Microscopic theory of multipole ordering in NpO$_2$

Katsunori Kubo and Takashi Hotta

Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
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In order to examine the mysterious ordered phase of NpO$_2$ from a microscopic viewpoint, we investigate an $f$-electron model on an fcc lattice constructed based on a $j$-$j$ coupling scheme. First, an effective model with multipole interactions is derived in the strong-coupling limit. Numerical analysis of the model clearly indicates that the interactions for $\Gamma_{4u}$ and $\Gamma_{5u}$ moments are relevant to the ground state. Then, by applying mean-field theory to the simplified model including only such interactions, we conclude that longitudinal triple-$\mathbf{q}$ $\Gamma_{5u}$ octupole order is realized in NpO$_2$ through the combined effects of multipole interactions and anisotropy of the $\Gamma_{5u}$ moment.

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The magnetism of actinide compounds has been one of the fascinating phenomena in the research field of condensed matter physics, since we have observed various ordered states at low temperatures due to the competition among several kinds of interactions between $5f$ electrons. Among them, the phase transition in NpO$_2$ is peculiar, and the determination of the order parameter has been a long-standing issue for many years. At first, this transition was expected to have a magnetic origin, due to the specific heat behavior similar to that of the antiferromagnet UO$_2$. In fact, a cusp in magnetic susceptibility has also been found at the transition temperature $T_0 \simeq 25$ K, as in an antiferromagnetic transition. However, no magnetic reflection has been observed in neutron diffraction experiments and more sensitive probes such as Mössbauer and $\mu$SR measurements have detected only a very small internal magnetic field. If it is caused by a dipole moment, the magnitude should be of the order of $0.01 \mu_B$. Thus, the transition is not the usual magnetic one, even though time reversal symmetry is broken.

Since the possibility of an ordinary magnetic transition is discarded, it may be natural to consider that the interesting properties of NpO$_2$ come from the orbital degeneracy of the $f$ electrons. However, typical orbital order, i.e., quadrupole order, does not break time reversal symmetry, and thus, we also discard this possibility. Finally, one may consider ordering of higher-order multipoles such as octupoles. In fact, recent results of resonant X-ray scattering experiments are consistent with this scenario. In order to explain superstructure Bragg peaks below $T_0$ due to longitudinal triple-$\mathbf{q}$ $\Gamma_{5u}$ quadrupole order, it has been proposed that longitudinal triple-$\mathbf{q}$ $\Gamma_{5u}$ octupole order is realized since it induces quadrupole order and breaks time reversal symmetry. Very recent experiments on the $^{170}$O NMR also support the triple-$\mathbf{q}$ ordered state.

In order to understand such multipole ordering, phenomenological theories have been developed up to now, assuming the existence of triple-$\mathbf{q}$ octupole order. These theories have consistently explained the experimental facts, such as a cusp in magnetic susceptibility, broken time reversal symmetry, no distortion from cubic structure a quadrupole moment observed in the resonant X-ray scattering, and the structure of $^{170}$O-NMR spectra. However, the origin of octupole order cannot be discussed in phenomenological theories. It was necessary to proceed to a microscopic theory to understand why such higher-order multipole order is realized in NpO$_2$, but it has been a very hard task to study multipole ordering from a microscopic level, since multipole moments originate from the complex combination of spin and orbital degrees of freedom of $f$ electrons.

In this paper, we attempt to overcome such a difficulty by considering a microscopic model based on a $j$-$j$ coupling scheme. Following the procedure to estimate the superexchange interaction in $d$-electron systems, we derive an effective multipole interaction model from a Hamiltonian on an fcc lattice corresponding to NpO$_2$. The correlation functions for multipole moments are numerically evaluated, suggesting that the interactions for $\Gamma_{4u}$ and $\Gamma_{5u}$ moments are relevant to the ground state. Then, we apply a mean-field theory to a simplified model including only such interactions. It is shown that the ground state has the longitudinal triple-$\mathbf{q}$ $\Gamma_{5u}$ octupole order, proposed phenomenologically for the low-temperature phase of NpO$_2$. We also evaluate specific heat and magnetic susceptibility for the triple-$\mathbf{q}$ octupole ordered state.

First we briefly explain our approximation to treat the multipole state. In general, Coulomb interaction, symbolically expressed by “$U$”, is larger than the spin-orbit interaction $\lambda$, leading to an LS coupling scheme, but the energy scale of the present problem is $T_0$, much smaller than both $U$ and $\lambda$. Since we find that the local ground state does not qualitatively depend on the order to take infinite limits of $\lambda/T_0$ and $U/T_0$, we prefer to use a $j$-$j$ coupling scheme, in which we accommodate $f$ electrons among sextet with total angular momentum $j=5/2$. For actinide dioxides, we propose to ignore further two states in the sextet. Due to crystalline electric field (CEF) effect for the CaF$_2$ structure, the sextet is split into $\Gamma_8$ quartet and $\Gamma_7$ doublet. In this case, the $\Gamma_7$ state is higher than the $\Gamma_8$ level and the splitting energy is defined as $\Delta$. When we accommodate two, three, and four electrons in the $\Gamma_8$ level, the ground states are $\Gamma_5$, $\Gamma_8^{(2)}$, and $\Gamma_1$, respectively, consistent with the CEF ground states of
\begin{align*}
\mathcal{H}_{\text{eff}} &= \sum_q (\mathcal{H}_{1q} + \mathcal{H}_{2q} + \mathcal{H}_{4u1q} + \mathcal{H}_{4u2q}), \\
\text{where } q \text{ is the wave vector. } \mathcal{H}_{1q} \text{ denotes the interactions between quadrupole moments, given by} \\
\mathcal{H}_{1q} &= a_1(O_{2x-z}^0O_{2y}^0c_xc_y + \text{c.p.}) \\
&\quad + a_3(O_{2y}^1O_{xy}^0s_xs_y + \text{c.p.}) \\
&\quad + a_4(O_{xy}^1O_{xy}^0c_xc_y + \text{c.p.}),
\end{align*}

(4)

where c.p. denotes cyclic permutations, \(e_v = \cos(q_ya/2)\), and \(s_v = \sin(q_ya/2)\) \((v = x, y, z)\). The definitions of the multipole operators and values of the coupling constants \(a_i\) are given in Tables II and III respectively. Note that \(O_{2y}^0\) transforms to \((\sqrt{3}O_{2y}^0 - O_{2y}^1)\) under c.p. \((x, y, z) \rightarrow (y, z, x)\) and \((x, y, z) \rightarrow (z, x, y)\). \(\mathcal{H}_{2q}\) and \(\mathcal{H}_{4unq}\) \((n = 1 \text{ or } 2)\) are the interactions between dipole and octupole moments, given by

\begin{align*}
\mathcal{H}_{2q} &= b_8[T_{zq}^5c_xc_z + c_zc_x + \text{c.p.}] \\
&+ b_9[T_{zq}^8s_xs_y + \text{c.p.}] \\
&+ b_{1q}T_{xy}c_zc_y + \text{c.p.},
\end{align*}

(6)

and

\begin{align*}
\mathcal{H}_{4unq} &= b_1^{(n)}[T_{zq}^{4un}c_xc_y + \text{c.p.}] \\
&+ b_2^{(n)}[T_{zq}^{4un}c_xc_z + c_zc_x + \text{c.p.}] \\
&+ b_3^{(n)}[T_{zq}^{4un}s_xs_y + \text{c.p.}] \\
&+ b_4^{(n)}[T_{xy}^{4un}s_xs_y + \text{c.p.}] \\
&+ b_5^{(n)}[T_{zq}^{4un}c_xc_y + \text{c.p.}] \\
&+ b_6^{(n)}[T_{zq}^{4un}c_xc_z + c_zc_x + \text{c.p.}],
\end{align*}

(7)

where values of the coupling constants \(b_i\) and \(b_i^{(n)}\) are shown in Table IV. The above Eqs. (4)-(7) are consistent with the general form of multipole interactions on the fcc
The multipole operators are represented by pseudospin operators: \[ \hat{q} = \sum_{r,r';\sigma} \hat{c}_{r\sigma}^\dagger \hat{c}_{r'\sigma} \] and \[ \hat{\sigma} = \sum_{r,\sigma \neq 0} \hat{c}_{r\sigma}^\dagger \hat{c}_{r\sigma} \] where \( \sigma \) are the Pauli matrices. We use notations \( \hat{q}^\pm = (\pm \sqrt{2} \tau^z \mp \tau^x)/2 \) and \( \hat{\sigma}^\pm = (\pm \sqrt{2} \tau^z \mp \sqrt{2} \tau^x)/2 \). The site label \( r \) is suppressed in this Table for simplicity.

| \( \Gamma_\gamma \) | \( \hat{X}_{\Gamma}^\gamma \) | \( \hat{O}_{xy}^\gamma \) | \( \hat{O}_{yz}^\gamma \) | \( \hat{J}_{4u}^\gamma \) | \( \hat{J}_{5u}^\gamma \) | \( \hat{J}_{6u}^\gamma \) |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 2u               | 3gv              | 3gy              | 4u1y             | 4u1y             | 4u1y             | 4u2y             |
| \( \hat{q}^\dagger \) | \( \hat{\sigma}^\dagger \) | \( \hat{\sigma}^\dagger \) | \( \hat{\sigma}^\dagger \) | \( \hat{\sigma}^\dagger \) | \( \hat{\sigma}^\dagger \) | \( \hat{\sigma}^\dagger \) |
| 12               | 64\( \sqrt{3} \) | 192              | 195              | -336             | 576              | -196             |
| \( b_{1}^{(1)} \) | \( b_{2}^{(1)} \) | \( b_{1}^{(1)} \) | \( b_{2}^{(1)} \) | \( b_{1}^{(1)} \) | \( b_{2}^{(1)} \) | \( b_{2}^{(1)} \) |
| \( 224\sqrt{3} \) | 0                | 0                | 4                | 193              | -336             | 64\( \sqrt{3} \) |
| \( 2\sqrt{3} \) | \( 12\sqrt{3} \) | \| \| \| \| \| |

FIG. 1: Correlation functions for the 8-site cluster for \( q = (0,0,0) \) (triangles), \( q = (0,0,1) \) (squares), and \( q = (1/2,1/2,1/2) \) (diamonds) in units of \( 2\pi/a \). The inset shows the fcc cluster (solid spheres) taken in the calculation.

We follow the notation in Ref. [23] for convenience.

When we apply a mean-field theory to the effective model, the effect of fluctuations may be strong enough to destroy the state obtained with mean-field theory. Thus, we first evaluate the correlation function in the ground state using an unbiased method such as exact diagonalization on the N-site lattice. We set \( N = 8 \), as shown in the inset of Fig. 1. The correlation function of the multipole operators is given by \( \chi_{q}^\gamma = \langle 1/N \rangle \sum_{r,r'} e^{i\mathbf{q} \cdot (r-r')} \langle X_{r}\rangle \langle X_{r'} \rangle \), where \((\cdots)\) denotes the expectation value using the ground-state wavefunction. Figure 1 shows results for the correlation functions. Although the interaction between \( \Gamma_\gamma \) moments \( (b_{10}) \) is large, the correlation function of the \( \Gamma_\gamma \) moment is not enhanced, indicating that the frustration effect is significant for an Ising-like moment such as \( \Gamma_{2u} \). Large values of correlation functions are obtained for \( J_{4u}^2, T_{5u}^2, \) and \( O_{xy} \) moments at \( q = (0,0,1) \) in units of \( 2\pi/a \). We note that there is no term in the effective model which stabilizes \( O_{xy} \) quadrupole order at \( q = (0,0,1) \). The enhancement of this correlation function indicates an induced quadrupole moment in \( \Gamma_{4u} \) or \( \Gamma_{5u} \) moment ordered states. Therefore, the relevant interactions are \( b_{2}^{(2)} \) and \( b_{8} \), which stabilize the \( J_{4u}^2 \) and \( T_{5u}^2 \) order, respectively, at \( q = (0,0,1) \). In the following, we consider a simplified model including only \( b_{2}^{(2)} \) and \( b_{8} \).

Next we study the ordered state by applying mean-field theory to our simplified model. The coupling constant \( b_{8} \) is slightly larger than \( b_{2}^{(2)} \), and \( \Gamma_{5u} \) order has lower energy than \( \Gamma_{4u} \) order. The interaction \( b_{8} \) stabilizes longitudinal ordering of the \( \Gamma_{5u} \) moments, but their directions are not entirely determined by the form of the interaction. In the \( \Gamma_{8} \) subspace, the \( \Gamma_{5u} \) moment has an easy axis along \( [111] \). Thus, taking the moment at each site along \([111]\) or other equivalent directions, we find that a triple-\( q \) state is favored, since it gains interaction energy in all the directions. In fact, the ground state has longitudinal triple-\( q \) \( \Gamma_{5u} \) octupole order with four sublattices, i.e., \( (T_{5u}^{x\gamma}, T_{5u}^{y\gamma}, T_{5u}^{z\gamma}) \propto \exp[i2\pi x/a], \exp[i2\pi y/a], \exp[i2\pi z/a] \). Note that this triple-\( q \) structure does not have frustration even in the fcc lattice. The ground state energy is \(-4b_{8} \) per site, and the transition temperature is given by \( k_{B}T_{0} = 4b_{8} \).

Let us evaluate physical quantities in the mean-field theory. Figures 2(a) and (b) show the temperature dependence of the specific heat and magnetic susceptibility, respectively. The calculated results are compatible with experimental ones for \( \text{NpO}_{2} \), but we should include higher energy states such as \( \Gamma_{7} \) for quantitative agreement, as already mentioned. This is one of future problems. Figures 2(c) and (d) show the magnetic field dependence of the magnetization at \( T = 0 \) and an \( H-T \) phase diagram, respectively. The magnetization is isotropic as \( H \rightarrow 0 \) due to the cubic symmetry, while anisotropy develops under a high magnetic field. Note that under a high magnetic field, sublattice structures change: \( (T_{5u}^{x\gamma}, T_{5u}^{y\gamma}, T_{5u}^{z\gamma}) \propto (0,0,\exp[i2\pi z/a]) \) for \( H \parallel [001] \), a two-sublattice structure with \( (T_{5u}^{x\gamma}, T_{5u}^{y\gamma}) \neq 0 \), and \( (T_{5u}^{z\gamma}) = 0 \) for \( H \parallel [110] \), and \( (T_{5u}^{x\gamma}, T_{5u}^{y\gamma}, T_{5u}^{z\gamma}) \propto \exp[i2\pi y/a], \exp[i2\pi x/a], \exp[i2\pi z/a] \) for \( H \parallel [111] \). Note also that the triple-\( q \) state is fragile under \( H \parallel [110] \). in order to confirm the octupole ordered state in \( \text{NpO}_{2} \), further experimental tests are required. One possibility is a neutron diffraction measurement under uniax-
sent the experimental values for ThO$_2$ from those for NpO$_2$.

(b) Temperature dependence of the magnetic susceptibility. The Landé $g$-factor is $g_J = 6/7$. Solid circles represent the experimental values for NpO$_2$. (c) Magnetic field dependence of the magnetization. (d) $H$-$T$ phase diagram. Solid symbols denote the $\Gamma_{5u}$ octupole transition, while open symbols denote transitions between $\Gamma_{5u}$ octupole ordered states with different sublattice structures. Note that $k_B T_0/(g_J \mu_B) = 43$ T for NpO$_2$.

In summary, multipole order in $f$-electron systems on the fcc lattice has been studied from a microscopic viewpoint. An effective model has been derived from a microscopic model based on the $j$-$j$ coupling scheme. Multipole correlation functions in the ground state of the effective model have been calculated by exact diagonalization. It has been revealed that the interactions for $\Gamma_{4u}$ and $\Gamma_{5u}$ moments are dominant. Mean-field theory has been applied to the simplified model including only such interactions, and longitudinal triple-$q$ $\Gamma_{5u}$ octupole order has been found to be realized.

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20. Even if we include the hopping via oxygen $p$ orbitals, the hopping matrix is written in the form of Eq. (2).
21. It is in sharp contrast to a model on a simple cubic lat-
In which the hopping integrals are real and the same form as for $e_g$ orbitals of $d$ electrons. In other words, there is no difference between the $\Gamma_8$ model for $f$ electrons and the $e_g$ orbital model for $d$ electrons on the simple cubic lattice in the absence of a magnetic field. For $e_g$ orbitals, we can always set the hopping integrals to be real, irrespective of the lattice type, by selecting appropriate basis wave-functions, while $\Gamma_8$ orbitals on the fcc lattice appear to be complex in nature, specific to $f$-electron systems with strong spin-orbit coupling.

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