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Journal of Alloys and Compounds 444–445 (2007) 162–167

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Multipoles in δ-Pu

Takashi Hotta*

Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

Received 26 June 2006; received in revised form 8 November 2006; accepted 8 November 2006
Available online 27 December 2006

Abstract

We propose a multipole scenario to understand the absence of magnetism in δ-Pu on the basis of a microscopic model constructed from a j–j coupling scheme. In order to determine the multipole state, we employ a concept of the optimization of multipole susceptibility. By using an exact diagonalization technique for 4-site fcc lattice, we depict the phase diagram, including the states characterized by quadrupole and octupole fluctuations. We discuss the region in our phase diagram with possible relevance to the actual situation for δ-Pu.

Keywords: δ-Pu; j–j Coupling scheme; Multipole

1. Introduction

Recently plutonium and its related compounds have attracted renewed attention in the research field of strongly correlated electron systems of condensed matter physics. It has been triggered by the discovery of superconductivity in $PuCoGa_5$ with high superconducting transition temperature $T_c = 18.5\,K$ [1]. This material is considered to be a heavy-fermion superconductor, since the coefficient of electronic specific heat γ has been estimated as $\gamma = 77\,mJ/mol\,K^2$, which is moderately enhanced relative to that for normal metals. In $PuRhGa_5$, superconductivity has been also found [2]. Although the value of $T_c = 8.7\,K$ is lower than that of $PuCoGa_5$, it is still high enough in comparison with other f-electron superconductors. Recently, high quality single crystal $PuRhGa_5$ has been synthesized [3] and the Ga-NQR measurement has been performed to reveal that d-wave superconductivity is realized in $PuRhGa_5$ [4]. This is consistent with the results of $PuCoGa_5$ from the Ga-NMR measurement [5] and the μSR measurement of the temperature dependence of penetration depth [6].

Another issue is the absence of magnetism in δ-Pu, which is one of solid phases of Pu. It has been widely recognized that actinide metal crystallizes in large varieties of structures, in comparison with other elements in the periodic table. In particular, Pu metal takes a remarkably anomalous position. The thermal expansion coefficient of Pu is large compared with other actinides, and the coefficient of δ-Pu is negative. Namely, in δ-Pu, the volume is decreased with increasing temperature. Furthermore, the density is smaller than that of the liquid phase. Such peculiar behavior has been basically understood from the competition between itineracy and localization of 5f electrons of Pu. From this viewpoint, for the understanding of negative thermal expansion coefficient, the localization tendency of 5f electron should be the strongest in δ-Pu, which requires the magnetism of δ-Pu. However, from the recent μSR measurement at low temperatures in δ-Pu which is stabilized by the doping of small amount of Ga, the limit of the magnetic moment has been found to be less than $10^{-3}\mu_B$ [7]. This result does not support the magnetic phase. Note also that in neutron scattering measurements, no magnetic moment has been detected thus far [8]. The competition between electron itineracy and localization is closely related to the emergence of magnetism, but it is difficult to understand why magnetism does not appear when localization tendency becomes strong. This seems to be a basic issue in condensed matter physics.

In order to attack such a problem, it is necessary to promote a couple of theoretical researches in parallel with different viewpoints. One is the analysis of the energy-band structure and Fermi surfaces by using the band-structure calculation techniques, in order to obtain correct information about the electronic properties around the Fermi energy. Another is the research from a viewpoint of strongly correlated electron systems. Namely, on the basis of a simplified electron model which reproduces the energy-band structure around the Fermi energy, we attempt to

* Tel.: +81 29 284 3521; fax: +81 29 282 5939.
E-mail address: hotta.takashi@jaea.go.jp (T. Hotta).

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doi:10.1016/j.jallcom.2006.11.028

include the effect of electron correlation. These two types of researches are complementary to each other to make significant progress in our understandings on novel magnetism and exotic superconductivity of actinide compounds. However, theoretical activities on Pu were limited in the sense that band-structure calculations and related techniques have been the main tools for the research of Pu and related materials. It is still important to improve the band-structure calculations, but we should make more effort to consider the problem also from the viewpoint of strongly correlated electron systems.

In this paper, we report our first trial to understand the absence of magnetism in δ-Pu by analyzing a multiorbital Hubbard-like model on an fcc lattice composed of Pu^{3+} ions on the basis of a *j–j* coupling scheme. When we depict the phase diagram for the multipole state on the plane of the Hund's rule interaction and the crystalline electric field (CEF) potential, the non-magnetic quadrupole state is found to exist next to the magnetic phase. We discuss possible relevance of the present result to the actual situation in δ-Pu.

2. Model Hamiltonian

First we briefly discuss the valence of Pu in the δ-phase. The LDA+U calculation suggested $5f^5$ electron state [9]. The analysis of the mixed-level model also suggested $5f^5$ configuration [10], but four electrons are in a localized multiple hybridizing with valence states, while one 5f electron forms a delocalized band state [11]. On the other hand, in the calculation of the LDA+U with spin–orbit coupling λ, δ-Pu phase had a non-magnetic ground state with Pu ion in f^6 configuration [12]. The LDA+U in combination with the mean-field theory indicated $n = 5.44$ [13], where n denotes the average f-electron number per site. It is difficult to conclude the exact valence of Pu, but the tendency of magnetism should be strong for $n = 5$ in comparison with the case of $n = 6$. It is considered to be a challenging problem to explain the absence of magnetism even for $n = 5$. Thus, in this paper, we consider the model for Pu^{3+} ions in an fcc lattice.

Next let us discuss the picture to describe the 5f-electron state. For the purpose, it is useful to refer the result on $PuIn_3$, which is a paramagnet with enhanced specific heat coefficient $\gamma \sim 100\,\mathrm{mJ/mol\,K^2}$. Recently, Haga et al. have grown single crystal of $PuIn_3$ and succeeded in the observation of de Haas-van Alphen (dHvA) signals [14]. The detected dHvA branch corresponds to a closed electron Fermi surface in good agreement with the theoretical result of the relativistic band-structure calculation on the basis of the itinerant 5f-electron states. Then, we take the itinerant picture for 5f electrons in this paper, but we do not intend to exclude the localized picture, since our purpose here is to provide an alternative scenario for the absence of magnetism in δ-Pu. The actual situation should be located in the middle of itinerant and localized pictures and there exist two routes to arrive at the actual situation from itinerant and localized sides, depending on the description of the 5f-electron states. We believe that the approach from the itinerant picture is complementary to previous scenarios on the basis of the localized picture for 5f electrons.

There are two typical approaches to consider f^n-electron state, LS and *j–j* coupling schemes. Since the f^n-electron state in the LS coupling scheme is continuously connected to that in the *j–j* coupling scheme [15,16], we can take one of them depending on the nature of the problem. In order to consider the problem from the itinerant side, we prefer to use the *j–j* coupling scheme [17]. Since individual f-electron states are first defined, we can include many-body effects using standard quantum-field theoretical techniques. In contrast, in the LS coupling scheme we cannot use such standard techniques, since Wick's theorem does not hold. Of course, when we consider the problem from the localized picture, the LS coupling scheme is useful.

By following the method to construct the f-electron Hamiltonian H on the basis of the *j–j* coupling scheme in Ref. [17], we obtain H as

$$H = \sum_{\mathbf{i},\mathbf{a},\mu,\nu} t^{\mathbf{a}}_{\mu\nu} f^{\dagger}_{\mathbf{i}\mu} f_{\mathbf{i}+\mathbf{a}\nu} + \sum_{\mathbf{i},\mu,\nu} B_{\mu\nu} f^{\dagger}_{\mathbf{i}\mu} f_{\mathbf{i}\nu} + \frac{1}{2} \sum_{\mathbf{i},\mu,\nu,\mu',\nu'} I_{\mu,\nu;\nu',\mu'} f^{\dagger}_{\mathbf{i}\mu} f^{\dagger}_{\mathbf{i}\nu} f_{\mathbf{i}\nu'} f_{\mathbf{i}\mu'}, \quad (1)$$

where $f_{\mathbf{i}\mu}$ is the annihilation operator for f electron with the z-component μ of total angular momentum $j = 5/2$ at a site $\mathbf{i}$ and $t^{\mathbf{a}}_{\mu\nu}$ is the overlap integral between the μ- and ν-states connected by a vector $\mathbf{a}$. For simplicity, here we consider only the $(ff\sigma)$ bond and the hopping amplitude t is defined by $t = 3(ff\sigma)/56$. The explicit expressions of $t^{\mathbf{a}}_{\mu\nu}$ for arbitrary direction are shown in Ref. [17]. The bandwidth W is given by $W = (50 + 2\sqrt{145})t \approx 74t$.

The second term denotes the one-electron CEF potential part. For the fcc lattice of Pu^{3+} with cubic symmetry, we obtain Γ_7 doublet and Γ_8 quartet. Then, we introduce the level splitting Δ between Γ_7 and Γ_8 states. By using Δ, we express $B_{\mu\nu}$ as $B_{\pm5/2,\pm5/2} = \Delta/6$, $B_{\pm3/2,\pm3/2} = -\Delta/2$, $B_{\pm1/2,\pm1/2}=\Delta/3$, $B_{\pm5/2,\mp3/2} = B_{\mp3/2,\pm5/2} = \sqrt{5}\Delta/6$, and zero for other μ and ν. Note that for $n = 5$, the ground state is Γ_8 for $\Delta > 0$, while Γ_7 for $\Delta < 0$ in the *j–j* coupling scheme, since we simply accommodate electrons in the one-electron levels.

The last term in Eq. (1) indicates the Coulomb interaction part and I is the Coulomb integral expressed by using three Racah parameters, E_0, E_1, and E_2 [17]. Among the Racah parameters, E_2 plays a key role of the Hund's rule interaction, which is important to determine the electron state.

3. Multipole susceptibility

In order to clarify the magnetic properties at low temperatures, we usually discuss the magnetic susceptibility, but in more general, we should consider the susceptibility of multipole moments such as dipole, quadrupole, and octupole. The multipole operator is given in the second-quantized form as

$$X_{\mathbf{i}\gamma} = \sum_{\mu,\nu} (X_\gamma)_{\mu\nu} f^{\dagger}_{\mathbf{i}\mu} f_{\mathbf{i}\nu}, \quad (2)$$

where X denotes the symbol of multipole with the symmetry of Γ_γ and γ indicates a set of indices for the irreducible representation. In this paper, we consider the multipoles up to rank 3.