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Multipoles in δ-Pu

Takashi Hotta*

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

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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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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.

As for dipole moments with Γ_{4u} symmetry, where "u" indicates ungerade, we express the matrices as

$$J_{4ux} = J_x,\ J_{4uy} = J_y,\ J_{4uz} = J_z, \tag{3}$$

where J_x, J_y, and J_z denote three angular momentum operators for $j = 5/2$. Quadrupole moments are classified into Γ_{3g} and Γ_{5g}, where "g" indicates gerade. Γ_{3g} quadrupole operators are given by

$$O_{3gu} = \frac{(2J_z^2 - J_x^2 - J_y^2)}{2}, \quad O_{3gv} = \frac{\sqrt{3}(J_x^2 - J_y^2)}{2}. \tag{4}$$

For Γ_{5g} quadrupole, we have three operators as

$$O_{5g\xi} = \frac{\sqrt{3}\overline{J_yJ_z}}{2}, \quad O_{5g\eta} = \frac{\sqrt{3}\overline{J_zJ_x}}{2}, \quad O_{5g\zeta} = \frac{\sqrt{3}\overline{J_xJ_y}}{2}, \tag{5}$$

where the bar denotes the operation to take all possible permutations in terms of Cartesian components.

Regarding octupole moments, there are three types as Γ_{2u}, Γ_{4u}, and Γ_{5u}. Among them, Γ_{2u} octupole is given by

$$T_{2u} = \frac{\sqrt{15}\overline{J_xJ_yJ_z}}{6}. \tag{6}$$

Γ_{4u} octupole operators are written as

$$T_{4ux} = \frac{(2J_x^3 - \overline{J_xJ_y^2} - \overline{J_xJ_z^2})}{2},$$
$$T_{4uy} = \frac{(2J_y^3 - \overline{J_yJ_z^2} - \overline{J_yJ_x^2})}{2},$$
$$T_{4uz} = \frac{(2J_z^3 - \overline{J_zJ_x^2} - \overline{J_zJ_y^2})}{2}, \tag{7}$$

while Γ_{5u} octupole operators are give by

$$T_{5ux} = \frac{\sqrt{15}(\overline{J_xJ_y^2} - \overline{J_xJ_z^2})}{6}, \quad T_{5uy} = \frac{\sqrt{15}(\overline{J_yJ_z^2} - \overline{J_yJ_x^2})}{6},$$
$$T_{5uz} = \frac{\sqrt{15}(\overline{J_zJ_x^2} - \overline{J_zJ_y^2})}{6}. \tag{8}$$

We redefine the multipole moments so as to satisfy the orthonormal condition $\mathrm{Tr}(X_\gamma X_{\gamma'}) = \delta_{\gamma\gamma'}$ [18], where $\delta_{\gamma\gamma'}$ is the Kronecker's delta.

In principle, the multipole susceptibility can be evaluated in the linear response theory [19], but in order to determine the multipole state, it is necessary to maximize the multipole susceptibility. Namely, we define the multipole operator as

$$M_{\boldsymbol{q}} = \sum_\gamma p_{\boldsymbol{q}\gamma} X_{\boldsymbol{q}\gamma}, \tag{9}$$

where $\boldsymbol{q}$ is the momentum and $X_{\boldsymbol{q}\gamma}$ is the Fourier transform of $X_{\mathbf{i}\gamma}$ in Eq. (2). Then, the coefficient $p_{\boldsymbol{q}\gamma}$ is determined by the eigenstate with the maximum eigenvalue of the susceptibility matrix, given by

$$\chi_{\gamma\gamma'}(\boldsymbol{q}) = \frac{1}{N}\sum_{\mathbf{i},\mathbf{i}'} \mathrm{e}^{-i\boldsymbol{q}\cdot(\mathbf{R_i}-\mathbf{R_{i'}})} \times \int_0^{1/T} \mathrm{d}\tau \frac{\mathrm{Tr}\{\mathrm{e}^{-H/T} X_{\mathbf{i}\gamma}(\tau) X_{\mathbf{i}'\gamma'}\}}{Z}, \tag{10}$$

where N is the number of sites, T the temperature, $\mathbf{R_i}$ denotes the position of site $\mathbf{i}$, $X_{\mathbf{i}\gamma}(\tau) = \mathrm{e}^{H\tau} X_{\mathbf{i}\gamma}\,\mathrm{e}^{-H\tau}$, and Z is the partition function.

Since the present model is the many-body Hamiltonian in three-dimensional (3D) environment, in any case, it is necessary to resort to an approximation to analyze it. Basically, there are two types of approaches for the problem. One is the mean-field-based technique, in which correlation effect is taken into account in the mean-field level, while the size of the system can be large enough to evaluate the physical quantities in the thermodynamic limit. Another is the exact-diagonalization-based method, in which electron correlation is treated exactly, but the system size is very limited. These two methods are complementary to each other.

In this paper, we prefer to use the exact diagonalization approach. Since the fcc lattice includes geometrical frustration, we may arrive at a conclusion irrelevant to actual phenomena, when we apply first the mean-field approximation to the problem concerning magnetism without any guidance. It is meaningful to employ an unbiased technique such as the exact diagonalization to consider the problem of the absence of magnetism in δ-Pu.

Here we note that each site includes three orbitals. Since it is necessary to keep numerous numbers of eigenstates to evaluate the multipole susceptibility, 4-site cluster is almost the limitation to run the code of the exact diagonalization method in our computational resources. Then, we take a tetrapod as the minimal cluster for the fcc lattice, as shown in Fig. 1. Although it is very difficult to conclude the ordered state from the calculations for such a small-sized cluster, it is possible to determine the dominant multipole fluctuation. The phase with strong fluctuations may grow into the long-range order, but this point will be examined by mean-field-based calculations. It is one of future tasks.

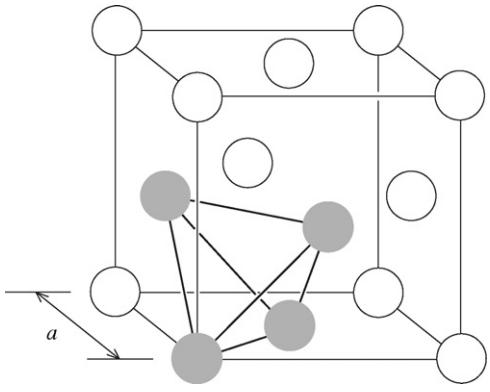

Fig. 1. A view of the fcc lattice with a lattice constant a. We consider that Pu^{3+} is placed at each site. Shaded spheres compose a tetrapod.

4. Result

After repeating numerical calculations of the multipole susceptibility, we depict the phase diagram for the 4-site fcc system in the plane of level splitting Δ and one of Racah parameters E_2, as shown in Fig. 2. Other parameters are set as $T = 10^{-8}$, $t = 10^{-3}$, $E_0 = 5$, and $E_1 = 2$ in the unit of eV. We fix $n = 5$ throughout the calculation. Each phase is determined by the multipole state which maximizes the multipole susceptibility.

First let us see the region of $\Delta > 0$ with Γ_8 quartet ground state for $n = 5$. Since Γ_8 quartet brings several types of multipoles, it may be easy to imagine the appearance of the phase with dominant multipole fluctuations. For $E_2 < 0.145$, we find the phase characterized by antiferro octupole (AFO) fluctuation, in which the optimized multipole is found to be

$$M_{\boldsymbol{q}} = T_{\boldsymbol{q}2\mathrm{u}}, \tag{11}$$

for $\boldsymbol{q} = (1, 0, 0)$, (0, 1, 0), and (0, 0, 1) in the unit of $2\pi/a$. When we increase E_2, the phase turns to be dominated by antiferro quadrupole (AFQ) fluctuations. The optimized multipole is given by

$$M_{\boldsymbol{q}} = -\left(\frac{\sqrt{3}}{2}\right) O_{\boldsymbol{q}3\mathrm{g}u} - \frac{O_{\boldsymbol{q}3\mathrm{g}v}}{2}, \tag{12}$$

for $\boldsymbol{q} = (1, 0, 0)$,

$$M_{\boldsymbol{q}} = \left(\frac{\sqrt{3}}{2}\right) O_{\boldsymbol{q}3\mathrm{g}u} - \frac{O_{\boldsymbol{q}3\mathrm{g}v}}{2}, \tag{13}$$

for $\boldsymbol{q} = (0, 1, 0)$, and

$$M_{\boldsymbol{q}} = O_{\boldsymbol{q}3\mathrm{g}v}, \tag{14}$$

for $\boldsymbol{q} = (0, 0, 1)$. Note that the quadrupole moment extends in the plane perpendicular to the momentum $\boldsymbol{q}$, i.e., $J_y^2 - J_z^2$ for $\boldsymbol{q} = (1, 0, 0)$, $J_z^2 - J_x^2$ for $\boldsymbol{q} = (0, 1, 0)$, and $J_x^2 - J_y^2$ for $\boldsymbol{q} = (0, 0, 1)$.

For $\Delta \approx 0$, we find a narrow phase characterized by antiferro magnetic (AFM) fluctuations. It seems natural that the magnetic phase appears in the orbital degenerate region, when we increase the Hund's rule interaction which stabilizes the local magnetic moment. The optimized magnetic moments are found to be longitudinal, given by

$$M_{\boldsymbol{q}} = \alpha J_{\boldsymbol{q}4\mathrm{u}x} + \beta T_{\boldsymbol{q}4\mathrm{u}x}, \tag{15}$$

for $\boldsymbol{q} = (1, 0, 0)$,

$$M_{\boldsymbol{q}} = \alpha J_{\boldsymbol{q}4\mathrm{u}y} + \beta T_{\boldsymbol{q}4\mathrm{u}y}, \tag{16}$$

for $\boldsymbol{q} = (0, 1, 0)$, and

$$M_{\boldsymbol{q}} = \alpha J_{\boldsymbol{q}4\mathrm{u}z} + \beta T_{\boldsymbol{q}4\mathrm{u}z}, \tag{17}$$

for $\boldsymbol{q} = (0, 0, 1)$. Thus, we call this phase "l-AFM". Note that the coefficients α and β depend on parameters, but they change in the ranges of $\alpha = 0.8$–0.97 and $\beta = 0.6$–0.25. We find that α increases with increasing E_2, while it decreases with increasing Δ.

Now we turn out attention to the region of $\Delta < 0$, where the ground state for $n = 5$ is Γ_7 doublet which brings only magnetic moment. Thus, we naively expect the appearance of the magnetic phase, but as observed in Fig. 2, there exists a wide region of the phase characterized by ferro quadrupole (FQ) fluctuations from excited Γ_8 near the degenerate region for negative values of Δ. The optimized multipoles are doubly degenerate, given by

$$M_{\boldsymbol{q}} = O_{\boldsymbol{q}3\mathrm{g}u},\ O_{\boldsymbol{q}3\mathrm{g}v}, \tag{18}$$

for $\boldsymbol{q} = (0, 0, 0)$. Here we note that $O_{3\mathrm{g}}$ quadrupoles indicate orbital degrees of freedom in the Γ_8 state. In general, orbitals tend to arrange themselves so as to gain the kinetic energy [20], but in 3D environment, ferro orbital order does not easily occur, since the optimal shape of the orbital cannot be determined only from the viewpoint of kinetic energy. Then, orbital (quadrupole) fluctuations significantly remain.

For large negative Δ, we expectedly find the region with AFM fluctuations. Except for a narrow region near $E_2 = 0$, the magnetic moments of the phase become transverse, given by

$$M_{\boldsymbol{q}} = \alpha' J_{\boldsymbol{q}4\mathrm{u}y} + \beta' T_{\boldsymbol{q}4\mathrm{u}y},\ \alpha' J_{\boldsymbol{q}4\mathrm{u}z} + \beta' T_{\boldsymbol{q}4\mathrm{u}z}, \tag{19}$$

for $\boldsymbol{q} = (1, 0, 0)$,

$$M_{\boldsymbol{q}} = \alpha' J_{\boldsymbol{q}4\mathrm{u}z} + \beta' T_{\boldsymbol{q}4\mathrm{u}z},\ \alpha' J_{\boldsymbol{q}4\mathrm{u}x} + \beta' T_{\boldsymbol{q}4\mathrm{u}x}, \tag{20}$$

for $\boldsymbol{q} = (0, 1, 0)$, and

$$M_{\boldsymbol{q}} = \alpha' J_{\boldsymbol{q}4\mathrm{u}x} + \beta' T_{\boldsymbol{q}4\mathrm{u}x},\ \alpha' J_{\boldsymbol{q}4\mathrm{u}y} + \beta' T_{\boldsymbol{q}4\mathrm{u}y}, \tag{21}$$

for $\boldsymbol{q} = (0, 0, 1)$. Thus, this phase is called "t-AFM". It is found that $\alpha' = 0.37$ and $\beta' = -0.93$ and these values are almost unchanged in the present parameter space. For $E_2 \approx 0$, the magnetic moment becomes longitudinal, given by the same expressions as Eqs. (15)–(17), but the coefficients α and β are replaced by α' and β'.

Let us try to set the realistic parameters for δ-Pu. Concerning E_2, it can be estimated as $E_2 \sim J_{\mathrm{H}}/49$ [17], where J_{H} is the original Hund's rule interaction among f electrons. Since J_{H} is considered to be in the order of eV, E_2 is expected to be 0.05–0.1 eV. As for Δ, we cannot find the value from the literatures, but we deduce its sign as follows: In the case of $CeIn_3$ with the fcc structure, it has been experimentally found that the CEF

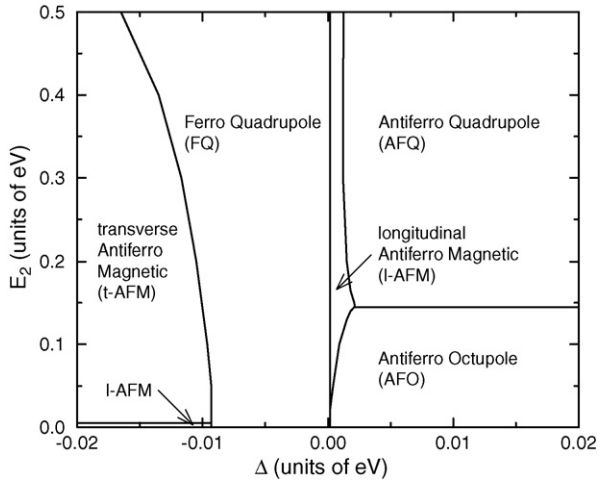

Fig. 2. Phase diagram for the 4-site fcc lattice. Meaning of each phase is explained in the maintext.

ground state of Ce^{3+} is Γ_7 and the excited state is Γ_8 with the excitation energy of 12 meV [21]. In the case of δ-Pu with the same fcc structure, since one Pu^{3+} is surrounded by others, the CEF potential has the reversed sign in comparison with the case of $CeIn_3$. Thus, Δ is negative and the Γ_8 level is lower. Note again that the CEF ground state for $n = 5$ is Γ_7 doublet for $\Delta < 0$.

In this paper, we have set $t = 10^{-3}$ eV, leading to $W = 0.074$ eV, which seems to be much smaller than $W = 1$–2 eV from the band-structure calculations [9,13]. However, if we regard H as an effective model for heavy quasi-particles with residual interactions, $W = 0.074$ eV is not extremely small, since we find the moderately enhanced value of γ as 60 mJ/mol K^2 for δ-Pu [8]. Thus, t may be larger than 10^{-3} eV, but it should be less than 0.01 eV in the present model. When t is increased, it is found that the overall structure of the present phase diagram is not qualitatively changed, but the boundary curve between FQ and t-AFM phases is shifted to the large negative value of Δ. We do not know the absolute value of Δ for δ-Pu, but it may be larger than 12 meV, since in general, the CEF potential for 5f electrons is larger than that for 4f. Then, the parameters for δ-Pu can be situated near the boundary between FQ and t-AFM phases. If we consider that δ-Pu is in the FQ phase, it seems to be consistent with the absence of magnetism, in the sense that magnetic fluctuations are not dominant.

5. Discussion and summary

We have discussed the multipole state of δ-Pu by evaluating the multipole susceptibility on the basis of numerical results for the 4-site fcc cluster. The present result has suggested that quadrupole fluctuations are significant in the ground state of δ-Pu. Here the key parameter is the CEF potential Δ. It may be interesting, if possible, to perform experiments to detect induced magnetic moment by applying pressure, assuming that the variation of the CEF potential is sensitive to the pressure. This seems to provide an alternative story to explain that the magnetic tendency becomes strong for the shrinkage of the volume. When we consider only the competition between the Coulomb interaction and the f-electron itineracy, it is concluded that the magnetic phase should be stabilized by the localization tendency. However, there exists another important ingredient, *orbital degree of freedom*, leading to multipole due to the combination with spin degree of freedom through strong spin–orbit interaction. In such a multiorbital system with active multipole degrees of freedom, the CEF potential plays a crucial role to determine the orbital state.

We have not mentioned superconductivity, but it is also possible to discuss the occurrence of superconductivity on the basis of the same model. For instance, for Ce-based heavy-fermion superconductors $CeMIn_5$ (M = Co, Rh, and Ir), d-wave superconductivity induced by AFM fluctuations has been suggested to occur based on the similar model [22,23], consistent with experimental results. In particular, the importance of the orbital state under a tetragonal CEF potential has been pointed out [23]. Concerning $PuMGa_5$ (M = Co and Rh), there is a simple idea using the electron-hole symmetry [17]. In the j–j coupling scheme, the f-electron state of $n = 5$ is considered to be the hole version of that of $n = 1$. Thus, it is expected that the d-wave superconductivity induced by AFM fluctuations also occurs in $PuMGa_5$. However, it may be premature to conclude it, since the relevant orbital state should be quite different from that of $CeMIn_5$. It is one of future tasks to perform actual calculations for $n = 5$ using the model with the tetragonal CEF.

In summary, we have proposed the idea that the ground state of δ-Pu is dominated by quadrupole fluctuations. When the CEF potential is controlled, for instance, by pressure, such a phase is changed to be magnetic, suggesting the induced magnetic moment. We believe that the multipole scenario provides us a hint to resolve a puzzle concerning the absence of magnetism in δ-Pu.

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