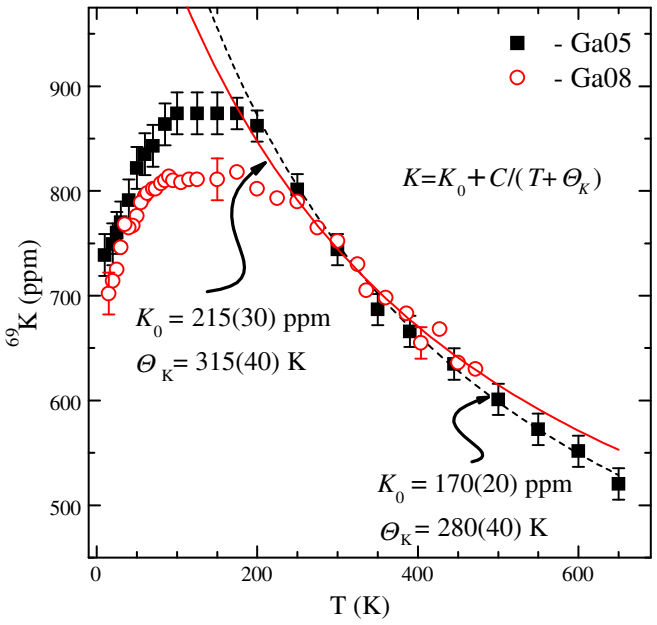

Fig. 2. Temperature dependences of Ga NMR shifts, ^{69}K, in $Pu_{0.95}Ga_{0.05}$ (■) and $Pu_{0.92}Ga_{0.08}$ (○). At $T > 200$ K for Ga05 and at $T > 250$ K for Ga08, the $^{69}K(T)$ data sets are fitted with an expression of the Curie–Weiss law form: $K(T) = K_0 + C/(T + \Theta_K)$ with $K_0 = 170(20)$ ppm, $\Theta_K = 280(20)$ K (dotted line) and $K_0 = 215(30)$ ppm, $\Theta_K = 315(40)$ K (solid line).

formed and where the state of the f-ions electron system is adequately described in the framework of the model considering a gas of noninteracting Kondo centers with a local spin susceptibility $\chi_{s,f}(T) \sim (T + \Theta)^{-1}$.

It was shown before [4], that the NMR line shift of Ga is mainly determined by the Knight shift $^{69}K_s$ due to the hyperfine interactions of the nuclear spin $\boldsymbol{I}$ with its electron environment. The contact Fermi interaction with the conduction band electrons $\gamma\hbar A\boldsymbol{I}\boldsymbol{S}^c$ forms a temperature independent contribution $K_{s,0}$. An additional uniform spin polarization of conduction electrons due to the indirect electron–nucleus interactions $\gamma\hbar\boldsymbol{I}(r_i)B\boldsymbol{S}^f(r_j)$ with stronger localized spins S^f of f-electrons is taken into account in the form of an additive contribution K_f to the total Knight shift

$$^{69}K_s(T) = K_{s,0} + K_f(T) = A\chi_{s,c} + B\chi_{s,5f}(T)/N_A, \quad (1)$$

where the constant B is assumed to be isotropic and has a physical meaning of the effective hyperfine field produced at the Ga nucleus by the 5f-electrons of the 12 nearest Pu atoms in the fcc structure of δ-Pu, N_A is the Avogadro number, and $\chi_{s,5f}$ is the molar spin susceptibility of 5f-electrons of Pu in the alloy.

Below T^*(Ga05) ~ 200 K and T^*(Ga08) ~ 250 K T-dependences of a shift $^{69}K(T)$ deviate from Curie–Weiss law showing similar nonmonotonic behavior with a broad maximum near $T \sim 150$ K, while bulk magnetic susceptibility $\chi(T)$ of the alloys (not shown) continues gradual growth with temperature decreasing.

Recently [5,6], we have shown that different behavior of $^{69}K(T)$ and $\chi(T)$ observed at $T < T^*$ in the Ga05 alloy can be explained reasonably following the two-fluid description of Kondo lattices developed by Pines et al. [10,11]. It was suggested that an additional coherent component of the heavy-fermion (HF) liquid state $\chi_{cf}(T)$ emerges in magnetic response of interacting f-electrons in δ-phase plutonium alloys below T^*. As temperature is decreased, the negative HF contribution K_{cf} (for details see [5]) to the total NMR shift increases in its absolute value following to the universal dependence $K_{cf}(T) = K_{cf}(0)\{(1 - T/T^*)\lg(T/T^*)\}$ [10]. The maximum in $^{69}K(T)$ dependence originates in the competition between $K_{cf}(T)$

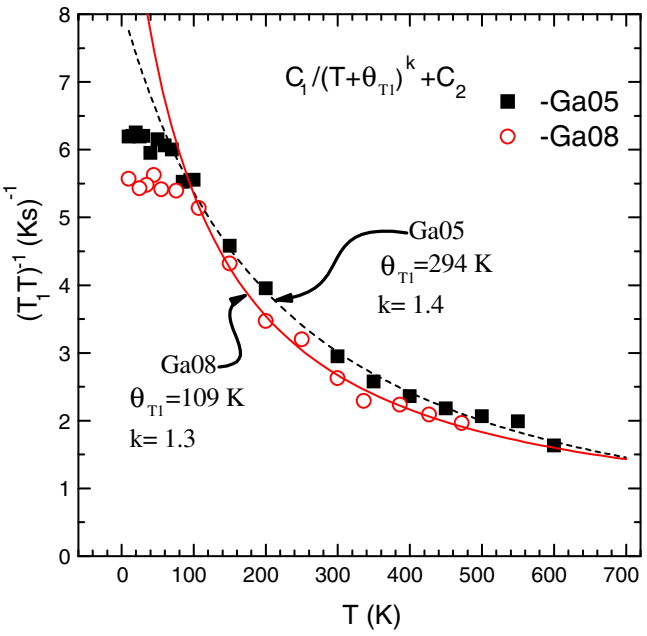

Fig. 3. Temperature dependences of $(^{69}T_1T)^{-1}$ in $Pu_{0.95}Ga_{0.05}$ (■) and $Pu_{0.92}Ga_{0.08}$ (○). Data sets are fitted with an expression $(^{69}T_1T)^{-1} = C_1/(T+\theta_{T_1})^k + C_2$.

and $K_f(T)$. A comparison of the ^{69}Ga NMR shifts temperature behavior in Ga05 and Ga08 alloys allows us to argue that forming of the coherent state of a heavy-fermion liquid in Ga08 takes place at higher temperature than in Ga05. It may be attributed to known shortening the interatomic distance Pu–Pu with Ga concentration increasing in the Pu–Ga alloys. Another possible reason is that the concentration equaled to 8 at.% Ga corresponds to one gallium atom for every 12 nearest plutonium atoms, e.g. each plutonium feels at least one gallium. In this connection, NMR experiments under high hydrostatic pressure allowing to vary Pu–Pu bonding without any change of Ga concentration in an alloy are the primary concern of today.

To elucidate peculiarities in the low-frequency spin dynamic of electrons in Ga-stabilized δ-Pu we have measured the temperature dependence nuclear spin-lattice relaxation (NSLR) rate $^{69}T_1^{-1}$ (Fig. 3). It was cleared up before [4,6] that NSLR in Ga05 was determined by time-dependent local field at the Ga sites created by spin fluctuations of the f-electrons via the RKKY interaction rather than the Fermi-contact interaction of nuclear spin with conducting electrons (Korringa contribution). Furthermore, the temperature dependence of the value $(T_1T)^{-1}$ at $T > 100$ K is close to the power–law curve $(T_1T)^{-1} \propto (T+\theta_{T_1})^{-1.5}$ observed in 3D nonmagnetic Kondo lattice, where the localized electron spins fluctuate without any macroscopic coherence and keeping themselves only the short-range spin correlations with $\omega_{sf} \sim T^{0.5}$ [12].

As the temperature is lowered $(T_1T)^{-1}$ becomes temperature independent indicating that the regime of spin fluctuations for f-electrons in the δ-Pu alloy is drastically changed. The relation $(T_1T) \approx$ constant is considered as a signature of the fermi-liquid state for electron in metallic compounds. The NSLR data confirm the conclusion that coherent state of a heavy-fermion liquid emerges in Ga08 at higher temperature than in Ga05.

In summary, the NMR parameters of ^{69}Ga measured in the present work on the fresh $Pu_{0.92}Ga_{0.08}$ alloy show nearly the same features that those in the aged $Pu_{0.95}Ga_{0.05}$ alloy. This is evidence that the revealed abnormal behavior of the static spin susceptibility and nuclear spin-lattice relaxation in Ga05 и Ga08 is the inherent property of a Ga-stabilized δ-Pu and it does not depend on alloy prehistory. The most pronounced of those peculiarities are the following. The temperature dependence of the spin susceptibility χ_s is nonmonotonic obeying the Curie–Weiss law at high temperature and displaying the broad maximum around $T \sim 150$ K. At the high temperature ($T > 100$ K) the product (T_1T) obey the power–law $(T_1T) \propto (T+\theta_{T_1})^{1.5}$ and becomes constant at low temperature. These features suggest that δ-Pu alloys $Pu_{1-x}Ga_x$ at $T > 200$ K belongs to the nonmagnetic Kondo lattice in which the incoherent regime of spin fluctuations for localized f-electrons is realized. Below 200 K the coherent state of a heavy-fermion liquid is formed, this state emerges in $Pu_{0.92}Ga_{0.08}$ at a little bit higher temperature (T^* (Ga08) = 250 K), than in $Pu_{0.95}Ga_{0.05}$.

Acknowledgments

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