Hidden Order and Low-Energy Excitations in NpO_2

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We investigate the nature of the hidden order parameter in the ordered phase of NpO_2, which had been identified with a staggered arrangement of Γ_5 magnetic multipoles. By analyzing the existing experimental data, we show that the most likely driving order parameter is not provided by octupoles, as usually assumed, but rather by the rank-5 triakontadipoles. Calculations of the coupled dynamics of spins, Γ_5 quadrupoles, and Γ_5 triakontadipoles in the ordered phase enable us to analyze the resulting structure of low-energy excitations. We show that the powder inelastic neutron scattering cross section should contain, in addition to the already-observed peak at 6.5 meV, a second weaker peak at about 14 meV.

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The low-temperature properties of NpO_2 have recently attracted much attention because its second-order phase transition, occurring at $T_0 \simeq 26$ K, has been proposed as the first example of ordering driven by a magnetic-multipole (MM) primary order parameter (OP) [1–10]. No experimental indication of magnetic dipole order has ever been found by neutron diffraction or Mössbauer spectroscopy. Only recently, resonant x-ray [3] and ^{17}O-NMR [9] measurements demonstrated the occurrence of longitudinal type-I (AF-I) triple-**q** ordering of Γ_5 electric quadrupoles, lowering the symmetry from $Fm\bar{3}m$ to $Pn\bar{3}m$. These quadrupoles have been interpreted as secondary OPs induced by a longitudinal type-I triple-**q** ordering of Γ_5 magnetic multipoles. In fact, both the saturating susceptibility as $T \rightarrow 0$ and μSR experiments [11] indicate that time-reversal symmetry is broken below T_0.

Although the symmetry of the OP has been unveiled, truly direct evidence of the MM primary OP is still lacking and the specific form of the leading primary OP is unknown. The resulting structure of the low-energy wave functions and excitations in the ordered phase are still unclear. In particular, there are four distinct triplets of operators belonging to Γ_5 which could drive the transition. One of these may be constructed from rank-3 (octupoles), one from rank-5 (triakontadipoles), and two from rank-7 operators. Here we show that existing information provides strong evidence that *rank-5* Γ_5-MMs are the driving force of the phase transition. The coupled dynamics of spins, Γ_5 quadrupoles, and Γ_5 triakontadipoles in the ordered phase is calculated by the random-phase approximation (RPA), and a proposal for a new inelastic neutron scattering (INS) experiment is put forward. Besides providing direct evidence of MM order, INS could be used to validate the present theoretical results about low-energy excitations.

In the high-temperature phase, NpO_2 has the fcc CaF_2 crystal structure. The ground $J = 9/2$ multiplet of each Np^{4+} ion is split by the cubic crystal field (CF) into two Γ_8 quartets separated by about 50 meV and a higher-lying Γ_6 doublet (Fig. 1) [12]. The effective CF Hamiltonian for the $J = 9/2$ multiplet is [13,14]

$$H_{\mathrm{CF}} = W\left[x\frac{O_4}{F(4)} + (1-|x|)\frac{O_6}{F(6)}\right] + H_{\mathrm{mix}}(x, W), \quad (1)$$

where $H_{\mathrm{mix}}(x, W)$ represents an additional term describing the weak J-mixing effects in II-order perturbation theory. Even if its effect is small, we include H_{mix} as we wish to adopt a model as realistic as possible, with the actual CF wave functions. The precise form of the Γ_8 wave functions is set primarily by the x parameter and to a smaller extent by W through H_{mix}. Two possible sets of CF parameters, having $x \simeq -0.75$ and $x \simeq -0.48$, had been identified on the basis of INS data [12], but we have recently shown that only the $x \simeq -0.48$ set scales satisfactorily over the whole (UO_2, NpO_2, PuO_2, AmO_2, CfO_2) series of compounds [14].

In the triple-**q** ordered phase below T_0, there are four inequivalent sublattices (Fig. 1). The most parsimonious

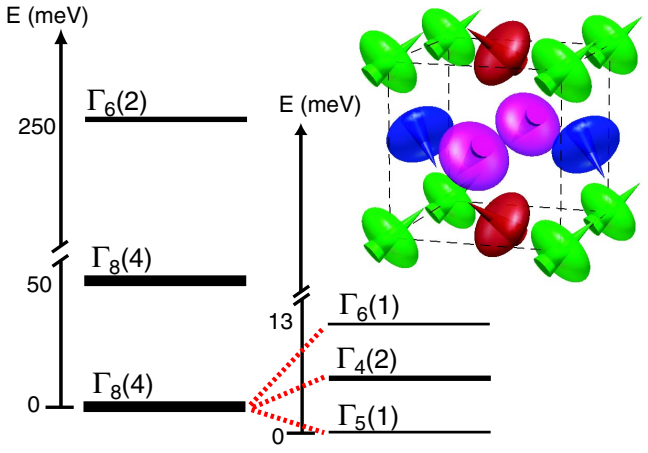

FIG. 1 (color online). Calculated cubic CF levels and mean-field splitting of the ground Γ_8 quartet in the ordered phase. The ($x = -0.48$, $W = -4.8$) CF set and the rank-5 Γ_5 MM OP have been used. Numbers in parentheses are degeneracies. The image represents the arrangement of the Γ_5 MMs (cones) and of the induced Γ_5 quadrupoles (ellipsoids) in the 4-sublattices triple-**q** ground state.

model for the ordering is one in which Eq. (1) is supplemented with the mean-field (MF) contribution from a Γ_5 MM OP (of superexchange origin) [3]:

$$H_{\mathrm{MF}}(s) = \lambda O(s)\langle O(s)\rangle, \tag{2}$$

where $s = 1$–4 labels the four sublattices, λ is the MF constant, and $O(s) = \sum_{l=1,2,3} O_l n_l(s)$. Here $\vec{n}(s)$ represents one of the four inequivalent $\langle 111\rangle$ directions, and O_l are the three components of the (so-far unspecified) Γ_5 MM. In the ordered phase, the point symmetry on Np ions lowers from O_h to D_{3d}, and a nondipolar magnetization density appears around each Np ion. In addition, a distortion of the charge density, corresponding to a nonzero quadrupole moment $Q \equiv \langle Q(s)\rangle \propto \langle 3(\vec{n}(s)\cdot\vec{J})^2 - J(J+1)\rangle$, is induced as secondary OP (Fig. 1) [3]. In principle, $H_{\mathrm{MF}}(s)$ should be supplemented with the MF contribution from the secondary OP itself $\lambda_Q Q(s)\langle Q(s)\rangle$, with λ_Q the MF constant for quadrupolar interactions. Although the latter are not expected to be qualitatively important, if strong enough they could affect quantitative details such as the rate of growth of the OPs or the precise value of excitation energies below T_0. In addition, as mentioned above, there are four independent and physically distinct triplets belonging to Γ_5: $O_l^{(3)}$, $O_l^{(5)}$, $O_l^{(7,a)}$, and $O_l^{(7,b)}$, with $l = 1, 2, 3$ [15] (ranks larger than 7 are irrelevant for f-electron shells [16]). All of these have nonzero average values below T_0, and all might provide distinct contributions to $H_{\mathrm{MF}}(s)$. Within the Γ_8-quartet CF ground state, these four triplets of observables are represented by matrices proportional to one another. Thus, if the Γ_8 quartet was completely isolated, the phase transition could be modeled with no need to distinguish these Γ_5 MMs. However, the presence of excited CF levels at $\sim$50 meV makes them inequivalent. This fact is inconsequential as far as the symmetry of the ordered phase is concerned but needs to be pondered if the actual structure of the ground state and of low-E excitations is sought. Since Ref. [3] focused on the symmetry of the OP, this problem had been bypassed by considering only the Γ_8 quartet below T_0. Here we focus on the specific nature of the OP, and we include the full CF spectrum in the self-consistent MF and RPA calculations.

The dynamics in the ordered phase appear to be the feature by which evidence and information on the nature of the primary OP is most likely to be experimentally obtainable. An ordering of Γ_5 MMs implies a splitting of the Γ_8 quartets into a D_{3d} Γ_4 doublet and a pair of singlets Γ_5 and Γ_6 (Fig. 1) which are degenerate in the presence of time-reversal invariance, whereas their degeneracy is removed when time reversal is broken. Therefore, if only Γ_5 quadrupolar order took place, the Γ_8 quartets would split in a pair of Kramers doublets. However, if a hidden order of Γ_5 MMs is behind the observed quadrupolar order, the Γ_8 quartets should split in three levels (one doubly degenerate, Fig. 1). Whether and how this actually occurs could be checked by INS. In fact, $\Gamma_5 \rightarrow \Gamma_4$, $\Gamma_6 \rightarrow \Gamma_4$, and $\Gamma_5 \rightarrow \Gamma_6$ are all allowed dipole transitions. Therefore, in the case of pure quadrupole order, a single MF magnetic transition exists, which physically corresponds to changing the charge density character from oblate to prolate along $\langle 111\rangle$. In the case of Γ_5 MM order, there are two MF magnetic transitions, which correspond to concurrent changes of the local magnetization and charge densities (see Fig. 3).

In the energy window between 3 and 11 meV, a single peak at about 6.4 meV had been identified by INS on powder samples [12]. Thus, either the order is purely quadrupolar, or a second peak exists outside the explored energy window. Recent measurements of the low-T specific heat [17] are inconsistent with the presence of excited MF levels at low energy, indicating that the second INS peak, if any, must be sought above 11 meV. As already mentioned, a purely quadrupolar OP must be excluded in view of μSR and susceptibility measurements. It is also totally inconsistent with the low-T specific heat [17], whose field independence evidences the lack of the residual low-T entropy. If instead Γ_5 MM order is assumed, the simplest possible choice for the OP is to identify O_l in Eq. (2) with the octupoles $O_l^{(3)}$. We have pointed out above that this choice for O_l is as good as any other within a model including the ground CF quartet only. However, it works badly if all CF states are included. The source of the problem is in the very low octupolar polarizability of the CF ground quartet (see below), which leads to an enhanced role of excited CF states in the ordering process: For CF parameters with $x \simeq -0.48$, the order occurs through a strongly first-order phase transition. Even assuming parameters with $x \simeq -0.75$ (which are now known to be unlikely for their lack of overall scaling properties [14]) does not solve the problem: A second-order transition occurs, but the Γ_4 doublet (Fig. 1) lies well below 3 meV, inconsistently with specific heat results. Moreover, the heavy mixing of the ground Γ_8-quartet wave functions with excited CF states below T_0 leads to a nonmonotonic T dependence of the secondary quadrupolar OP Q [Fig. 2(a)], in disagreement with resonant x-ray scattering results [3]. Thus, we are led to conclude that the driving MM cannot be an octupole. It must be stressed that the strength of multipolar two-ion superexchange interactions is not correlated in obvious way with the multipole rank, so that the contributions of rank-5 and rank-7 MMs are not, in general, smaller than that of octupoles [7,16]. A key factor in selecting which of these MMs plays a driving role is the CF potential equation (1), because this dominant interaction may strongly affect the size of the corresponding multipolar moments. We investigate this effect for the four possible Γ_5 MMs by comparing the effective multipolar paramagnetic moment μ_{CF} associated with the ground Γ_8-quartet CF wave functions with the corresponding free-ion moment μ_0 [18]. Figure 2(b) shows the ratio $r = \mu_{\mathrm{CF}}^2/\mu_0^2$ as a function of the CF parameter x. This quantity measures how much the multipolar susceptibility of the Γ_8 quartet is reduced ($r < 1$) or increased ($r > 1$) by

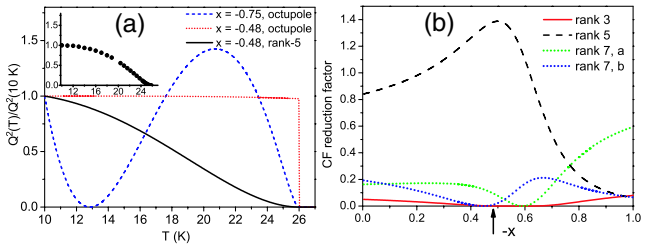

FIG. 2 (color online). (a) T dependence of the square of the secondary quadrupolar OP Q^2 normalized to its value at 10 K, calculated for the three different models of Γ_5 MM order discussed in the text (the MF transition temperature has been set to T_0). Inset: The same quantity measured by x-ray scattering [3]. (b) CF reduction factor for the Γ_8 ground quartet, $\mu^2_{\mathrm{CF}}/\mu^2_0$, as a function of the CF parameter x ($W < 0$). The arrow indicates the most likely value of x.

the CF, and it is the factor by which the MF ordering temperature is changed in passing from the full degenerate $J = 9/2$ multiplet to the Γ_8 CF ground state. For this specific calculation, we have neglected H_{mix} in Eq. (1) (the conclusions are not minimally affected by this), since in this way we can focus on the relevant CF parameter x. Figure 2 shows that the octupolar moment is greatly reduced by the CF and nearly completely quenched for $x \simeq -0.48$, where also the two rank-7 moments are heavily reduced. On the contrary, the rank-5 moment is increased by the CF and peaks at $x = -0.5$. This shows that for $x \simeq -0.48$ the rank-5 MM is by far the most likely driving OP and that the MF model equation (2) with O_l identified with $O_l^{(5)}$ provides the most reasonable approximation. If $O_l^{(5)}$ are used in (2), the role of excited CF states is much smaller and the resulting growth of Q is monotonic as in experiments [Fig. 2(a)]. In this case, the usual approximation of retaining only the lowest CF quartet is a very good one.

In the following, we investigate the implications of this finding on the low-energy dynamics in the ordered phase, and we propose an INS experiment which can directly validate this model. In particular, we calculate dynamical susceptibilities in the ordered phase by including fluctuations around the 4-sublattice MF configuration within the RPA approach [19] and using Eqs. (1) and (2) (with $O_l \equiv O_l^{(5)}$) as a single-ion Hamiltonian. In the simplest conceivable model, the joint dynamics of magnetic dipoles (J_1, J_2, J_3) and Γ_5 MMs (O_1, O_2, O_3), corresponding to $24 = (3 \times 2) \times (4$ sublattices) degrees of freedom per cell, is obtained in ($\mathbf{q}$, E) Fourier space by solving the following 24×24 RPA system (here J_l and O_l are to be understood as mean values of the corresponding operators):

$$dJ_\alpha(\mathbf{q},E) = \sum_\beta \chi^{\alpha,\beta}_{JJ}\, dH^\beta_{\mathrm{ext}}(\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta),E/\hbar) + \sum_{\beta,\gamma} \chi^{\alpha,\beta}_{JJ} I^{\beta,\gamma}_J((\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta))dJ_\gamma(\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta),E) + \sum_{\beta,\gamma} \chi^{\alpha,\beta}_{JO} I^{\beta,\gamma}_O((\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta))dO_\gamma(\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta),E), \quad (3a)$$

$$dO_\alpha(\mathbf{q},E) = \sum_{\beta,\gamma} \chi^{\alpha,\beta}_{OO} I^{\beta,\gamma}_O((\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta))dO_\gamma(\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta),E) + \sum_{\beta,\gamma} \chi^{\alpha,\beta}_{OJ} I^{\beta,\gamma}_J((\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta))dJ_\gamma(\mathbf{q}+\mathbf{q}_{\mathrm{AF}}(\alpha,\beta),E). \quad (3b)$$

Here $\chi^{\alpha,\beta}_{AB}$ represents the single-ion cross-susceptibility for observables A_α and B_β, calculated from the self-consistent MF eigenstates for one of the four sublattices. $H^\beta_{\mathrm{ext}}(\mathbf{q},\omega)$ is the external magnetic field, $I^{\alpha,\beta}_A(\mathbf{q})$ is the Fourier transform of two-ion couplings between observables A_α and A_β [20], and $\mathbf{q}_{\mathrm{AF}}(\alpha,\beta)$ is zero for $\alpha = \beta$; otherwise, it is the ith wave vector of the AF-I star [$\mathbf{q}_1 = 2\pi/a(1,0,0)$; $\mathbf{q}_2 = 2\pi/a(0,1,0)$; $\mathbf{q}_3 = 2\pi/a(0,0,1)$], with $i \neq \alpha, \beta$. The most parsimonious choice is to neglect anisotropic contributions to two-ion couplings [i.e., $I^{\alpha,\beta}_J(\mathbf{q}) = I_J(\mathbf{q})\delta_{\alpha,\beta}$ and $I^{\alpha,\beta}_O(\mathbf{q}) = I_O(\mathbf{q})\delta_{\alpha,\beta}$] and to consider nearest-neighbor (n.n.) interactions only. The resulting model contains two free parameters only, the n.n. dipole-dipole (I^0_J) and the n.n. triakontadipole-triakontadipole (I^0_O) coupling constants. The former is estimated from the static magnetic susceptibility in the paramagnetic phase [21], yielding $I^0_J \simeq 0.1$ meV. The latter parameter is determined as $I^0_O = 4.7 \times 10^{-7}$ meV by fitting to 6.5 meV the position of the lowest-E peak in the $Q = 1.9$ Å^{-1} powder INS cross section [12,22]. We have also made calculations without the simplifying assumptions, but existing experimental data are insufficient to fix more than two parameters. Anyway, our conclusions are not affected by these assumptions.

The $\mathbf{q}$ dependence of low-E excitations is obtained by calculating the poles of the absorptive part of the dynamical magnetic susceptibility $\mathrm{Im}\chi^{\alpha,\beta}_{JJ}(\mathbf{q},E)$, which is numerically derived from Eqs. (3). This quantity is directly probed by INS, whose cross section $\partial\sigma/\partial\Omega\partial E \propto S = \sum_{\alpha,\beta}(\delta_{\alpha\beta} - Q_\alpha Q_\beta/Q^2)\mathrm{Im}\chi^{\alpha,\beta}_{JJ}(\mathbf{Q},E)$. Figure 3(a) shows the intensity of INS transitions along $\langle 001\rangle$ directions calculated for $T \ll T_0$. The two allowed MF transitions from the ground state yield dispersive branches, whose details depend on the specific assumptions on two-ion couplings made in the present calculation. The spherically averaged (powder) INS cross section [Fig. 3(b)] is less sensitive to details and displays two broad peaks whose centers are rather close to the energies of the two MF transitions. Figure 3(b) shows that the calculated shape and width of the 6.5 meV peak are in very good agreement with available experimental data. A *second* weaker peak is predicted at about 13.8 meV for $Q = 1.9$ Å^{-1}. This energy range has been investigated only by using unpolarized neutrons [23], but the spectra were contaminated by a very broad spurious contribution preventing conclusions about the presence of a second peak [24]. We have also

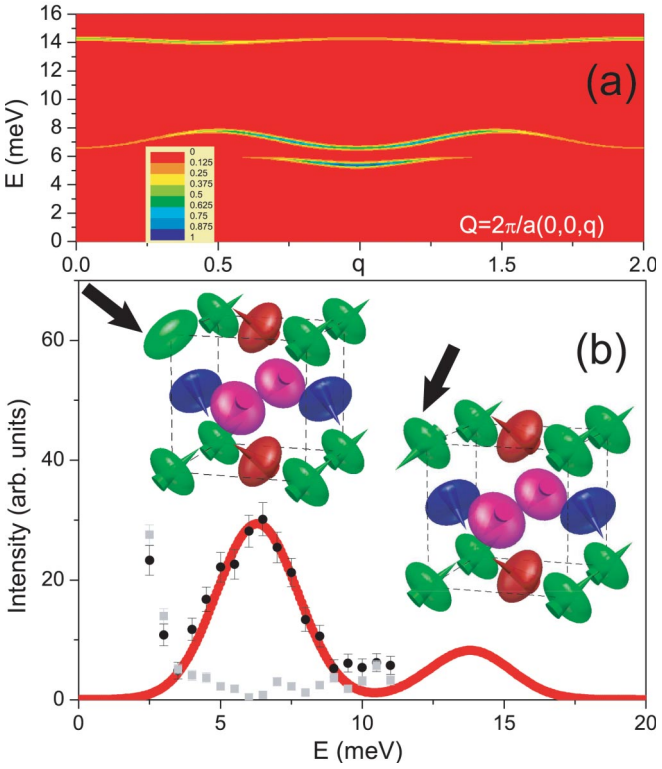

FIG. 3 (color online). (a) Intensity plot showing the calculated $T = 0$ momentum-transfer and energy dependence of the scattering function S along $\langle 001 \rangle$. (b) Measured powder INS spectrum for $Q = 1.9$ Å^{-1} [12] (black squares: spin flip; gray circles: non-spin flip). Line: Present calculation convoluted with the 3 meV Gaussian resolution function. The left-hand peak involves excited states where typically 1 Np ion (indicated by an arrow) has its quadrupole reverted and vanishing Γ_5 MM moment (i.e., the Γ_4 MF excited state in Fig. 1). The right-hand peak involves excited states where typically 1 Np ion has its Γ_5 MM moment reverted (i.e., the Γ_6 MF excited state in Fig. 1).

checked the effect of adding two-ion interactions between the Γ_5 quadrupolar secondary OPs, which requires adding a self-consistent quadrupolar term in Eq. (2) and increasing the size of the RPA system to 36. Sufficiently strong quadrupolar interactions significantly change the rate of growth of OPs below the critical region and may slightly change the ratio between the energy positions of the two powder INS peaks and/or their integrated intensities.

In conclusion, we have investigated the nature of the hidden order parameter in the AF-I triple-**q** ordered phase of NpO_2. This OP had been identified with a Γ_5 magnetic multipole. We have shown that, among the possible distinct MMs of this symmetry, rank-5 triakontadipoles are the most likely driving order parameters. Evidence and information on this OP can be obtained by probing the dynamics in the ordered phase. In particular, we have calculated the coupled dynamics of spins, Γ_5 quadrupoles, and Γ_5 triakontadipoles in the ordered phase, and we have shown that the powder INS cross section should contain, besides the already-observed peak at 6.5 meV [12], a second weaker peak at about 14 meV. Therefore, new polarized INS experiments will allow one to validate this scenario for the hidden OP. In addition, (more difficult) single-crystal INS measurements will provide very rich and detailed information about the actual fine structure of two-ion multipolar interactions.

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