Triple-$q$ octupolar ordering in NpO$_2$

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We report the results of resonant X-ray scattering experiments performed at the Np $M_{4.5}$ edges in NpO$_2$. Below $T_0 = 25$ K, the development of long-range order of Np electric quadrupoles is revealed by the growth of superlattice Bragg peaks. The electronic transition is not accompanied by any measurable crystallographic distortion, either internal or external, so the symmetry of the system remains cubic. The polarization and azimuthal dependence of the intensity of the resonant $\mu$E1-processes ($3d_{3/2,5/2} \leftrightarrow 5f$) is well reproduced assuming anisotropic tensor susceptibility (ATS) scattering from a triple-$q$ longitudinal antiferroquadrupolar structure. Electric quadrupole order in NpO$_2$ could be driven by the ordering at $T_0$ of magnetic octupoles of $\Gamma_5$ symmetry, splitting the Np ground state quartet and leading to a singlet ground state with zero dipole magnetic moment.

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For half a century the low temperature properties of NpO$_2$ have mystified theorists and experimentalists alike. Upon cooling from room temperature a single phase transition is observed at $T_0 \approx 25.5$ K [5]. Similarities with UO$_2$ [3] suggested a magnetic nature of the phase transition, but no magnetic order was found by neutron diffraction [3] nor by Mößbauer spectroscopy [1], which established an upper limit of $\approx 0.01 \mu_B$ for the ordered magnetic moment $\vec{\mu}_{ord}$. However, Np$^{4+}$ ions in NpO$_2$ are Kramers ions ($5f^3$, $4I_{9/2}$). In the absence of interactions breaking time-reversal symmetry the ground state has to carry a magnetic moment, $\vec{\mu}$, whatever the crystalline environment. A fluctuating magnetic moment of finite size would be revealed by a Curie-like divergence of the susceptibility at low temperatures, whereas the experiments reveal a flat susceptibility between 15 and 5 K [5]. Moreover, no evidence for a crystallographic distortion, neither external nor internal, has been found by synchrotron experiments [1].

Another element of the puzzle was recently provided by muon spin relaxation experiments, showing the abrupt appearance of a precession signal below $T_0$ [6]. This implies that the order parameter (OP) sets up a magnetic field at the muon stopping site and provides definitive evidence that the OP breaks invariance under time reversal. By assuming antiferromagnetic (AF) order of the same kind of that established for UO$_2$, i.e. a type-I, triple-$q$ structure, the authors deduced an ordered moment $\mu_{ord} \approx 0.1 \mu_B$, a value much larger than the upper limit compatible with Mößbauer spectroscopy. In parallel with this finding, direct evidence for long-range order in NpO$_2$ was obtained through the observation below $T_0$ of superlattice reflections in resonant X-ray scattering (RXS) experiments at the Np $M_{4.5}$ absorption edges [5]. The superstructure Bragg peaks occur at $\vec{Q} = \vec{G} + (0 \, 0 \, 1)$ positions, where $\vec{G}$ is a reciprocal lattice vector. This is the same periodicity found for the AF phase in UO$_2$, and the observations were taken as evidence for the occurrence of longitudinal triple-$q$ AF order. Santini and Amoretti [5] pointed out the possibility of explaining the whole body of experimental evidence assuming magnetic-octupole order instead of magnetic-dipole order. Octupolar order would lift the degeneracy of the $\Gamma_8$ Np ground state and generate an interstitial magnetic field, in agreement with neutron spectroscopy [5] and muon spin resonance results. However, octupolar order can be directly observed in RXS only through E2-resonances, whilst the resonances observed in [6] are at the E1 absorption edge. Indeed, all previous experimental data taken at the actinide $M_{4.5}$ edges indicates a very strong dominance of E1-processes ($3d_{3/2,5/2} \leftrightarrow 5f$). To our knowledge there is no evidence for E2 contributions ($3d_{3/2,5/2} \leftrightarrow 6g$), and indeed matrix elements involving E2 promotion to 6g states are expected to be too small to allow for any observable signal.

To clarify the above confusion, we have undertaken a new RXS experiment at the magnetic scattering beamline, ID20, of the ESRF. We performed polarization analysis of the diffracted radiation and measured the dependence of the intensity from the azimuthal angle, $\psi$ (the angle describing the rotation of the crystal about the scattering vector). These analyzes were not possible in the experiment reported earlier in [6], preventing an unambiguous determination of the origin of the resonance.
FIG. 1: Energy scans through the Np M\textsubscript{4} absorption edge. The $\sigma \rightarrow \pi$ (main panel) and $\sigma \rightarrow \sigma$ (not shown) resonances of the (0 0 3) superstructure peak have a Lorentzian-squared (solid line) rather than a Lorentzian (dashed line) line shape. The maximum at the resonance lies at the absorption edge as measured at the (0 0 2) Bragg reflection (insert).

Indeed, the results we present in this Letter show that the superlattice peaks in NpO\textsubscript{2} are not magnetic, but arise from the asphericity of the Np 5\textit{f} electron density leading to an anomalous tensor component in the atomic scattering factor. In other words, the superlattice peaks signal the occurrence of electric-quadrupole long range order below T\textsubscript{0}. This conclusion is incompatible with the particular octupolar model given in Ref. [8], which predicts an undistorted charge density for the 5\textit{f} ground state, with vanishing quadrupole moment.

The experiment was performed on a single crystal of 0.7 $\times$ 0.7 $\times$ 0.2 mm\textsuperscript{3} in volume, with a flat (0 0 1) surface. A closed-cycle refrigerator equipped with an azimuthal-rotation stage provided a base temperature of 12 K. An Au(1 1 1) single crystal was used to analyze whether the polarization of the scattered beam was parallel ($\pi$) or perpendicular ($\sigma$) to the scattering plane. The incident beam had $\sigma$ polarization and the scattering plane was vertical.

Fig. 1 shows the $\sigma \rightarrow \pi$ intensity of the $\vec{Q} = (0 0 3)$ superlattice reflection as a function of the photon energy, E, around the Np M\textsubscript{4} absorption edge. The data can be fit to a Lorentzian squared line-shape, centered near the E1 threshold. The presence of a resonance in the $\sigma \rightarrow \sigma$ channel (not shown) excludes that the scattering arises from dipole-magnetic order, as this would give only $\sigma \rightarrow \pi$ resonant scattering. Studies measuring magnetic order at actinide M edges have shown Lorentzian energy profiles, whereas we clearly observe a Lorentzian-squared form, as it is expected when the intermediate state splitting is much smaller than the core hole life time.

The dependence of polarization and intensity of the scattered radiation on $\psi$ can be modeled with satisfactory agreement by assuming a triple-$\vec{q}$ antiferroquadrupolar ordering of ($\Gamma_5$) quadrupoles, and using the ATS cross section, with the Stokes parameter $P_1 = (I_{\sigma \rightarrow \pi} - I_{\sigma \rightarrow \sigma})/(I_{\sigma \rightarrow \sigma} + I_{\sigma \rightarrow \pi})$ and $P_2 = (I_+ - I_-)/(I_+ + I_-)$ [11], for the (0 0 1) and (0 0 3) reflections. $P_2$ can be considered as a measure of the phase relation between the two polarization channels and is defined by the intensities measured with the analyzer oriented at $\pm 45^\circ$ with respect to the scattering plane,

$$I_{\pm} \propto \frac{1}{\sqrt{2}} |F_{\sigma \rightarrow \sigma} \pm F_{\sigma \rightarrow \pi}|^2$$

where $F_{\sigma \rightarrow \sigma}$ and $F_{\sigma \rightarrow \pi}$ are the $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ scattering amplitudes.

The dependence of polarization and intensity of the scattered radiation on $\psi$ can be modeled with satisfactory agreement by assuming a triple-$q$ antiferroquadrupolar ordering of ($\Gamma_5$) quadrupoles, and using the ATS cross section.
Above \( T_0 \), \( \text{NpO}_2 \) crystallizes in the Fluorite structure with space group (SG) \( Fm\overline{3}m \), \( \text{Np}^{4+} \) at \( 4a \) and \( \text{O}^{2-} \) ions at \( 8c \) Wyckoff positions. A periodic distribution of electric quadrupoles can be Fourier expanded, wherever the type of order. A triple-\( q \) structure is obtained when 3 components of the star of the propagation vector \( \mathbf{q} \) enter in the Fourier sum. For \( \mathbf{q}_1 = (1 \ 0 \ 0) \), \( \mathbf{q}_2 = (0 \ 1 \ 0) \) and \( \mathbf{q}_3 = (0 \ 0 \ 1) \), the arrangement schematically shown in Fig. \( 3 \) is obtained, with charge distribution distorted along the \( (1 \ 1 \ 1) \) directions of the cubic unit cell. The SG symmetry is lowered from \( Fm\overline{3}m \) to \( Pn\overline{3}m \), the only maximal non-isomorphic subgroup of \( Fm\overline{3}m \) that is non-symmetric and simple cubic. Within this SG, \( \text{Np} \) ions can be accommodated on the \( 4b \) positions, with reduced point symmetry \( D_{4h} \) but the same crystallographic extinction rules of the FCC para-quadrupolar SG. Oxygen ions can occupy two inequivalent positions (\( 2a \) and \( 6d \)), where all coordinates are uniquely fixed by symmetry alone, so that this electronic phase transition does not allow a shift of the oxygen ions. The symmetry of the ordered state remains cubic and, apart from a possible change of the lattice parameter \( f \), the transition will not be accompanied by any distortion. In that case, the quadrupolar OP cannot be measured with neutron or conventional X-ray diffraction techniques.

RXS from quadrupolar order has recently been observed in several systems [12, 13, 14]. It is well described within the framework of ATS scattering [12, 13, 14], which occurs when the photon energy is tuned to an absorption edge of an atom. The anisotropy of this atom’s polarizability may lead to a finite scattering cross section at reflections which are normally forbidden due to glide plane or screw axis extinction rules. The scattering amplitude arising from E1 transitions can be described by second rank tensors, which are invariant under the point symmetry of the scattering atom.

The scattering amplitude for the induced quadrupolar order must be represented by a symmetric tensor \( \tilde{F}(Q) \). For \( \bar{Q} = (0 \ 0 \ L) \), with \( L \) odd, the scattering length is given by \( F(\bar{Q}) = \bar{e} \cdot \tilde{F}(\bar{Q}) \cdot \bar{e} = \tilde{F}(\epsilon_x \epsilon_y + \epsilon_y \epsilon_x) \), where \( \epsilon \) and \( \bar{e} \) are the vectors of the incident and scattered beam, and \( \tilde{F} \) is proportional to the Fourier component of the quadrupolar operator, \( \Phi \). With incident \( \sigma \) polarization and \( \tilde{h} = (1 \ 0 \ 0) \) as azimuthal reference vector, we find

\[
F_{\sigma \rightarrow \sigma} = \tilde{F}(\sigma) = \tilde{F}(\epsilon_x \epsilon_y + \epsilon_y \epsilon_x) \quad (2)
\]

\[
F_{\sigma \rightarrow \pi} = \tilde{F}(\pi) = \tilde{F}(\epsilon_x \epsilon_y + \epsilon_y \epsilon_x) \quad (3)
\]

where \( \theta \) is the Bragg angle. The resulting scattered intensities are \( I_{\sigma \rightarrow \pi} \propto |F_{\sigma \rightarrow \pi}|^2 \) and \( I_{\sigma \rightarrow \pi} \propto |F_{\pi \rightarrow \pi}|^2 \). As shown in Fig. 2(a), the experimental data are well matched by this model with one overall scale factor. This factor can be eliminated by calculating the Stokes parameter \( P_1 \). The data are shown in Fig. 2(b), along with model calculations.

The quantities \( I_{\pm} \) defined in eq. 1 are given by

\[
I_{\pm} \propto |\tilde{F}(\sigma)|^2 (1 - \cos^2(\theta) \cos^2(2\psi) \pm \sin(\theta) \sin(4\psi)) \quad (4)
\]

The Stokes parameter \( P_2 \) can be calculated, and is in good agreement with the experiments, Fig. 2(c).

However, the quadrupolar order alone is not a sufficient ingredient, as it cannot explain the absence of a disordered magnetic moment [15] and the breaking of invariance under time reversal [16]. The lowest-rank multipolar OP consistent with the experimental findings (no ordered and fluctuating dipoles, broken time reversal symmetry) is an octupole. Under octahedral symmetry, the seven octupolar operators belong to irreducible representations \( \Gamma_2, \Gamma_4 \) or \( \Gamma_5 \). A \( \Gamma_4 \)-octupole OP must be ruled out. In fact, this would always be accompanied by an ordering of dipoles as the latter belong to \( \Gamma_4 \) as well. A \( \Gamma_2 \) OP is consistent with most properties of \( \text{NpO}_2 \), but it cannot explain the RXS results, as it does not carry an electric quadrupole moment and the \( \sigma \rightarrow \pi \) signal would vanish [17]. \( \Gamma_5 \) octupolar operators are given by symmetrized combinations of \( O_{3z} = J_z (J_z^2 - J_x^2) \), where \( ijk = xyz \), \( xyz \) or \( zzy \). The little cogroup of the ordering wavevector is \( D_{4h} \). \( \Gamma_5 \) decomposes into the tetragonal representations \( \Gamma_4^{(1)} \) (1-d) and \( \Gamma_5^{(2)} \) (2-d), which identify two possible type-I octupolar orders, a “longitudinal” one and a “transverse” one. For a single-\( q \) structure, both types of OPs are inconsistent with the observed quenching of dipoles and with the present RXS results. There is just one single type of order which can explain all observations, and this is a triple-\( q \) longitudinal structure, in which the \( \Gamma_4^{(1)} \) OPs associated with the three wavevectors...
of the star of \( \vec{q} \) have the same amplitude, \( \rho \). The simplest conceivable mean-field (MF) Hamiltonian for each of the four sublattices \( s \) includes the crystal field (CF) potential \( \xi \) and a self-consistent octupolar interaction term

\[
\lambda O(\vec{n}(s))(O(\vec{n}(s)))(T),
\]

where \( \vec{n}(s) \) represents one of the four inequivalent \((1\,1\,1)\) directions, \( O(\vec{n}(s)) = \sum_{i=x,y,z} O_{ni}(s) \), \( \lambda \) is a MF constant, and \( (O(\vec{n}(s)))(T) \) is the self-consistent average value of \( O(\vec{n}(s)) \), which does not depend on \( s \) and is nonzero for \( T < T_0 \). The MF potential lowers the symmetry of the \( Np \) Hamiltonian from \( O_h \) to \( D_{3d} \) and splits the \( \Gamma_8 \)-quartet CF ground state into two singlets, \( \Gamma_5 \) and \( \Gamma_6 \), and one doublet, \( \Gamma_4 \), of \( D_{3d} \). \( \Gamma_5 \) and \( \Gamma_6 \) are complex-conjugate representations, which are degenerate for a time-reversal invariant Hamiltonian, whereas their degeneracy is lifted by the time-odd OP. By choosing the value of \( \lambda \) which reproduces the observed \( T \rightarrow 0 \) sequence at \( T = 0 \) is found to be singlet-doublet-singlet. The ground state has zero dipole moment and the susceptibility saturates for \( T \rightarrow 0 \), as observed [3]. These properties do not depend on the details of the CF Hamiltonian (i.e. on the precise value of the CF parameter \( x \) or whether \( J \)-mixing is taken into account).

This octupolar OP induces the observed triple-\( \vec{q} \) structure of \( \Gamma_5 \) quadrupoles as secondary OP, with an amplitude \( \propto \rho^2 \) in MF near \( T_0 \). The charge density is distorted along \( \vec{n}(s) \), as quantified by the quadrupolar operator along \( \vec{n}(s) \), \( \Phi(\vec{n}(s)) \propto \alpha [3(\vec{n}(s) \cdot \vec{J})^2 - J(J+1)] \) where \( \alpha \) is a Stevens coefficient. \( \Phi \) is negative in the ordered phase, indicating a charge distribution “oblate” along \( \vec{n}(s) \). This quadrupolar secondary OP is the quantity observed in the RXS experiment.

The model we propose excludes a lattice distortion or a shift of the oxygen positions. The reduction of the local symmetry at the \( Np \) site leads to an electric field gradient along the \((1\,1\,1)\) directions. This explains the line broadening observed below \( T_0 \) in Mößbauer spectroscopy [1]. The octupolar order breaks time reversal symmetry and thus allows the occurrence of interstitial magnetic fields as evidenced by \( \mu \)SR [4].

Finally, we remind the reader that we have inferred the triple-\( \vec{q} \) symmetry and octupolar order from the boundary conditions set out by previous experimental observations, such as the absence of lattice distortions, the analogy to \( UO_2 \), and from the excellent agreement of our data with the model. At the \( E2 \) edge, the principal OP, i.e., the \( \Gamma_5 \) magnetic octupole, is expected to give a resonant contribution to the scattered intensity [7], comparable to that expected at the same energy from the secondary OP, the \( \Gamma_5 \) electric quadrupoles. However, no signal has been detected at the \( E2 \) edge, indicating that both contributions are below the sensitivity of the experimental device we used. At the \( E1 \) edge the intensity is almost entirely of quadrupolar origin, Indeed, the \( \sigma \rightarrow \sigma \) intensity has no magnetic contributions, and we can fit both the \( \sigma \rightarrow \sigma \) and \( \sigma \rightarrow \pi \) intensities using a single scaling factor, which should not be possible with a sizable magnetic contribution in the \( \sigma \rightarrow \pi \) channel. Such a contribution could originate from an ordered magnetic moment in the bulk, but Mößbauer spectroscopy establishes it unambiguously to be vanishing, or from dipolar order around defects, but this would give broad peaks which are not observed.

Whilst we have no direct evidence for a triple-\( \vec{q} \) magnetic structure, and cannot directly prove the octupolar model, several predictions about the low temperature properties can be investigated. Octupolar order will split the \( \Gamma_8 \) CF ground state into a singlet ground state and two excited levels. Inelastic neutron scattering [8] has shown an excitation near 6.5 meV, but the second one is expected to lie below 2 meV, outside the explored energy range. Low temperature specific heat measurements should also show the characteristic signature of the CF spectrum. The integrated entropy from lowest temperatures up to the phase transition should be \( R \ln(4) \), with a significant contribution from a Schottky anomaly below 8 K. If large single crystals would become available, octupolar order could also be directly observed by neutron diffraction, with a form factor peaking at a finite value of the momentum transfer and reflecting the Fourier transform of the static magnetization density below \( T_0 \).

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