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Magnetic state of f electrons in δ-phase of Pu–Ga alloys studied by Ga NMR

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Abstract

^{69}Ga nuclear magnetic resonance (NMR) line shift (^{69}K) and nuclear spin–lattice relaxation rate ($^{69}T_1{}^{-1}$) are measured for $Pu_{0.95}Ga_{0.05}$ alloy, stabilized in δ-phase, in the temperature range 10 and 650 K at magnetic field of 9.4 T. The shift and $^{69}T_1{}^{-1}$ are determined correspondingly by the static and fluctuating-in-time 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 $T > 200$ K, the temperature dependent part of the shift $^{69}K(T)$ scales macroscopic magnetic susceptibility $\chi(T)$, following the Curie–Weiss law, and the product ($^{69}T_1T$) increases with temperature proportionally $(T + 255)^{1.5(1)}$. Both of the NMR observations are typical of the incoherent spin fluctuation regime of f electrons in nonmagnetic 3D Kondo lattice. An estimate of the effective magnetic moment $\mu_{\mathrm{eff,5f}}(g_e = 2) = 0.15(5)\mu_B$ per Pu atom points out a strong suppression of the spin magnetism in the alloy.

Keywords: Actinide alloys; Electronic properties; Spin dynamics; Nuclear resonances

The rich phase diagram of plutonium [1] presents six polymorphous transitions. The unique structural, transport and magnetic properties are determined by the degree of itinerancy for 5f electrons in each of the Pu allotropes. Many efforts are undertaken to elucidate the ground state of the f electron system in δ-Pu, in the stabilized δ-phase alloys, and magnetic state of f electrons in δ-Pu is a problem of real challenge in the fundamental physics of actinides. The very narrow ($\Delta W \sim 700$ K) peak, observed in density of states near the Fermi energy [2], the large value of the Sommerfeld coefficient ($\gamma_{\mathrm{el}} \approx 60$ mJ K^{-2} mol^{-1}) [3] indicate, that an effective mass of carriers in conducting band is greatly increased at low temperature in this material. In addition, an abnormal temperature dependence of static spin susceptibility χ_s, displayed by ^{69}Ga NMR shift [4], and magnetic instability, arisen due to self-damage in δ-Pu alloy at low temperature [5], suggest to consider this material approaching in electronic properties to the heavy-fermion compounds.

The NMR technique is an appropriate local tool for studying the peculiar electron instability, emerging with temperature in the stabilized δ-phase plutonium alloys. From ^{27}Al [6] and ^{69,71}Ga [4,7] NMR studies, it was found that magnetic part of the NMR line shift (the Knight shift, K) and the nuclear spin–lattice relaxation rate ($T_1{}^{-1}$) are determined by local magnetic fields that arise at the NMR probe nucleus due to the spin polarization transferred from the f electron shells of the neighboring Pu. 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 $T \sim 150$ K [4]. Its temperature-reversible behavior points out that, as T decreases, the electron spectrum of the δ-phase develops an instability, which is accompanied by a decrease in the spin contributions to the susceptibility of the alloy below 150 K. However, the NMR data obtained in the limited temperature interval 5–350 K [4] were insufficient to clear up the magnetic state of f electrons in the high-temperature region.

In this report the temperature dependence of spin susceptibility and spin dynamics of f electrons are discussed on the basis of the ^{69}Ga NMR and static magnetic susceptibility measurements performed in a wide temperature range for the $Pu_{0.95}Ga_{0.05}$ alloy, stabilized in δ-phase. The ^{69}Ga NMR measurements were

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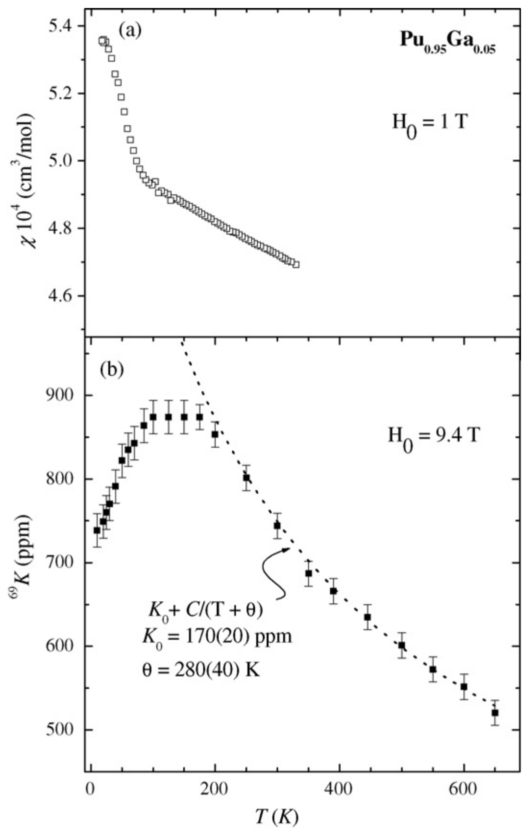

Fig. 1. Magnetic susceptibility (a) and Ga NMR shift (b) vs. T in $Pu_{0.95}Ga_{0.05}$ alloy.

performed in the temperature range (10–650) K at magnetic field $H_0 = 94$ kOe using a sample of alloy, prepared as a set of electrochemically polished plates ∼200 μm in thickness. The details of the NMR technique and sample preparation are described in Ref. [8]. The macroscopic magnetic susceptibility $\chi(T)$ was measured in 10–350 K temperature range and $H_0 = 10$ kOe. The macroscopic magnetic susceptibility $\chi(T)$ was measured in 10–350 K temperature range and $H_0 = 10$ kOe. These measurements allow us to estimate the spin contribution of f electrons to static magnetic susceptibility of the alloy and to clear up their magnetic state in the high-temperature region as an incoherent regime of spin fluctuation, observed in the nonmagnetic 3D Kondo lattice.

The temperature dependence of the NMR line magnetic shift $^{69}K(T)$ measured in $Pu_{0.95}Ga_{0.05}$ alloy is shown in Fig. 1b. At $T > 200$ K, the $^{69}K(T)$ data set is well fitted with an expression in the form of the Curie–Weiss law: $K(T) = K_0 + C/(T + \theta)$ with the parameters $K_0 = 170(20)$ ppm and $\theta = 280(40)$ K. The corresponding fitting curve is drawn by dotted line in Fig. 1b.

It was shown [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 $\mathbf{I}$ with its electron environment. The contact Fermi interaction with the electrons of the conduction band $\gamma\hbar A\mathbf{I}\mathbf{S}^c$ forms a temperature-independent contribution $K_{s,0}$. An additional uniform spin polarization of conduction electrons due to indirect electron–nucleus interactions $\gamma\hbar \mathbf{I}(r_i) B S^f(r_j)$ 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

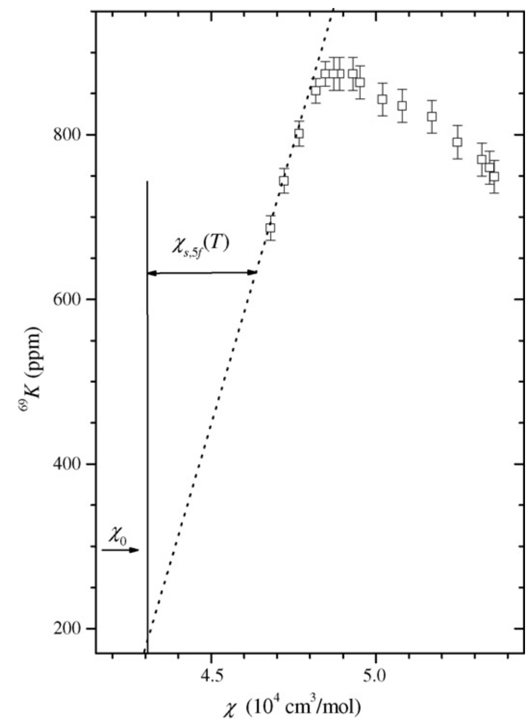

Fig. 2. Parametric dependence $^{69}K(\chi)$ and the results of separating the contributions to the spin susceptibility of the $Pu_{0.95}Ga_{0.05}$ alloy. The dotted line shows the linear fit of $^{69}K(\chi)$ data, measured in the T-range (200–350) K.

shift:

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

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, the constant A characterizes the Ga on-site contact hyperfine coupling, N_A is the Avogadro number, and $\chi_{s,5f}$ is the molar spin susceptibility of 5f electrons of Pu in the alloy. It is necessary to note here, that at the nominal concentration of gallium, $C_{Ga} = 0.05$, more than half plutonium atoms in the alloy contribute to the second term in Eq. (1). For the high-temperature region one should expect, that magnetic shift of the ^{69}Ga NMR traces variation with temperature of macroscopic spin susceptibility: $^{69}K_s(T) \sim \chi_{s,5f}(T)$. As shown in [9], macroscopic magnetic susceptibility of the alloy does not depend on external magnetic field reflecting the bulk properties of the material. Above 200 K its slight decrease with temperature increasing (Fig. 1a) is consistent with negative slope $(\Delta\chi/\Delta T)$ <0 observed in $\chi_{s,5f}(T)$ for $Pu_{0.94}Ga_{0.06}$ alloy [10] with nearly the same concentration of gallium.

The linear shift increase portion observed in the parametric dependence $^{69}K(\chi)$ (Fig. 2) evidences in favor, that Eq. (1) can be applied to describe spin magnetism of 5f electrons in the alloy above 200 K. The extrapolation T to infinity gives an estimate of the temperature-dependent contribution $\chi_{s,5f}$, whose value $\sim 0.08(1)\chi$ is small and it corresponds to the effective spin magnetic moment of the f shell of a Pu atom in the alloy: $\mu_{eff,5f}(g_e = 2) = 0.15(5)\mu_B$. It follows from the estimated $\chi_{s,5f}$, that above 200 K the dominant contribution to macroscopic magnetic susceptibility is determined by the orbital state of f electrons in the alloy. The strong inequality $\chi_{s,5f} \ll \chi$ gives a constraint for possible f shell configurations of actinide in δ-Pu. In particular, the Ga NMR results are not consistent with a scenario of the atomic-like f^5 configuration [11], where a nearly complete compensation of the large spin and orbital contributions to magnetism in δ-Pu is expected. We note also, that an idea to treat the temperature dependence of $\chi_{s,5f}$ (T) in terms of the narrow band effects [12] is hard to perform for strong T-dependence of $^{69}K_s(T)$. An appropriate fitting curve presumes the DOS peak with a width $\Delta W \sim 100$ K, that is much narrower than the observed in the spectrum of photoemission for the Ga-stabilized δ-Pu alloy [2].

The relation $K(T) \sim \chi(T)$ is broken with decreasing temperature below $T^* \sim 200$ K. A similar breakdown of the proportionality between $K(T)$ and $\chi(T)$ occurs at low temperature in many metallic compounds, demonstrating the heavy-fermion (HF) behavior, and this phenomenon is considered to occur at the expense of the f electron system [13].

Recently [8], we have discussed the difference between the $^{69}K(T)$ and $\chi(T)$ dependences, observed in the $Pu_{0.95}Ga_{0.05}$ alloy below T^*, in the frame of the two-fluid description of Kondo lattices developed by Pines and co-workers [14]. There were suggested, that the energy scale T^* is of a multiparticle character and is determined by the intensity of interaction between Kondo centers. According to the proposed two-fluid description of concentrated Kondo lattices, at temperatures $T < T^*$, the system of localized f electrons $(\boldsymbol{S}^f(r_i))$ and conduction electrons $(\boldsymbol{S}^c(r_i))$ with a total spin $\boldsymbol{S} = \sum_i \boldsymbol{S}^f(r_i) + \sum_i \boldsymbol{S}^c(r_i)$ acquires an additional spin component associated with the coherent behavior f electrons below T^*. An additional contribution to macroscopic spin susceptibility of the emergent heavy-fermion component $\chi_{cf}(T) = (1/N)\sum_{i,j}\langle \boldsymbol{S}^f(r_i)\boldsymbol{S}^c(r_j)\rangle$ follows the universal dependence $\chi_{cf}(T) \sim (1 - T/T^*)\log(T/T^*)$, where the factor $(1 - T/T^*)$ determines the fraction of the HF component of f electrons.

It is shown in Ref. [13], that corresponding HF contribution to the total Knight shift $K_{cf}(T) \sim \chi_{cf}(T)$ can be visualized taking into account experimental data on $K(T)$ and macroscopic magnetic susceptibility. By addressing for details to Ref. [8], we reproduce in Fig. 3 the $K_{cf}(T)$ results, obtained for $Pu_{0.95}Ga_{0.05}$ with the use of experimental data on $^{69}K(T)$ and $\chi(T)$ presented in Fig. 1. Solid line is the fitting curve $K_{cf}(0)\{(1-T/T^*)\log(T/T^*)\}$, that with parameters $K_{cf}(0) = -950(80)$ ppm and $T^* = 235(40)$ K reproduces the $K_{cf}(T)$ results over change T/T^* on the order of magnitude.

We should note, that the tendency of $K_{cf}(T)$ to flatten out at $T < 30$ K may be reasoned in an additional upturn, observed in $\chi(T, H_0 = 10\,\text{kOe})$ data below 75 K. The results of magnetization measurement, reported in Ref. [9], incline us to attribute this $\chi(T)$-upturn to a precursor phenomenon of the static magnetic ordering, occurring in our sample of $Pu_{0.95}Ga_{0.05}$ alloy below 10 K and $H_0 \leq 10$ kOe.

Now we draw attention to the ^{69}Ga nuclear spin–lattice relaxation time (T_1) probing the low-frequency spin dynamics of f electrons in $Pu_{0.95}Ga_{0.05}$ alloy (δ-Pu phase). The measurements were performed in magnetic field 94 kOe and the temperature range (10–650) K. Assuming the *scenario of completely itinerant* f *electrons*, we should expect the temperature dependence of the product $(T_1T) \sim K_s^{-2}$, that predicts steeper rise of (T_1T) with T than it follows from the experimental data set shown in Fig. 4. The corresponding power-law fit curve $(T_1T) \sim (T + \theta_{T1})^{1.5(1)}$ with $\theta_{T1} = 255(20)$ K is mapped by grey curve in Fig. 4.

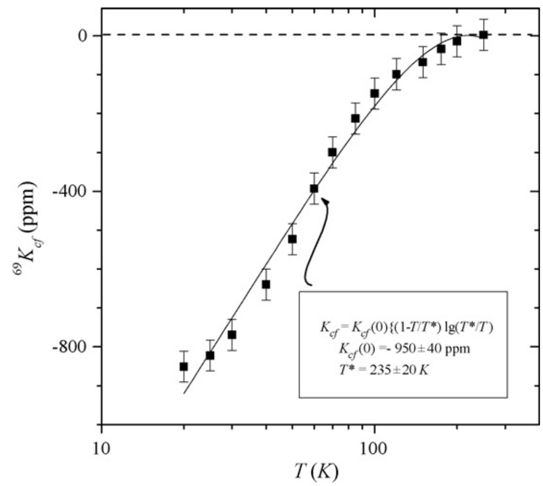

Fig. 3. The coherent HF component of the Knight shift vs. T in T in $Pu_{0.95}Ga_{0.05}$ alloy. The black curve is a fit with the expression $K_{cf}(T) = K_{cf}(0)\{(1 - T/T^*)\log(T/T^*)\}$ according Ref. [13] at $K_{cf}(0) = -950(80)$ ppm and $T^* = 235(40)$ K.

In the more general *case of partially localized behavior of* f *electrons* the nuclear spin–lattice relaxation rate is defined usually in terms of the q-weighted imaginary part of the dynamic spin susceptibility $\chi''(q, \omega \approx \omega_{NMR})$:

$$(T_1T)^{-1} \propto \sum_q H_f^2(q)\frac{\chi''_{s,5f}(q, \omega_{NMR})}{\omega_{NMR}}. \quad (2)$$

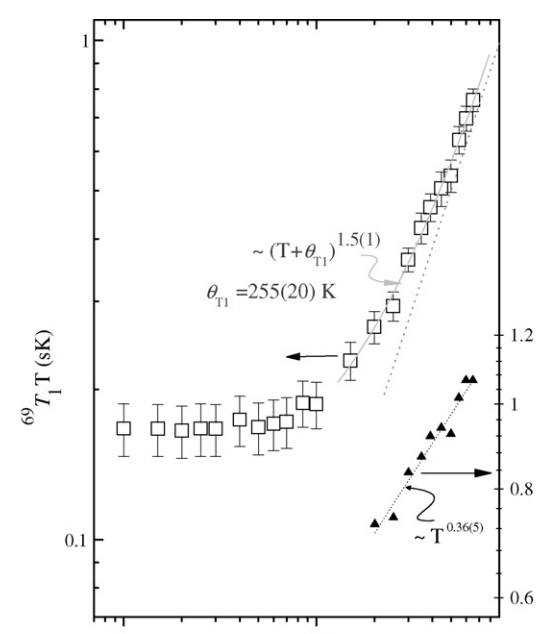

Fig. 4. The product $^{69}T_1T$ and Γ_f vs. T in $Pu_{0.95}Ga_{0.05}$.

Here $H_f(q)$ is a hyperfine coupling form-factor, determining hyperfine magnetic field at the Ga nuclei from 5f electrons of Pu. At high temperature range we can ignore both the spin correlations among f electrons and the q-dependence of $\chi_{s,5f}$. Then the expression (2) can be reduced to the following proportionality: $(T_1T)^{-1} \sim zH_f^2\chi_{s,5f}(T)/\Gamma_f(T)$, where z is a number of the nearest neighbors of Pu around ^{69}Ga, $\chi_{s,5f}(T) = \mu_B K_s(T)/zH_f$ is a static spin susceptibility of f electrons. So that for independently 3D-fluctuating moments coupled through conducting electrons the characteristic energy of f spin fluctuations $\Gamma_f(T)$ follows to the NMR product (T_1TK_s). The variation with T of $\Gamma_f(T)$ in the $Pu_{0.95}Ga_{0.05}$ alloy is shown by up-triangles in Fig. 4, which for the power-law fit $\Gamma_f(T) \sim T^{0.36(5)}$ is close to the T-dependence of $\Gamma_f(T) \sim T^{0.5}$, predicted for 3D-Kondo systems at high temperature [15].

So, the temperature dependence of nuclear spin relaxation at $T > 100$ K is close to the observed in nonmagnetic Kondo lattice, where the localized electron spins fluctuate independently each other without any macroscopic coherence.

At low $T < 100$ K the product (T_1T) becomes temperature independent, signaling to drastic changes in the regime of spin fluctuations for f electrons in the δ-Pu alloy. As usually the relation $(T_1T) \approx$ constant is considered as a signature of the fermi-liquid state for electron in metallic compounds. At $T \sim 10$ K the product $(T_1T) = 0.18(2)$ sK leads to an estimate of the effective mass of carriers $m^* = 25(3)\ m_e$, that is approximately twice less of the estimate, following from the Sommerfeld coefficient in the δ-$Pu_{0.95}Al_{0.05}$ alloy [3].

In summary, the subsequent joint analysis of the static magnetic susceptibility, the Ga Knight shift, and nuclear spin–lattice relaxation rate measured in a wide range of temperature has allowed to find out the following peculiarities of the magnetic state of f electrons in the $Pu_{0.95}Ga_{0.05}$ alloy:

- The temperature dependence of spin susceptibility and spin dynamics at $T > T^*$ is typical for nonmagnetic 3D Kondo lattice, where the localized electron spins fluctuate independently each other without any macroscopic coherence.
- The spin contribution of the f electrons $\chi_{s,5f}$ to the total magnetic susceptibility is estimated as $\chi_{s,5f} \sim 0.08(1)\chi$. This estimate correspond to the localized f electrons with very small value of magnetic moment $\mu_{eff,5f}(g_e = 2) = 0.15(5)\mu_B$/at. Pu, pointing out suppression of the spin magnetism in δ-Pu. Apparently, the T-independent orbital term determines macroscopic magnetic susceptibility of the alloy.

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