Analysis of $f$-$p$ model for octupole ordering in NpO$_2$

Katsunori Kubo and Takashi Hotta

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

(Dated: March 23, 2022)

In order to examine the origin of octupole ordering in NpO$_2$, we propose a microscopic model constituted of neptunium 5$f$ and oxygen 2$p$ orbitals. To study multipole ordering, we derive effective multipole interactions from the $f$-$p$ model by using the fourth-order perturbation theory in terms of $p$-$f$ hopping integrals. Analyzing the effective model numerically, we find a tendency toward $\Gamma_{5u}$ antiferro-octupole ordering.

PACS numbers: 75.30.Et, 71.10.Fd, 75.40.Cx

In the research field of condensed matter physics, it is one of currently important issues to unveil the mechanism of multipole ordering phenomena frequently observed in $f$-electron systems. It has been widely recognized that quadrupole ordering realizes in several $f$-electron compounds, but recently, in addition to dipole and quadrupole ordering, a possibility of ordering of higher order magnetic multipoles, i.e., octupoles, has been discussed intensively.

A typical candidate with octupole ordering is the low-temperature ordered phase of NpO$_2$ since time reversal symmetry is broken in this phase but the detected internal field is too weak to be ascribed to dipole ordering. Indeed, several experimental facts can be consistently explained by assuming longitudinal triple-$q$ $\Gamma_{5u}$ octupole ordering. In addition, recent experiments on the $^{171}$O NMR also support the triple-$q$ ordered state.

In order to understand why such higher-order multipole order is realized in NpO$_2$, it has been highly required to proceed to the microscopic research. In general, it is difficult to develop a microscopic theory for complex multipole ordering in $f$-electron systems beyond the phenomenological level, but it has been recently proposed to construct a microscopic $f$-electron model on the basis of a $j$-$j$ coupling scheme. Following this proposal, we have studied the $f$-electron model on an fcc lattice composed of Np ions with hopping integrals via $(f f \sigma)$ bonding, and actually found the triple-$q$ octupole ordering. However, as shown in Fig. 1(a), oxygen anions exist between Np ions in actual crystal structure. Thus, it is important to clarify how the octupole ordering in the $f$-electron model is affected by oxygen anions.

In this paper, we construct a more realistic model including also $p$ orbitals of oxygen anions in addition to $f$ orbitals of Np ions. We derive an effective multipole interaction model by evaluating the exchange of $f$ electrons via $p$ orbitals within the fourth-order perturbation with respect to $p$-$f$ hopping integrals. By analyzing the effective model, we again find a tendency toward the triple-$q$ octupole ordered phase, indicating that the $f$-electron model on the fcc lattice have grasped the essential point on the appearance of octupole ordering of NpO$_2$.

Let us discuss local $f$-electron states of actinide dioxides based on the $j$-$j$ coupling scheme, in which we first include the spin-orbit interaction and consider only the states with total angular momentum $j=5/2$. From a quantitative viewpoint, this simplification may not be appropriate for actinide dioxides, since they are insulators, and the $LS$ coupling scheme is expected to work well to describe $f$-electron states in these materials. However, both schemes are continuously connected to each other by changing the ratio of the strength of the spin-orbit interaction and the Coulomb interaction, as long as the symmetry of the ground state is not changed. Thus, on the basis of a spirit of adiabatic continuation, we expect that qualitative properties at low temperatures can be grasped whether we choose the $j$-$j$ coupling or the $LS$ coupling schemes as a starting approximation. The $j=5/2$ states split into $\Gamma_7$ doublet and $\Gamma_8$ quartet under a cubic crystalline electric field (CEF). Since the $\Gamma_7$ wavefunction extends along the [111] direction and an oxygen anion locates in this direction, the $\Gamma_7$ level is expected to be higher than the $\Gamma_8$ level. If we assume that the level splitting $\Delta$ between $\Gamma_8$ and $\Gamma_7$ is large enough, CEF ground states for $f^2$, $f^3$, and $f^4$ are obtained by accommodating two, three, and four electrons into $\Gamma_8$ levels, leading to $\Gamma_5$, $\Gamma_8$, and $\Gamma_1$, respectively, consistent with experimental results for UO$_2$ and PuO$_2$ respectively. Thus, we ignore the $\Gamma_7$ state to discuss the ground state of actinide dioxides in the $j$-$j$ coupling scheme.

We have three comments on the CEF level scheme. (i) In our picture, the first excited state of PuO$_2$ should include three $\Gamma_8$ and one $\Gamma_7$ electrons, indicating that the excitation energy provides the lower limit for $\Delta$. Since
the CEF excitation energy of PuO$_2$ is 123 meV $\Delta$, should be larger than 1400K, consistent with the initial assumption. (ii) The $f^3$ state in NpO$_3$ is regarded as the one-hole state in $\Gamma_8$. In the following, we use a hole picture and “electron” denotes such a hole. (iii) Among the $f^2$ states, the $\Gamma_5$ triplet is the ground state as observed in UO$_2$. Since the CEF excitation energy in UO$_2$ is as large as 150 meV $\Delta$, we consider only the $\Gamma_5$ triplet among $f^2$ intermediate states to study exchange processes of $f^3$ ions in NpO$_2$.

The $\Gamma_8$ quartet consists of two Kramers doublets, and it is convenient to introduce orbital index $\tau (= \alpha, \beta)$ to label the two Kramers doublets and spin index $\sigma (= \uparrow, \downarrow)$ to distinguish the two states in each Kramers doublet. In the second-quantized form, annihilation operators for $\Gamma_8$ electrons are defined by $f_{\alpha\tau \uparrow} = \sqrt{5/6}a_{\alpha\tau \uparrow} + \sqrt{1/6}a_{\alpha\tau \downarrow}$, $f_{\alpha\tau \downarrow} = \sqrt{5/6}a_{\alpha\tau \downarrow} - \sqrt{1/6}a_{\alpha\tau \uparrow}$, and $f_{\beta\tau \pm} = a_{\beta\tau \pm}/2$, where $a_{\rho\tau \pm}$ is the annihilation operator for an $f$ electron with the $z$-component $j_z$ of the total angular momentum $j = 5/2$ at site $\bf r$. Multipole operators are usually expressed as $X_{\tau \gamma}^{\rho}$, where $\Gamma_\gamma$ denotes symmetry. The explicit forms of $X_{\tau \gamma}$ in the $\Gamma_8$ subspace are found in Ref. 13.

Now we show the $f$-$p$ model for NpO$_2$, given by

$$\mathcal{H} = \mathcal{H}_f + \mathcal{H}_p + \mathcal{H}_{\text{kin}}, \quad (1)$$

where $\mathcal{H}_f$ and $\mathcal{H}_p$ are the local $f$- and $p$-electron terms, respectively, and $\mathcal{H}_{\text{kin}}$ denotes the hybridization term between $f$ and $p$ electrons. Among them, the local $f$-electron term is explicitly given by

$$\mathcal{H}_f = \epsilon_f \sum_{\bf r, \tau} n_{\tau \uparrow} + U \sum_{\bf r, \tau} n_{\tau \uparrow} n_{\tau \downarrow} + U' \sum_{\bf r} n_{\rho \alpha} n_{\rho \beta}$$

$$+ J \sum_{\bf r, \sigma, \sigma'} f_{\rho \tau \sigma}^{\dagger} f_{\tau \rho \sigma'} f_{\rho \tau \sigma'} f_{\tau \rho \sigma}$$

$$+ J' \sum_{\bf r, \tau \neq \tau'} f_{\tau \tau'}^{\dagger} f_{\rho \tau'} f_{\rho \tau'}^{\dagger} f_{\tau \tau'}, \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quan
effective oxygen sites. For instance, along the [110] direction, the effective $f-f$ hopping integral is given by $T^{(a)/2,a/2,0}_{\sigma\sigma'}(\alpha/a,0,0) = T^{(a)/2,a/2,0}_{\sigma\sigma'}(\alpha/a,0,0) + T^{(a)/2,a/2,0}_{\sigma\sigma'}(\alpha/a,0,0)$, where $\alpha$ is the lattice constant. Using $T^{\mu}_{\sigma\sigma'}$, we express $I^{(a)}$ as

$$I^{(a)}_{\sigma\sigma';\mu} = - (U' - J)^{-1} \sum_{\nu,\mu,\nu'} \left[ (T^{\nu}_{\sigma\sigma'})^* P_{\nu\sigma}^* P_{\mu\nu} T_{\mu\nu}^{\nu} - (\mu\nu)^* P_{\mu\nu}^* P_{\nu\sigma} T_{\nu\sigma}^{\nu} \right]$$

where $P_{\nu\sigma}$ denotes the inner product between one of the $\Gamma_5$ triplet states denoted by $\nu$ and the $f^2$ state labeled by $\sigma$ and $\sigma'$.

We note that the effective $f-f$ hopping integrals have the same form as those via $(f\sigma f)$ bonding. For instance,

$$T^{(a)/2,a/2,0}_{\sigma\sigma'} \propto \delta_{\sigma\sigma'} \delta_{\sigma\sigma'} + c_1 \sigma_{\tau\tau}^z \delta_{\sigma\sigma'} + c_2 \sigma_{\tau\tau}^y \sigma_{\tau\tau}^z ,$$

where $\sigma$ are Pauli matrices, and $c_1$ and $c_2$ are constants depending on $(pf\sigma)$ and $(pf\pi)$. This fact indicates that the form of the hopping integrals are restricted by $f$-electron symmetry, and the simple $(f\sigma f)$ model may grasp properties of actual materials with complex structures.

Concerning processes (b)–(e), we consider the effect of the Coulomb interaction at oxygen sites, symbolically expressed as “$U_p$”. In this paper, we study two limiting cases, $U_p=0$ and $U_p=\infty$. For $U_p=0$, multipole interaction contains all the processes (b)–(e), given by

$$I^{(b)}_{\sigma\sigma';\mu} = 2(\epsilon_p - \epsilon_f)^{-1} \sum_{\nu,\mu,\nu'} T^{\mu}_{\sigma\sigma'} T^{\nu-\mu}_{\sigma\sigma'} ,$$

$$I^{(c)}_{\sigma\sigma';\mu} = 2(\epsilon_p - \epsilon_f)^{-1} \sum_{\nu,\mu,\nu'} T^{\mu}_{\sigma\sigma'} T^{\nu-\mu}_{\sigma\sigma'} ,$$

$$I^{(d)}_{\sigma\sigma';\mu} = 2(\epsilon_p - \epsilon_f)^{-1} \sum_{\nu,\mu,\nu'} S^{\mu}_{\sigma\sigma'} S^{\nu-\mu}_{\sigma\sigma'} ,$$

and

$$I^{(e)}_{\sigma\sigma';\mu} = - I^{(d)}_{\sigma\sigma';\mu} ,$$

respectively, where

$$S^{\mu}_{\sigma\sigma'} = (\epsilon_f - \epsilon_p)^{-1} \sum_{\nu,\mu,\nu'} (T^{\nu}_{\mu\sigma\sigma'})^* T^{\nu}_{\mu\sigma\sigma'} .$$

Note that the sum of processes (d) and (e) merely becomes energy shift, since $I^{(e)}_{\sigma\sigma';\mu} + I^{(d)}_{\sigma\sigma';\mu} \propto \delta_{\sigma\sigma'} \delta_{\sigma\sigma'}$, and such terms can be eliminated in the present discussion. After all, the multipole interaction for $U_p=0$ is given by

$$I^{\mu}_{\sigma\sigma'} = I^{(a)}_{\sigma\sigma'} + 2(\epsilon_p - \epsilon_f)^{-1} T^{\mu}_{\sigma\sigma'} ,$$

Note that this term is expressed by only the effective $f-f$ hopping integral.

FIG. 3: Phase diagrams obtained from the multipole correlation functions. Here 3gF denotes $I_{3g}$ moment with $q = (0,0,0)$, and so on. The antiferro (AF) ordering vector is $q = (0,0,1)$ in units of $2\pi/a$ for all the AF phases. (a) Phase diagram for $U_p=0$. (b) Phase diagram for $U_p=0$ in a magnified scale around $(U'-J)/(\epsilon_p - \epsilon_f + U' - J)=0.145$ and $(pf\pi)=0$. (c) Phase diagram for $U_p=\infty$.

Now we move on to another limiting case $U_p=\infty$, in which the effect of $U_p$ is included by prohibiting processes (c) and (e). Thus, the effective interaction for $U_p=\infty$ is given by

$$I^{\mu}_{\sigma\sigma'} = I^{(a)}_{\sigma\sigma'} + I^{(b)}_{\sigma\sigma'} + I^{(d)}_{\sigma\sigma'} .$$

It should be noted that in the process (b), a couple of electrons exchange their sites by avoiding the effect of Coulomb interactions. Such a term is characteristic to the crystal structure of NpO$_2$, and it has a tendency to stabilize the octupole ordering, as shown later.
Using the effective Hamiltonian, we evaluate numerically the multipole correlation function, $\chi_{q}^\Gamma = \langle 1/N \sum_{r} e^{i q \cdot (r-r')} (X_{r}^\Gamma X_{r'}^\Gamma) \rangle$, where $\langle \cdots \rangle$ denotes the expectation value using the ground-state wavefunction. Here we take $N=8$, as shown in Fig. 11(b). Figures 2(a) and (c) show phase diagrams, presenting the multipole moment which has the largest value in the correlation function at each parameter set, for $U_p=0$ and $U_p=\infty$, respectively. For $U_p=0$, as shown in Fig. 2(b) in a magnified scale, there is a very small, but finite region of the $\Gamma_5u$ antiferro-octupole [$q=(0,0,1)$ in units of $2\pi/a$, 5uAF] phase. For $U_p=\infty$, on the other hand, the region of the 5uAF phase becomes much larger than that for $U_p=0$. The 5uAF phase locates in the parameter region with $\epsilon_p - \epsilon_f - U' - J$, in which processes (b) and (d) work effectively. Since process (d) provides only a quadrupole interaction, we conclude that the stabilization of the 5uAF phase originates from the process (b).

Note that the Coulomb energy in the $f^2$ intermediate state $U' - J$ is expected to be in the order of 1 eV, but we cannot estimate the difference of the energy levels of $p$ and $f$ electrons $\epsilon_p - \epsilon_f$ within the present theory. We also note that in the phase diagrams, the 5uAF phase appears for $(pf\pi) \simeq 0$. Since $(pf\sigma)$ and $(pf\pi)$ are treated as parameters in this paper, we have no clear answer why the absolute value of $(pf\pi)$ should be so small for the appearance of the 5uAF phase. In order to confirm the reality of the parameter region for the octupole phase obtained in this study is realistic or not, it is highly requested to perform the band-structure calculations for NpO$_2$. This is one of future problems.

In summary, on the basis of the $f$-$p$ model for NpO$_2$, we have found a finite region of the 5uAF phase for both cases of $U_p=0$ and $U_p=\infty$. Thus, we expect that this property is retained in the actual situation for NpO$_2$ with finite $U_p$. While the ordered state cannot be entirely determined within the present small-cluster calculation, it is confirmed that among structures with $q=(0,0,1)$ and equivalent ones, the triple-$q$ structure is energetically favorable since the $\Gamma_{5u}$ moment in the $\Gamma_8$ subspace has the easy axis along the [111] direction. We emphasize that the $\Gamma_{5u}$ antiferro-octupole phase is also realized in the simple $(ff\sigma)$ hopping model on an fcc lattice even without oxygen $p$ orbitals. These findings indicate that the tendency toward $\Gamma_{5u}$ antiferro-octupole ordering is common to $\Gamma_8$ models on fcc lattices.

We thank S. Kambe, N. Metoki, H. Onishi, Y. Tokunaga, K. Ueda, R. E. Walstedt, and H. Yasuoka for useful discussions. One of the authors (K. K.) is supported by the REIMEI Research Resources of Japan Atomic Energy Research Institute. Another author (T. H.) is supported by Japan Society for the Promotion of Science and by the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

References

1. P. Santini and G. Amoretti, Phys. Rev. Lett. 85, 2188 (2000); J. Phys. Soc. Jpn. 71 (Suppl.), 11 (2002).
2. B. D. Dunlap, G. M. Kalvius, D. J. Lam, and M. B. Brodsky, J. Phys. Chem. Solids 29, 1365 (1968); J. M. Friedt, F. J. Litterst, and J. Rebizant, Phys. Rev. B 32, 257 (1985).
3. W. Kopmann, F. J. Litterst, H. H. Klauf, M. Hillberg, W. Wagener, G. M. Kalvius, E. Schreier, F. J. Burghart, J. Rebizant, and G. H. Lander, J. Alloys Compd. 271-273, 463 (1998).
4. L. Heaton, M. H. Mueller, and J. M. Williams, J. Phys. Chem. Solids 28, 1651 (1967); D. E. Cox and B. C. Frazer, ibid. 28, 1649 (1967); R. Caciufo, G. H. Lander, J. C. Spirlet, J. M. Fournier, and W. F. Kuhs, Solid State Commun. 64, 149 (1987).
5. E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne, J. Chem. Phys. 21, 419 (1953).
6. J. W. Ross and D. J. Lam, J. Appl. Phys. 38, 1451 (1967); P. Erdős, G. Solt, Z. Zohner, A. Blaise, and J. M. Fournier, Physica B & C 102B, 164 (1980).
7. D. Mannix, G. H. Lander, J. Rebizant, R. Caciufo, N. Bernhoeft, E. Lidström, and C. Vettier, Phys. Rev. B 60, 15187 (1999).
8. S. W. Lovesey, E. Balcar, C. Detlef, G. van der Laan, D. S. Sivia, and U. Staub, J. Phys.: Condens. Matter 15, 4511 (2003).
9. J. A. Paixão, C. Detlef, M. J. Longfield, R. Caciufo, P. Santini, N. Bernhoeft, J. Rebizant, and G. H. Lander, Phys. Rev. Lett. 89, 187202 (2002); R. Caciufo, J. A. Paixão, C. Detlef, M. J. Longfield, P. Santini, N. Bernhoeft, J. Rebizant, and G. H. Lander, J. Phys.: Condens. Matter 15, S2287 (2003).
10. Y. Tokunaga, Y. Homma, S. Kambe, D. Aoki, H. Sakai, E. Yamamoto, A. Nakamura, Y. Shiokawa, R. E. Walstedt, and H. Yasuoka, Phys. Rev. Lett. 94, 137209 (2005).
11. O. Sakai, R. Shiina, and H. Shibai, J. Phys. Soc. Jpn 74, 457 (2005).
12. T. Hotta and K. Ueda, Phys. Rev. B 67, 104518 (2003).
13. K. Kubo and T. Hotta, Phys. Rev. B 71, 140404(R) (2005).
14. T. Hotta, J. Phys. Soc. Jpn. 74, 1275 (2005).
15. S. Kern, C.-K. Loong, and G. H. Lander, Phys. Rev. B 32, 3051 (1985); G. Amoretti, A. Blaise, R. Caciufo, J. M. Fournier, M. T. Hutchings, R. Osborn, and A. D. Taylor, Phys. Rev. B 40, 1856 (1989).
16. J. M. Fournier, A. Blaise, G. Amoretti, R. Caciufo, J. Larroque, M. T. Hutchings, R. Osborn, and A. D. Taylor, Phys. Rev. B 43, 1142 (1991); G. Amoretti, A. Blaise, R. Caciufo, D. Di Cola, J. M. Fournier, M. T. Hutchings, G. H. Lander, R. Osborn, A. Severing, and A. D. Taylor, J. Phys.: Condens. Matter 4, 3459 (1992).
17. S. Kern, C.-K. Loong, G. L. Goodman, B. Cort, and G. H. Lander, J. Phys.: Condens. Matter 2, 1933 (1990); S. Kern, R. A. Robinson, H. Nakotte, G. H. Lander, B. Cort, P. Watson, and F. A. Vigil, Phys. Rev. B 59, 104 (1999).
18. K. Takemagahara, Y. Aoki, and A. Yanase, J. Phys. C: Solid St. Phys. 13, 583 (1980).