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LETTER TO THE EDITOR

Observation of quadrupolar x-ray diffraction peaks in NdMg

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Abstract. In a previous paper, we discussed the use of multiaxial magnetic structures in rare-earth compounds as test systems for x-ray scattering by orbital non-collinear 4f structures. We here present an experiment using synchrotron radiation, which, meanwhile, has given encouraging results regarding this use of x-ray diffraction: the scattering of x-rays by NdMg within its multiaxial magnetic phase yields tiny Bragg reflections which are very likely to be of quadrupolar origin. Indeed, these peaks have been found at the positions and with the intensities expected for such a charge scattering.

1. Introduction

Recently, we have pointed out that with the availability of high flux x-ray sources scattering experiments revealing details of the 4f charge distribution of rare-earth ions within a crystal may be reasonably envisaged [1]. In particular, the Thompson scattering should be the direct probe for $\boldsymbol{q} \neq \mathbf{0}$ orderings which involve only the orbital degrees of freedom of the rare earth (what is usually called antiferroquadrupolar ordering). Such types of ordering have been controversially evoked for various lanthanide and actinide systems. Once established as an effective experimental technique, simple Thompson multipolar scattering may clarify these questions up to a quantitative level. Indeed, as well as the multipolar scattering amplitudes, the non-collinear arrangement of the aspherical 4f shells may be described using the Stevens equivalent operators [2], thus allowing a rigorous relationship between magnetic microscopic models and scattering experiments. In the absence of an unambiguous archetype of antiferroquadrupolar order, we have proposed to validate this x-ray technique using multiaxial magnetic structures, the associated charge density of which could play the role of an antiferroquadrupolar arrangement.

We have ourselves undertaken an experimental study looking first for a well adapted rare-earth cubic system displaying a multiaxial magnetic structure. Although neodymium is far from being the most favourable rare earth as one considers the involved scattering intensities [1, 3]. NdMg appeared as a really promising system thanks to the surface quality of the single crystals. Indeed, the state of the surface of the sample is crucial to the feasibility of such an experiment, involving very weak scattering amplitudes. NdMg shows, among the rare-earth metallic compounds, an uncommon reluctance to oxidize and the single crystals cleave easily perpendicularly to fourfold directions, thus producing clean regular surfaces.

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2. Magnetic and quadrupolar structures of NdMg

The CsCl-type cubic compound NdMg orders antiferromagnetically at $T_N = 61$ K and displays a second magnetic transition at $T_R = 35$ K. From neutron diffraction, it has been established that the transition at T_R corresponds to a change from a collinear structure, at high temperature, to a multiaxial one, at low temperature. Both structures are based on wave vectors from the $\langle 1/2\,0\,0\rangle$ star [4]. NdMg's magnetic multiaxial structure consists of a double-k structure, with moments along twofold axes. At any j site of the lattice, located by the position vector $\boldsymbol{R}_j$, the magnetic moment reads as

$$\boldsymbol{M}_j = \boldsymbol{m}_1 \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}_1\cdot\boldsymbol{R}_j} + \boldsymbol{m}_2 \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}_2\cdot\boldsymbol{R}_j}$$

where the respective Fourier components and wave vectors are $\boldsymbol{m}_1 = [1/\sqrt{2}\,0\,0]$, $\boldsymbol{k}_1 = [1/2\,0\,0]$, $\boldsymbol{m}_2 = [0\,1/\sqrt{2}\,0]$ and $\boldsymbol{k}_2 = [0\,1/2\,0]$ (the moment amplitude is here unity). As stated in [1], such a structure preserves the rare-earth sites as centres of symmetry and, therefore, cannot originate a periodic displacement of the atoms and the related Bragg peaks. Starting from this Fourier description of the magnetic structure and using equation (5) from [1], one determines the corresponding quadrupolar arrangement, that is the expression at any j site for the five quadrupolar components (here defined at Stevens' equivalent operators in the cubic axes [2]):

$$\left\langle O_2^0 \right\rangle_j = -\tfrac{1}{2} Q_0$$

$$\left\langle P_{xy} \right\rangle_j = \tfrac{1}{4}\left[Q_0 - Q_1 \right] \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_j} \qquad \boldsymbol{q} = [1/2\,1/2\,0]$$

$$\left\langle O_2^2 \right\rangle_j = 0 \qquad \left\langle P_{yz} \right\rangle_j = 0 \qquad \left\langle P_{zx} \right\rangle_j = 0$$

where Q_0 and Q_1 are the ordered quadrupolar components on a local coordinate system (with the magnetic moment direction as z axis) and $\boldsymbol{q}$ is the quadrupolar wave vector propagating the $\langle P_{xy}\rangle$ component ($\boldsymbol{q} = \boldsymbol{k}_1 + \boldsymbol{k}_2$). One observes that the $\langle O_2^0\rangle$ component is non-zero and constant from site to site and thus has the same periodicity as the lattice, which results, through the magnetoelastic coupling, in a macroscopic tetragonal strain mode [5].

However, in the (xy) plane defined by the moments' directions, the double-k magnetic structure corresponds to an antiferroquadrupolar arrangement for the $\langle P_{xy}\rangle$ component which propagates with a wave vector $\boldsymbol{q} = [1/2\,1/2\,0]$. In its basal (xy) plane, NdMg's double-k magnetic structure is then suitable for the observation of x-ray antiferroquadrupolar diffraction peaks, at reciprocal space nodes $\boldsymbol{Q} = [h\,k\,l] + [1/2\,1/2\,0]$, where $[h\,k\,l]$ is a reciprocal lattice vector.

3. X-ray quadrupolar scattering

Expressing the Thompson scattering amplitude beyond the simple hypothesis of a spherical rare-earth ion, one obtains the quadrupolar, octupolar and dodecapolar scattering amplitudes [1, 3]. For rare-earth ions located at sites of cubic symmetry, the expectation values for the octupolar and dodecapolar operators mainly result from the crystalline electric field, whereas the quadrupolar terms develop as a result of dipolar or quadrupolar pair interactions. Consequently, out of the Brillouin-zone centre, the dominant contribution to the multipolar scattering is of quadrupolar origin. Thus, in the analysis of the multipolar scattering in

NdMg, we will here restrict ourselves to the quadrupolar scattering amplitude:

$$A_2(\boldsymbol{Q}) = \alpha_J F_2(Q)\left[\frac{1}{2}\left(3\frac{Q_z^2}{Q^2}-1\right)\left\langle O_2^0\right\rangle + \frac{3}{2}\left(\frac{Q_x^2-Q_y^2}{Q^2}\right)\left\langle O_2^2\right\rangle + 6\left(\frac{Q_xQ_y}{Q^2}\langle P_{xy}\rangle + c.p.\right)\right] \quad (1)$$

where $\boldsymbol{Q} = [Q_x\ Q_y\ Q_z]$ is the scattering vector and $\alpha_J F_2(Q)$ represents the quadrupolar form factor. Furthermore, in the case of NdMg's multiaxial structure, the $\langle O_2^0\rangle$ component is the same on all sites and, outside the Brillouin-zone centre, the scattering amplitude should arise from the $\langle P_{xy}\rangle$ term. The effective scattering amplitude then reduces to

$$A_2(\boldsymbol{Q}) = \alpha_J F_2(Q) 6\frac{Q_xQ_y}{Q^2}\langle P_{xy}\rangle. \quad (2)$$

In contrast with the spherical scattering amplitude, the multipolar ones are maximum for non-zero scattering angle, the optimum being reached for $\sin\theta/\lambda \approx 0.5$ Å^{-1} for the quadrupolar scattering [1]. Considering the $\boldsymbol{Q}$ dependence of the above quadrupolar amplitude, the most favourable reflection for giving evidence of the quadrupolar scattering in NdMg should occur for the [5/2 5/2 0] scattering vector.

4. Experiment

The experiment was performed at the ESRF, BM2 beamline, using the seven-circle goniometer and a closed-cycle helium refrigerator for cooling the sample below $T_R = 35$ K. As very weak scattering intensities had to be measured, the signal to background ratio had to be optimized. In view of this, a short x-ray wavelength $\lambda = 0.8943$ Å, which is an energy well above the neodymium L absorption edges, was used. To further decrease the background level, a Ge(111) analyser was mounted in front of the detector.

The single crystal of NdMg used for this experiment is part of an ingot processed with the Bridgman technique. It has a parallepipedic shape ($3 \times 1 \times 6$ mm^3) due to the aptitude of this cubic system for cleaving perpendicularly to fourfold directions. The illuminated face of the crystal was then unaffected by mechanical stress or any other damage associated with a spark or mechanical cutting. This face, perpendicular to the reference [1 0 0] direction of the crystal, was tilted with a 45° angle with respect to the goniometer's φ axis, in order to have this axis coincident with the twofold [1 1 0] direction. All measurements were performed in reflection conditions. With this geometry, having conveniently fixed the φ angle, numerous reflections were accessible within the ($h\,k\,0$) first quadrant of the crystal, with the same x-ray incident and emerging angles with respect to its surface.

The sample was then cooled down to 19 K. Scanning the lattice reflections, it appeared that the low temperature tetragonal strain was large enough to resolve the peaks associated with the three magnetic domains (figure 1).

As only one domain could result in quadrupolar diffraction peaks in the accessible ($h\,k\,0$) plane, we had to focus on the corresponding reciprocal lattice. Identifying this particular domain was possible since the tetragonal magnetostriction mode results in the expansion, in real space, of the ($x\,y$) plane containing the magnetic moments. Unfortunately, this domain appeared to be the least represented one, its associated Bragg reflections being approximately ten times less than for the two other domains.

Once the orientation matrix was determined for the selected domain, we focused on the [5/2 5/2 0] quadrupolar reflection which, from equation (2) and the $\boldsymbol{Q}$ dependence of the quadrupolar form factor, is calculated as the most intense. First, the background counting level was estimated about the [5/2 5/2 0] node, its value being a little less than 2 counts s^{-1} (2×10^{-5} per monitor count). Considering the order of magnitude of the

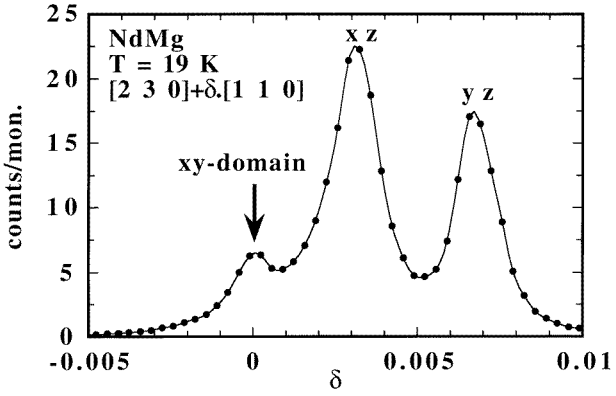

Figure 1. Low temperature $[2+\delta,\ 3+\delta,\ 0]$ scan across the [2 3 0] lattice node at $T = 19$ K. Each peak corresponds to one of the three domains associated with the tetragonal symmetry lowering of NdMg, (xy) represents the domain for which subsequent measurements were carried out. The line is a guide for the eye.

expected quadrupolar reflection (some tenths of a count per second), counting times of at least ten minutes per point were necessary for the peak to emerge from the background. Due to the ω extension of the Bragg reflections, a diagonal scan in the $(h\,k\,0)$ plane appeared to be the most appropriate process. An additional advantage of this $h\,k$ scan was to also measure the equivalent [5/2 5/2 0] nodes of the two other domains, which allows one to check the systematic emergence of peaks at such positions, in relation, for instance, to the $\lambda/2$ harmonic of the monochromator. As a result of these scans, with total counting time of 20 minutes per point (10^8 monitor counts), only one peak was clearly defined and located at the expected position for the quadrupolar scattering (figure 2, upper part), whereas no $\lambda/2$ peaks were identifiable. The maximum of the peak reached some more than 200 counts above the background, that is about 0.2 counts per second, which is typically the expected order of magnitude.

Looking for another reflection with favourable theoretical intensity and a low enough background level, we initiated equivalent measurements on the [3/2 5/2 0] reflection, the path in reciprocal space being parallel with the [5/2 5/2 0] one. This scan also revealed a peak at the expected position, even better defined than the previous one (figure 3, upper part). In both cases, the peaks' full widths at half maximum are comparable to the FWHM of neighbouring lattice reflections.

An h scan has also been carried out across the [5/2 0 0] position, in order to establish the order of magnitude of a magnetic x-ray reflection [6]. This scan, with a counting time of 15 minutes per point, showed no evidence of any peak of magnetic or $\lambda/2$ origin. This agrees with the results of the calculations, which show that the quadrupolar x-ray scattering is much larger than the magnetic one, and confirms, if necessary, that the observed peaks cannot be ascribed to multiple magnetic scattering.

The next step was to warm the sample up to a temperature higher than T_N and then to carry out scans equivalent to the low temperature ones. The background level had increased by about 40%, due to the thermal incoherent scattering of the lattice, but peaks could no longer be identified at the [5/2 5/2 0] and [3/2 5/2 0] positions (figures 2 and 3, lower parts). This confirms the quadrupolar nature of the low temperature intensities.

An estimate of the ordered quadrupolar component $\langle P_{xy} \rangle$ can be achieved using

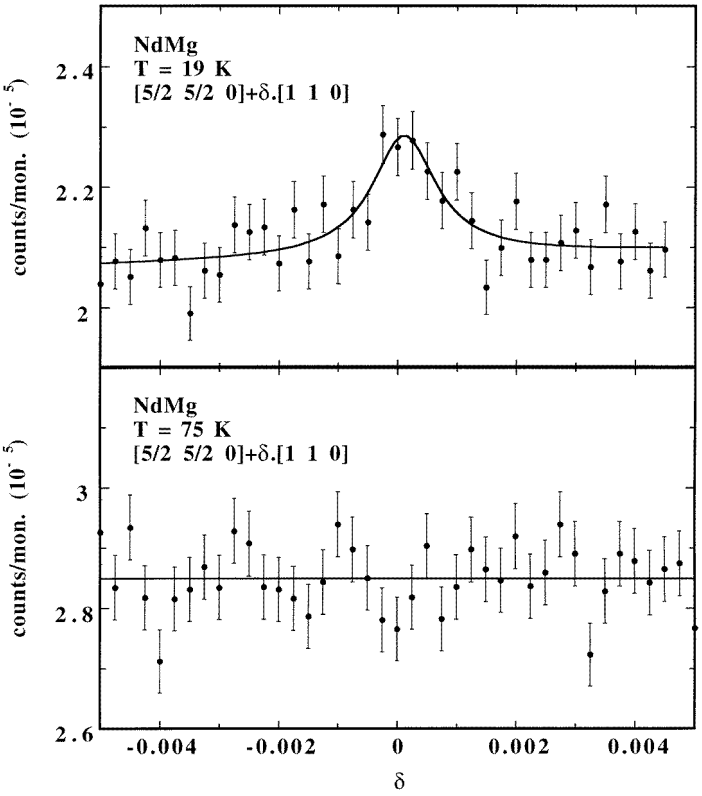

Figure 2. Upper part: scan along the [1 1 0] direction across the [5/2 5/2 0] quadrupolar node at $T = 19$ K, within the double-k ordered phase of NdMg. The line is a Lorentzian fit to the peak. Lower part: scan along the [1 1 0] direction across the [5/2 5/2 0] quadrupolar node at $T = 75$ K, above the Néel temperature.

equation (2). The absolute intensities for the [3/2 5/2 0] and [5/2 5/2 0] reflections can be obtained by scaling them with neighbouring lattice Bragg peaks and neglecting the effect of primary extinction. Within these conditions, one obtains $\langle P_{xy} \rangle = 2.2 \pm 0.6$. Because of the lack of a crystalline electric field determination in NdMg, no theoretical value is at present available for $\langle P_{xy} \rangle$. However, one may compare the $\langle P_{xy} \rangle$ value obtained for NdMg with that computed in the isomorphous compound NdZn [7], which displays below 18 K the same double-k magnetic structure at NdMg: the measured $\langle P_{xy} \rangle$ value is in qualitative agreement with the calculated one, $\langle P_{xy} \rangle \approx 5$.

5. Summary

In summary, the existence of diffraction peaks, at the positions and with the order of magnitude expected for quadrupolar x-ray reflections, has been established in NdMg. These peaks are not of magnetic origin, cannot be ascribed to a $\lambda/2$ contamination and disappear as the temperature is raised to the paramagnetic range. Thus, although additional measurements are necessary to check the $\boldsymbol{Q}$ dependence of this scattering, the observed reflections can be reasonably ascribed to x-ray quadrupolar diffraction. They have been observed despite

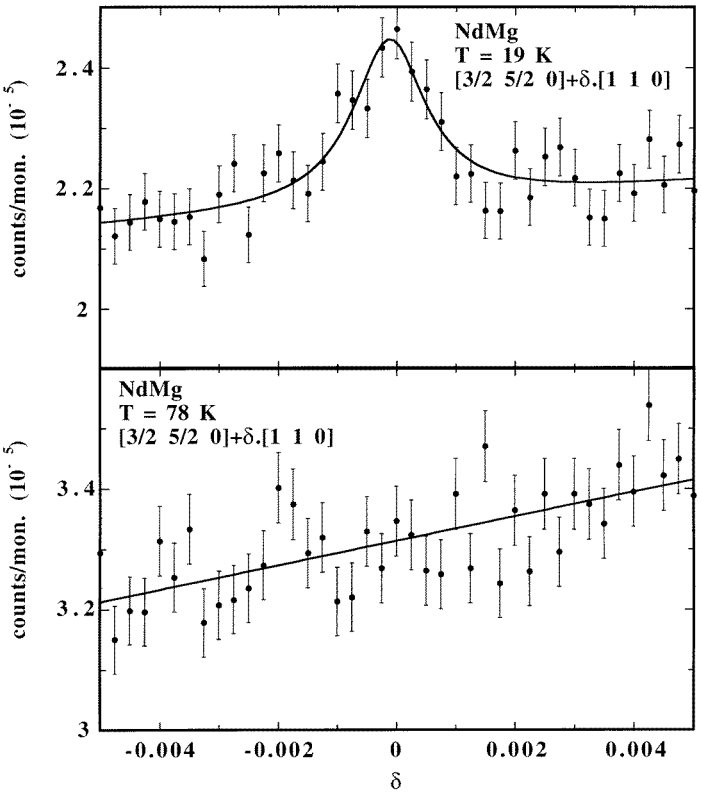

Figure 3. Upper part: scan along the [1 1 0] direction across the [3/2 5/2 0] quadrupolar node at $T = 19$ K, within the double-k ordered phase of NdMg. The line is a Lorentzian fit to the peak. Lower part: scan along the [1 1 0] direction across the [3/2 5/2 0] quadrupolar node at $T = 78$ K, above the Néel temperature.

an unfavourable domain partition of the crystal and using a neodymium based sample, which does not correspond to the maximum quadrupolar scattering amplitude among the rare earths. The results of this experiment are thus very encouraging with regard to the use of x-ray diffraction as a probe for multiaxial orbital and/or magnetic orderings in rare-earth compounds.

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