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# Magnetic structures and x-ray 4f multipolar scattering in cubic systems

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## Abstract

Thomson scattering by rare-earth multipoles is a valuable technique for determining orbital structures in rare-earth systems. In the present paper, the formalism describing the relation between the magnetic and multipolar structures in cubic systems is extended to the fourth- and sixth-order multipoles. The associated x-ray scattering amplitudes are written using the cubic irreducible representations and calling in play appropriate Stevens equivalent operators. This paper is intended to provide a rigorous framework for the interpretation of multipolar scattering experiments on magnetically or orbitally ordered systems.

## 1. Introduction

In rare-earth systems, the asphericity of the unfilled 4f shell is related to many low temperature properties of crystallographic and magnetic nature. Within a crystal, this asphericity is first the consequence of the crystal electric field (CEF), but, for highly symmetrical systems, the 4f distribution keeps degrees of freedom which may be involved in ordering phenomena. This orbital degeneracy is particularly influential for rare-earth ions in cubic symmetry, in which case the electric quadrupoles are not ordered by the CEF. The scope of this paper is actually restricted to cubic systems and, for further simplification, to these with a single rare-earth site per crystallographic cell.

In most of these systems, a magnetic ordering occurs and secondly affects the shape of the 4f shell. The 4f orbital arrangement which then develops is characteristic of the magnetic structure. However, in some rare cases, independently of any magnetic order, the interactions between the 4f shells drive orderings in which their electronic density no longer respects the initial symmetries. In such cases, the primary order parameter is not of magnetic, but of orbital nature. As the additional 4f asphericity is usually well described by the emergence of quadrupolar components, this state of the system is called quadrupolar order. According to the

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associated change in the lattice translational symmetries, one distinguishes ferroquadrupolar or anti-ferroquadrupolar order by analogy with the ferromagnetic and anti-ferromagnetic situations.

From an experimental point of view, probing the 4f asphericity is a delicate task; it is a microscopic property related to a few electrons from an inner electronic shell. In the paramagnetic state, spectroscopic techniques (mainly neutron inelastic scattering) can provide one with the crystal electric field energy scheme. Then from a single site approach, using a quantum description of the atom, one can determine the 4f aspherical distribution due to the crystal field.

Within a magnetically or orbitally ordered phase the single site treatment fails and deriving the 4f asphericity from a spectroscopic experiment becomes very delicate. If the change in the asphericity propagates at the centre of the Brillouin zone ( $\mathbf{q} = 0$ ), instead of spectroscopy, direct macroscopic (dilatometry) or microscopic (x-ray, neutron diffraction) techniques may be valuable for detecting the strain mode resulting from magnetoelastic couplings. However, such techniques are useless if the 4f asphericity develops with ( $\mathbf{q} \neq 0$ ) wave vectors for which the macroscopic strain is cancelled. Then, depending on whether or not the rare-earth sites lose the inversion symmetry in the ordered state, one should distinguish between the following two situations.

In the first one, a 4f ion is no longer located at the centre of inversion and will move with respect to the other ions of the crystal. The lattice will therefore display a change in its period which coincides with that of the 4f even multipoles. For displacements of sufficient amplitude neutron nuclear scattering or spherical x-ray Thomson scattering give rise to Bragg peaks associated with the new periodicity [1]. Multipolar x-ray scattering represents a negligible contribution to such x-ray satellites and this phenomenon will not be further considered in this paper.

In the second case, the ordered system preserves the rare-earth sites as centres of symmetry and the only change in charge distribution is related to the 4f shell itself. Then, no ( $\mathbf{q} \neq 0$ ) movement of the atoms occurs. This is a rather common situation in cubic systems where constant amplitude magnetic structures, collinear or multi-axial, usually preserve the rare-earth sites as inversion centres. In this case the only effective probe remains x-rays, which directly couple to the 4f shell electronic distribution. In concomitance with the magnetic/multipolar ordering, additional diffraction peaks of a multipolar nature should appear in agreement with the new charge periodicity of the system. From an experimental point of view, the observation of such weak peaks is possible even in the less favourable case of neodymium [2, 3].

In principle, this technique allows determination of the multipolar structures, that is, the involved wave vectors and multipolar operators. Therefore, in the case of a primary order parameter of multipolar nature, as in the anti-ferroquadrupolar ordering case, this experimental method represents the most direct characterization of the ordered phase. In the more commonly occurring situation of a magnetic order having consequences for the 4f asphericity, x-ray scattering will provide one with indirect information on the magnetic structure itself. Note that although it is weak, this charge scattering is three to four orders of magnitude larger than x-ray magnetic scattering. In many cases, it will represent an alternative or complementary technique to neutron magnetic scattering. This could be of particular interest in the case of the non-availability of crystals large enough for neutron scattering experiments or in the case of excessive neutron absorption lengths for the nuclei involved.

In a previous paper [4], we described a method for relating a magnetic structure to its quadrupolar counterpart and also developed a formalism for describing the multipolar scattering by a rare-earth ion using 'isotropic' equivalent operators. In the present paper, we first generalize, beyond the quadrupolar case, the analysis for determining the relation between

a given magnetic structure and its multipolar counterpart. As an example, the technique is applied to the double- $k$  magnetic structure of NdMg. Second, we write, using the multipolar equivalent operators relevant for the cubic symmetry, the scattering amplitudes of order four and six. In the appendixes, one will find useful definitions regarding the multipolar equivalent operators involved.

## 2. From the magnetic structure to the multipolar one

Our goal here is to qualitatively establish the multipolar 4f structure which can be expected to coexist, in a cubic system, with a given high-symmetry magnetic structure. By high symmetry structure we mean magnetic structures in which all magnetic sites are crystallographically equivalent, with cubic point group  $O_h$ , in the paramagnetic state, and which, within the ordered range, carry a magnetic moment of the same amplitude with a direction belonging to a unique crystallographic family. In addition, the magnetic sites have to keep the inversion symmetry. Despite these apparently very selective conditions, these structures are largely represented in cubic rare-earth compounds.

The scope then is to determine the consequences on the 4f asphericity of the occurrence of a magnetic order. This asphericity being described in terms of multipolar operators, we shall identify those which are non-zero and determine their associated wave vectors. We have, in previous papers, already discussed the connection between a given anti-ferromagnetic structure and the coexisting quadrupolar structure. To solve this question we proposed two methods: one based on the systematic analysis of the rare-earth site magnetic symmetry lowering similar to the treatment of a crystal field problem [4], the other based on the assumption that multipoles develop as a result of the mean bilinear exchange field [5]. Since they both account for the local magnetic symmetry lowering, these two approaches are equivalent. However, we will prefer the latter here as it can easily be extended to higher order multipoles.

### 2.1. Method

The method is based on the transformation properties of multipoles which are considered as consequences of the mean bilinear exchange field applied to a site of cubic symmetry. For high-symmetry magnetic structures, the mean field is simply proportional to the magnetic moment and all magnetic sites are equivalent to the origin's one except for a cubic point group transformation [5]. As a consequence of the mean field, additional, even multipolar components have to develop at the origin site 0. Obviously, any  $j$  site of the lattice will display changes in its asphericity in agreement with the changes at 0.

Any multipolar component is defined, at first, as a function of the space coordinates of the 4f electrons. Then, to deduce from the origin's ones the multipolar components developing at the  $j$  site, one should know how to transform the space coordinates going from 0 to  $j$ . The only difference between the conditions at sites 0 and  $j$  lies in the possible different orientation of the magnetic moment, hence of the mean field. This difference in orientation can be ascribed to a combination of rotations only, all of which belong to the cube's point group. As for rotations, the space coordinates  $(x, y, z)$  transform exactly as the magnetic components  $(\langle m_x \rangle, \langle m_y \rangle, \langle m_z \rangle)$ ; within a magnetic structure one can relate any multipole to a proper combination of magnetic components. For instance, let us consider the cubic  $\Gamma_3$  case for which the quadrupolar components, in terms of Stevens' average operators,  $\{\langle O_2^0 \rangle, \sqrt{3}\langle O_2^2 \rangle\}$ , transform as the space coordinates' basis functions  $\{3z^2 - r^2, \sqrt{3}(x^2 - y^2)\}$ . This basis may be replaced by a 'magnetic' one:  $\{3\langle m_z \rangle^2 - m^2, \sqrt{3}(\langle m_x \rangle^2 - \langle m_y \rangle^2)\}$  which transforms identically. Consequently, at any  $j$  site, the quadrupolar components can be simply related to

the local magnetic moment  $\mathbf{m}_j = (\langle m_x \rangle_j, \langle m_y \rangle_j, \langle m_z \rangle_j)$  by the equations

$$\langle O_2^0 \rangle_j = (\alpha_J \langle r^2 \rangle)^{-1} \left\langle \sum_i (3z_i^2 - r_i^2) \right\rangle = c_2^\gamma (3\langle m_z \rangle_j^2 - m^2)$$

$$\langle O_2^0 \rangle_j = (\alpha_J \langle r^2 \rangle)^{-1} \left\langle \sum_i (x_i^2 - y_i^2) \right\rangle = \frac{c_2^\gamma}{\sqrt{3}} (\langle m_x \rangle_j^2 - \langle m_y \rangle_j^2)$$

where  $c_2^\gamma$  is a scalar, common to all rare-earth sites, which can be expressed as a function of the values at the origin of the magnetic and quadrupolar moments. The centre member of the equations recalls the 4f electron coordinates' definition of the quadrupolar moments ( $\alpha_J$  is the Stevens coefficient and  $\langle r^2 \rangle$  the average second-order radial integral for a 4f electron). All quantitative aspects of the system are confined in the  $c_2^\gamma$  scalar. In other words, the problem is then factorized and one may define the quadrupolar wave vectors by replacing  $(\langle m_x \rangle, \langle m_y \rangle, \langle m_z \rangle)$  with their Fourier definitions.

Using the appropriate magnetic polynomials, it is then possible to generalize this method to all the multipolar operators of order two, four and six. Instead of the general multipolar operators, defined in [4], it is much more convenient to use operators transforming according to the irreducible representation of the cubic  $O_h$  group. As we shall see (section 2.2), results for one representation then generalize at any order: second, fourth or sixth. The cubic multipolar operators we use in the following are those defined by Morin and Schmitt in [6] and are listed in appendix C.

The question of defining the existence and wave vectors for all the 27 multipolar components then reduces to writing the magnetic polynomials which can serve as the basis vectors for the  $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5$  representations associated with even multipoles. Starting from the basis of functions of the space coordinates, one can easily define the associated basis of the magnetic polynomials which appear in table 1. The table is organized so that, within a cubic representation, the equivalent basis vectors of order two, four or six share the same line.

The fully symmetric  $\Gamma_1$  terms are already ordered by the crystal field but may be slightly affected by the magnetic order. As they stay identical on all sites, they cannot introduce a new charge periodicity, but only a slight volume effect. Depending on the magnetic Fourier components and wave vectors, the  $\Gamma_2, \Gamma_3, \Gamma_4$  and  $\Gamma_5$  terms may be associated with non-zero charge wave vectors, which may be identified by x-ray scattering experiments. Multipolar components associated with the zone centre will, thanks to the magnetoelastic couplings, result in strain modes characteristic of the magnetic structure.

## 2.2. Magnetic moments along threefold, twofold or fourfold axes

In cubic systems, the anisotropy will force the magnetic moments to develop along fourfold, threefold or twofold axes. Within these conditions, one observes in table 1 that the  $\Gamma_2$  and  $\Gamma_4$  multipolar components cancel; these two representations which are specific to the fourth and sixth orders will not influence the 4f asphericity. Moreover, the expressions of table 1 for the fourth and sixth order multipolar components belonging to the  $\Gamma_3$  and  $\Gamma_5$  are then drastically simplified. As already appears at the level of quadrupoles, structures with moments along the fourfold axes will have multipolar components only within the  $\Gamma_3$  representation, whereas structures with magnetic moments along threefold axes will have components only within the  $\Gamma_5$  one. Twofold axes structures will mix components from the  $\Gamma_3$  and  $\Gamma_5$  representations. The reduced expressions for the relevant multipolar components are listed in table 2, for moments along fourfold or threefold axes, and table 3 for moments along twofold axes. One important benefit of this representational analysis approach is to show that the multipolar components

**Table 1.** Relation, for a high symmetry magnetic structure, between the cubic multipolar components and the statistical magnetic moment  $\mathbf{m} = (m_x, m_y, m_z)$ . The lines correspond to the cubic irreducible representations and the columns to the three orders of even multipoles. The  $\Delta$  symbols appearing in the  $\Gamma_1$  expressions recall that these multipolar components are already ordered by the crystal field. The  $c_n^\mu$  factors are temperature-dependent but common to all rare-earth sites.

	Quadrupole	Hexadecapole	Hexacontatetrapole
$\Gamma_1$ —		$\Delta\langle O_4^\alpha \rangle = c_4^\alpha (m_x^4 + m_y^4 + m_z^4 - \frac{3}{5}m^4)$	$\Delta\langle O_6^\alpha \rangle = c_6^\alpha [2(m_x^6 + m_y^6 + m_z^6) + 180m_x^2m_y^2m_z^2 - 15(m_x^2m_z^4 + m_z^2m_x^4 + m_x^2m_y^4 + m_y^2m_x^4 + m_y^2m_z^4 + m_z^2m_y^4)]$
$\Gamma_2$ —		—	$\langle O_6^\beta \rangle = c_6^\beta [m_x^4(m_y^2 - m_z^2) + m_y^4(m_z^2 - m_x^2) + m_z^4(m_x^2 - m_y^2)]$
	$\langle O_2^0 \rangle = c_2^\gamma (3m_z^2 - m^2)$	$\langle O_4^{\gamma,1} \rangle = c_4^\gamma [7m_z^4 + 14m_x^2m_y^2 - 4m^2m_z^2 - m^4]$	$\langle O_6^{\gamma,1} \rangle = c_6^\gamma [2m_z^6 - m_x^6 - m_y^6 + 15(m_x^4 + m_y^4)m_z^2 - 15(m_x^2 + m_y^2)m_z^4]$
$\Gamma_3$	$\langle O_2^{\gamma} \rangle = \frac{c_2^\gamma}{\sqrt{3}} (m_x^2 - m_y^2)$	$\langle O_4^{\gamma,2} \rangle = c_4^\gamma (m_x^2 - m_y^2) \times (m^2 - 7m_z^2)$	$\langle O_6^{\gamma,2} \rangle = c_6^\gamma (m_x^2 - m_y^2)(m^4 - 7m^2m_z^2 + 11m_z^4 - 11m_x^2m_y^2)$
—		$\langle O_4^{\delta,1} \rangle = c_4^\delta m_x m_y (m_x^2 - m_y^2)$	$\langle O_6^{\delta,1} \rangle = c_6^\delta m_x m_y (m_x^2 - m_y^2)(11m_z^2 - m^2)$
$\Gamma_4$ —		$\langle O_4^{\delta,2} \rangle = c_4^\delta m_z m_x (m_z^2 - m_x^2)$	$\langle O_6^{\delta,2} \rangle = c_6^\delta m_y m_z (m_y^2 - m_z^2)(11m_x^2 - m^2)$
—		$\langle O_4^{\delta,3} \rangle = c_4^\delta m_y m_z (m_y^2 - m_z^2)$	$\langle O_6^{\delta,3} \rangle = c_6^\delta m_z m_x (m_z^2 - m_x^2)(11m_y^2 - m^2)$
	$\langle P_{xy} \rangle = c_2^\epsilon m_x m_y$	$\langle O_4^{\epsilon,1} \rangle = c_4^\epsilon m_x m_y (7m_z^2 - m^2)$	$\langle O_6^{\epsilon,1,1} \rangle = c_6^{\epsilon 1} m_x m_y (33m_z^4 - 18m^2m_z^2 + m^4)$ $\langle O_6^{\epsilon,2,1} \rangle = c_6^{\epsilon 2} m_x m_y (3m_x^4 - 10m_x^2m_y^2 + 3m_y^4)$
$\Gamma_5$	$\langle P_{yz} \rangle = c_2^\epsilon m_y m_z$	$\langle O_4^{\epsilon,2} \rangle = c_4^\epsilon m_y m_z (7m_x^2 - m^2)$	$\langle O_6^{\epsilon,1,2} \rangle = c_6^{\epsilon 1} m_y m_z (33m_x^4 - 18m^2m_x^2 + m^4)$ $\langle O_6^{\epsilon,2,2} \rangle = c_6^{\epsilon 2} m_y m_z (3m_y^4 - 10m_y^2m_z^2 + 3m_z^4)$
	$\langle P_{zx} \rangle = c_2^\epsilon m_z m_x$	$\langle O_4^{\epsilon,3} \rangle = c_4^\epsilon m_z m_x (7m_y^2 - m^2)$	$\langle O_6^{\epsilon,1,3} \rangle = c_6^{\epsilon 1} m_z m_x (33m_y^4 - 18m^2m_y^2 + m^4)$ $\langle O_6^{\epsilon,2,3} \rangle = c_6^{\epsilon 2} m_z m_x (3m_z^4 - 10m_z^2m_x^2 + 3m_x^4)$

will not scatter over many points of the first Brillouin zone, but will concentrate at particular points. Indeed, all components sharing the same line, in tables 2 or 3, are proportional to the same combination of the magnetic components and, therefore, will have common wave vectors. This means that, for structures with constant amplitude magnetic moments lying along the fourfold, twofold or threefold axes, accounting for the fourth and sixth order terms, do not introduce additional charge wave vectors. These new terms only confirm the charge periodicities which develop at the quadrupolar level.

### 2.3. The example of the double-k anti-ferromagnetic structure of NdMg

To illustrate the advantages of the above analysis, let us consider the concrete example of the magnetic multi-axial structure of NdMg. We used this structure for demonstrating the

**Table 2.** Reduction of table 1 to the special cases of structures with magnetic moments along fourfold ( $\Gamma_3$ ) or threefold ( $\Gamma_5$ ) axes.

	Quadrupole	Hexadecapole	Hexacontatetrapole
$\Gamma_3$ $m//\langle 100 \rangle$	$\langle O_2^0 \rangle = c_2^\gamma (3m_z^2 - m^2)$	$\langle O_4^{\gamma,1} \rangle = c_4^\gamma m^2 (3m_z^2 - m^2)$	$\langle O_6^{\gamma,1} \rangle = c_6^\gamma m^4 (3m_z^2 - m^2)$
	$\langle O_2^2 \rangle = \frac{c_2^\gamma}{\sqrt{3}} (m_x^2 - m_y^2)$	$\langle O_4^{\gamma,2} \rangle = c_4^\gamma m^2 (m_x^2 - m_y^2)$	$\langle O_6^{\gamma,2} \rangle = c_6^\gamma m^4 (m_x^2 - m_y^2)$
$\Gamma_5$ $m//\langle 111 \rangle$	$\langle P_{xy} \rangle = c_2^\varepsilon m_x m_y$	$\langle O_4^{\varepsilon,1} \rangle = \frac{4}{3} c_4^\varepsilon m^2 m_x m_y$	$\langle O_6^{\varepsilon,1,1} \rangle = -\frac{4}{3} c_6^{\varepsilon,1} m^4 m_x m_y$
			$\langle O_6^{\varepsilon,2,1} \rangle = -\frac{4}{9} c_6^{\varepsilon,2} m^4 m_x m_y$
	$\langle P_{yz} \rangle = c_2^\varepsilon m_y m_z$	$\langle O_4^{\varepsilon,2} \rangle = \frac{4}{3} c_4^\varepsilon m^2 m_y m_z$	$\langle O_6^{\varepsilon,1,2} \rangle = -\frac{4}{3} c_6^{\varepsilon,1} m^4 m_y m_z$
			$\langle O_6^{\varepsilon,2,2} \rangle = -\frac{4}{9} c_6^{\varepsilon,2} m^4 m_y m_z$
	$\langle P_{zx} \rangle = c_2^\varepsilon m_z m_x$	$\langle O_4^{\varepsilon,3} \rangle = \frac{4}{3} c_4^\varepsilon m^2 m_z m_x$	$\langle O_6^{\varepsilon,1,3} \rangle = -\frac{4}{3} c_6^{\varepsilon,1} m^4 m_z m_x$
		$\langle O_6^{\varepsilon,2,3} \rangle = -\frac{4}{9} c_6^{\varepsilon,2} m^4 m_z m_x$	

**Table 3.** Reduction of table 1 to the special case of a structure with magnetic moments along twofold axes.

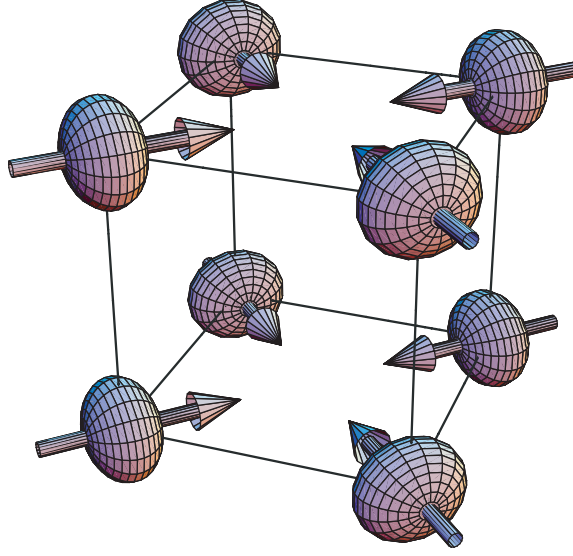
	Quadrupole	Hexadecapole	Hexacontatetrapole
$\Gamma_3$	$\langle O_2^0 \rangle = c_2^\gamma (3m_z^2 - m^2)$	$\langle O_4^{\gamma,1} \rangle = -\frac{5}{2} c_4^\gamma m^2 (3m_z^2 - m^2)$	$\langle O_6^{\gamma,1} \rangle = \frac{1}{4} c_6^\gamma m^4 (3m_z^2 - m^2)$
	$\langle O_2^2 \rangle = \frac{c_2^\gamma}{\sqrt{3}} (m_x^2 - m_y^2)$	$\langle O_4^{\gamma,2} \rangle = -\frac{5}{2} c_4^\gamma m^2 (m_x^2 - m_y^2)$	$\langle O_6^{\gamma,2} \rangle = \frac{1}{4} c_6^\gamma m^4 (m_x^2 - m_y^2)$
$\Gamma_5$	$\langle P_{xy} \rangle = c_2^\varepsilon m_x m_y$	$\langle O_4^{\varepsilon,1} \rangle = -c_4^\varepsilon \frac{4}{3} m^2 m_x m_y$	$\langle O_6^{\varepsilon,1,1} \rangle = c_6^{\varepsilon,1} m^4 m_x m_y$
			$\langle O_6^{\varepsilon,2,1} \rangle = -c_6^{\varepsilon,2} m^4 m_x m_y$
	$\langle P_{yz} \rangle = c_2^\varepsilon m_y m_z$	$\langle O_4^{\varepsilon,2} \rangle = -c_4^\varepsilon \frac{4}{3} m^2 m_y m_z$	$\langle O_6^{\varepsilon,1,2} \rangle = c_6^{\varepsilon,1} m^4 m_y m_z$
			$\langle O_6^{\varepsilon,2,2} \rangle = -c_6^{\varepsilon,2} m^4 m_y m_z$
	$\langle P_{zx} \rangle = c_2^\varepsilon m_z m_x$	$\langle O_4^{\varepsilon,3} \rangle = -c_4^\varepsilon \frac{4}{3} m^2 m_z m_x$	$\langle O_6^{\varepsilon,1,3} \rangle = c_6^{\varepsilon,1} m^4 m_z m_x$
		$\langle O_6^{\varepsilon,2,3} \rangle = -c_6^{\varepsilon,2} m^4 m_z m_x$	

feasibility of the multipolar scattering experiments thanks to synchrotron radiation [3]. Our analysis was then restricted to quadrupoles. We can now generalize it to all multipolar terms.

The magnetic multiaxial structure of NdMg consists of a double- $k$  structure, with moments along twofold axes (figure 1). Three anti-ferromagnetic domains can exist and here we restrict to a particular one. At any  $j$  site of the lattice, located by the position vector  $\mathbf{R}_j$ , the magnetic moment reads

$$\mathbf{m}_j = \mathbf{m}_1 e^{ik_1 R_j} + \mathbf{m}_2 e^{ik_2 R_j}$$

where the respective Fourier components and wave vectors are  $\mathbf{m}_1 = m[\frac{1}{\sqrt{2}} \ 0 \ 0]$ ,  $\mathbf{k}_1 = [\frac{1}{2} \ 0 \ 0]$ ,  $\mathbf{m}_2 = m[0 \ \frac{1}{\sqrt{2}} \ 0]$  and  $\mathbf{k}_2 = [0 \ \frac{1}{2} \ 0]$  ( $m$  is the moment amplitude).



**Figure 1.** Double- $k$  anti-ferromagnetic structure of NdMg. The associated 4f shell asphericity is represented by an ellipsoid with its shorter axis along the magnetic moment (the Stevens  $\alpha_J$  multiplying factor is negative for neodymium).

To determine which multipolar components develop in agreement with this magnetic structure with moments along the twofold axes, we just have to use this Fourier description for writing down the polynomials defined in table 3. One immediately observes that non-zero terms will appear only for two lines of table 3. In the first line, within the  $\Gamma_3$  representation:

$$\begin{aligned}\langle O_2^0 \rangle_j &= -c_2^\gamma m^2 = \langle O_2^0 \rangle_0 \\ \langle O_4^{\gamma,1} \rangle_j &= \frac{5}{2} c_4^\gamma m^4 = \langle O_4^{\gamma,1} \rangle_0 \\ \langle O_6^{\gamma,1} \rangle_j &= -\frac{1}{4} c_6^\gamma m^6 = \langle O_6^{\gamma,1} \rangle_0.\end{aligned}$$

In the third line, within the  $\Gamma_5$  representation:

$$\begin{aligned}\langle P_{xy} \rangle_j &= \frac{c_2^\varepsilon}{2} m^2 e^{i(k_1+k_2)R_j} = \langle P_{xy} \rangle_0 e^{iqR_j} & \mathbf{q} &= \left[ \frac{1}{2} \frac{1}{2} 0 \right] \\ \langle O_4^{\varepsilon,1} \rangle_j &= -\frac{c_4^\varepsilon}{2} m^4 e^{iqR_j} = \langle O_4^{\varepsilon,1} \rangle_0 e^{iqR_j} \\ \langle O_6^{\varepsilon 1,1} \rangle_j &= \frac{c_6^{\varepsilon 1}}{2} m^6 e^{iqR_j} = \langle O_6^{\varepsilon 1,1} \rangle_0 e^{iqR_j} \\ \langle O_6^{\varepsilon 2,1} \rangle_j &= -\frac{c_6^{\varepsilon 2}}{2} m^6 e^{iqR_j} = \langle O_6^{\varepsilon 2,1} \rangle_0 e^{iqR_j}\end{aligned}$$

A schematic representation of this 4f asphericity, which develops with the magnetic order, is given in figure 1.

In the above equations, one observes that the  $\Gamma_3$  terms do not depend on  $\mathbf{R}_j$  and define the same symmetry lowering on all sites. The magnetoelastic couplings will force a strain mode of the same symmetry, which corresponds to the tetragonal mode  $\varepsilon_1^\gamma$ . Considering only



one-ion magnetoelastic couplings, the strain may be related to the values of the multipolar operators [6]:

$$\varepsilon_1^\gamma = \frac{1}{C_0^\gamma} [B_2^\gamma \langle O_2^0 \rangle + B_4^\gamma \langle O_4^{\gamma,1} \rangle + B_6^\gamma \langle O_6^{\gamma,1} \rangle]$$

where  $C_0^\gamma = C_{11}^0 - C_{12}^0$  is the tetragonal mode background elastic constant and the  $B_n^\gamma$  are the second-, fourth- and sixth-order tetragonal mode magnetoelastic coupling constants.

All remaining aspherical terms belong to the  $\Gamma_5$  representation and propagate according to the  $\mathbf{q} = [\frac{1}{2} \frac{1}{2} 0]$  wave vector in the plane defined by the magnetic moment directions. In an x-ray experiment this zone boundary wave vector gives rise to well-identifiable Bragg peaks at reciprocal space nodes  $\mathbf{Q} = [h k l] + [\frac{1}{2} \frac{1}{2} 0]$ , where  $[h k l]$  is a reciprocal lattice vector [3]. Thanks to rather larger magnetoelastic couplings, the tetragonal strain mode is also observable by x-ray diffraction or dilatometric measurements [7].

### 3. Scattering amplitudes in cubic symmetry

As shown in the above example of NdMg, in the case of a multipolar structure of high symmetry, only a few multipolar operators are necessary for describing the 4f asphericity. For interpreting the results of a multipolar x-ray scattering experiment, instead of considering the 27 multipolar contributions to the Thomson scattering amplitude, it is much more convenient to restrict to those whose existence may be expected from symmetry considerations (see section 2). Obviously, taking advantage of the symmetry analysis, one should use the definitions of multipolar operators appropriate to the cubic symmetry considered here. To write down the scattering amplitude of a rare-earth ion at a site which is a centre of inversion, the first analytical step is to decompose this amplitude  $A(\mathbf{Q})$  into a sum of terms representing the four even orders of scattering [4]:

$$A(\mathbf{Q}) = A_0(\mathbf{Q}) + A_2(\mathbf{Q}) + A_4(\mathbf{Q}) + A_6(\mathbf{Q})$$

where  $\mathbf{Q}$  is the scattering vector,  $A_0(\mathbf{Q})$  is the usual, spherical, scattering amplitude and  $A_2(\mathbf{Q})$ ,  $A_4(\mathbf{Q})$  and  $A_6(\mathbf{Q})$  are, respectively, the quadrupolar, hexadecapolar and hexacontatetrapolar scattering amplitudes.

The second step which is introduced here is to decompose each of the above terms into contributions related to the cubic irreducible representations. This is obtained by rewriting the expressions of the scattering amplitudes of [4] in which the multipolar components are replaced by linear combinations of the cubic multipolar components (see appendix C).

- *Quadrupolar term:* Within the  $O_h$  point group symmetry, the quadrupolar representation decomposes into  $\Gamma_3 + \Gamma_5$ . Thus, the quadrupolar scattering amplitude can be written as a sum of two terms:

$$A_2(\mathbf{Q}) = A_2^\gamma(\mathbf{Q}) + A_2^\varepsilon(\mathbf{Q}).$$

- *Hexadecapolar term:* The fourth-order, hexadecapolar, multipolar representation decomposes into  $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$  and the associated scattering amplitude reads as a sum of four terms.

$$A_4(\mathbf{Q}) = A_4^\alpha(\mathbf{Q}) + A_4^\gamma(\mathbf{Q}) + A_4^\delta(\mathbf{Q}) + A_4^\varepsilon(\mathbf{Q}).$$

- *Hexacontatetrapolar term:* The last, sixth-order, multipolar representation decomposes into  $\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$ . The associated scattering amplitude reads as a sum of six terms:

$$A_6(\mathbf{Q}) = A_6^\alpha(\mathbf{Q}) + A_6^\beta(\mathbf{Q}) + A_6^\gamma(\mathbf{Q}) + A_6^\delta(\mathbf{Q}) + A_6^{\varepsilon 1}(\mathbf{Q}) + A_6^{\varepsilon 2}(\mathbf{Q}).$$

**Table 4.** Expressions for the multipolar scattering amplitudes for a scattering vector  $\mathbf{Q} = (h, k, l)$ . Each line corresponds to a cubic irreducible representation and the columns refer to the three even orders of scattering.  $\alpha_J, \beta_J$  and  $\gamma_J$  are the Stevens multiplying factors [8].  $F_2(Q), F_4(Q)$  and  $F_6(Q)$  are the second-, fourth- and sixth-order multipolar scattering form factors [4].

	$A_2^\mu(\mathbf{Q}) \times \frac{Q^2}{\alpha_J F_2(Q)}$	$A_4^\mu(\mathbf{Q}) \times \frac{Q^4}{\beta_J F_4(Q)}$	$A_6^\mu(\mathbf{Q}) \times \frac{Q^6}{\gamma_J F_6(Q)}$
$\Gamma_1(\mu = \alpha)$ —	—	$\frac{35}{24}(h^4 + k^4 + l^4 - \frac{3}{5}Q^4) \times \langle O_4^\alpha \rangle$	$\frac{1}{16} [2(h^6 + k^6 + l^6) - 15(h^2 l^4 + c.p.) + 180h^2 k^2 l^2] \langle O_6^\alpha \rangle$
$\Gamma_2(\mu = \beta)$ —	—	—	$\frac{1155}{32} [h^4(k^2 - l^2) + k^4(l^2 - h^2) + l^4(h^2 - k^2)] \langle O_6^\beta \rangle$
$\Gamma_3(\mu = \gamma)$	$\frac{1}{2} \left\{ \begin{array}{l} (3l^2 - Q^2) \langle O_2^0 \rangle \\ + 3(h^2 - k^2) \langle O_2^2 \rangle \end{array} \right\}$	$\frac{5}{24} \left\{ \begin{array}{l} [7l^4 + 14h^2 k^2 - 4Q^2 l^2 - Q^4] \times \langle O_4^{\gamma,1} \rangle \\ + \sqrt{3}(h^2 - k^2) \times \langle O_4^{\gamma,2} \rangle \end{array} \right\}$	$\frac{7}{16} \left\{ \begin{array}{l} [2l^6 - h^6 - k^6 + 15(h^4 + k^4)l^2 - 15(h^2 + k^2)l^4] \langle O_6^{\gamma,1} \rangle + \sqrt{3} \\ \times (h^2 - k^2) (Q^4 - 7Q^2 l^2 \\ + 11l^4 - 11h^2 k^2) \langle O_6^{\gamma,2} \rangle \end{array} \right\}$
$\Gamma_4(\mu = \delta)$ —	—	$\frac{35}{2} \left\{ \begin{array}{l} hk(h^2 - k^2) \langle O_4^{\delta,1} \rangle \\ + lh(l^2 - h^2) \langle O_4^{\delta,2} \rangle \\ + kl(k^2 - l^2) \langle O_4^{\delta,3} \rangle \end{array} \right\}$	$\frac{63}{4} \left\{ \begin{array}{l} hk(h^2 - k^2)(11l^2 - Q^2) \langle O_6^{\delta,1} \rangle \\ + lh(l^2 - h^2)(11k^2 - Q^2) \langle O_6^{\delta,2} \rangle \\ + kl(k^2 - l^2)(11h^2 - Q^2) \langle O_6^{\delta,3} \rangle \end{array} \right\}$
$\Gamma_5(\mu = \varepsilon 1)$	$6 \left\{ \begin{array}{l} hk \langle P_{xy} \rangle \\ + kl \langle P_{yz} \rangle \\ + lh \langle P_{zx} \rangle \end{array} \right\}$	$5 \left\{ \begin{array}{l} hk(7l^2 - Q^2) \langle O_4^{\varepsilon,1} \rangle \\ + kl(7h^2 - Q^2) \langle O_4^{\varepsilon,2} \rangle \\ + lh(7k^2 - Q^2) \langle O_4^{\varepsilon,3} \rangle \end{array} \right\}$	$\frac{105}{16} \left\{ \begin{array}{l} hk(33l^4 - 18Q^2 l^2 + Q^4) \langle O_6^{\varepsilon 1,1} \rangle \\ + kl(33h^4 - 18Q^2 h^2 + Q^4) \langle O_6^{\varepsilon 1,2} \rangle \\ + lh(33k^4 - 18Q^2 k^2 + Q^4) \langle O_6^{\varepsilon 1,3} \rangle \end{array} \right\}$
$\Gamma_5(\mu = \varepsilon 2)$ —	—	—	$\frac{231}{32} \left\{ \begin{array}{l} hk(3h^4 - 10h^2 k^2 + 3k^4) \langle O_6^{\varepsilon 2,1} \rangle \\ + kl(3k^4 - 10k^2 l^2 + 3l^4) \langle O_6^{\varepsilon 2,2} \rangle \\ + lh(3l^4 - 10l^2 h^2 + 3h^4) \langle O_6^{\varepsilon 2,3} \rangle \end{array} \right\}$

All terms appearing in the definitions of these multipolar scattering amplitudes are detailed in table 4. Each column of table 4 corresponds to a given order of scattering, whereas the rows correspond to the cubic irreducible representations. As clearly appears in the expressions for the scattering amplitudes, the diffraction indices  $(h, k, l)$  play a very selective role.

For instance, in the case of multipolar components from the  $\Gamma_5$  representation, no scattered intensity can be observed if two indices are simultaneously zero (scattering vector along a fourfold axis). If only one index is zero, only one component from these three-dimensional representations will contribute to the scattering amplitude. In the case of multipolar components from the  $\Gamma_3$  representation, the scattering amplitude cancels if all indices are equal (scattering vector along a threefold axis).

This selectivity is reminiscent of that used to analyse the magnetic and magnetoelastic properties in the paramagnetic range of the cubic rare-earth systems [6]. Here, instead of the applied magnetic field or the strain mode, the symmetry-selective actor is the scattering vector which may separate the  $\Gamma_3$  and  $\Gamma_5$  properties.

However, in practical conditions this selection may not be as effective as desirable. Indeed, the scattering vector cannot be chosen along any direction as it also has to comply

with the multipolar wave vectors of the system. The analysis may then be less straightforward than one could first imagine, but, by checking the existence and comparing the intensities of a few reflections, the involved multipolar representations can be easily identified. This multipolar information will be in its turn selective within the set of models of consistent magnetic structures.

In the same way, if multipolar scattering is used for studying a supposed anti-ferroquadrupolar system, it will be not only the most direct technique for evidencing the new charge periodicity, but also the most simple means of identification of the quadrupolar order parameter. Up to now, such identification has never been achieved, even in the case of the popular, presumed anti-ferroquadrupolar, phase of CeB<sub>6</sub>.

We shall now apply this method to our example of the double- $k$  magnetic structure of NdMg in order to establish the expression for the total multipolar scattering amplitude. Starting with the results of section 2 and using table 4, one may immediately identify the relevant scattering amplitude terms. For this magnetic structure, the analysis showed that all aspherical terms originating in multipolar Bragg peaks belong to the  $\Gamma_5$  representation. Moreover, for the chosen magnetic domain, the only non-zero terms are those related to the Cartesian coordinates' function  $xy$ . Extracting the relevant terms from the fifth and sixth lines of table 4, one gets the expression of the multipolar scattering amplitude from a rare-earth site  $j$  for the scattering vector  $\mathbf{Q} = [h k l]$ ,

$$A_j(\mathbf{Q}) = hk \left\{ \begin{aligned} & \frac{\alpha_J F_2(\mathbf{Q})}{Q^2} 6 \langle P_{xy} \rangle_j + \frac{\beta_J F_4(\mathbf{Q})}{Q^4} 5(7l^2 - Q^2) \langle O_4^{\varepsilon,1} \rangle_j \\ & + \frac{\gamma_J F_6(\mathbf{Q})}{Q^6} \left[ \frac{105}{16} (33l^4 - 18Q^2l^2 + Q^4) \langle O_6^{\varepsilon,1,1} \rangle_j \right. \\ & \left. + \frac{231}{32} (3h^4 - 10h^2k^2 + 3k^4) \langle O_6^{\varepsilon,2,1} \rangle_j \right] \end{aligned} \right\}$$

then, using the simple Fourier descriptions of the multipolar components obtained in section 2

$$A_j(\mathbf{Q}) = hk \left\{ \begin{aligned} & \frac{\alpha_J F_2(\mathbf{Q})}{Q^2} 6 \langle P_{xy} \rangle_0 + \frac{\beta_J F_4(\mathbf{Q})}{Q^4} 5(7l^2 - Q^2) \langle O_4^{\varepsilon,1} \rangle_0 \\ & + \frac{\gamma_J F_6(\mathbf{Q})}{Q^6} \left[ \frac{105}{16} (33l^4 - 18Q^2l^2 + Q^4) \langle O_6^{\varepsilon,1,1} \rangle_0 \right. \\ & \left. + \frac{231}{32} (3h^4 - 10h^2k^2 + 3k^4) \langle O_6^{\varepsilon,2,1} \rangle_0 \right] \end{aligned} \right\} e^{i\mathbf{q}\mathbf{R}_j} \quad \mathbf{q} = \left[ \frac{1}{2} \frac{1}{2} 0 \right]$$

where the index 0 refers to the origin site,  $\mathbf{R}_j$  is the position vector of site  $j$ ,  $(\alpha_J, \beta_J, \gamma_J)$  are the Stevens multiplying factors [8] and  $(F_2(\mathbf{Q}), F_4(\mathbf{Q}), F_6(\mathbf{Q}))$  are the second-, fourth- and sixth-order multipolar scattering form factors as defined in [4].

In this example, the  $\Gamma_5$  selectivity of the diffraction indices clearly appears through the  $hk$  factor. All the involved  $\Gamma_5$  terms have identical transformation properties here (those of the  $xy$  function) and thus contribute to the same Bragg peaks associated with the wave vector  $\mathbf{q} = [\frac{1}{2} \frac{1}{2} 0]$ . Thanks to the use of Stevens equivalent operators, the description of the observed scattering intensities may be rather easily achieved. The statistical values for all relevant operators may be computed using a microscopic magnetic model based on the ground state multiplet of the involved rare earth.

#### 4. Summary

The method for relating a given high-symmetry magnetic structure to its multipolar charge counterpart has been generalized to all relevant orders in 4f cubic systems. This method makes use of the mean field approximation, in view of a quantitative analysis, but only as a practical way of expressing the magnetic order symmetry lowering. It should then escape the usual criticisms against the mean field approximation and will be very useful for the analysis

of experiments based on macroscopic (magnetostriction) or microscopic (x-ray diffraction) techniques.

Although they are generally neglected, apart from those due to the crystal field in the paramagnetic range, multipolar terms beyond the quadrupolar ones may become important in the ordered range. Indeed, the involved interaction fields can exceed by far the values of the applied magnetic field used for studying the paramagnetic phase. However, here we have demonstrated that for the commonly occurring high symmetry structures, the wave vectors, according to which the fourth- and sixth-order multipoles propagate, are identical to the quadrupolar ones. Therefore, in the case of a multipolar x-ray scattering study on such a magnetic structure no extra fourth- or sixth-order peaks can be observed. The fourth- and sixth-order scattering amplitudes may not be negligible but will contribute to the same Bragg reflections as the quadrupolar amplitudes. Accounting for these contributions should no longer be a problem thanks to the symmetry-related expressions introduced here. All these expressions show rather simple dependence on the scattering vector and on the cubic, multipolar, components. This should make it easy to identify, in addition to the charge wave vectors, the cubic representations to which the involved multipolar components belong. This is very useful for the study of a purely orbital order with wave vectors out of the zone centre, i.e. the anti-ferroquadrupolar order. Then, the x-ray multipolar scattering is not only the most direct technique for determining the 4f asphericity periodicity, but also the only one allowing identification of the quadrupolar order parameter independently of any model-dependent interpretation.

One can also consider multipolar x-ray diffraction as usable for determining a magnetic structure with the advantage, with respect to x-ray magnetic scattering, of significant scattering amplitudes. However, as the relation between charge and magnetic order is not bijective, x-ray scattering on a single crystal cannot be used alone for a magnetic structure determination. The structure that may be actually determined is the multipolar one which, in general, is consistent with several magnetic models. If used for a magnetic structure determination, this x-ray technique should then be a complementary tool, which is efficient once the magnetic wave vector is already known from powder neutron diffraction. In such cases, it may be useful for proving the multi-axial nature of an anti-ferromagnetic structure, without need for a neutron diffraction experiment on a single crystal under applied magnetic field. In other cases, neutron diffraction experiments may be delicate for absorption cross-section problems or because of difficulties in obtaining large enough single crystals. Then x-ray multipolar scattering may be a practical, alternative technique.

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## Appendix A. Errata regarding [4]

In our previous paper on ‘X-ray scattering by rare-earth multipoles in multiaxial structures’, we improperly called the fourth-order terms octupolar and sixth-order terms dodecapolar. For  $2^n$  multipoles with  $n = 4, 6$ , the appropriate adjectives should be, respectively, hexadodecapolar and hexacontatetrapolar.

In the same paper, some factors appearing in the definitions of the fourth- and sixth-order scattering amplitudes are erroneous; they should be replaced by:

$$C_4^{1c}(\mathbf{Q}) = (\sqrt{10}/4Q^4)Q_a Q_c (7Q_c^2 - 3Q^2)$$

$$\begin{aligned}
C_6^{2c}(\mathcal{Q}) &= (\sqrt{210}/32\mathcal{Q}^6)(\mathcal{Q}_a^2 - \mathcal{Q}_b^2)(33\mathcal{Q}_c^4 - 18\mathcal{Q}_c^2\mathcal{Q}^2 + \mathcal{Q}^4) \\
C_6^{2s}(\mathcal{Q}) &= (\sqrt{210}/32\mathcal{Q}^6)2\mathcal{Q}_a\mathcal{Q}_b(33\mathcal{Q}_c^4 - 18\mathcal{Q}_c^2\mathcal{Q}^2 + \mathcal{Q}^4) \\
C_6^{4c}(\mathcal{Q}) &= (3\sqrt{7}/16\mathcal{Q}^6)(\mathcal{Q}_a^4 - 6\mathcal{Q}_a^2\mathcal{Q}_b^2 + \mathcal{Q}_b^4)(11\mathcal{Q}_c^2 - \mathcal{Q}^2) \\
C_6^{4s}(\mathcal{Q}) &= (3\sqrt{7}/16\mathcal{Q}^6)4\mathcal{Q}_a\mathcal{Q}_b(\mathcal{Q}_a^2 - \mathcal{Q}_b^2)(11\mathcal{Q}_c^2 - \mathcal{Q}^2).
\end{aligned}$$

## Appendix B

Multipolar operators of the fourth and sixth orders as defined in [4] and written here starting from the spherical harmonics equivalent operators given by Buckmaster in [9]. The second member from the left of the equations relates these multipolar operators to the definitions of Hutchings [10].

### Order 4

$$\begin{aligned}
O_4^0 &= 35J_z^4 - [30J(J+1) - 25]J_z^2 - 6J(J+1) + 3J^2(J+1)^2 \\
O_4^{1c} &= 2\sqrt{10}O_4^1 = \sqrt{10} \left\{ [7J_z^2 - 3J(J+1) - 1] J_z J_x + J_x J_z [7J_z^2 - 3J(J+1) - 1] \right\} \\
O_4^{1s} &= 2\sqrt{10}O_4^1(s)^b = \sqrt{10} \left\{ [7J_z^2 - 3J(J+1) - 1] J_z J_y + J_y J_z [7J_z^2 - 3J(J+1) - 1] \right\} \\
O_4^{2c} &= 2\sqrt{5}O_4^2 = \sqrt{5} \left\{ [7J_z^2 - J(J+1) - 5] O_2^2 + O_2^2 [7J_z^2 - J(J+1) - 5] \right\} \\
O_4^{2s} &= 2\sqrt{5}O_4^2(s)^b = 2\sqrt{5} \left\{ [7J_z^2 - J(J+1) - 5] P_{xy} + P_{xy} [7J_z^2 - J(J+1) - 5] \right\} \\
O_4^{3c} &= 2\sqrt{70}O_4^3 = \sqrt{\frac{35}{2}} \left\{ J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3)J_z \right\} \\
O_4^{3s} &= 2\sqrt{70}O_4^3(s)^b = \sqrt{\frac{35}{2}}i \left\{ J_z(J_-^3 - J_+^3) + (J_-^3 - J_+^3)J_z \right\} \\
O_4^{4c} &= \sqrt{35}O_4^4 = \frac{\sqrt{35}}{2}(J_-^4 + J_+^4) \\
O_4^{4s} &= \sqrt{35}O_4^4(s)^b = \frac{\sqrt{35}}{2}i(J_-^4 - J_+^4).
\end{aligned}$$

### Order 6 (from [10])

$$\begin{aligned}
O_6^0 &= \left\{ 231J_z^6 - 105[3J(J+1) - 7]J_z^4 + [105J^2(J+1)^2 - 525J(J+1) + 294]J_z^2 \right. \\
&\quad \left. - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1) \right\} \\
O_6^{1c} &= 2\sqrt{21}O_6^1 = \frac{\sqrt{21}}{2} \left( \begin{aligned} &\{33J_z^5 - 15[(2J(J+1)) - 1]J_z^3 + [5J^2(J+1)^2 - 10J(J+1)] \\ &+ 12J_z\}(J_- + J_+) + (J_- + J_+)\{33J_z^5 - 15[(2J(J+1)) - 1]J_z^3 \\ &+ [5J^2(J+1)^2 - 10J(J+1) + 12]J_z\} \end{aligned} \right) \\
O_6^{1s} &= 2\sqrt{21}O_6^1(s)^b = \frac{\sqrt{21}}{2}i \left( \begin{aligned} &\{33J_z^5 - 15[(2J(J+1)) - 1]J_z^3 + [5J^2(J+1)^2 \\ &- 10J(J+1) + 12]J_z\}(J_- - J_+) + (J_- - J_+)\{33J_z^5 \\ &- 15[2J(J+1) - 1]J_z^3 + [5J^2(J+1)^2 \\ &- 10J(J+1) + 12]J_z\} \end{aligned} \right)
\end{aligned}$$

$$\begin{aligned}
O_6^{2c} &= \frac{\sqrt{105}}{\sqrt{2}} O_6^2 = \frac{\sqrt{105}}{4\sqrt{2}} \left( \begin{array}{l} \{33J_z^4 - [18J(J+1) + 123]J_z^2 + J^2(J+1)^2 + 10J(J+1)\} \\ + 102 \} (J_-^2 + J_+^2) + (J_-^2 + J_+^2) \{33J_z^4 - [18J(J+1) \\ + 123]J_z^2 + J^2(J+1)^2 + 10J(J+1) + 102\} \end{array} \right) \\
O_6^{2s} &= \frac{\sqrt{105}}{\sqrt{2}} O_6^{2(s)b} = \frac{\sqrt{105}}{4\sqrt{2}} i \left( \begin{array}{l} \{33J_z^4 - [18J(J+1) + 123]J_z^2 + J^2(J+1)^2 \\ + 10J(J+1) + 102\} (J_-^2 - J_+^2) + (J_-^2 - J_+^2) \{33J_z^4 \\ - [18J(J+1) + 123]J_z^2 + J^2(J+1)^2 \\ + 10J(J+1) + 102\} \end{array} \right) \\
O_6^{3c} &= \sqrt{210} O_6^3 = \frac{\sqrt{105}}{2\sqrt{2}} \left( \begin{array}{l} \{11J_z^3 - [3J(J+1)J_z - 59]J_z\} (J_-^3 + J_+^3) \\ + (J_-^3 + J_+^3) \{11J_z^3 - [3J(J+1)J_z - 59]J_z\} \end{array} \right) \\
O_6^{3s} &= \sqrt{210} O_6^{3(s)b} = \frac{\sqrt{105}}{2\sqrt{2}} i \left( \begin{array}{l} \{11J_z^3 - [3J(J+1)J_z - 59]J_z\} (J_-^3 - J_+^3) \\ + (J_-^3 - J_+^3) \{11J_z^3 - [3J(J+1)J_z - 59]J_z\} \end{array} \right) \\
O_6^{4c} &= 3\sqrt{7} O_6^4 = \frac{3\sqrt{7}}{4} \left( \begin{array}{l} \{11J_z^2 - J(J+1) - 38\} (J_-^4 + J_+^4) \\ + (J_-^4 + J_+^4) \{11J_z^2 - J(J+1) - 38\} \end{array} \right) \\
O_6^{4s} &= 3\sqrt{7} O_6^{4(s)b} = \frac{3\sqrt{7}}{4} i \left( \begin{array}{l} \{11J_z^2 - J(J+1) - 38\} (J_-^4 - J_+^4) \\ + (J_-^4 - J_+^4) \{11J_z^2 - J(J+1) - 38\} \end{array} \right) \\
O_6^{5c} &= 3\sqrt{154} O_6^5 = \frac{3\sqrt{77}}{2\sqrt{2}} \{J_z(J_-^5 + J_+^5) + (J_-^5 + J_+^5)J_z\} \\
O_6^{5s} &= 3\sqrt{154} O_6^{5(s)b} = \frac{3\sqrt{77}}{2\sqrt{2}} i \{J_z(J_-^5 - J_+^5) + (J_-^5 - J_+^5)J_z\} \\
O_6^{6c} &= \frac{\sqrt{231}}{\sqrt{2}} O_6^6 = \frac{\sqrt{231}}{2\sqrt{2}} (J_-^6 + J_+^6) \quad O_6^{6s} = \frac{\sqrt{231}}{\sqrt{2}} O_6^{6(s)b} = \frac{\sqrt{231}}{2\sqrt{2}} i (J_-^6 - J_+^6).
\end{aligned}$$

### Appendix C

Symmetrized multipolar equivalent operators according to the cubic symmetry (after [6]).

Order 4

$$\begin{aligned}
O_4^\alpha &= O_4^0 + 5O_4^4 = O_4^0 + \sqrt{\frac{5}{7}} O_4^{4c} \quad \Gamma_1 \\
\left. \begin{aligned} O_4^{\gamma,1} &= O_4^0 - 7O_4^4 = O_4^0 - \sqrt{\frac{7}{5}} O_4^{4c} \\ O_4^{\gamma,2} &= -4\sqrt{3} O_4^2 = -2\sqrt{\frac{3}{5}} O_4^{2c} \end{aligned} \right\} \Gamma_3 \\
\left. \begin{aligned} O_4^{\delta,1} &= O_4^4(s)^b = \frac{1}{\sqrt{35}} O_4^{4s} \\ O_4^{\delta,2} &= O_4^1 - O_4^3 = \frac{1}{2\sqrt{10}} O_4^{1c} - \frac{1}{2\sqrt{70}} O_4^{3c} \\ O_4^{\delta,3} &= -O_4^1(s)^b - O_4^3(s)^b = -\frac{1}{2\sqrt{10}} O_4^{1s} - \frac{1}{2\sqrt{70}} O_4^{3s} \end{aligned} \right\} \Gamma_4 \\
\left. \begin{aligned} O_4^{\varepsilon,1} &= O_4^2(s)^b = \frac{1}{2\sqrt{5}} O_4^{2s} \\ O_4^{\varepsilon,2} &= -\frac{1}{2} O_4^1(s)^b + \frac{7}{2} O_4^3(s)^b = -\frac{1}{4\sqrt{10}} O_4^{1s} + \frac{\sqrt{7}}{4\sqrt{10}} O_4^{3s} \\ O_4^{\varepsilon,3} &= -\frac{1}{2} O_4^1 - \frac{7}{2} O_4^3 = -\frac{1}{4\sqrt{10}} O_4^{1c} - \frac{\sqrt{7}}{4\sqrt{10}} O_4^{3c} \end{aligned} \right\} \Gamma_5.
\end{aligned}$$

## Order 6

$$\begin{aligned}
O_6^\alpha &= O_6^0 - 21O_6^4 = O_6^0 - \sqrt{7}O_6^{4c} & \Gamma_1 \\
O_6^\beta &= O_6^2 - O_6^6 = \sqrt{\frac{2}{105}}O_6^{2c} - \sqrt{\frac{2}{231}}O_6^{6c} & \Gamma_2 \\
\left. \begin{aligned}
O_6^{\gamma,1} &= O_6^0 + 3O_6^4 = O_6^0 + \frac{1}{\sqrt{7}}O_6^{4c} \\
O_6^{\gamma,2} &= \frac{5\sqrt{3}}{2}O_6^2 + \frac{11\sqrt{3}}{2}O_6^6 = \sqrt{\frac{5}{14}}O_6^{2c} + \sqrt{\frac{11}{14}}O_6^{6c}
\end{aligned} \right\} & \Gamma_3 \\
\left. \begin{aligned}
O_6^{\delta,1} &= O_6^4(s)^b = \frac{1}{3\sqrt{7}}O_6^{4s} \\
O_6^{\delta,2} &= -\frac{1}{2}O_6^1 - \frac{5}{4}O_6^3 + \frac{11}{4}O_6^5 = -\frac{1}{4\sqrt{21}}O_6^{1c} - \frac{\sqrt{5}}{4\sqrt{42}}O_6^{3c} + \frac{\sqrt{11}}{12\sqrt{14}}O_6^{5c} \\
O_6^{\delta,3} &= \frac{1}{2}O_6^1(s)^b - \frac{5}{4}O_6^3(s)^b - \frac{11}{4}O_6^5(s)^b = \frac{1}{4\sqrt{21}}O_6^{1s} - \frac{\sqrt{5}}{4\sqrt{42}}O_6^{3s} - \frac{\sqrt{11}}{12\sqrt{14}}O_6^{5s}
\end{aligned} \right\} & \Gamma_4 \\
\left. \begin{aligned}
O_6^{\varepsilon^{1,1}} &= O_6^2(s)^b = \sqrt{\frac{2}{105}}O_6^{2s} \\
O_6^{\varepsilon^{1,2}} &= \frac{1}{4}O_6^1(s)^b - \frac{9}{8}O_6^3(s)^b + \frac{33}{8}O_6^5(s)^b = \frac{1}{8\sqrt{21}}O_6^{1s} - \frac{9}{8\sqrt{210}}O_6^{3s} + \frac{\sqrt{11}}{8\sqrt{14}}O_6^{5s} \\
O_6^{\varepsilon^{1,3}} &= \frac{1}{4}O_6^1 + \frac{9}{8}O_6^3 + \frac{33}{8}O_6^5 = \frac{1}{8\sqrt{21}}O_6^{1c} + \frac{9}{8\sqrt{210}}O_6^{3c} + \frac{\sqrt{11}}{8\sqrt{14}}O_6^{5c}
\end{aligned} \right\} & \Gamma_5 \\
\left. \begin{aligned}
O_6^{\varepsilon^{2,1}} &= O_6^6(s)^b = \sqrt{\frac{2}{231}}O_6^{6s} \\
O_6^{\varepsilon^{2,2}} &= \frac{3}{4}O_6^1(s)^b + \frac{5}{8}O_6^3(s)^b + \frac{3}{8}O_6^5(s)^b = \frac{1}{8}\sqrt{\frac{3}{7}}O_6^{1s} + \frac{1}{8}\sqrt{\frac{5}{42}}O_6^{3s} + \frac{1}{8}\frac{1}{\sqrt{154}}O_6^{5s} \\
O_6^{\varepsilon^{2,3}} &= \frac{3}{4}O_6^1 - \frac{5}{8}O_6^3 + \frac{3}{8}O_6^5 = \frac{1}{8}\sqrt{\frac{3}{7}}O_6^{1c} - \frac{1}{8}\sqrt{\frac{5}{42}}O_6^{3c} + \frac{1}{8}\frac{1}{\sqrt{154}}O_6^{5c}
\end{aligned} \right\} & \Gamma_5.
\end{aligned}$$

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