The peculiarities of $\delta$-plutonium electronic structure and magnetic susceptibility

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Abstract. The calculations of electronic density of states, exchange-enhanced spin and orbital magnetic susceptibility of plutonium in its $\delta$-phase existing region are performed in terms of a generalized s(p)df-model, which enables to take the intra-site Hubbard ff-, dd-interactions and inter-site df-exchange interaction into account along with s,p,f and d-electrons band movement and orbital splitting of $f$-states. It is shown that the splitting of the electronic spectra induced by fluctuating exchange fields leads to appearing of the temperature-induced local magnetic moments, to changing of d,f-bands occupation numbers with temperature and to appearing of charge fluctuations induced by spin fluctuations. A good agreement with the experimental data on temperature dependencies of magnetic susceptibility of Pu$_{0.95}$Ga$_{0.05}$ and Pu$_{0.957}$Ga$_{0.043}$ alloys is obtained.

1. Introduction
Elucidation of the nature of plutonium and its alloys anomalous electronic properties is extremely important both from scientific and practical points of view. On the one hand it is necessary for the definition of type and concentrations of defects, which appears as a consequence of plutonium's radioactive decay. On another hand the question remains open on the fundamental difference among plutonium and other f-metals, which connected with Kondo or Kondo-like behavior of its susceptibility and resistivity [1,2].

In [3] in terms of ab initio LDA+U+SO method it is shown that magnetic moments in the case of plutonium’s ground state disappear due to strong (comparing to exchange) spin-orbit interaction. However the experiments reveal both orbital and spin magnetic susceptibility already in the low-temperature region [4,5]. In the recent article [6] in terms of combination of DMFT method and density functional theory (DFT) a transformation from Pauli-like local magnetic susceptibility to Curie-Weiss susceptibility is demonstrated. Calculated in such a framework density of states demonstrates a considerable overlap between 7/2 and 5/2 multiplets comparing to [3], while the compensation of the local magnetic moments due to spin-orbit coupling gets broken. However, in terms of this model only a qualitative agreement with experimental data can be achieved and only in the range of relatively high temperatures (T>400 K).

It is worth noting that plutonium can be attributed to the group of nearly magnetic metals, which electronic system is unstable to the formation of magnetic ordering [7]. Previously in terms of the Hubbard model for d-electrons and a generalized Hubbard sd-model [8,9] it was shown that the fluctuating inner exchange fields ($\xi_n$) which appear in nearly magnetic systems, lead to the fluctuations of charge fields ($\eta_n$) and to the splitting of electronic spectrum, which increases with increasing temperature. In the range of low temperatures exchange fields fluctuate both in direction and
magnitude (transverse and longitudinal fluctuations). For the temperatures higher than some temperature $T^*$ the longitudinal spin and charge fluctuations disappear and the transverse spin fluctuations lead to Curie-Weiss law for magnetic susceptibility, which is analogous to the picture of appearing of local magnetic moments (LMM). The last in terms of the fluctuation theory is interpreted as formation of the temperature-induced LMM.

In the present study we develop a self-consistent procedure which combines an ab initio calculation of electronic structure using LDA+U+SO method (within FP-LAPW) with model representations on spin and charge fluctuations in the d,f-electrons system. A generalized s(p)df-model is considered, where along with s,p,f and d-electrons band movement and orbital splitting of f-states the intra-site Hubbard ff-, dd-interactions and interstitial exchange df-interaction are taken into account.

2. Model description

In order to calculate the free energy and electronic densities of states we use an approach, which was previously developed in [8,9] with regard to the two band Hubbard sd-model. In the present self-consistent model calculation combined with ab initio calculation along with spin magnetic moments the orbital magnetic moments are taken into account. Therefore in the expression for magnetic susceptibility along with spin susceptibility a Van Vleck-type terms appears:

$$\chi = \chi_s + \chi_{\text{orb}}$$

(1)

Here

$$\chi_{\text{orb}} = 2\sum_{\sigma} n \left[N_f - N_s \right] \left[N_s (\Delta_s + U^{(s)} m^{(s)} (\alpha - \alpha')) \right]$$

(2)

$$\chi_s = \chi_s^{(s)} + \chi_s^{(p)} + I \chi_s^{(f)}$$

(3)

where $N_s$ is the value of orbital degeneracy of the band with an $l$ quantum number ($l=f,d$), $2n_s$ is the averaged energetic distance between multiplets (which are splitted due to coulomb and spin-orbital interaction), $U^{(l)}$ is the parameter of the Hubbard’s repulsion of electrons of the band with an $l$ quantum number, $I$ is the uniform part of the inter-site f-d exchange interaction,

$$\chi_s^{(s)} = 2g_{s}^{(s)} (\mu)$$

(4)

$$\chi_s^{(p)} = 2\left[ \frac{2}{3} \chi_s^{(s)} + \frac{1}{3} \chi_s^{(f)} \right] D^{(s)}$$

(5)

are paramagnetic susceptibilities of s,p- (4) and d,f- (5) electrons,

$$D^{(s)} = 1 - \frac{2}{3} U^{(s)} \chi_s^{(s)} - \frac{1}{3} U^{(f)} \chi_s^{(f)}$$

(6)

is the susceptibility exchange-enhancement factor of d- or f-electrons,

$$\chi_s^{(s)} = \sum_{\alpha=\pm} \alpha \left[ \frac{d e g_{s}^{(s)} (\varepsilon) f (\varepsilon - \mu - U^{(s)} \eta_s^{(s)} - \alpha U^{(s)} m^{(s)}) / (2U^{(s)} m^{(s)}) }{1 + 4 \left( f D^{(s)} / U^{(s)} U^{(s)} \right) \left( D^{(s)} - (B^{(s)} / B^{(s)}) D^{(s)} \right)} \right]$$

(7)

corresponds to the transverse, and

$$\chi_s^{(f)} = \sum_{\alpha=\pm} 2g_{s}^{(s)} (\mu + U_{\eta_s^{(s)} + \alpha U_{m_s}}) / \sum_{\alpha} g_{s}^{(s)} (\mu + U_{\eta_s^{(s)} + \alpha U_{m_s}})$$

(8)

to the longitudinal components of the paramagnetic susceptibility of non-interacting f- or d-electrons ($l=f,d$), the mean-squared amplitude of spin fluctuations (square root from the spin-spin correlator on a site) is

$$m^{(s)} = B^{(s)} (D^{(s)} / U^{(s)} T / U^{(s)}) \left\{ [1 + 4 \left( f D^{(s)} / U^{(s)} U^{(s)} \right) \left( D^{(s)} - (B^{(s)} / B^{(s)}) D^{(s)} \right)] \times \left[ 2 - (B^{(s)} / B^{(s)}) D^{(s)} \right] \left( B^{(s)} / B^{(s)} \right) D^{(s)} \right\}^{1/2}$$

(9)

$$\eta_s^{(s)} = \eta_s^{(s)} + \Delta n_s$$

$$\Delta n_s = \int \frac{d \varepsilon}{\pi} \frac{d g_{s}^{(s)} (\varepsilon) f (\varepsilon - \mu - \alpha U^{(s)} m^{(s)} + U^{(s)} \Delta n_s)}{d \varepsilon - \eta_s^{(s)}}$$

while the amplitude of the charge fluctuations is defined as follows

$$\delta \eta_{s,f} = \left( \frac{\varepsilon_s^{(s)} - (U^{(s)} m_s)}{m} \left[ \sum_{\alpha=\pm} \alpha \frac{d e g_{s}^{(s)} (\mu - U \Delta n_s + \alpha U m_s)}{\sum_{\alpha=\pm} \alpha \frac{d e g_{s}^{(s)} (\mu - U \Delta n_s + \alpha U m_s)}} \right] \right)$$

(10)
$B^{(l)}$ and $X^{(l)}$ parameters are the coefficients of the expansion of Pauli susceptibility in the effective mass approximation, $n_l(0)$ is the occupancy of electrons belonging to the band with an $l$ quantum number in the ground state, $g^{(l)}(e)$ is the uniform density of states of electrons belonging to the band with an $l$ quantum number ($l=f,d$) which is calculated using LDA+U+SO approximation (in the FP-LAPW basis). The calculation of the ground state was performed with FP-LAPW Elk code [10]. We use experimental values [11] for the lattice parameters of considered dilute alloys, a 32x32x32 k-point grid, an LSDA exchange-correlation potential as parameterized by Perdew-Wang [12] and a interpolation scheme between around mean field and fully localized limits for LDA+U calculation (see [13]). The intra-site $f$-$f$ exchange parameter $J_H$ was determined automatically by implementing method described in [10]. Other parameters of the band calculations have been checked for the stable convergence.

While performing the self-consistent calculation along with magnetic susceptibility we have defined the electronic spectra, splitting of which is accounted by the replacement $\epsilon_{k,j}^{(l)} \rightarrow \epsilon_{k,j}^{(l)} + \alpha U^{(l)}m^{(l)}(T)$. Along with this a formation of the temperature-induced local magnetic moments is observed, which is accompanied by filling of the d,f-states analogously to how it occurs in Kondo effect. The states with energy $\epsilon_{k,j}^{(l)} - U^{(l)}m^{(l)}(T)$ are filled both by states of another bands (with $l \neq l'$) and by states of the same band with energy $\epsilon_{k,j}^{(l)} + U^{(l)}m^{(l)}(T)$. Thus appearing difference of occupancies corresponds to the effective concentration of electrons in the expression for spin magnetic susceptibility, which appears due to the transverse spin fluctuations.

3. Results and discussion
The results of the calculations of temperature dependencies of magnetic susceptibility are presented in figures 1, 2. Agreement with the experimental data [1,2] is obtained by taking two different values of the Fermi energy (see figures captions) and with single values of electrons interaction: $U^{(f)}=2.67$ eV, $J_{H}=0.5$ eV (in the ab initio calculations [3], where exchange-enhancement effect is not taken into account, $U^{(f)}=2.5$ eV). The averaged distance between multiplets’ energies is $\Delta_e=2$ eV, which corresponds to the half of energy distance between centers of gravity of the bands which correspond do 5/2 and 7/2 multiplets and the value of spin-orbit coupling is 0.35 eV, as in [3]. Also while performing the self-consistent calculation of densities of states (figure 3) and of magnetic

![Figure 1](image1.png)  Figure 1. Temperature dependence of Pu$_{0.95}$Ga$_{0.05}$ alloy magnetic susceptibility: 1 – experimental data [4]; 2 – calculation in the present study using the equation (1) and the DOS (figure 3) with Fermi energy equals to $-0.02$ eV; 3 – Van Vleck contribution (calculated with (2)); 4 – spin contribution (calculated with (3))

![Figure 2](image2.png)  Figure 2. Temperature dependence of Pu$_{0.957}$Ga$_{0.043}$ alloy magnetic susceptibility: 1 – experimental data [5]; 2 – calculation in the present study using the equation (1) and the DOS (figure 3) with Fermi energy equals to 0.02 eV; 3 – Van Vleck contribution (calculated with (2)); 4 – spin contribution (calculated with (3))
susceptibility (figure 1, 2) we used the value of \( I=0.1U^f \) for the inter-site \( f\text{-}d \)-exchange interaction and the following values for imaginary part of Pauli susceptibility of non-interacting electrons: \( B^{(0)}=1 \) and \( B^{(\epsilon)}=B^{(0)}U^f g^{(\epsilon)}(\varepsilon_f)/(U^d g^{(0)}(\varepsilon_d)) \), respectively.

Additionally let us note that the orbital susceptibility renormalized by spin fluctuations accounts for somewhat greater than 70\% of the value of full magnetic susceptibility, which is in agreement with the experimental estimations [4]. Moreover, the developed model of plutonium’s electronic structure describes instability to the formation of magnetic ordering. By shifting the Fermi level to the left on energy scale by amount of 0.1 eV, we obtain a ferromagnetic solution (divergence of spin susceptibility). With temperature change in the deltha-phase existing range the factor of exchange enhancement changes from 11 to 7 for \( f \)-electrons and from 1.6 to 1.5 for \( d \)-electrons.

In the \( T>T^* \) temperature range (for Pu\(_{0.95}\)Ga\(_{0.05}\) \( T^*=200\) K and for Pu\(_{0.957}\)Ga\(_{0.043}\) \( T^*=150\) K) the spin-fluctuation renormalization of \( \delta \)-plutonium electronic spectrum leads to disappearance of longitudinal spin fluctuations (\( \chi_{//}^{(r)} \gg \chi_{\perp}^{(r)} \)) and a state with temperature-induced local spin magnetic moments appears (figure 1, 2).

The densities of states (DOS) at different temperatures are shown in figure 3. Changing of DOS with temperature leads to decrease of the averaged occupation numbers of \( f,d \)-electrons while the occupancy of sp-bands increases. For example at \( T=400 \) K we obtain \( \Delta n_f = -0.2 \) electrons/site and \( \Delta n_d = -0.013 \) electrons/site. The obtained change of valence with temperature is accompanied by charge fluctuations, specifically the maximal mean-squared value of fluctuation of on-site electrons number is \( \sqrt{\sum \delta n^2_{i_f}/N_o} \sim 0.01 \) electrons/site for \( f \)-electrons, and is smaller by an order of magnitude

Figure 3. Temperature dependence of \( \delta \)-plutonium \( f \)-electrons DOS: \( 1 \rightarrow 0 \) K, \( 2 \rightarrow 100 \) K, \( 3 \rightarrow 200 \) K, \( 4 \rightarrow 300 \) K, \( 5 \rightarrow 400 \) K; the dashed curve shows the position of chemical potential.
for d-electrons. However, the obtained changes of DOS with temperature are only in qualitative agreement with the photoemission experiments [14], because maximum of the calculated spectral function is shifted by 0.4 eV from the experimental one.

Thus when the temperature-induced LMM are emerging in δ-plutonium a temperature dependence of spin and orbital susceptibility is appeared which is consistent with the experimental data. Thus appearing temperature-dependent renormalization of the electronic DOS leads to the effects of charge fluctuations and variable valence.

Other mechanisms for LMM formation are defects and impurities. However, in the present study we discussed experimental data [4,5] on magnetic susceptibility of specimens, which have undergone a special heat processing, which eliminates defects produced by radioactive decay and leads to conserving of electrons concentration.

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