An orbital-based scenario for the magnetic structure of neptunium compounds

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Abstract. In order to understand the key role of the orbital degree of freedom in the magnetic structure of some recently synthesized neptunium compounds, NpTGa₅ (T = Fe, Co and Ni), we propose to discuss the magnetic phase of an effective two-orbital model, which has been constructed based on a $j-j$ coupling scheme to explain the magnetic structure of the uranium compounds UTGa₅. By analysing the model with the use of numerical techniques such as exact diagonalization, we obtain the phase diagram including several kinds of magnetic states. An orbital-based scenario is discussed to understand the change in magnetic structure among C-, A- and G-type antiferromagnetic phases, observed experimentally in NpFeGa₅, NpCoGa₅ and NpNiGa₅.

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1. Introduction

Recently, it has been widely recognized that the orbital degree of freedom plays an essential role in understanding the novel magnetism in transition metal oxides [1]. A typical material is manganese oxide, exhibiting remarkable colossal magneto-resistance phenomena [2]. Due to the competition and interplay among spin, charge and orbital degrees of freedom, a rich phase diagram has been revealed [1], but a recent trend is to further unveil new phases both from experimental and theoretical investigations. In fact, even in undoped RMnO$_3$ (R = rare earth lanthanide ions), a novel antiferromagnetic (AF) phase called the ‘E-type’ spin structure has been reported as the ground state for R = Ho [3, 4]. Here, we follow the definitions of spin structure given in [5]. The origin of the E-AF phase has been clarified theoretically [6] on the basis of a band-insulator scenario in the e$_g$-orbital systems [7]–[9]. It should be noted that the ground state of undoped manganites was just considered to be well understood, since for most R ions, the A-type AF insulating phase appears with the C-type ordering of the $(3x^2-r^2)$ and $(3y^2-r^2)$ orbitals [10]–[24]. Moreover, also for the half-doped manganese L$_{a0.5}$Ca$_{0.5}$MnO$_3$, a charge-ordered ferromagnetic phase (FM phase) has been found in experiments [25, 26], as predicted theoretically [27, 28]. These facts clearly indicate the importance of both experimental and theoretical efforts to unveil new phases in manganites in addition to explaining the complex phases already observed. Efforts have also been made to find new phases in other transition metal oxides, for instance ruthenates [29, 30] and nickelates [31].

A trend to look for new magnetic as well as superconducting phases has been also found in the f-electron system, which is another type of spin–charge–orbital complex. Of the many kinds of f-electron materials, in recent years, f-electron compounds with an HoCoGa$_5$-type tetragonal crystal structure (see figure 1(a)), frequently referred to as ‘115’, have been intensively investigated both in experimental and theoretical research fields of condensed matter physics. Such vigorous activities are certainly motivated by the high superconducting transition temperature $T_c$ observed in some 115 compounds. In particular, the amazingly high value of $T_c = 18.5$ K was reported for PuCoGa$_5$ [32]–[34] and the mechanism is discussed theoretically in [35, 36]. Of 115 compounds, interesting magnetic properties have been reported for UTGa$_5$, where T is a transition metal ion [37]–[48]. In particular, neutron scattering experiments have revealed that UNiGa$_5$ exhibits the G-type AF phase, while UPdGa$_5$ and UPtGa$_5$ have the A-type AF state [44, 48]. Note that G-type indicates a three-dimensional Néel state, while A-type denotes a layered AF structure in which spins align ferromagnetically in the $ab$ plane and AF along the $c$-axis [5]. It is quite interesting that the magnetic structure is different for U-115 compounds, which differ only by the substitution of transition metal ions.

Quite recently, 115 compounds including neptunium have been skilfully synthesized and several kinds of physical quantities have been successfully measured [49]–[56]. Especially, the de Haas–van Alphen (dHvA) effect has been observed in NpNiGa$_5$ [50], which is the first observation of dHvA signal in transuranium compounds. For NpCoGa$_5$, the dHvA oscillations have been also detected and a couple of cylindrical Fermi surfaces are found [52]. For NpFeGa$_5$, the magnetic moment at Fe site has been suggested in neutron scattering experiments [56] and it has been also detected by $^{57}$Fe Mössbauer spectroscopy [55]. Interestingly enough, the magnetic structure of Np-115 compounds also depends sensitively on transition metal ion [53, 56]: C-AF for NpFeGa$_5$, A-AF for NpCoGa$_5$ and G-AF for NpNiGa$_5$, as shown in figures 1(b)–(d). Note that, for NpNiGa$_5$, the G-AF structure is composed of canted Np moments and the peak in the neutron scattering intensity grows after the FM transition occurs [53, 56]. In any case, it is
Figure 1. (a) Crystal structure of NpTGa$_5$. Schematic representation of magnetic structures composed of magnetic moments of Np ions for (b) NpFeGa$_5$, (c) NpCoGa$_5$ and (d) NpNiGa$_5$. For NpFeGa$_5$, magnetic moments at Fe sites are also depicted.

characteristic of U-115 and Np-115 compounds that the magnetic properties are sensitive to the choice of transition metal ions.

The appearance of several kinds of AF states reminds us of the magnetic phase diagram of manganites and, thus, we envisage a scenario to understand the complex magnetic structure of actinide compounds based on an orbital degenerate model similar to that of manganites. However, one must pay close attention to the meanings of ‘spin’ and ‘orbital’ in f-electron systems. Since they are tightly coupled with each other through a strong spin–orbit interaction, distinguishing them is not straightforward in comparison with d-electron systems. This point can create serious problems when we attempt to understand microscopic aspects of magnetism and superconductivity in f-electron compounds. Thus, it is necessary to carefully define the terms ‘orbital’ and ‘spin’ for f electrons in a microscopic discussion of magnetism and superconductivity in actinide compounds.

In order to overcome such problems, we have proposed to employ a $j$–$j$ coupling scheme to discuss f-electron systems [35]. Here, we stress the advantages of the $j$–$j$ coupling scheme. Firstly, it is quite convenient for the inclusion of many-body effects using standard quantum-field theoretical techniques, since individual f-electron states are clearly defined. In contrast, in the LS coupling scheme, we cannot use such standard techniques, since Wick’s theorem does not hold. Secondly, we can, in principle, include the effects of valence fluctuations. In some uranium compounds, the valence of the uranium ion is neither definitely U$^{3+}$ nor U$^{4+}$, indicating that the f-electron number takes a value between 2 and 3. In the $j$–$j$ coupling scheme, this is simply regarded as the average number of f electrons per uranium ion.

In this paper, we attempt to explain the complex magnetic structure of Np-115 based on the effective two-orbital model, which has been constructed from the $j$–$j$ coupling scheme in order to understand the magnetic properties of U-115 compounds [57]. We depict the Fermi surfaces of the kinetic term of the 5f electron based on the $j$–$j$ coupling scheme in comparison with those obtained from the dHvA experiments. The agreement seems to be quite good, but the present itinerant picture should be critically discussed. Then, we apply the exact diagonalization technique to the model in a small $2 \times 2 \times 2$ cube to obtain a clue to understand the complex magnetic structure of NpTGa$_5$. The phase diagrams are found to include G-, A- and C-type AF states, consistent with experimental observations in Np-115.

The organization of this paper is as follows. In section 2, we will introduce an effective Hamiltonian, called the $\Gamma_8$ model, for actinide 115 systems. In section 3, we show the calculated...
results of the model Hamiltonian. The Fermi-surface structure is discussed in comparison with dHvA experimental results. We show numerical results for the magnetic structure obtained by using the exact diagonalization technique. Finally, in section 4, future developments are discussed and the paper is summarized. Throughout the paper, we use units such that $\hbar = k_B = 1$.

2. Model Hamiltonian

In this section, we show an effective model based on the $j$–$j$ coupling scheme for Np-115 compounds, which is the same as the model for U-115 [57]. We emphasize that the model with orbital degree of freedom is applicable to actinide 115 materials in common.

2.1. Local f-electron state

In order to construct a microscopic Hamiltonian for f-electron systems, it is necessary to include simultaneously the itinerant nature of f electrons as well as strong electron correlation and the effect of crystalline electric field (CEF). For the purpose, we have proposed to use the so-called $j$–$j$ coupling scheme [35]. As shown in figure 2, we include the spin–orbit coupling so as to define the state labelled by the total angular momentum. For $f$ orbitals with $\ell = 3$, we immediately obtain an octet with $j = 7/2$ ($= 3 + 1/2$) and a sextet with $j = 5/2$ ($= 3 - 1/2$), which are well separated by the spin–orbit interaction. In general, the spin–orbital coupling is as large as 1 eV in actinide elements and, thus, in the $j$–$j$ coupling scheme, we consider only the $j = 5/2$ sextet.

In actual compounds, due to the electrostatic potential from ligand ions surrounding the actinide ion, the six-fold degeneracy of $j = 5/2$ is lifted, as shown in figure 2. Note that, in the $j$–$j$ coupling scheme, it is enough to define the one-electron potential, which is deduced from the CEF level scheme of the corresponding $f^1$-electron system. Firstly, we consider the one f-electron state in the AuCu$_3$-type cubic crystal structure, since this is the mother structure of the HoCoGa$_5$-type tetragonal compound. The effects of tetragonality will be discussed later. For the
Figure 3. (a) The two orbitals $a$ and $b$ in the $\Gamma_8$ model. Level scheme for (b) CeIn$_3$, (c) UGa$_3$ and (d) NpGa$_3$ based on the $j$–$j$ coupling scheme. Here, we assume trivalent actinide ions as $U^{3+}$ ($5f^3$) and $Np^{3+}$ ($5f^4$). It should be noted that up and down arrows denote pseudospins to distinguish the states in the Kramers doublet. Note also that, for NpGa$_3$, a couple of electrons in $\Gamma_1$ orbitals form a local triplet, leading to $\Gamma_5$.

In order to proceed with the discussion, we need to know which is lower, $\Gamma_7$ or $\Gamma_8$, in the one f-electron picture. For some crystal structures, it is possible to determine the level scheme from intuitive discussions on f-electron wavefunctions and the positions of ligand ions. However, this is not the case for the AuCu$_3$-type crystal structure. For this case, we invoke certain experimental results on CeIn$_3$, a typical AuCu$_3$-type Ce-based compound, where $\Gamma_7$ and $\Gamma_8$ have been reported as ground and excited states, respectively, with an energy difference of 12 meV [58]. Thus, we take $\Gamma_7$ to be lower for the present considerations, as shown in figure 3(b).

In the $j$–$j$ coupling scheme for UGa$_3$ and NpGa$_3$, it is necessary to accommodate three or four electrons in the one-electron energy states $\Gamma_7$ and $\Gamma_8$. We immediately notice that there are two possibilities, i.e., low- and high-spin states, depending on the Hund’s rule interaction and the splitting between the $\Gamma_7$ and $\Gamma_8$ levels. As discussed in [35], the effective Hund’s rule interaction becomes small in the $j$–$j$ coupling scheme and, thus, the low-spin state should be realized, as shown in figures 3(c) and (d). We emphasize that the low-spin state is consistent with the $LS$ coupling scheme. In the electron configuration shown in figures 3(c) and (d), the $\Gamma_7$ level is fully occupied to form a singlet. If this $\Gamma_7$ level is located well below the $\Gamma_8$, the occupying electrons will not contribute to the magnetic properties. Thus, we ignore the $\Gamma_7$ electrons in the following discussion. See [57] for details to validate the suppression of the $\Gamma_7$ level. We also mention another theoretical effort based on the $j$–$j$ coupling scheme, in which the dual nature, itinerant and localized, of 5f electrons has been emphasized [59]–[61].

As shown in figure 1(a), since 115 compounds have a tetragonal structure, we need to include the effect of tetragonality. In the tetragonal structure, the quartet $\Gamma_8$ is further split into two doublets, $\Gamma_6$ and $\Gamma_7$, as shown in figure 2. Namely, there appear three Kramers doublets with one $\Gamma_6$ and two $\Gamma_7$. Note that two $\Gamma_7$ states are obtained from the mixture of $\Gamma_7$ and $\Gamma_8$ in the cubic symmetry. However, for simplicity, we ignore the change of wavefunctions from cubic to tetragonal systems, since we believe that the existence of orbital degrees of freedom is a key issue to understand the complex magnetic structure of actinide compounds. For the purpose of
improving the present theory from the quantitative viewpoint, it may be important to include
dehdration of the local f-electron wavefunction, but we postpone such a study for the future.
In this paper, we consider the splitting energy between $\Gamma_8$ orbitals in order to take into account
the tetragonality in the 115 compounds.

2.2. The $\Gamma_8$ model

After tedious calculations, we obtain the Hamiltonian including $\Gamma_8$ orbitals in the form of [35, 57]

$$H = H_{\text{kin}} + H_{\text{CEF}} + H_C,$$

where $H_{\text{kin}}$ denotes the kinetic term of 5f electrons, $H_{\text{CEF}}$ is the CEF potential term and $H_C$
indicates the Coulomb interaction term among $\Gamma_8$ electrons.

Concerning the kinetic term, one traditional way is to consider the hybridization process
between f and conduction electrons. For 115 systems, from the band-structure calculations [36],
p electrons of Ga ion play an important role informing the conduction band. However, based
on a picture that 5f electrons are itinerant, we can consider another way to construct the kinetic
term for f electrons within a tight-binding approximation. In actual compounds, there should
occur several processes through other ligand ions, in addition to the direct process of f electrons.
However, when we include correctly the local symmetry of relevant f orbitals, it is believed that
we can grasp qualitative point of kinetic term of f electrons, even within the simple tight-binding
approximation. This point will be discussed elsewhere in future. Here, we do not consider the
hybridization process. Then, the kinetic term is given in the tight-binding approximation for
f electrons as

$$H_{\text{kin}} = \sum_{i,a,\tau,\tau', \sigma, \sigma'} t_{\tau\tau'} a^\dagger_i f_{\tau\sigma} f_{a \tau'\sigma'},$$

where $f_{\tau\sigma}$ is the annihilation operator for an f electron with pseudospin $\sigma$ in the $\tau$ orbital at site $i$
and $t_{\tau\tau'}^a$ is the f-electron hopping matrix element between $\tau$ and $\tau'$ orbitals along the $a$
direction. Indices $a$ and $b$ denote the $\Gamma_8^a$ and $\Gamma_8^b$ orbitals, respectively. In the $xy$ plane and along the $z$-axis,$t_{\tau\tau'}^a$ is given by

$$t_{\tau\tau'}^x = t \begin{pmatrix} 3/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & 1/4 \end{pmatrix}$$

for the $x$ direction,

$$t_{\tau\tau'}^y = t \begin{pmatrix} 3/4 & \sqrt{3}/4 \\ \sqrt{3}/4 & 1/4 \end{pmatrix}$$

for the $y$ direction and

$$t_{\tau\tau'}^z = \begin{pmatrix} 0 & 0 \\ 0 & t_{bb}^z \end{pmatrix}$$
for the \( z \) direction. Note that \( t = (3/7)(ff\sigma) \), where \((ff\sigma)\) is a Slater–Koster overlap integral between \( f \) orbitals through the \( \sigma \) bond. In the following, \( t \) is taken as an energy unity. Note that we introduce another hopping amplitude along the \( z \)-axis. In AnTGA\(_5\) (An = U and Np), the AnGa\(_2\) layer is sandwiched by two AnGa\(_3\) sheets, indicating that the hopping of the \( f \) electron along the \( z \)-axis should be reduced compared with that in AnGa\(_3\). However, it is difficult to estimate the reduction quantitatively, since it is necessary to include correctly the hybridization with \( d \) electrons in transition metal ions and \( p \) electrons in Ga ions. Thus, in this paper, we consider the effective reduction by simply treating \( t^\prime_{bb} \) as a parameter. For a practical purpose, we introduce a non-dimensional parameter \( t_z = t^\prime_{bb}/t \).

We point out that the hopping amplitudes among \( \Delta \Gamma_8 \) orbitals are just the same as those for the \( e_g \) orbitals of 3d electrons [1, 9]. Readers can intuitively understand this point from the shapes of \( \Delta \Gamma_8 \) orbitals shown in figure 3(a), which are similar to \( e_g \) orbitals. Mathematically, this is quite natural, if we recall the fact that \( \Delta \Gamma_8 \) is isomorphic to \( \Delta \Gamma_3 \times \Delta \Gamma_6 \), where \( \Delta \Gamma_3 \) indicates \( E \) representation for the orbital part and \( \Delta \Gamma_6 \) denotes the spin part. Note, however, that the agreement between \( f \)- and \( d \)-electron hopping amplitudes is due to the choice of special axis directions. If we take the \((1, 1, 0)\) direction in an fcc lattice, \( f \)-electron hopping amplitude becomes complex, leading to the stabilization of octupole ordering in NpO\(_2\) [62].

The CEF term is given by

\[
H_{CEF} = -\Delta \sum_i (\rho_{i\uparrow} - \rho_{i\downarrow})/2, \tag{6}
\]

where \( \rho_{i\sigma} = f^\dagger_{i\sigma} f_{i\sigma} \), \( \rho_{i\tau} = \sum_\sigma \rho_{i\sigma\tau} \), and \( \Delta \) is the level splitting, which expresses the effect of tetragonal CEF, as discussed above. We note that, in actuality, \( \Delta \) should be related to the value of \( t_z \), since both quantities depend on the lattice constant along the \( z \)-axis. However, the relation between \( t_z \) and \( \Delta \) is beyond the scope of this paper and thus, here, we simply treat them as independent parameters.

The Coulomb interaction term is expressed by

\[
H_C = U \sum_i \rho_{i\uparrow\uparrow} \rho_{i\downarrow\downarrow} + U' \sum_i \rho_{i\uparrow\downarrow} \rho_{i\downarrow\uparrow} + J \sum_{i,\sigma,\sigma'} f^\dagger_{i\sigma \downarrow} f_{i\sigma\uparrow} f^\dagger_{i\sigma' \downarrow} f_{i\sigma'\uparrow} + J' \sum_{i,\tau\neq\tau'} f^\dagger_{i\uparrow\downarrow} f_{i'\uparrow\downarrow} f^\dagger_{i\uparrow\downarrow} f_{i'\uparrow\downarrow}, \tag{7}
\]

where the Coulomb interactions \( U, U', J \) and \( J' \) denote intra-orbital, inter-orbital, exchange and pair-hopping interactions among \( \Delta \Gamma_8 \) electrons, respectively, expressed by using the Racah parameters [63]. Note that the relation \( U = U' + J + J' \) holds, ensuring rotational invariance in pseudo-orbital space for the interaction part. For \( d \)-electron systems, one also has the relation \( J = J' \). When the electronic wavefunction is real, this relation is easily demonstrated from the definition of the Coulomb integral. However, in the \( j-j \) coupling scheme, the wavefunction is complex and \( J \) is not equal to \( J' \) in general. For simplicity, we shall assume here that \( J = J' \), noting that essentially the results are not affected. Since double occupancy of the same orbital is suppressed owing to the large value of \( U \), pair-hopping processes are irrelevant in the present case.

3. Results

Now, let us show our calculated results based on the two-orbital model. Firstly, we discuss the electronic properties of \( H_{\text{kin}} \) in the non-interacting limit by focusing on the Fermi-surface
Figure 4. Fermi-surface sheets of the $\Gamma_8$ tight-binding model for (a) $n = 2, t_z = 1, \Delta = 0$, (b) $n = 2, t_z = 0.1, \Delta = -0.4$, (c) $n = 1.5, t_z = 1, \Delta = 0$ and (d) $n = 1.5, t_z = 0.1, \Delta = -0.4$. The bounding box indicates the first Brillouin zone for a simple cubic lattice. The $\Gamma$ point is located at the centre of the box, while the apices denote R points.

structure, in order to gain an insight into interpretation of the dHvA experiments on Np-115 compounds. Next, the magnetic properties are discussed. We attempt to understand the appearance of three kinds of magnetic phases based on the orbital-based scenario similar to that of manganites.

3.1. Fermi-surface structure

Let us consider the structure of Fermi-surface sheets of the $\Gamma_8$ tight-binding model $H_{\text{kin}}$. In the following, we define $n$ as the number of f electrons included in the $\Gamma_8$ state. Namely, the local f-electron number per actinide ion is $n + 2$, by adding $\Gamma_7$ electrons.

As shown in figure 3(d), in our picture, there are two $\Gamma_8$ electrons in trivalent neptunium ion. Then, it is quite natural to consider first the case of $n = 2$. The results for $(t_z, \Delta) = (1, 0)$ and $(0.1, -0.4)$ are shown in figures 4(a) and (b), respectively. For the cubic case with $t_z = 1$ and $\Delta = 0$, there exist two kinds of cube-like Fermi surfaces. One is centred at the $\Gamma$ point, while the centre of another cube is the R point. When we change $t_z$ and $\Delta$ to consider the tetragonality, cubes gradually change to cylinders. As shown in figure 4(b), we can clearly observe two kinds of cylindrical Fermi surfaces. Note that the Fermi-surface structure does not sensitively depend on the value of $\Delta$, as long as the absolute value is not so large as $|\Delta| < 0.5$. It is important to have quasi-orbital degeneracy, to reproduce a couple of cylindrical Fermi surfaces.

It is interesting to recall the dHvA experiment on NpCoGa$_5$, which has revealed two kinds of cylindrical Fermi surfaces [52]. In the relativistic band-structure calculations for the paramagnetic phase, it has been difficult to understand the appearance of a couple of cylindrical Fermi surfaces [36]. Note that the folding of the magnetic Brillouin zone cannot explain the discrepancy between the experimental results and the band-calculation ones for NpCoGa$_5$. A direct way to understand...
the dHvA experimental results is to improve the band-structure calculation method, but, as shown in figure 4(b), even in a simple tight-binding model for itinerant 5f electrons, we obtain two kinds of cylindrical Fermi surfaces due to the effect of the $\Gamma_8$ orbital degree of freedom. We do not claim that the dHvA results can be understood only by the present simple calculations, but a hint to understand the electronic structure of Np-115 is believed to be hidden in the construction of our model with the $\Gamma_8$ orbital degree of freedom.

We point out that in actual Np-115 compounds $n$ is not definitely determined. Especially, due to a change of the transition metal ion, $n$ seems to have changed effectively. In fact, in the relation between the superconducting transition temperature $T_c$ and the ratio of lattice constants $c/a$, the curve of $T_c$ versus $c/a$ for solid solution (U,Np,Pu)CoGa$_5$ is similar to that for another solid solution Pu(Fe,Co,Ni)Ga$_5$ [64, 65]. Namely, in actinide 115 materials, the effect of the change of f-electron number due to the substitution of actinide ion seems to be similar to that of the substitution of transition metal ion. Thus, when we consider the change of the magnetic structure among NpTGa$_5$ ($T$ = Fe, Co and Ni) based on the effective two-orbital model, there is no strong reason to fix firmly $n = 2$.

In figures 4(c) and (d), we show the Fermi-surface sheets for $n = 1.5$, in which the number of f electrons is slightly decreased. We can observe that the Fermi-surface structure is not changed so much, although the cylinder centred at the $\Gamma$ point becomes slender. Thus, as long as we are based on the simple tight-binding model, it is concluded that the structure of Fermi-surface sheets is not changed sensitively by the value of $n$ around $n = 2$. This result suggests that it is possible to change the value of $n$ when considering the magnetic structure of Np-115 compounds.

3.2. Magnetic structure

Now we consider the magnetic properties of the $\Gamma_8$ model. Of several methods to analyse the microscopic model, in this paper we resort to an exact diagonalization technique on a $2 \times 2 \times 2$ lattice. Although this has a demerit that it is difficult to enlarge the system size, we see a clear advantage that it is possible to deduce the magnetic structure by including the effect of electron correlation. In order to discuss the ground-state properties, it is useful to measure the spin and orbital correlations, which are, respectively, defined by

$$S(q) = (1/N) \sum_{ij} \langle \sigma_i^z \sigma_j^z \rangle e^{i\mathbf{q} \cdot (i-j)},$$

with $\sigma_i^z = \sum_{\tau} (n_{i\tau\uparrow} - n_{i\tau\downarrow})/2$, and

$$T(q) = (1/N) \sum_{ij} \langle \tau_i^z \tau_j^z \rangle e^{i\mathbf{q} \cdot (i-j)},$$

where $\tau_i^z = \sum_{\sigma} (n_{i\sigma\uparrow} - n_{i\sigma\downarrow})/2$. Here, $N$ is the number of sites.

Firstly, let us consider the case of $n = 2$, which is corresponding to the trivalent Np ion. In figure 5(a), we show the spin correlation as a function of $\Delta$ for $U' = 5$, $J = 0$ and $t_c = 1$. At $t_c = 1$ and $\Delta = 0$ (cubic system), local triplet composed of a couple of f electrons is formed at each site and the G-type AF structure is stabilized due to the so-called superexchange interaction. As can be easily observed, even when $\Delta$ is introduced as the tetragonal CEF effect, the G-AF structure remains robust for $|\Delta| < 1$. When $|\Delta|$ is larger than unity, two electrons simultaneously
occupy the lower orbital, leading to the non-magnetic state composed of local $\Gamma_1$, irrelevant to the present study for considering the magnetic phase. In figure 5(b), the spin correlation is shown as a function of $t_z$ for $\Delta = 0$. Again, the G-type AF structure is stabilized, but we find that the spin correlation of $q = (\pi, \pi, 0)$ comes to be equivalent to that of $q = (\pi, \pi, \pi)$ with decrease of $t_z$, since the AF structure is stabilized in each $xy$ plane due to superexchange interaction and the planes are decoupled for small $t_z$.

At the first glance, it seems difficult to understand the variety of magnetic phases observed in NpTGa$_5$ when we consider only the trivalent Np ion. However, there is no a priori reason to fix the valence as Np$^{3+}$, as mentioned in the previous subsection. In NpTGa$_5$, the d-electron band originating from transition metal ions may significantly affect the valence of Np ion. In addition, we also stress that the actual compounds exhibit AF metallic behaviour. In the band-structure calculation, the average number of f electrons at Np ion is easily decreased from four. Thus, we treat the local f-electron number as a parameter.

We may consider another reason to decrease effectively the number of f electrons from $n = 2$ in NpGa$_3$. In the present two-orbital model, the G-AF structure is robust, which is natural from the theoretical viewpoint within the model. However, in the experimental result on NpGa$_3$, the low-temperature ground state is ferromagnetic, although the AF phase has been observed around $T = 60$ K [66]. In order to understand the occurrence of the FM phase in the two-orbital model, it is necessary to inject some amount of ‘hole’ into the AF phase, since the double-exchange mechanism works to maximize the kinetic motion of electrons, as will be discussed later in the main text. It is difficult to determine the amount of doped holes required to obtain the FM phase, but, at least qualitatively, the effective decrease of $n$ seems to be physically meaningful in NpGa$_3$ as well as NpTGa$_5$.

Now, we consider the case of $n = 1.5$. As discussed in the previous subsection, the Fermi-surface structure does not change so much from that of the case of $n = 2$, when $|\Delta|$ is not so large. In figure 6(a), we show the ground-state phase diagram in the $(U', J)$ plane at $n = 1.5$ for the cubic case with $t_z = 1$ and $\Delta = 0$. At $J = 0$, a G-type AF structure is stabilized due to superexchange interaction in the same way as the case of $n = 2$. However, the G-AF structure is immediately changed to a C-AF structure by a small value of the Hund’s rule interaction. With

![Figure 5](http://www.njp.org/)
increase in $J$, the magnetic phase changes in the order of G-AF, C-AF, A-AF and FM phases, except for the C-AF phase in the large $J$ region. The spin structure of each phase is shown in figure 6(b). This result is quite natural, since we are now considering the magnetic structure based on the two-orbital model, in which the FM tendency is due to the optimization of kinetic motion of electrons.

In order to understand the underlying mechanism of the appearance of various magnetic structures in addition to the G-AF structure for $n = 1.5$, we consider the case of $J = 0$. In figure 7(a), we show typical results of the spin correlation as a function of $\Delta_1$ for $U' = 5$, $J = 0$ and $t_z = 1$. At $\Delta_1 = 0$, the dominant component of $S(q)$ appears at $q = (\pi, \pi, \pi)$, indicating the G-type AF structure. On the other hand, in the region of positive small $\Delta_1$, the spin correlation of $q = (\pi, \pi, 0)$ turns out to be dominant, indicating the C-type AF structure. This phase is defined as C-AF(I). Concerning the orbital correlation, we find no remarkable structure in the C-AF(I) phase, as shown in figure 7(b). Note that, in the G-AF phase with positive $\Delta$ , the orbital correlation of $q = (0, 0, 0)$ has a significant value in comparison with other regions, since electrons tend to doubly occupy lower $\Gamma_8^a$ orbitals. This G-AF phase is called G-AF(I). On the other hand, in the G-AF phase with negative $\Delta$, there is no indication of the development of the orbital correlation of $q = (0, 0, 0)$, since the lower $\Gamma_8^b$ orbitals are singly occupied. We label this G-AF phase as G-AF(II) to distinguish it from G-AF(I). It is interesting to see different types of the G-AF phases due to the change of the orbital state.

Let us now discuss the reason for the appearance of the C-AF(I) phase in the region of positive small $\Delta$. For $\Delta > 0$, the energy level of $\Gamma_8^a$ is lower than that of $\Gamma_8^b$ by definition. Then, the $\Gamma_8^a$ orbital is first occupied by one electron at each site. The rest of the electrons are accommodated in $\Gamma_8^b$ orbitals to avoid the effect of intra-orbital Coulomb interaction when $\Delta$ is not large so much. The electrons in $\Gamma_8^b$ orbitals hop to the $\Gamma_8^a$ orbital at the nearest-neighbour site, since the $\Gamma_8^b$ has a higher energy. Since the electrons in $\Gamma_8^a$ orbitals move only in the $xy$ plane, the AF structure is stabilized in each $xy$ plane independently due to superexchange interaction.
as schematically shown in figure 7(c). On the other hand, the electrons in $\Gamma^b_8$ orbitals can move itinerantly within the network composed of $\Gamma^b_8$ orbitals due to the existence of holes in $\Gamma^b_8$ orbitals. Since the hopping amplitude along the $z$-axis is dominant in the region near $t_z = 1$, the motion of $\Gamma^b_8$ electrons causes an FM spin arrangement of $\Gamma^a_8$ electrons along the $z$-axis to gain kinetic energy. Namely, even though localized $t_{2g}$ spins do not exist in the present case, the so-called double-exchange mechanism is always active in the two-orbital model. Note that the C-AF structure disappears for large $\Delta$, since all the electrons tend to occupy $\Gamma^a_8$ orbitals and the double-exchange mechanism is no longer active in that situation.

After calculations of the spin and orbital correlations for several parameter sets, we obtain the ground-state phase diagram in the $(\Delta, t_z)$ plane, as shown in figure 7(d). It is found that the C-AF(I) phase discussed above extends to a wide region of $t_z < 1$ in the phase diagram. Note that, for small values of $t_z$, another C-AF phase, which we call C-AF(II), appears in the region of negative small $\Delta$, in which the spin correlations of $\pi, 0, \pi$ and $0, \pi, \pi$ are dominant. For small $t_z$ and large negative $\Delta$, there appears yet another G-AF phase, called G-AF(III), for the same reason as that for the occurrence of G-AF(I) phase for positive $\Delta$, but the occupied orbital
Figure 8. Ground-state phase diagram of the magnetic structure in the \((\Delta, t_z)\) plane for \(n = 1.5\), \(U' = 5\), (a) \(J = 0.5\) and (b) \(J = 4\).

is changed from \(\Gamma_{1a}^\delta\) to \(\Gamma_{1b}^\delta\). In any case, for \(J = 0\), we can observe several kinds of C- and G-AF phases, but the A-AF phase does not occur.

Although we increase the value of \(J\) as \(J = 0.5\), no new phases appear in the phase diagram for \(n = 1.5\), as shown in figure 8(a). There are three phases, but they are two C-AF and one G-AF states. As labelled explicitly in the phase diagrams, C-AF(I), C-AF(II) and G-AF(I) are the same as those in the phase diagram of figure 7(d). Due to the effect of \(J\), G-AF(II) and G-AF(III) disappear, since the number of FM bonds should be increased to gain the kinetic energy. As shown in figure 8(b), when we further increase the value of \(J\) as \(J = 4\), the G-AF phase completely disappears and, instead, we observe the A-AF phase sandwiched by two C-AF phases. As described above, due to the double-exchange mechanism in the two-orbital model, the A-AF phase is considered to appear when \(J\) is increased.

4. Discussion and summary

In this paper, we have proposed an effective model with active orbital degree of freedom to understand the magnetic structure of neptunium 115 compounds from the microscopic viewpoint. By analysing the model with the use of the exact diagonalization technique, we have obtained the ground-state phase diagrams including three kinds of AF phases corresponding to NpTG\(_5\).

In the experiments for NpTG\(_5\), C-, A- and G-AF magnetic phases have been found in NpFeGa\(_5\), NpCoGa\(_5\) and NpNiGa\(_5\). Here we have a question: what is the key parameter to understand the change of the magnetic structure? In the case of UTGa\(_5\), it has been claimed that the level splitting \(\Delta\) is important to explain the difference in magnetic structure as well as the magnetic anisotropy for a fixed value of \(n = 1\) [57]. Roughly speaking, \(\Delta\) is positive for \(T = \text{Fe}\), small positive for \(T = \text{Co}\) and negative for \(T = \text{Ni}\). Among UTGa\(_5\) (\(T = \text{Ni}, \text{Pd and Pt}\)), when we assume that the absolute value of \(\Delta\) is increased in the order of \(\text{Ni}, \text{Pd and Pt}\), it is possible to understand qualitatively the change in magnetic anisotropy, in addition to the change in magnetic structure of G-AF for \(T = \text{Ni}\) and of A-AF for \(T = \text{Pd and Pt}\). It has been found that the value of \(t_z\) is not so crucial to explain qualitatively the magnetic properties of U-115 based on the two-orbital model for \(n = 1\).
For \( n = 2 \), as emphasized in the previous section, we always obtain the G-AF phase. However, for \( n = 1.5 \), we have observed three kinds of AF magnetic structure in the phase diagrams. Let us summarize the change in the magnetic structure for a fixed value of \( t_z = 0.8 \). Note that this value is larger than \( t_z = 0.1 \), which we have considered to reproduce two kinds of cylindrical Fermi-surface sheets of Np-115. However, in the small-sized cluster calculations, it is difficult to compare directly with the values in the thermodynamic limit. Thus, we do not discuss further the quantitative point on the values of \( t_z \) here. As shown in figure 7(d), for \( J = 0 \) and \( t_z = 0.8 \), we see the change in the magnetic structure as G-AF (\( \Delta < 0 \)), C-AF (\( 0 < \Delta < 0.4 \)) and G-AF (\( \Delta > 0.4 \)). For \( J = 0.5 \) and \( t_z = 0.8 \), as shown in figure 8(a), the C-AF phases are always observed, but they have different orbital structures. Finally, for \( J = 4 \) and \( t_z = 0.8 \), we observe C-AF (\( \Delta < -0.15 \)), A-AF (\( -0.15 < \Delta < 0.3 \)) and C-AF (\( \Delta > 0.3 \)), as shown in figure 8(b).

In order to understand the appearance of three types of AF phases, we may consider an explanation due to the combination of changes in \( \Delta \) and \( n \). For instance, by assuming that \( J = 4 \) for NpTGa5 and that the change in \( \Delta \) for NpTGa5 is just the same as that for UTGa5, we consider that \( n \approx 2 \) with \( \Delta < 0 \) for \( T = \text{Ni} \), \( n \approx 1.5 \) with \( \Delta \approx 0 \) for \( T = \text{Co} \) and \( n \approx 1.5 \) with \( \Delta > 0 \) for \( T = \text{Fe} \). Then, it seems to be possible to relate our theoretical AF phases with the experimental observations in NpTGa5. However, it is difficult to claim that the above parameter assignment for three Np-115 materials is the best explanation for the magnetic structure of Np-115, since, in actual compounds, there are other important ingredients which have not been included in the present model. For instance, we have never discussed the direction of the magnetic moment of Np ion. Especially, the canted AF structure cannot be considered at all for the G-AF phase of NpNiGa5. Thus, we need to recognize some distance between the actual magnetic states and the theoretically obtained phases. Our theory should be improved by taking into account other ingredients of the 115 structure.

In summary, we have analysed the orbital degenerate model appropriate for NpTGa5 by using the exact diagonalization technique. Our phase diagram includes C-, A- and G-AF phases. We have proposed the manganite-like scenario to understand the appearance of three kinds of AF spin structure in Np-115. Namely, the double-exchange mechanism works also in some actinide compounds based on the model with active orbital degree of freedom. We believe that the present model can grasp some important points of the actinide compound by regarding it as a charge–spin–orbital complex.

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