# Magnetic-Octupole Order in Neptunium Dioxide?

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The phase transition occurring at 25 K in $NpO_2$, discovered almost 50 years ago, is the most long-lasting mystery in the physics of actinide compounds. Theories based on magnetic or electric-quadrupole order lead inevitably to fundamental, qualitative inconsistencies with observations. We show that the phenomenology of $NpO_2$ can be understood if the order parameter is assumed to be a magnetic octupole of $\Gamma_2$ $(xyz)$ symmetry. $NpO_2$ is the first compound for which indications of an octupolar phase transition have been found.

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Actinide compounds display rich and complex physical properties, which result from the interplay of a great number of microscopic interaction mechanisms [1]. The complexity of the Hamiltonian describing these compounds is mainly due to the combined effect of two factors. The former, which differentiates actinide from rare-earth compounds (excluding some of Ce), is the fairly great spatial extent of the partially filled $f$ orbitals. This makes $5f$ electrons display a wide range of localization degrees in the different compounds or, sometimes, in a given compound for different values of external parameters. Well localized, quasi-ionic regimes (e.g., $UO_2$ or $UPd_3$), fairly delocalized, Kondo fluctuations (e.g., UTe or $NpSn_3$) or mixed-valence regimes (e.g., PuS or PuSe), and itinerant regimes (i.e., with $5f$ electrons contributing to the volume enclosed by the Fermi surface), with strong (e.g., elemental Pu or $UPt_3$) or weak (e.g., elemental U or UC) electron correlations, are all represented. The second source of complexity, differentiating actinide from most transition-metal compounds, is the fact that the orbital angular momentum $\mathbf{L}$ is never quenched by the crystal field (CEF). Even when $5f$ electrons are itinerant it plays a qualitatively important role. The charge degrees of freedom associated with $\mathbf{L}$ are usually coupled to phonons, with resulting magnetoelastic and dynamical Jahn-Teller (DJT) phenomena. In addition, the unquenched $\mathbf{L}$ and the large radius of the $5f$ orbitals concur in complicating the electronic Hamiltonian considerably. In particular, magnetism is rarely described by a Heisenberg spin-only Hamiltonian, since interactions involving the orbital momentum come into play. These interactions are strongly anisotropic and involve magnetic-dipole as well as high-rank multipole moments of the $5f$ shell. Electric-multipole interactions transmitted by phonons, as well as exchange interactions between electric and magnetic multipoles of any allowed rank are to be expected. In intermetallic compounds, these latter interactions are mainly transmitted by conduction $(k)$ electrons through multipolar $k$-$f$ exchange coupling [2], while they are mostly of superexchange type in insulators [3].

Because of these effects, phase diagrams of compounds ordering magnetically may be particularly complex (e.g., U and Np monopnictides). Also, the existence of sizable multipolar interactions makes phase transitions governed by a nondipolar order parameter (OP) possible. Because of their definite parity, $f^n$ configurations possess only even-rank electric- and odd-rank magnetic-multipole degrees of freedom. While phase transitions driven by an electric-quadrupole OP are now known to occur in a certain number of rare-earth and actinide compounds, no multipolar OP of higher rank has ever been observed. By OP we intend a *primary* OP: when spherical symmetry is broken by the CEF, a primary OP involving the magnetic-dipole of the ion (which belongs to a certain representation, say $\Gamma_d$, of the point group) induces a *secondary* OP (to leading order proportional to the primary OP) involving magnetic octupoles of the ion belonging to $\Gamma_d$ (this is because of a bilinear dipole-octupole invariant in the Landau free energy). In cubic symmetry $\Gamma_d = \Gamma_4$, and dipolar ordering induces ordering of $\Gamma_4$ octupoles, and vice versa. Thus, in a cubic CEF only four out of seven octupoles are actually distinct from the dipoles. These belong either to the three-dimensional $\Gamma_5$ representation or to the one-dimensional $\Gamma_2$ representation. In lower symmetries the number of these octupoles is even lower: in tetragonal symmetry only two octupoles are distinct from dipoles, and only one in orthorhombic symmetry. In most compounds, moreover, these remaining purely octupolar degrees of freedom are quenched by the CEF. In cubic symmetry, of the eight possible representations ($\Gamma_1$ to $\Gamma_8$) to which the CEF ground state (GS) may belong, only two, i.e., $\Gamma_3$ and $\Gamma_8$, carry $\Gamma_2$ or $\Gamma_5$ magnetic-octupole degrees of freedom. Thus, even if octupolar ion-ion couplings are likely to be strong in actinides and Ce compounds, these might drive a purely octupolar phase transition in quite a limited number of cases. We propose such a phase transition to occur in $NpO_2$.

Dioxides are among the most studied actinide compounds (for a recent review, see Ref. [1]). They are cubic insulators with rather well localized $5f$ electrons (the

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ionization state of the actinide is 4+), and thus they are among the simplest compounds. In spite of this, many of their interesting physical properties are still awaiting a satisfactory theoretical interpretation. These properties result from three ingredients: CEF, coupling of $5f$ electrons to phonons, and complex superexchange interactions. The CEF potential is known with great precision from inelastic neutron scattering (INS) experiments, and is remarkably stable in $UO_2$, $NpO_2$, and $PuO_2$. Coupling to phonons is responsible for spectacular effects in $UO_2$ (anticrossing of spin-wave and phonon branches, DJT phenomena), in $NpO_2$ (bound state between CEF excitations and optical phonons) and also in $PrO_2$ (strong reduction of the magnetic moment). In $UO_2$, magnetic superexchange drives a phase transition towards a type-I antiferromagnetic (AFM) state at $T_N \sim 31$ K. The noncollinear $3\mathbf{k}$ structure, the first-order character, the reduction of the ordered moment, and the anomalous dispersion of spin waves, are all manifestations of the complexity of interactions in $UO_2$. These contain anisotropic dipolar as well as quadrupolar contributions. In $NpO_2$, even more complex properties are to be expected: while the $\Gamma_5$-triplet CEF GS of the $U^{4+}$ ions carries only magnetic-dipole and electric-quadrupole degrees of freedom, the $\Gamma_8$ quartet CEF GS of the $Np^{4+}$ ions carries, in addition, $\Gamma_2$ and $\Gamma_5$ magnetic-octupole degrees of freedom.

At $T_0 \sim 25.5$ K sizable anomalies in various macroscopic quantities indicate the occurrence of a phase transition in $NpO_2$. Discovered almost 50 years ago, this phase transition constitutes the most long-lasting mystery of the physics of actinide compounds. In fact, none of the several neutron-diffraction or Mössbauer experiments could provide any evidence for some type of magnetic order. Note that Mössbauer spectroscopy is an extremely reliable and sensitive technique for probing magnetic moments on Np ions, no matter what the magnetic structure is. Only a tiny, sample-dependent broadening of the resonance line is observed below $T_0$. Mössbauer results *definitely* rule out conventional magnetic order. On the one hand, spectra with an applied field disagree with what is expected in an antiferromagnet [4]. On the other hand, the tiny upper limit $\mu \sim 0.01\mu_B$ which is found for the ordered moment is impossible to reconcile with the large value of $T_0$, with the large size of the paramagnetic moment observed just above $T_0$ ($\sim 3\mu_B$), and with the large size of the macroscopic anomalies. In addition, INS shows that below $T_0$ the $\Gamma_8$ quartet is split by the OP molecular field by about 6.3 meV [5]. However, the molecular field associated with such a tiny $\mu$ would be far too small to produce the observed splitting. Another problem is that a magnetic transition would remove an entropy of the order of $k_B \log 4$ per Np ion, while the observed value is close to $k_B \log 2$ [6].

Since a dipolar OP is to be excluded, an electric-quadrupole OP $Q$ has been considered in Refs. [5,7,8] ($Q_{xy}$) and Ref. [4] ($Q_{3z^2-r^2}$). However, *any* quadrupolar OP encounters two fundamental problems: the first is that sizable *distortions* of the lattice would be produced by the strong magnetoelastic coupling of $Q$ to oxygen displacements of the same symmetry. Such distortions, for example, exist in the ordered phase of $UO_2$. No distortion has ever been detected in $NpO_2$, neither by neutrons [9,10], nor, more recently, by high-sensitivity x-ray measurements [11]. Only an anomaly in the $T$ dependence of the lattice parameter is observed at $T_0$. The second problem is that $Q$ would split the $\Gamma_8$ quartet into two Kramers doublets, possessing an anisotropic magnetic moment. Thus, the magnetic susceptibility $\chi(T)$ would display Curie-Weiss behavior as $T \to 0$ [4,5,8] (and, eventually, magnetic order would set in), while the observed $\chi$ is constant below $\sim 12$ K [8].

Two recent results increased, if possible, the mystery. Muon-spin rotation ($\mu$SR) experiments [12] display the sudden appearance of a precessing signal below $T_0$, which was interpreted as an indication of AFM ordering in $NpO_2$. By comparing the precession frequency with that observed in $UO_2$, an ordered moment of the order of $0.1\mu_B$ was deduced. More recently, resonant x-ray scattering experiments [11] detected a signal at $\mathbf{q} = \langle 100 \rangle$ which was interpreted as being due to AFM type-I order. The $\mu$SR result tells us that time-reversal symmetry is broken below $T_0$, and this again rules out a quadrupolar OP. As far as a dipolar OP is concerned, according to Mössbauer the ordered moment should be smaller than 0.01 $\mu_B$. As discussed above, this value is far too small to account for any property of $NpO_2$, and appears to be too small to account for $\mu$SR, as well.

We show in the following that the phenomenology of $NpO_2$ can be explained if $\Gamma_2$-type *magnetic octupole* order of $5f$ electrons is assumed to drive the phase transition. In particular, a model with a single free parameter can explain the value of $T_0$, the value of the splitting observed by INS below $T_0$, the value of the entropy removed by the order, the saturating behavior of $\chi(T)$ below $T_0$, the lack of any lattice distortion, the anomaly in the lattice parameter at $T_0$, the $\mu$SR precession signal, the sample-dependent Mössbauer line broadening below $T_0$, and, possibly, the x-ray results.

The simplest conceivable model Hamiltonian for the $Np^{4+}$ ions is

$$H = W\left[x\,\frac{O_4}{F(4)} + (1 - |x|)\,\frac{O_6}{F(6)}\right] - \lambda_{xyz} O_{xyz} \langle O_{xyz} \rangle (T)\,. \quad (1)$$

The first part represents the cubic CEF, in the usual notation [13], with $-1 \le x \le 1$. $H$ acts within the $^4I_{9/2}$ Russell-Saunders ground manifold only, thus $J$ mixing is neglected. The values of the CEF parameters $x$ and $W$ are derived from those of $UO_2$ through the appropriate scaling coefficients for Stevens factors and average powers of ionic radii. Using $x_{UO_2} = 0.9$, $W_{UO_2} = 4.3$ meV [14] leads to $x_{NpO_2} = -0.75$, $W_{NpO_2} = -1.74$ meV. With these values of $x$ and $W$ the first excited CEF state is a $\Gamma_8$ quartet, 49 meV above a $\Gamma_8$ quartet GS, in agreement with INS

results. The second excited state is a $\Gamma_6$ doublet at 123 meV (for details on these states see Ref. [13]).

The second term in Eq. (1) is an octupolar (superexchange) interaction decoupled in mean-field (MF), with $O_{xyz} = 1/6[J_xJ_yJ_z + \text{permutations}]$ the operator equivalent for the $\Gamma_2$ octupole moment of the Np ion, and $\langle O_{xyz}\rangle(T)$ its self-consistent mean value. As is well known, the *ab initio* calculation of superexchange interaction parameters is an extremely tough problem, even in the simpler case of dipole interactions with quenched orbital momentum. Thus, $\lambda_{xyz}$ is left as a free parameter. The interaction produces a second-order phase transition towards a state with octupolar order, i.e., $\langle O_{xyz}\rangle \neq 0$, at a transition temperature $T_0$ given by the usual MF relation $\chi^{-1}_{xyz}(T_0) = \lambda_{xyz}$, with $\chi_{xyz}(T)$ the single-ion $\Gamma_2$-octupole susceptibility. Below $T_0$ time reversal symmetry is broken, and the $\Gamma_8$ GS quartet splits into two *non-Kramers* doublets, belonging to the $\Gamma_6$ and $\Gamma_7$ representations of the tetrahedral group. The entropy removed is then $k_B \log 2$ per Np ion, as observed. If only the $\Gamma_8$ GS is considered, an analytic calculation of $T_0$ and of the splitting $\Delta$ between the doublets is possible. We find that

$$\Delta(T = 0) = 2k_B T_0 . \tag{2}$$

The measured value $\Delta(T = 0) \sim 6.3$ meV gives $T_0 \sim 36$ K, 41% larger than the actual $T_0$. This result is satisfactory given the crudity of the model, the MF approximation, and the fact that even in $UO_2$ the exchange deduced from INS leads to overestimating $T_N$ by $\sim$35% [15].

Note that the octupolar OP has no quadrupolar or dipolar secondary OP's associated: Since the representation of $O_{xyz}$, $\Gamma_2$, is one dimensional, the only possible secondary OP's, $\eta$, involve either time-odd quantities belonging to $\Gamma_2$ [$\eta = \mathcal{O}(\langle O_{xyz}\rangle)$] or time-even, symmetric quantities belonging to $\Gamma_1$ [in particular, a contribution $\eta = \mathcal{O}(\langle O_{xyz}\rangle^2)$ to $\langle O_4\rangle$ and $\langle O_6\rangle$; see Eq. (1)]. This has three consequences, which agree with observations: the static magnetic moment on the Np sites is zero; no distortion of the lattice occurs below $T_0$; an anomaly in the $T$ derivative of the lattice parameter at $T_0$ is produced by the magnetoelastic coupling of the $\Gamma_1$ secondary OP's to the fully symmetric volume strain. What is remarkable is that besides lacking a static magnetic moment, the two doublets have an effective paramagnetic moment $\mu_p$ close to zero. It appears that $\mu_p$ is zero at $x = -0.73$ and remains very small in a large interval of values of $x$ (e.g., $\mu_p < 0.3\mu_B$ for $-0.77 < x < -0.685$) [16]. Therefore, all components of the magnetic susceptibility $\chi(T)$ tend to saturate below $T_0$ (see Fig. 1). When $x$ is not exactly equal to $-0.73$, $\chi(T)$ increases again at very low $T$. This increase, and the residual $k_B \log 2$ entropy, must eventually be removed by a second phase transition. This would be characterized by tiny-moment magnetic order and by local lattice distortions with a trigonal component (see the following discussion about Mössbauer). Measurements at very low $T$ on high-quality, newly prepared samples would be needed to check this.

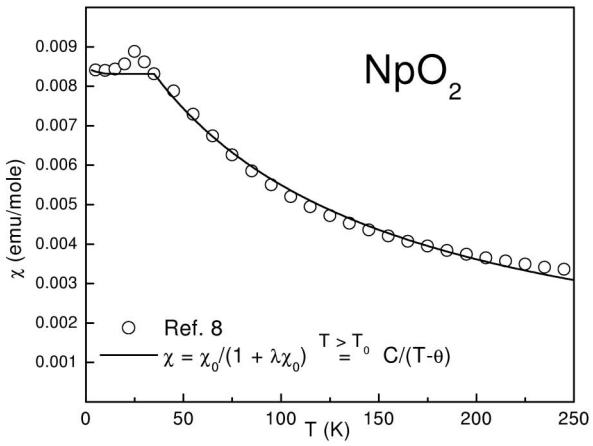


FIG. 1. Magnetic susceptibility of $NpO_2$ from the MF model. $\chi_0$ is the MF susceptibility from Eq. (1). Only the $\Gamma_8$ CEF GS has been included. The value used for $\lambda$, 88 mol/emu, corresponds to the paramagnetic Curie temperature $\theta = -92$ K.

Although the magnetic moment on the Np sites is zero, the octupole produces a *magnetic* field in interstitial regions (multipole expansion of the magnetic field). The key point is that the field produced by a sizable octupole may be comparable in strength with the field produced by a very small dipole. This may explain the $\mu$SR results, since muons probe interstitial regions locally. The octupolar interstitial field has spin and orbital contributions which were calculated in Ref. [17] in terms of the orbital and spin angular momentum operators of the ion. Consider a Np ion at the origin, a given point $\mathbf{R}$ and a reference system $(x', y', z')$ with the $z'$ axis along $\mathbf{R}$. By projecting $\mathbf{L}$ and $\mathbf{S}$ onto $\mathbf{J}$, we find that the orbital and spin parts of the (magnetostatic) coupling between the octupole moment of the Np ion and the magnetic moment $\mathbf{I}$ of a muon at $\mathbf{R}$ are given by

$$\begin{aligned} H_{\text{spin}} &= -12\mu_B(g_J - 1)\alpha_J\langle r^2\rangle R^{-5}\hat{T} , \\ H_{\text{orb}} &= -3\mu_B(2 - g_J)\alpha_J\langle r^2\rangle R^{-5}\hat{T} , \\ \hat{T} &= 2I_{z'}O_3^0(\mathbf{J}') + \sqrt{3/4}[I_+O_3^{-1}(\mathbf{J}') + I_-O_3^1(\mathbf{J}')] , \end{aligned} \tag{3}$$

where $I_\pm = I_{x'} \pm iI_{y'}$, $\langle r^2\rangle$ is the average square radius of $5f$ orbitals, $g_J$ and $\alpha_J$ are, respectively, the Landé and second-order Stevens factors, and the $O_3^Q(\mathbf{J}')$ are rank-3 tensor operators defined in Ref. [18]. When $\langle O_3^Q(\mathbf{J}')\rangle \neq 0$, $Q = 0, 1, -1$, the muon experiences an average static magnetic field. By performing a rotation of the tensor operators from the local (primed) reference system to the standard (unprimed) cubic-axes reference system, we calculate the quantities $\langle O_3^Q(\mathbf{J}')\rangle$ in terms of the static octupolar moment $\langle O_{xyz}\rangle$ on the Np ion, which is proportional to $\langle O_3^2(\mathbf{J}) - O_3^{-2}(\mathbf{J})\rangle$. The total field at $\mathbf{R}$ is obtained by summing over all Np ions within a large enough cutoff distance from $\mathbf{R}$. We show in Fig. 2 a map of the interstitial magnetic field at $T = 0$, assuming type-I antiferro-octupolar order with modulation wave vector $\mathbf{k} = 2\pi/a(001)$ (a similar result is obtained for

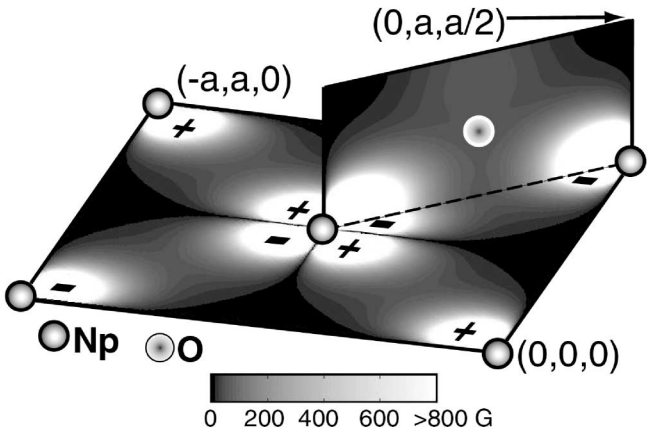


FIG. 2. Interstitial magnetic field intensity in the antiferro-octupolar-ordered phase at $T = 0$. A cut along a cubic face and one along its diagonal are shown. The field on the face is along $z$, with the sign indicated. The field observed in $\mu$SR is of the order of 500 G [12].

ferro-octupolar order). The octupole field has the same order of magnitude as the field detected by $\mu$SR in many interstitial regions. Thus, the present model may explain the existence of the interstitial field detected by $\mu$SR, in the lack of an atomic magnetic moment.

We come now to the Mössbauer line broadening below $T_0$. Since the interstitial field produced by the octupoles is zero at the Np sites, it gives no hyperfine effects. A direct coupling between the electronic and nuclear octupole moments is allowed by symmetry (octupole-octupole interaction), but the associated Mössbauer line broadening is expected to be extremely small. The strong dependence of the broadening on the sample and on its preparation suggests a defect origin, in particular imperfect stoichiometry or self-irradiation damage [19]. But why should static, $T$-independent defects give a sudden $T$-dependent broadening for $T < T_0$? This is expected from the model: below $T_0$ small *structural* perturbations may induce, locally, tiny *magnetic* moments on Np ions. The reason of this unusual "structure"-induced magnetism is the time-reversal symmetry breaking by the OP. As a consequence of this, it can be shown that local trigonal strains around an Np ion (coupling to the ionic quadrupole moments $Q_{xy}$, $Q_{xz}$, $Q_{yz}$) split the two doublets in the same way as a local magnetic field (coupling to $J_z$, $J_y$, $J_x$), inducing therefore a small magnetic moment. The $T$ dependence of these defect-induced moments reflects that of the OP, and is sensed by Mössbauer spectroscopy in defect-rich samples.

At last, we would like to comment on the resonant x-ray scattering results. Although these had been fitted to a model assuming longitudinal type-I AFM order [11], such assumption disagrees with Mössbauer results, which rule out magnetic order. An x-ray signal may have two possible origins within the present model: the first is resonant scattering from octupole moments [20]. The second possibility is that the x-ray signal arise from the defect mechanism outlined above in connection with Mössbauer. Below $T_0$, areas of the sample under strain fields with a trigonal component would develop tiny-moment magnetic order with the same wave vector as the underlying octupolar order. In particular, strained near-surface regions would be good candidates, given the small penetration depth of x rays in resonance conditions. The large correlation length (~6000 Å) inferred from the experiment would result from the fact that strain fields are usually long ranged.

In conclusion, the phase transition of $NpO_2$ can be understood if the OP is assumed to be the $\Gamma_2$ magnetic octupole of the $Np^{4+}$ ion. Interestingly, it has recently been discovered [21] that strong AF interactions between $\Gamma_2$ octupoles play an important role in the physics of $CeB_6$, which shares with $NpO_2$ a $\Gamma_8$ CEF ground state.

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