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Neptunium octupole and hexadecapole motifs in NpO_2 directly from electric dipole (E1) enhanced x-ray Bragg diffraction

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Abstract
The phase transition in NpO_2 at $T_0 \approx 25.5$ K is accompanied by the onset of superlattice reflections in the x-ray Bragg diffraction pattern, with intensity enhanced by an electric dipole (E1) event. Additional experiments using other techniques indicate no ordering at T_0 of Np magnetic moments. Absence of long-range magnetic order below T_0 fits with the outcome of a polarization analysis of superlattice intensities at 12 K; signals are observed in both the unrotated ($\sigma'\sigma$) and rotated ($\pi'\sigma$) channels of scattering while magnetic (dipole) moments would contribute only in the rotated channel. We demonstrate that these empirical findings, together with a narrow energy profile of the Bragg intensity at the Np M_4 edge, are consistent with magnetic and charge contributions to the E1 Bragg amplitude described by Np 5f multipoles of ranks 3 (octupole) and 4 (hexadecapole). Key to our understanding of the x-ray diffraction data gathered in the vicinity of the Np M_4 edge is recognition of an exchange field creating $3d_{3/2}$ core-level structure. The particular importance of the exchange field at the Np M_4 edge is emphatically revealed in calculations of the corresponding x-ray absorption spectrum with and without the core–valence interaction. From the experimental information about NpO_2 we can infer a ground-state wavefunction for the Np $5f^3$ valence shell and estimate saturation values for the octupole and hexadecapole. We are led to null values for Np multipoles of ranks 2 (quadrupole) and 5 (triakontadipole).

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1. Introduction

At room temperature NpO_2 adopts the fluorite structure $Fm\bar{3}m$ (number 225) and it undergoes a phase transition at $T_0 \approx 25.5$ K. Bragg diffraction experiments [1, 2] performed below T_0 show superlattice peaks, $(00L)$ with L an odd integer, that can be indexed on the structure $Pn\bar{3}m$ (224) derived from the room-temperature structure through a continuous, non-ferroic phase transition [2]. Long-range magnetic order is not observed below T_0 with Mössbauer [3] or neutron diffraction techniques [4]. On the other hand, muon spin-relaxation experiments show at T_0 the abrupt appearance of a precession signal [5]. In an attempt to reconcile these observations it has been proposed that below T_0 Np ions possess a zero magnetic dipole moment and a non-zero octupole moment [6].

The Bragg diffraction experiments in question, with the sample held at 12 K, exploit enhancement of the x-ray intensity found at Np M_4 and M_5 absorption edges. Intensity at the superlattice position (003) was gathered, with primary polarization (σ) normal to the plane of scattering, in the unrotated ($\sigma'\sigma$) and rotated ($\pi'\sigma$) secondary channels. Most importantly, the intensity was measured as a function of the rotation of the crystal about (003). A narrow energy profile at the M_4 edge, together with the favoured description of the low-temperature crystal structure, convinces us that a conventional framework for the interpretation of resonance enhanced x-ray diffraction is not appropriate. We submit that the superlattice amplitude is partly magnetic, and it is described in our model by Np multipoles of ranks 3 (octupole) and 4 (hexadecapole). Furthermore, we can infer a Np^{4+} ($5f^3$) ground-state wavefunction and obtain estimates of the saturation values for the Np multipole moments.

The following section describes both the conventional framework for scattering enhanced by an electric dipole resonance event, and the dependence of the Bragg amplitude of NpO_2 at $(00L)$ on azimuthal angle. Sections 3 and 4 develop the amplitude that occurs when core-level structure is included and the result can lead to a narrow energy profile (intensity) similar to a Lorentzian-squared form. A model wavefunction for Np^{4+} inferred from various measurements on NpO_2 is constructed in section 5 and applied to Np multipoles that appear in the Bragg amplitude. The energy profile calculated for the Np M_4 edge is successfully compared with available data in section 6, and opinions are then reached about the magnitudes of the Np quadrupole, octupole and hexadecapole. Conclusions about NpO_2 drawn from our study of resonant x-ray Bragg diffraction are gathered in section 7.

2. Bragg diffraction amplitude

For the crystal structure below T_0 we follow the authors of [2] and use space group 224. Neptunium ions occupy sites which have symmetry $\bar{3}m$ (D_{3d}), down from O_h in space group 225. Also, we ascribe enhancement of the x-ray signal to an electric dipole (E1) absorption event in which electrons photo-ejected from the core state $3d_{3/2}$ are promoted to hole states in the $5f^3$ valence state.

The E1 amplitude is of the form

$$F = \sum_{K=0}^{2} \boldsymbol{X}^K \cdot \boldsymbol{\Psi}^K, \tag{1}$$

where the spherical tensor $\boldsymbol{X}^K$ is constructed solely from polarization vectors of the primary and secondary x-ray beams, and $\boldsymbol{\Psi}^K$ is a unit-cell structure factor. In the construction of $\boldsymbol{\Psi}^K$ Np ions are placed at sites 4b in space group 224. Ions in pairs with a common value of the z-position parameter ($z = 0$ or $1/2$) are related to each other by rotation by π about the crystal c-axis. For a superlattice peak $(00L)$ with L an odd integer, the contributions to $\boldsymbol{\Psi}^K$

from pairs with $z = 0$ and $1/2$ are of opposite sign. Lastly, the two ions with $z = 1/2$ are related to the corner site (000) symmetry by rotation by π about the crystal a- and b-axes. With this information we have $(-K \leqslant q \leqslant K)$

$$\Psi_q^K = \{1 + (-1)^q\}\{\langle T_q^K\rangle - (-1)^K\langle T_{-q}^K\rangle\}, \tag{2}$$

in which atomic tensors $\langle T_q^K\rangle$ describe the $5f^3$ (Np^{4+}) valence shell of an ion at the corner site of the unit cell. Tensors of even (odd) rank K describe time-even (time-odd) properties. A necessary condition for scattering is that the projection q is not an odd integer.

For the moment, let us consider time-even, or non-magnetic, properties. In this instance, $\Psi_q^K = -\Psi_{-q}^K$ and $\Psi_0^K = 0$. Since the maximum K in X_q^K is 2 (this property of X_q^K arises from its construction from two vectors) it follows that $q = \pm 2$ and

$$\Psi_2^2 = 4\mathrm{i}\langle T_2^2\rangle'', \tag{3}$$

where $\langle\ \rangle'' = \mathrm{Im}\langle\ \rangle$ and we have used $\langle T_q^K\rangle^* = (-1)^q\langle T_{-q}^K\rangle$. Values of F in (1) for the unrotated ($\sigma'\sigma$) and rotated ($\pi'\sigma$) polarization channels are

$$\begin{aligned} F(\sigma'\sigma) &= -\mathrm{i}\Psi_2^2\sin(2\psi), \\ F(\pi'\sigma) &= -\mathrm{i}\Psi_2^2\sin\theta\cos(2\psi), \end{aligned} \tag{4}$$

where θ is the Bragg angle. The dependences of F on θ and the azimuthal angle ψ, which measures rotation of the crystal about the Bragg wavevector $(00L)$, are the same as those reported in [2] and the ψ-dependence is in full agreement with data gathered at (003).

The magnitude of F is set by $\langle T_2^2\rangle$. We express $\langle T_q^K\rangle$ in terms of the tensor $\langle T_q^K\rangle_{(\xi\eta\zeta)}$ calculated in orthogonal principal axes $(\xi\eta\zeta)$ that contain the triad axis of the point group D_{3d}. Let the ζ-axis coincide with the triad and, following a standard convention [7], the η-axis coincide with a diad of the point group. With respect to crystal axes (abc) the η-axis is $(1, -1, 0)$ and this is preserved in rotation to principal axes. One finds

$$\langle T_q^K\rangle = \sum_Q \exp(\mathrm{i}(q - Q)\pi/4)d_{qQ}^K(\beta)\langle T_Q^K\rangle_{(\xi\eta\zeta)}, \tag{5}$$

where the argument β of the (purely real) rotation matrix $d_{qQ}^K(\beta)$ is determined by $\sin\beta = -(2/3)^{1/2}$ and $\cos\beta = (1/3)^{1/2}$. $\langle T_Q^K\rangle_{(\xi\eta\zeta)}$ can be different from zero for $Q = 0, \pm 3$ which are the allowed values for D_{3d}, and $Q = \pm 3$ is only possible for $K > 2$. Thus, the Np quadrupole is diagonal in the principal axes and

$$\langle T_2^2\rangle = \mathrm{i}d_{20}^2(\beta)\langle T_0^2\rangle_{(\xi\eta\zeta)},$$

which is purely imaginary because the diagonal component of a spherical tensor is purely real.

It is possible that the diagonal component of the Np quadrupole moment $\langle T_0^2\rangle_{(\xi\eta\zeta)} = 0$, and such a result has been predicted [2, 6]. Even so, diffraction with E1 enhancement could still take place if higher-order Np multipoles were different from zero. We are motivated to explore this scenario both because one should not exclude a null quadrupole moment and, secondly, because the energy profile at the Np M_4 edge is exceptionally narrow [2] and suggestive of effective coherence between various contributions to the Np Bragg amplitude.

3. Magnetic contributions to scattering and the energy profile

A re-examination of the structure factor includes possible magnetic contributions to scattering. In this context we note that $\boldsymbol{X}^1(\sigma'\sigma) = 0$, whereas intensity is observed in the $\sigma'\sigma$ channel [2]. Independent measurements on NpO_2 strongly suggest that the Np magnetic (dipole) moment is very small and possibly zero [3, 4] in which case we can assume $\langle T_Q^1\rangle_{(\xi\eta\zeta)} = 0$, and $\Psi_q^1 = 0$,

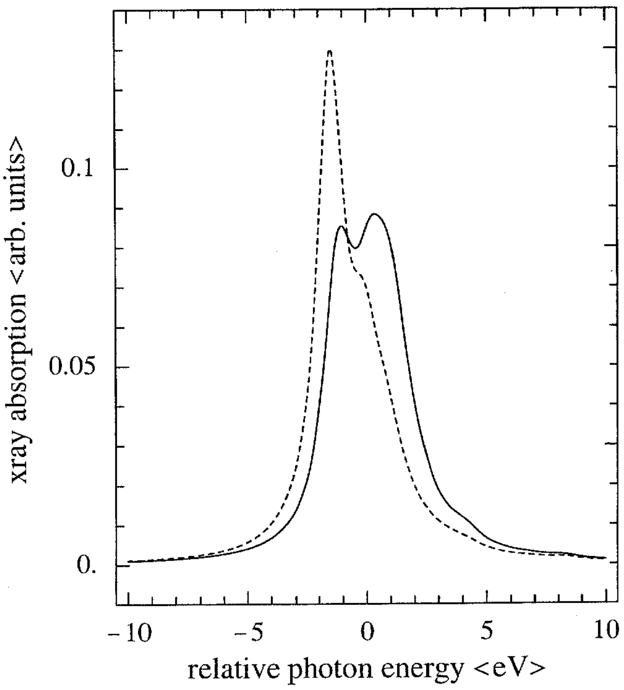

Figure 1. The M_4 x-ray absorption spectrum, or XAS (full curve), for Np f^3 ion in spherical symmetry calculated using Cowan's code [11] and broadened with a Lorentzian of width = 0.7 eV. The energy spread of the levels is evidenced by the comparison to the calculated spectrum (dashed curve) where the 3d–5f exchange interactions G^1, G^3 and G^5 are set to zero.

to a good approximation. However, $\boldsymbol{X}^2\,(\sigma'\sigma)$ and $\boldsymbol{X}^2(\pi'\sigma)$ are different from zero and we will attribute the observed intensity to contributions through this component of the E1 amplitude.

Implicit in the argument given thus far is that the E1 absorption event is adequately represented by a single oscillator. In reality, the dependence of the Bragg intensity on the x-ray energy E in the vicinity of the Np M_4 edge is definitely not a simple Lorentzian profile consistent with a single oscillator and it resembles a Lorentzian-squared [2].

In place of a single oscillator we argue for $2\bar{J} + 1 = 4$ oscillators that arise from action of the exchange field H_s on the core state $3d_{3/2}$. The corresponding amplitude is

$$\sum_{\bar{M}} \frac{A_q^K(\bar{M})}{E - \Delta_0 - \varepsilon(\bar{M}) + \mathrm{i}\Gamma}. \tag{6}$$

Here, E is the x-ray energy, and $\varepsilon(\bar{M}) = \bar{M}(g-1)H_s$ where $\bar{M} = \pm 1/2, \pm 3/2$ and $g = 4/5$ is the Landé factor. The importance of including the exchange field is reinforced by calculations of the XAS spectrum. Calculations displayed in figure 1 of the spectrum of $5f^3$ at the M_4 edge made with and without a core–valence interaction show a dramatic difference, and in this respect XAS spectra at M_4 and M_5 edges are shown to be quite different.

In (6) we write the amplitude factor $A_q^K(\bar{M}) = S_q^K(\bar{M}) + R_q^K(\bar{M})$ where the first (second) term is an even (odd) function of $\bar{M}$. We arrive at a Bragg amplitude:

$$\sum_{\bar{M}>0} \frac{2\{\varepsilon(\bar{M})R_q^K(\bar{M}) + (E - \Delta_0 + \mathrm{i}\Gamma)S_q^K(\bar{M})\}}{(E - \Delta_0 + \mathrm{i}\Gamma)^2 - \varepsilon^2(\bar{M})}. \tag{7}$$

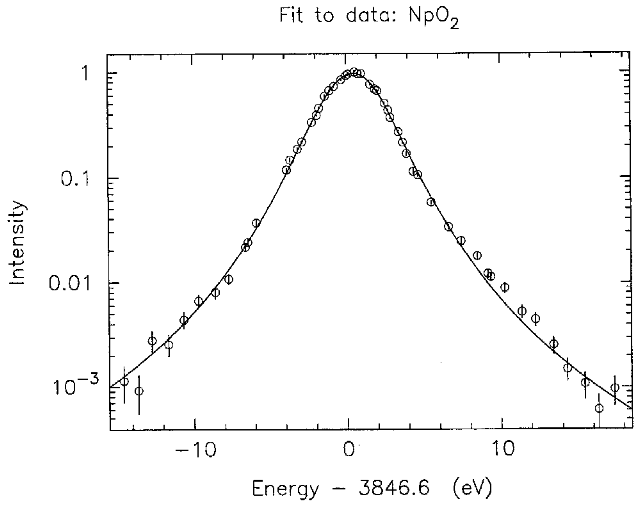

Figure 2. Data for the energy profile at the Np M_4 edge in the rotated channel of scattering are compared with the profile calculated from the amplitude (7). A fit described in section 6 produces $\Delta_0 = 3846.6$ eV, $\Gamma = 2.63 \pm 0.04$ eV and the magnitude of $(g-1)H_s/2$ is 1.0 ± 0.02 eV. The ratio of the hexadecapole and octupole moments is 0.70 ± 0.12 and the quadrupole is taken to be zero.

Should the even components of the amplitude factor sum to zero, the energy profile (intensity) derived from (7) is similar to a Lorentzian-squared form. We will find that S_q^K (R_q^K) is a linear combination of time-even (time-odd) atomic tensors; therefore, the numerator of (7) has S_q^K (R_q^K) married to a time-even (time-odd) quantity, and the whole expression has one signature with respect to the time reversal operation. Turning to figure 2, the energy profile observed in the vicinity of the Np M_4 edge is in excellent agreement with a result derived from (7) and ingredients described in following sections.

We refer to [8] for additional information about (6) and an expression for $A_q^K(\bar{M})$ that can be written as

$$A_q^K(\bar{M}) = (-1)^{\bar{J}-\bar{M}} \sum_r (2r+1) \begin{pmatrix} \bar{J} & r & \bar{J} \\ -\bar{M} & 0 & \bar{M} \end{pmatrix} \sum_x \begin{pmatrix} K & r & x \\ -q & 0 & q \end{pmatrix} \Psi_q^x(r). \tag{8}$$

This expression is evaluated for $K = 2$ and $q = \pm 2$. Inputs to the structure factor $\Psi_q^x(r)$ are chemical and magnetic symmetries of the unit cell and in these respects it is not different from the structure factor considered hitherto. In particular, the projection q is found to be ± 2. New features introduced with $\Psi_q^x(r)$ are atomic tensors that depend on an index $r = 0, 1, \ldots, 2\bar{J} = 3$, and their rank $x = |K - r|, \ldots, K + r$. Reduced matrix elements for $\Psi_q^x(r)$ are listed in table 1. A property of the $3j$ symbol tells us that $A_q^K(\bar{M})$ and $A_q^K(-\bar{M})$ differ in a factor $(-1)^r = (-1)^x$ where the equality follows from the selection rule $x+r =$ even on the reduced matrix elements in $\Psi_2^x(r)$. Thus $S_q^K(\bar{M})$ can be a linear combination of even-rank tensors and $R_q^K(\bar{M})$ can be a linear combination of odd-rank tensors. As regards $S_q^K(\bar{M})$, it contains tensors of rank $x = 2$ and 4, and the tensor $x = 0$ does not contribute because $q = \pm 2$ (recall also that $\Psi_0^x = 0$). A property of (8) is that a sum with respect to $\bar{M}$ of $S_q^K(\bar{M})$ is proportional to $\Psi_q^K(0)$. In the sum, contributions proportional to $\Psi_q^x(r)$ which have x different from K add up to zero. In the application at hand, $K = 2$, $\bar{J} = 3/2$ and in $S_q^K(\bar{M})$ tensors of rank 4 sum to zero, as shown explicitly in (11). As regards $R_q^K(\bar{M})$, it contains

Table 1. Reduced matrix elements for $\Psi^x_q(r)$ are subject to $x + r =$ even integer. Also tensors of rank $x = 0, 1$ are not present in $\Psi^x_2(r)$. Entries in the table are reduced matrix elements for $K = 2$ and an electric dipole (E1) absorption event with core angular momentum $\bar{J} = 3/2$.

	x		
r	2	3	4
0	$-\frac{1}{165}(\frac{2}{55})^{1/2}$	0	0
1	0	$\frac{497}{825}(\frac{2}{143})^{1/2}$	0
2	$\frac{2}{825}(\frac{1}{77})^{1/2}$	0	$-\frac{172}{275}(\frac{3}{1001})^{1/2}$
3	0	$-\frac{142}{2475}(\frac{14}{429})^{1/2}$	0

only the octupole ($x = 3$); the dipole ($x = 1$) does not contribute because $q = \pm 2$ and the triakontadipole ($x = 5$) derived from (5) is found to be identically zero.

4. Magnetic multipole motif

According to (2), even- and odd-rank tensors in $\Psi^x_2(r)$ appear as different combinations and, in turn, they lead to different dependences on the azimuthal angle. We do not reproduce the observed azimuthal-angle dependence of the (003) reflection if we use in (8) the result (2) which actually describes AF type I order of odd-rank tensors. Instead, we propose an AF type II motif of tensors (quantization axes for the four ions in a unit cell are in the star {1/2, 1/2, 1/2}) described by the structure factor

$$\Psi^x_q = \{1 + (-1)^q\}\{\langle T^x_q\rangle - \langle T^x_{-q}\rangle\} \tag{9}$$

and $\Psi^x_2 = 4\mathrm{i}\langle T^x_2\rangle''$. With $\Psi^x_q = -\Psi^x_{-q}$, Bragg amplitudes depend on the azimuthal angle ψ as shown in (4).

In principal axes we anticipate atomic tensors are purely real. From (5) we readily find $\langle T^2_2\rangle'' = \langle T^2_0\rangle_{(\xi\eta\zeta)}/\sqrt{6}$. Slightly more work is required to prove $\langle T^5_2\rangle'' = 0$, a result mentioned above, and

$$\begin{aligned}\langle T^3_2\rangle'' &= \tfrac{1}{3}\{(5/2)^{1/2}\langle T^3_0\rangle_{(\xi\eta\zeta)} + 2^{1/2}\langle T^3_3\rangle_{(\xi\eta\zeta)}\},\\ \langle T^4_2\rangle'' &= \tfrac{1}{9}\{10^{1/2}\langle T^4_0\rangle_{(\xi\eta\zeta)} + (7/2)^{1/2}\langle T^4_3\rangle_{(\xi\eta\zeta)}\}.\end{aligned} \tag{10}$$

In our results for the amplitude factors in (6) we take out the common factor $(\mathrm{i}\,284/297)(7/1430)^{1/2}$:

$$\begin{aligned}A^2_2(\pm\tfrac{1}{2}) &= -\tfrac{9}{5}\langle T^2_2\rangle'' \times 0.011 + \langle T^4_2\rangle'' \times 0.353 \mp \tfrac{3}{5}\langle T^3_2\rangle'',\\ A^2_2(\pm\tfrac{3}{2}) &= -\langle T^2_2\rangle'' \times 0.011 - \langle T^4_2\rangle'' \times 0.353 \mp \langle T^3_2\rangle''.\end{aligned} \tag{11}$$

Notice that the coefficient of $\langle T^4_2\rangle''$ in $A^2_2(\bar{M})$ is of equal magnitude and opposite sign for $|\bar{M}| = 1/2$ and 3/2. What remains to complete the description of Bragg diffraction are estimates of the atomic tensors $\langle T^2_0\rangle_{(\xi\eta\zeta)}$, $\langle T^3_0\rangle_{(\xi\eta\zeta)}\langle T^3_3\rangle_{(\xi\eta\zeta)}$, $\langle T^4_0\rangle_{(\xi\eta\zeta)}$ and $\langle T^4_3\rangle_{(\xi\eta\zeta)}$.

5. Np 5f wavefunction

A calculation reported in [2] for Np states in the presence of octupole ordering points to a singlet ground state derived from Γ_8 states in $\mathrm{O_h}$ symmetry. In terms of states $|M\rangle$ drawn from the $J = 9/2$ manifold of ${}^4\mathrm{I}_{9/2}$ representing $5\mathrm{f}^3$ we find, in the principal axes $(\xi\eta\zeta)$, a ground state spanned by

$$|\psi\rangle = \alpha|{-7/2}\rangle + \beta|{-1/2}\rangle + \gamma|5/2\rangle. \tag{12}$$

The real coefficients α, β and γ satisfy $\alpha^2 + \beta^2 + \gamma^2 = 1$. Mean values of J_ξ, J_η and J_ζ are all zero when $7\alpha^2 + \beta^2 = 5\gamma^2$. The coefficients in (12) can be expressed in terms of one parameter t. We find $\alpha^2 = 7/18 + t$, $\beta^2 = 1/18 - 2t$ and $\gamma^2 = 10/18 + t$ with the obvious requirement $-7/18 < t < 1/36$.

Using $(J = 9/2)$

$$\langle M|T^x_m|M'\rangle = (-1)^{J-M}\begin{pmatrix} J & x & J \\ -M & m & M' \end{pmatrix},$$

we find

$$\langle\psi|T^2_0|\psi\rangle = \tfrac{3}{2}(\tfrac{3}{55})^{1/2}t, \qquad \langle\psi|T^3_0|\psi\rangle = -\tfrac{1}{2}(\tfrac{5}{3003})^{1/2}(\tfrac{8}{3} + 9t),$$
$$\langle\psi|T^4_0|\psi\rangle = -\tfrac{1}{6}(\tfrac{1}{715})^{1/2}(17 + 75t)$$

and, extracting a common factor $(1/858)^{1/2}$,

$$\langle\psi|T^3_3|\psi\rangle = -\beta(4\alpha + 5\gamma), \qquad \langle\psi|T^4_3|\psi\rangle = \beta(8\alpha - 5\gamma)/\sqrt{3}. \tag{13}$$

The first result reveals that the parameter t is proportional to the Np quadrupole moment. Expressing this in terms of the standard definition $\{3l_z^2 - l(l+1)\}/2$ of the quadrupole operator $\boldsymbol{Q}$, we find that the first result translates to $\langle Q_0\rangle_{(\xi\eta\zeta)} = (945/242)t$. We note in passing that correlations included in an intermediate-coupling scheme applied to the free ion configuration $5f^3$ reduce the magnitude of the quadrupole moment by nearly 30% [9].

6. Confirmation of the agreement between data and the model calculation

We have confronted data for the energy profile at the Np M_4 absorption edge with intensity calculated from (7) and (11). In searches for optimal agreement, the atomic tensors $\langle T^x_2\rangle''$ in the amplitude factors (11) were varied together with the resonance parameters Γ and H_s. Because the experimental data are not on an absolute scale, information on atomic tensors is restricted to ratios.

In the absence of any prior knowledge about the Np octupole moment we initially set it equal to zero, and thereby start with an interpretation in terms of two non-magnetic Np moments of ranks 2 and 4. On setting the octupole tensor equal to zero a search returns an extremely small value of $\langle T^2_2\rangle''/\langle T^4_2\rangle''$. This finding fits well with the result $\langle T^2_2\rangle'' = 0$ from Santini and Amoretti [6] in their model calculation. In our case, $\langle T^2_2\rangle'' = 0$ is achieved in (13) with $t = 0$. In this instance, the amplitude at large distances from the resonance behaves like $1/E^2$ while a single-oscillator amplitude behaves like $1/E$. The $1/E^2$ dependence arises when $\langle T^2_2\rangle'' = 0$ because the coefficients of $\langle T^4_2\rangle''$ for $\bar{M} = 1/2$ and $3/2$ are equal in magnitude and opposite in sign.

Now setting $\langle T^2_2\rangle'' = 0$ and allowing the octupole to be different from zero, a search returns $\langle T^4_2\rangle''/\langle T^3_2\rangle'' = 0.70 \pm 0.12$ which is very robust with respect to latitude in the search. The value returned for the ratio of the hexadecapole and octupole moments is very similar to the value for the ratio calculated with the inferred wavefunction, namely $\langle T^4_2\rangle''/\langle T^3_2\rangle'' = 0.48$ and $\alpha = -0.624$, $\beta = 0.236$, and $\gamma = 0.745$ which are obtained when $t = 0$.

Figure 2 shows the fit to data for the energy profile. The resonance parameters from the fit are $\Gamma = 2.63 \pm 0.04$ eV and $|(g - 1)H_s| = 1.0 \pm 0.02$ eV. This value for the exchange field is consistent with the calculated XAS spectrum. Including the energy resolution of the instrument (FWHH = 0.7 eV) does not have a significant effect on values derived from the fit to data. The similarity between derived and calculated values of $\langle T^4_2\rangle''/\langle T^3_2\rangle''$ and the quality and robustness of the fit shown in figure 2 give us confidence in the inferred wavefunction, a null value for the Np quadrupole and a non-zero Np octupole. In fact, from (10), (13) and the forgoing coefficients in the Np wavefunction, one finds a saturation value $\langle T^3_2\rangle'' = -0.033$ for the observed component of the octupole moment. A standard definition of the octupole moment Λ is based on the operator $\{3l(l+1) - 5l_z^2 - 1\}l_z/2$ and for this quantity the corresponding value is $\langle \Lambda_2 \rangle = -2.18$. Note that $\langle T_q^3 \rangle$ and $\langle \Lambda_q \rangle$ differ only by a numerical factor, usually called a reduced matrix element, that is equal to 65.44 in the present case of f^3.

7. Conclusions

High-order neptunium multipoles are found to be responsible for diffraction by NpO_2 at superlattice reflections, $(00L)$ with L odd, that are a signature in the resonant x-ray diffraction pattern of the phase transition at $T_0 \approx 25.5$ K. The Np multipoles of ranks 3 and 4 possess an AF type II motif. The interpretation uses a Bragg amplitude with enhancement by an electric dipole (E1) event at the Np M_4 edge and the amplitude is independent of the Np magnetic (dipole) moment. A fit to the energy profile measured in the vicinity of the absorption edge strongly suggests a null value for the Np quadrupole moment, and our calculation shows the moment of rank 5 is also zero. Our proposal accounts for the observed azimuthal-angle dependence of the Bragg intensity and the narrow energy profile seen at Np M_4 edge, and it exploits a space group $(Pn\bar{3}m)$ that accommodates the superlattice reflections.

The narrow energy profile is attributed to an exchange interaction that lifts the core-state degeneracy. The interaction is pronounced in a calculated M_4 XAS spectrum, and it is very pronounced compared to the corresponding finding at the M_5 absorption edge. Other interactions which can influence XAS, and produce in calculated spectra departures from an effective exchange interaction, evidently have minimal influence on the resonant Bragg intensity.

A Np ground-state wavefunction can be inferred from experimental findings. By assuming that the Np magnetic moment is zero, which is suggested by several experiments, we obtain an estimate for the ratio of octupole and hexadecapole moments in the Bragg amplitude that is consistent with data gathered at (003) in the rotated $(\pi'\sigma)$ channel of scattering.

We end by noting that the corresponding magnetic neutron diffraction pattern is predicted to be zero, for $(00L)$ and an AF type II motif [10]. On the other hand, a type I AF motif, which appears to be ruled out by data for azimuthal-angle scans in x-ray diffraction, will provide intensity at $(00L)$ in the neutron diffraction pattern.

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