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Magnetic multipole order and symmetry considerations on the ground state of Np^{4+} ions in NpO_2

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Abstract

The ground-state symmetries of Np ions in the low temperature phase of NpO_2 are discussed with reference to the results of resonant X-ray scattering experiments suggesting the occurrence of long-range multipolar order with electric quadrupole secondary order parameter. Two models have been proposed in the literature: one based on a Γ_4 doublet (in D_{3d} point group), the other on a Γ_5 (Γ_6) singlet. We show, through a theoretical group analysis, that the Γ_4 doublet is not compatible with the available experimental data. Our analysis supports the hypothesis of a singlet ground state.

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1. Introduction

The low-temperature properties of NpO_2 have recently attracted much attention due to some peculiar aspects of its magnetic ground-state [1–9]. A convincing picture has become available only in the last 5 years, after the key indication of a time-reversal breaking order parameter below $T_0 \simeq 25\,\mathrm{K}$ [10], the absence of crystallographic distortions [1], and the proposal of a magnetic octupole as primary order parameter [11].

The origin of the controversy about the ground-state properties aroused from the absence of a sizeable magnetic dipole order, as indicated by negative Mössbauer spectroscopy, and neutron diffraction results [3]. The existence of a static magnetic field distribution around the Np ions in the ordered phase was revealed by μSR experiment [10]. This experimental evidence paved the way to the hypothesis that higher-order magnetic multipoles could play the role of order parameter at the transition. Quadrupole magnetic moments being excluded, because Np positions are inversion centres, magnetic octupole moments were considered [11] and in particular the components transforming like Γ_2 (singlet) and Γ_5 (triplet) in octahedral fields. The first possibility is maintained in Ref. [11] and appears compatible with a Γ_4 doublet ground-state in D_{3d}. The second type of symmetry for the octupole has been advanced in Refs. [2,3] and assumes a Γ_5 (Γ_6) singlet ground-state.

In this brief report we restate the theoretical analysis of the ground-state symmetry, from the perspective of the D_{3d} local symmetry at Np^{4+}-sites, which is now universally accepted after the results of Refs. [2,9], trying to clarify some subtleties related to time-reversal symmetry. This also opens the way to a straightforward identification of the allowed order parameters and a direct classification of the possible ground states. The analysis supports the conclusions reported in Ref. [12], where a singlet ground state was proposed for NpO_2 on the basis of specific heat measurements.

While the symmetry of the primary order parameter is now known, it must be noticed that direct experimental evidence about its true nature is still lacking. In the following we will consider the ordering of magnetic octupoles (which is the most commonly accepted for NpO_2 today), but similar results and considerations could be made for any kind of odd-rank magnetic multipole distinct from the dipole. We have recently proposed a inelastic neutron scattering experiment to clarify this situation, based on the theoretical analysis of the ground-state dynamics [13].

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2. Symmetry analysis

In the high-temperature phase, NpO_2 crystallises in the $Fm\bar{3}m$ space group. The (0 0 3) Bragg reflection in such a group is forbidden by symmetry at all orders, even in resonant conditions. Therefore, its detection at Np M_4 edge in the low-temperature phase [1] shows that the local symmetry of Np^{4+}-ions below T_0 is a subgroup of the cubic group $m\bar{3}m$ (O_h). As described in Ref. [2], the only maximal nonisomorphic subgroup of $Fm\bar{3}m$ that is non-symmorphic and simple cubic is $Pn\bar{3}m$, which has the same diffraction pattern as $Fm\bar{3}m$ for both Np and O atoms, thus explaining why usual diffraction is not sensitive to any symmetry-lowering below T_0. The Np ions are accommodated at positions 4b, with reduced local symmetry $\bar{3}m$ (D_{3d}), that allows for both $\sigma\sigma$ and $\sigma\pi$ RXS reflections at (0 0 3). Therefore, in what follows, we shall directly exploit the character table of D_{3d} (double) group, instead of O_h, in order to derive the ground state symmetry and the allowed octupolar components (see e.g., pp. 522–523 of Ref. [14]).

The seven degenerate components of the octupole magnetic moment in spherical symmetry $SO(3)$ split, in D_{3d} symmetry, into two doublets Γ_3, two singlets Γ_2 and one singlet Γ_1, the latter corresponding to the totally symmetric irreducible representation of $L = 3$ in D_{3d}. However the experimental evidence of the absence of dipolar long-range order forces us to consider only those components of magnetic octupole not belonging to the same representations as the dipole, otherwise this latter would be induced as secondary order parameter. This constraint, which in O_h symmetry selects four out of seven octupolar components, is much more restrictive in the case of D_{3d} symmetry, as only one octupolar component has the desired property, the one belonging to the totally symmetric representation Γ_1. This latter can be written in terms of spherical harmonics with quantization axis along the trigonal [1 1 1] direction: $O \propto Y_{33} + Y_{3-3}$. Following the convention of Ref. [14] we have chosen the two-fold axis of D_{3d} along y. Therefore its expression in terms of equivalent angular momentum operators is: $O \propto \hat{J}_y^3 - 3\overline{\hat{J}_y^2\hat{J}_x}$, where we introduced the symmetrized form $\overline{\hat{J}_y^2\hat{J}_x} \equiv (\hat{J}_y^2\hat{J}_x + \hat{J}_y\hat{J}_x\hat{J}_y + \hat{J}_x\hat{J}_y^2)/3$. When we re-express this quantity according to the quantization axis usually adopted in the literature, i.e. the one along the original four-fold axis of the cubic group, we recover back in a simple fashion the representation used in Ref. [2]: $O \propto \overline{\hat{J}_{z'}\hat{J}_{y'}^2} - \overline{\hat{J}_{z'}\hat{J}_{x'}^2}$ + permutations of (xyz). The rotation matrix from the non-primed to the primed reference system is expressed in terms of the three orthonormal vectors $\vec{v}_1 = \left(-1/\sqrt{6}, -1/\sqrt{6}, 2/\sqrt{6}\right)$, $\vec{v}_2 = \left(-1/\sqrt{2}, -1/\sqrt{2}, 0\right)$, and $\vec{v}_3 = \left(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3}\right)$ as $M_{\alpha\beta} = (\vec{v}_\beta)_\alpha$, and transformed vectors are given by: $r'_\alpha = M_{\alpha\beta}r_\beta$.

When we analyze how the Γ_8 ground-state quartet of O_h branches into D_{3d}, we find that it splits into a doublet Γ_4 and a couple of Kramers-related singlets Γ_5 and Γ_6. Even though they belong to two different representations of the D_{3d} double group, the latters are degenerate in presence of time-reversal symmetry, and their degeneracy splits only when time-reversal is broken (see e.g., p. 159 of Ref. [14]). Therefore, if there is no magnetic order, we would get just two energy levels, one for Γ_4 states, the other for Γ_5 and Γ_6 states. In order to understand the characteristics of each state, and to help visualizing their behavior under time-reversal symmetry, it is useful to write them down explicitly. Choosing the natural quantization direction in D_{3d} along the three-fold symmetry axis, we have the following expressions for the four states in terms of the basis $\| J = 9/2, J_z\rangle$ [14]:

$$|\Gamma_5\rangle = \frac{\sqrt{7}}{3\sqrt{5}}\left(1+\frac{\mathrm{i}}{\sqrt{2}}\right)\left\|\frac{9}{2},\frac{9}{2}\right\rangle + \frac{2\mathrm{i}}{\sqrt{15}}\left\|\frac{9}{2},\frac{3}{2}\right\rangle + \frac{2}{\sqrt{15}}\left\|\frac{9}{2},-\frac{3}{2}\right\rangle + \frac{\sqrt{7}}{3\sqrt{5}}\left(\mathrm{i}-\frac{1}{\sqrt{2}}\right)\left\|\frac{9}{2},-\frac{9}{2}\right\rangle \quad (1)$$

$$|\Gamma_6\rangle = \frac{\sqrt{7}}{3\sqrt{5}}\left(\mathrm{i}+\frac{1}{\sqrt{2}}\right)\left\|\frac{9}{2},\frac{9}{2}\right\rangle + \frac{2}{\sqrt{15}}\left\|\frac{9}{2},\frac{3}{2}\right\rangle + \frac{2\mathrm{i}}{\sqrt{15}}\left\|\frac{9}{2},-\frac{3}{2}\right\rangle + \frac{\sqrt{7}}{3\sqrt{5}}\left(1-\frac{\mathrm{i}}{\sqrt{2}}\right)\left\|\frac{9}{2},-\frac{9}{2}\right\rangle \quad (2)$$

$$|\Gamma_4^{(1)}\rangle = -\frac{\sqrt{7}}{3\sqrt{15}}\left\|\frac{9}{2},\frac{7}{2}\right\rangle - \frac{4}{3\sqrt{15}}\left\|\frac{9}{2},\frac{1}{2}\right\rangle - \frac{4\sqrt{7}}{3\sqrt{15}}\left\|\frac{9}{2},-\frac{5}{2}\right\rangle \quad (3)$$

$$|\Gamma_4^{(2)}\rangle = \frac{\sqrt{7}}{3\sqrt{15}}\left\|\frac{9}{2},-\frac{7}{2}\right\rangle - \frac{4}{3\sqrt{15}}\left\|\frac{9}{2},-\frac{1}{2}\right\rangle + \frac{4\sqrt{7}}{3\sqrt{15}}\left\|\frac{9}{2},\frac{5}{2}\right\rangle \quad (4)$$

Notice that we chose the phase convention of Ref. [14] for time-reversal, such that the action on spherical tensors $||J, J_z\rangle$ brings the phase $(-)^{J-J_z}$, besides making the complex conjugate. Therefore the time-reversal of $|\Gamma_5\rangle$ is $|\Gamma_6\rangle$ and in the doublet subspace $|\Gamma_4\rangle$ we have chosen the two states $|\Gamma_4^{(1)}\rangle$ and $|\Gamma_4^{(2)}\rangle$ in such a way that they are the time-reversed one of the other. Of course, in the presence of a time-reversal symmetry they are degenerate and any linear combination of the two could equally well describe the $|\Gamma_4\rangle$-subspace: the degeneracy of the $|\Gamma_4^{(1)}\rangle$ and $|\Gamma_4^{(2)}\rangle$ states is lifted only in a magnetic dipole ordered phase, but persists if time reversal is broken by the totally symmetric representation Γ_1 of magnetic octupole. We point out that our choice of reference frame, albeit different from that commonly used for cubic systems [4,8], can express the same physics in a more convenient way (for example the numerical coefficients can be fixed by symmetry considerations only).

A discussion on the role of finite spin-orbit interaction in determining localized 5f-electron wavefunctions has to keep into account the influence of J-mixing and intermediate coupling.

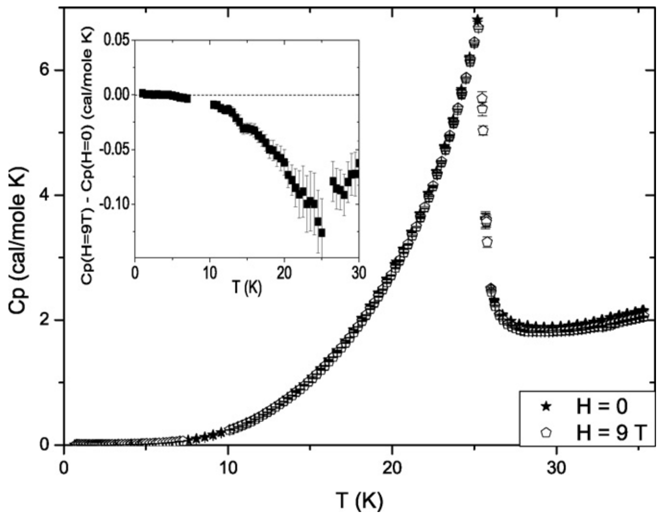

Fig. 1. Specific heat of NpO_2 as a function of temperature, without (from Ref. [12]) and with applied magnetic field (9 T). Inset: calculated difference between the two data sets.

However, we have recently proposed a perturbative procedure [15] which allows to retain the usual crystal-field formalism. As expected, the transformed effective Hamiltonian maintains the cubic symmetry and all of the following qualitative considerations hold their validity.

3. Discussion and conclusions

There are several interesting perspectives that can be derived from the explicit form of the states. In first place, we can easily exclude a Γ_4 ground-state in presence of a time-reversal symmetry breaking. In fact, in the case of magnetic dipole order the double degeneracy would be lifted and only one of $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$ would be low-lying. However, each of this states carries a net dipolar moment given by $\pm(0.22^2 \times 7/2 + 0.34^2 \times 1/2 - 0.91^2 \times 5/2)\hbar = \pm 1.84\hbar$, against the experimental evidence of absence of magnetic moment. The only way to avoid this is to suppose that the coefficient of Γ_4 states can be chosen arbitrarily with the constraint that the ground state has zero dipolar moment. The $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$ states remain degenerate if time reversal symmetry is broken by magnetic octupolar order, while the application of an external magnetic field would remove the degeneracy and a non-zero magnetic dipole moment would appear. We have verified that this possibility is excluded by performing low temperature specific-heat measurements with and without the application of a 9 T magnetic field [12] (Fig. 1). The results show no significant variation between the two data sets; moreover, the obtained magnetic entropy curve is not compatible with a residual degeneracy of the ground state persisting below $T = 0.7$ K [12].

Therefore, we can safely suppose that the ground state of Np in the low-temperature phase is $|\Gamma_5\rangle$ ($|\Gamma_6\rangle$). The structure of the Γ_5 ground state is such that the average value of any component of the magnetic moment J_a ($a = x, y, z$) is zero: in fact, on one hand both states with $\pm J_z$ appear with the same weight and therefore $\langle\Gamma_5|J_z|\Gamma_5\rangle = 0$. On the other hand, the raising and lowering operators $J_\pm$ cannot connect the different J_z components, which differ by $3\hbar$ (9/2, 3/2, $-3/2$, $-9/2$). This property is interesting because it shows that only trilinear objects $J_a J_b J_c$ (e.g., the odd-rank magnetic multipoles) can have expectation values different from zero. As it turns out, the symmetry of the primary order parameter also leads to the ordering of the Γ_5 electric quadrupoles [8] as secondary order parameter, which is confirmed by resonant X-ray scattering experiments [2].

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