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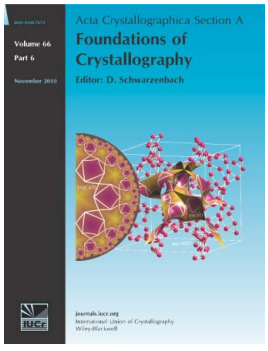

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Magnetic space and superspace groups, representation analysis: competing or friendly concepts?

Václav Petříček,* Jiří Fuksa and Michal Dušek

Institute of Physics of the Academy of Sciences of the Czech Republic, v.v.i., Na Slovance 2, 182 21 Praha 8, Czech Republic. Correspondence e-mail: petricek@fzu.cz

Although encoded in theoretical works, relationships between the diffraction symmetry of magnetic structures and magnetic space/superspace groups are often ignored in practical applications. It is shown that magnetic symmetry operations have a direct impact through the rotation parts in the diffraction symmetry of the crystal and can be used to simplify calculations of magnetic structure factors. Besides, the translation parts can introduce specific systematic extinctions of magnetic reflections. Another point is that the efficiency and stability of refinement of magnetic crystal structures, in analogy with the refinement of nuclear structures, depend on direct application of the magnetic symmetry in the structure-factor formula. Magnetic symmetry also allows diffractionally independent magnetic domains and their mutual spatial orientations to be recognized. The selection of one irreducible representation can provide extra relationships between magnetic moments which do not directly affect diffraction symmetry. Thus the combination of both methods seems to be the most effective way to analyze and refine magnetic structures.

1. Introduction

Ordering of magnetic moments in a crystal can be described either by magnetic symmetry or by representation analysis of symmetry properties of the phase transition. The first approach yields a magnetic (Shubnikov) space group, the second yields a set of possible irreducible representations (henceforth irrep) from which we have to select the correct one or, more generally, the correct combination of several irreps. Both methods are applicable not only to magnetic structures having their translation periodicity identical with the nuclear lattice but also to those being commensurate or incommensurate with the nuclear translation symmetry. Respective additional periodicities will be expressed through magnetic propagation vectors $\mathbf{k}_i$.

Magnetic space groups are composed of nuclear symmetry elements combined with a time inversion sign (see *e.g.* Belov *et al.*, 1957*a*,*b*). Any magnetic symmetry operation can be written in the form

$$\hat{\mathbf{S}} = (\mathbf{R}, \theta|\mathbf{s}) \tag{1}$$

where $\mathbf{R}, \theta = \pm 1$ and $\mathbf{s}$ are the proper or improper rotation matrix, the time inversion sign and the translation part of the symmetry operation, respectively. Further, we shall concentrate mainly on so-called *proper magnetic groups* (Souvignier, 2006) which do not contain the pure time inversion element $\hat{\mathbf{S}} = (\mathbf{E}, -1|0)$; these groups allow some ordering of magnetic moments. The magnetic moment of the atom μ related to the atom ν by the equation $\mathbf{r}_\mu = \hat{\mathbf{S}}\mathbf{r}_\nu = \mathbf{R}\mathbf{r}_\nu + \mathbf{s}$ is then

$$\mathbf{M}_\mu = \hat{\mathbf{S}}\mathbf{M}_\nu = \theta \det(\mathbf{R})\mathbf{R}\mathbf{M}_\nu. \tag{2}$$

The factor $\det(\mathbf{R})$ is respecting the fact that the magnetic vector is an axial vector. The concept of magnetic space group has been generalized to magnetic modulated structures by Janner & Janssen (1980) by applying superspace theory (de Wolff, 1974; de Wolff *et al.*, 1981).

The magnetic space and superspace groups give a phenomenological description of magnetic structures. The symmetry operations of the magnetic group define a unique way of calculating magnetic moments of all atoms of the magnetic orbit from one representative atom of the orbit.

Magnetic structures can arise after phase transitions from a parent paramagnetic phase for which some symmetry elements will be lost; the space group of that parent phase is a direct product of the nuclear space group with time inversion $1'$. This implies that atoms belonging to a paramagnetic orbit (which coincides just with the nuclear atomic orbit) may belong to several magnetic orbits. Such a lowering of symmetry is often accompanied by the occurrence of magnetic domains globally related by proper or improper rotations corresponding to lost symmetry elements.

Symmetry considerations on the determination of magnetic structures were given by Alexander (1962), who used irreducible representations of the non-magnetic space group

(nuclear space group) to find corresponding magnetic configurations. Later the representation analysis was successfully applied to a series of magnetic structures by Bertaut (1968), and since then it has been used as a basic method for the description and refinement of magnetic structures. Instead of individual magnetic moments, coefficients of basis functions belonging to a single selected irrep, defined in the carrier space made of individual magnetic moments, are used to describe the magnetic structure. Such an approach is closely connected to the assumption that a magnetic ordering behaves according to the Landau theory of second-order phase transitions. Furthermore, the representation analysis allows different irreps to be combined for distinct magnetic atoms in the structure [see, for example, $TbFeO_3$ in Bertaut *et al.* (1967) and Bertaut (1968)].

A more consistent approach starts from the magnetic space group of the paramagnetic phase and its irreducible representations. Ordering of magnetic moments can be characterized by kernels and epikernels (Ascher, 1977) of those irreps; one may note that, for example, Stokes & Hatch (1988) refer to such subgroups as isotropy subgroups.

In relation to this we would like to point out that irreducible co-representations introduced by Wigner (1959) represent a common and effective means of handling incommensurate structures allowing prediction of not only possible orderings of magnetic moments but also other characteristics such as magnetically driven ferroelectricity (Tolédano *et al.*, 2009). The co-representations of the paramagnetic space group have been used in the analysis of multiferroic systems such as that of Ribeiro (2007) and Tolédano (2009).

For $\mathbf{k} = 0$ the three-dimensional periodic magnetization density $\boldsymbol{\rho}_{\rm mag}(\mathbf{r})$ can be expanded into a Fourier series with coefficients $\mathbf{F}_{\rm mag}(\mathbf{H})$, so-called magnetic structure factors,

$$\boldsymbol{\rho}_{\rm mag}(\mathbf{r}) = \sum_{\mathbf{H}} \mathbf{F}_{\rm mag}(\mathbf{H}) \exp(-2\pi i \mathbf{H}\cdot\mathbf{r}). \qquad (3)$$

The summation runs over vectors $\mathbf{H} = \sum_{i=1}^{3} H_i \mathbf{a}_i^*$. The magnetization density can be written as a sum of individual contributions $\boldsymbol{\rho}_{\nu,\rm mag}(\mathbf{r})$ of all magnetic atoms in the structure,

$$\boldsymbol{\rho}_{\rm mag}(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{\nu=1}^{N_{\rm mag}} \boldsymbol{\rho}_{\nu,\rm mag}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_\nu - \mathbf{n}).$$

The first summation runs over all unit cells in the crystal $\mathbf{n} = \sum_{i=1}^{3} n_i \mathbf{a}_i$ and the second sum runs over all magnetic atoms in the first (reference) cell. Then the magnetic structure factor $\mathbf{F}_{\rm mag}(\mathbf{H})$ is directly related to the individual atomic magnetic moments $\mathbf{M}_\nu$ according to the equation

$$\mathbf{F}_{\rm mag}(\mathbf{H}) = p \sum_{\nu=1}^{N_{\rm mag}} f_\nu(|\mathbf{H}|) \mathbf{M}_\nu T_\nu(\mathbf{H}) \exp(2\pi i \mathbf{H}\cdot\mathbf{r}_\nu), \qquad (4)$$

where f_ν, $T_\nu(\mathbf{H})$ and $\mathbf{r}_\nu$ are the magnetic form factor, the anisotropic dispalcement parameter factor and the position of an atom ν in the unit cell, respectively. The coefficient $p = r_{\rm e}\gamma/2$ converts the magnetic structure factor from Bohr magnetons to the neutron scattering length in barns (10^{-12} cm) in order to unify scales.

The intensity of magnetic diffraction for a non-polarized neutron beam is related to the magnetic structure factor according to the fundamental formula of Halpern & Johnson (1939),

$$I_{\rm mag}(\mathbf{H}) = \left|\mathbf{F}_{\rm mag}(\mathbf{H})\right|^2 - \left[\mathbf{e}\cdot\mathbf{F}_{\rm mag}(\mathbf{H})\right]^2, \qquad (5)$$

where $\mathbf{e} = \mathbf{H}/|\mathbf{H}|$ is the unit vector along the scattering vector $\mathbf{H}$. As nuclear and magnetic diffractions are independent, each having generally its own distribution of mosaic blocks, the overall intensity for $\mathbf{k} = 0$ is a sum of two independent contributions,

$$I(\mathbf{H}) = I_{\rm nucl}(\mathbf{H}) + I_{\rm mag}(\mathbf{H}). \qquad (6)$$

The description of magnetic ordering by means of magnetic space and superspace groups is used more and more in theoretical analysis (see, for example, Schobinger-Papamantellos & Janssen, 2006). However, in practical solution and refinement of magnetic structures against neutron diffraction data the symmetry is usually reduced to the trivial symmetry, with atomic positions restricted by the nuclear space group and with atomic magnetic moments expressed as a linear combination of basic functions belonging to the set of active irreps, determined by a Monte Carlo or annealing procedure (Wills, 2000). In such an approach magnetic symmetry is respected but it is not efficiently used, as in the structure-factor formula the summation runs over all atomic positions although several of them are often related by magnetic symmetry operations. Apart from that, it happens for hexagonal and cubic families that for certain irreps some basis functions imply that any two of three magnetic moments belonging to three different magnetic orbits determine the third (see an example in §3).

On the other hand the magnetic symmetry allows the number of generated reflections for powder diffraction to be restricted to independent ones, and for single-crystal data collection it allows symmetry averaging of measured reflections. This stabilizes the refinement process and makes calculations more effective. Probably even more important is that direct use of magnetic symmetry gives a better basis for further interpretation of results.

For the direct application of magnetic space groups in structure determination the two following questions need to be answered:

(i) How does the magnetic space group affect the diffraction pattern and systematic extinctions of magnetic reflections? Can we draw some conclusions about magnetic symmetry directly from the diffraction pattern? These problems of diffraction symmetry have not been explicitly discussed in the literature, maybe because they are too basic, simple and obvious. Nevertheless, such discussion seems to be necessary because many magnetic structures solved from diffraction data are published without mention of magnetic point and space group and without using a symmetry analysis of the diffraction for finding the correct solution.

(ii) What are the consequences of all restrictions on the ordering of magnetic moments following from a single irrep?

We shall answer these questions in §2 and §3. Finally, in §4, the results will be generalized to the superspace in order to extend the description to incommensurate and commensurate magnetic structures.

2. Magnetic diffraction symmetry for k = 0

Once the magnetic space group of the studied crystal is known, the magnetic moments of all symmetry-related atoms of the magnetic orbit can be calculated from a selected representative position following (2). The fact that the density distribution function is to be invariant with respect to symmetry operation (1) can be expressed by

$$\hat{\mathbf{S}} \cdot \boldsymbol{\rho}_{\rm mag}(\mathbf{r}) = \theta \det(\mathbf{R}) \mathbf{R} \boldsymbol{\rho}_{\rm mag}\left\{\mathbf{R}^{-1}(\mathbf{r}-\mathbf{s})\right\} = \boldsymbol{\rho}_{\rm mag}(\mathbf{r}),$$

which leads to

$$\mathbf{F}_{\rm mag}(\mathbf{HR}) = \theta^{-1} \det\left(\mathbf{R}^{-1}\right) \exp(-2\pi i \mathbf{H}\cdot\mathbf{s}) \mathbf{R}^{-1} \cdot \mathbf{F}_{\rm mag}(\mathbf{H}). \quad (7)$$

According to (5) the intensity of the symmetry-related point is then

$$\begin{aligned} I_{\rm mag}(\mathbf{HR}) &= \left\{\mathbf{F}_{\rm mag}(\mathbf{HR}_k)\right\}^2 - \left\{\mathbf{e}\cdot\mathbf{R}\cdot\mathbf{F}_{\rm mag}(\mathbf{HR}_k)\right\}^2 \\ &= \mathbf{F}_{\rm mag}(\mathbf{H})^2 - \left\{\mathbf{e}\cdot\mathbf{F}_{\rm mag}(\mathbf{H})\right\}^2 \\ &= I_{\rm mag}(\mathbf{H}). \end{aligned} \quad (8)$$

This means that each symmetry operation of the magnetic point group induces rotation symmetry (proper or improper) in the magnetic diffraction pattern. Similarly to nuclear structures an inversion centre is always present even for non-centrosymmetric groups if anomalous-scattering effects are neglected. Hence, the magnetic diffraction pattern follows classical Laue symmetry without any influence of time inversion signs. Thus the observed diffraction symmetry cannot be directly used for determination of the actual magnetic symmetry from the list of possible magnetic groups obtained by combination of nuclear point-group symmetry operations with the time inversion.

In the case of an invariant subspace of the reciprocal space containing all vectors **H** being fixed by the condition **HR** = **R**, equation (7) yields

$$\mathbf{F}_{\nu,\rm mag}(\mathbf{H}) = \theta^{-1} \det\left(\mathbf{R}^{-1}\right) \exp(-2\pi i \mathbf{H}\cdot\mathbf{s}) \mathbf{R}^{-1} \cdot \mathbf{F}_{\nu,\rm mag}(\mathbf{H}). \quad (9)$$

An analogous equation for the scalar nuclear density leads directly to systematic extinctions related to the factor $\exp(-2\pi i\mathbf{H}\cdot\mathbf{s})$. For magnetic structure factors, because they contain the vector quantity of magnetic moment, we obtain three equations which should be taken into account simultaneously and this fact considerably reduces the possible systematic extinctions. However, for translations (cell centerings), equation (9) splits into three separate conditions for each component, and therefore such extinctions are directly related to the factor $\exp(-2\pi i\mathbf{H}\cdot\mathbf{s})$.

For symmetry elements having the rotational part different from a unit matrix, the extinction rules can still be found from (9) but additional restrictions of magnetic moments following from Wyckoff positions are to be taken into account as well. This can be demonstrated in the following example.

Table 1
Independent magnetic Co atoms in $Ba_5Co_5ClO_{13}$.

			Magnetic vector	
Atom	Wyckoff position	Coordinates	$P6_3/mm'c'$	$P6'_3/m'm'c$
Co1	(2*a*) $\bar{3}m$	(0, 0, 1/2)	$(0, 0, M_z)$	$(0, 0, M_z)$
Co2	(4*e*) $3m$	(0, 0, 0.418)	$(0, 0, M_z)$	$(0, 0, M_z)$
Co3	(4*f*) $3m$	(1/3, 2/3, 0.314)	$(0, 0, M_z)$	$(0, 0, M_z)$

The paramagnetic phase of $Ba_5Co_5ClO_{13}$ (Mentré *et al.*, 2008) has the nuclear symmetry $P6_3/mmc$ and it contains three independent magnetic atoms Co (see Table 1). The two magnetic space groups listed there are those that give non-zero magnetic moments parallel to the *c* axis for all three Co atoms. The three equations (9) then reduce to one. In the case of $P6_3/mm'c'$ the glide plane c' gives the same extinction condition $l = 2n+1$ (h, h, l) for both magnetic and nuclear contributions. While in the case of $P6'_3/m'm'c$ the extinction condition for magnetic reflections is $l = 2n$, there is a chance to observe a non-zero intensity (h, h, l) for $l = 2n+1$ in the diffraction pattern of the compound, to which the nuclear structure does not contribute. On the other hand, if any of the magnetic atoms were not located at the special positions but at general ones, no systematic extinctions would be induced.

As already mentioned in the *Introduction*, the ordering of magnetic moments can reduce both translation and rotation symmetry of the nuclear structure. In the case that some of the nuclear point-group operators are forbidden owing to magnetic ordering, rotationally non-equivalent magnetic domains may appear. The number of independent domains is equal to the ratio of the number of symmetry elements in the paramagnetic (HT) and magnetic (LT) point group.

3. Representation analysis for k = 0

As mentioned above, the complete analysis of the magnetic ordering should start with the paramagnetic space group and its irreducible representations. For **k** = 0 two families of irreps can be recognized. The first one is formed by irreps where the pure time inversion element $\hat{\mathbf{S}} = (\mathbf{E}, -1|0)$ is represented by a unit matrix. The minimal allowed symmetry group is then $P1'$, which is paramagnetic and does not support any magnetic ordering.

The second family contains irreps where the time inversion is given as a negative unit matrix. Some of these irreps may allow non-zero magnetic moments, in which case magnetic reflections would be observed. The ordering of magnetic moments can be analyzed, without losing generality, by the method proposed by Bertaut (1968), *i.e.* by restriction to the nuclear space group of the paramagnetic phase. Such a technique relies on a one-to-one correspondence between the irreps of the nuclear space group and the irreps of the paramagnetic space group belonging to the second family; for the latter irreps matrices of the operations that do not belong to the nuclear space group are obtained from matrices of the

Table 2
Two-dimensional irreducible representation E of the space group $P422$ for $\mathbf{k} = 0$.

Symmetry code	#1 x, y, z	#2 $-x, -y, z$	#3 $-y, x, z$	#4 $y, -x, z$	#5 $-x, y, -z$	#6 $x, -y, -z$	#7 $y, x, -z$	#8 $-y, -x, -z$
Representation matrix	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$
Basis function #1	(1 0 0)	(1 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #2	(0 1 0)	(0 1 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #3	(0 0 1)	(0 0 −1)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #4	(0 0 0)	(0 0 0)	(1 0 0)	(1 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #5	(0 0 0)	(0 0 0)	(0 1 0)	(0 1 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #6	(0 0 0)	(0 0 0)	(0 0 1)	(0 0 −1)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #7	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(1 0 0)	(1 0 0)	(0 0 0)	(0 0 0)
Basis function #8	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 1 0)	(0 1 0)	(0 0 0)	(0 0 0)
Basis function #9	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 1)	(0 0 −1)	(0 0 0)	(0 0 0)
Basis function #10	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(1 0 0)	(1 0 0)
Basis function #11	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 1 0)	(0 1 0)
Basis function #12	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 1)	(0 0 −1)

former irreps simply by multiplying by a negative unit matrix. This approach will be adopted throughout this section to make a closer relationship with the basic original papers. However, for magnetic modulated phases *i.e.* $\mathbf{k} \neq 0$ in §4.2, the full irreps of the paramagnetic space group have to be used.

We note that the correspondence mentioned above was used by Opechowski & Dreyfus (1971) in the proof of their $C1'$–$C2$ linking theorem through which they argued that description of spin arrangements by magnetic groups and description by means of their representations which admit non-zero magnetic moments are equivalent.

As has been shown (Niggli, 1959; Indenbom, 1959), there is one-to-one correspondence between one-dimensional real representations of nuclear space groups and magnetic space groups of the same geometric class. In relation to this we note that concerning the symmetry of a diffraction pattern there is a fundamental difference between displacive and magnetic phase transitions driven by a one-dimensional real irrep. For displacive phase transitions when testing all such irreps one obtains for each a generally distinct set of restrictions to atomic displacements expressed as linear combinations of corresponding basis functions. For magnetic phase transitions, the restrictions to magnetic moments obtained through basis functions can be unequivocally transformed to magnetic symmetry which will yield for each irrep the same diffraction symmetry (see the conclusion in §2). This means that in the former case the actual irrep can, in principle, be recognized or confirmed from the symmetry of a diffraction pattern while in the latter case establishing the correct magnetic symmetry need not be so straightforward.

Let φ_i, $i = 1, \ldots, n$, be a set of basis functions defined on the carrier space of atomic magnetic moments and belonging to a single irrep. Then the actual magnetic moments φ are linear combinations of n basis functions φ_i,

$$\varphi = \sum_{i=1}^{n} \eta_i \varphi_i.$$

The coefficients η_i $(i = 1, \ldots, n)$, not all of which are necessarily non-zero, form a so-called order-parameter direction. The application of a symmetry operator g to the moments φ leads to

$$g\varphi = \sum_{j=1}^{n} \left[\sum_{i=1}^{n} D_{ji}(g)\eta_i \right] \varphi_j,$$

where $D_{ji}(g)$ are matrix elements of the single irrep. From this we can see that the minimal (kernel) symmetry induced by the single irrep is built from symmetry operations mapped to unit or negative unit matrices (it appears as a consequence of the technique in use; see the text at the beginning of this paragraph). The latter means that these operations are to be combined with the time inversion.

Following the methods developed by Stokes & Hatch (1988) we can look for isotropy subgroups that correspond to other (higher than kernel) allowed symmetries by searching for possible solutions of the equation

$$\eta_j = \sum_{i=1}^{n} D_{ji}(g)\eta_i,$$

where η_i is the order parameter. According to Ascher (1977), these isotropy subgroups are called epikernels. We shall confine the following discussion and examples to the kernel symmetry connected with a minimal diffraction symmetry assured by the selected irrep.

3.1. Example 1: the two-dimensional irreducible representation *E* of the space group *P*422

For an atom at a general position there are 12 independent basis functions (see Table 2) in the carrier space made of magnetic moments at each of eight symmetry-equivalent atomic positions. The kernel symmetry is $P2'$ which implies the minimal diffraction symmetry to be monoclinic.

From the basis functions listed in Table 2 independent components of magnetic moments can be found as the magnetic moments at points #1, #3, #5 and #7. The remaining moments are related by the operations of the magnetic symmetry $P2'$. This implies that the selection of the two-dimensional irrep E and the use of its basis functions is fully equivalent to Opechowski's classification,

Table 3
Two-dimensional irreducible representation E_1 of the space group $P622$ for $\mathbf{k} = 0$.

$\varepsilon = -1/2 + \sqrt{3}/2i$.

Symmetry code	#1 x, y, z	#2 $-y, x-y, z$	#3 $-x+y, -x, z$	#4 $-x, -y, z$	#5 $y, -x+y, z$	#6 $x-y, x, z$
Representation matrix	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon^* \end{pmatrix}$	$\begin{pmatrix} \varepsilon^* & 0 \\ 0 & \varepsilon \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\varepsilon & 0 \\ 0 & -\varepsilon^* \end{pmatrix}$	$\begin{pmatrix} -\varepsilon^* & 0 \\ 0 & -\varepsilon \end{pmatrix}$
Basis function #1	(1 0 0)	(0 0 0)	(1 1 0)	(1 0 0)	(0 0 0)	(1 1 0)
Basis function #2	(0 1 0)	(0 0 0)	(−1 0 0)	(0 1 0)	(0 0 0)	(−1 0 0)
Basis function #3	(0 0 1)	(0 0 0)	(0 0 −1)	(0 0 −1)	(0 0 0)	(0 0 1)
Basis function #4	(0 0 0)	(1 0 0)	(0 −1 0)	(0 0 0)	(1 0 0)	(0 −1 0)
Basis function #5	(0 0 0)	(0 1 0)	(1 1 0)	(0 0 0)	(0 1 0)	(1 1 0)
Basis function #6	(0 0 0)	(0 0 1)	(0 0 −1)	(0 0 0)	(0 0 −1)	(0 0 1)
Basis function #7	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #8	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #9	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #10	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #11	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #12	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)

Symmetry code	#7 $y, x, -z$	#8 $x-y, -y, -z$	#9 $-x, -x+y, -z$	#10 $-y, -x, -z$	#11 $-x+y, y, -z$	#12 $x, x-y, -z$
Representation matrix	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \varepsilon^* \\ \varepsilon & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \varepsilon \\ \varepsilon^* & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\varepsilon^* \\ -\varepsilon & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\varepsilon \\ -\varepsilon^* & 0 \end{pmatrix}$
Basis function #1	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #2	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #3	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #4	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #5	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #6	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)	(0 0 0)
Basis function #7	(1 0 0)	(0 0 0)	(0 −1 0)	(1 0 0)	(0 0 0)	(0 −1 0)
Basis function #8	(0 1 0)	(0 0 0)	(1 1 0)	(0 1 0)	(0 0 0)	(1 1 0)
Basis function #9	(0 0 1)	(0 0 0)	(0 0 −1)	(0 0 −1)	(0 0 0)	(0 0 1)
Basis function #10	(0 0 0)	(1 0 0)	(1 1 0)	(0 0 0)	(1 0 0)	(1 1 0)
Basis function #11	(0 0 0)	(0 1 0)	(−1 0 0)	(0 0 0)	(0 1 0)	(−1 0 0)
Basis function #12	(0 0 0)	(0 0 1)	(0 0 −1)	(0 0 0)	(0 0 −1)	(0 0 1)

$$\left[P422;\ \ P2';\ \ \mathbf{M}(\mathbf{r}_1), \mathbf{M}(\mathbf{r}_3), \mathbf{M}(\mathbf{r}_5), \mathbf{M}(\mathbf{r}_7)\right].$$

In this example all 12 basic functions are transformed into the relationships between atoms in the four magnetic orbits and therefore a description of the magnetic structure as a combination of 12 basic functions and a description by explicit use of relationships following from the magnetic symmetry are equivalent.

3.2. Example 2: the two-dimensional representation E_1 of $P622$

For an atom occupying a general position there are again 12 independent basis functions (see Table 3) in the carrier space made of magnetic moments of 12 atomic positions. As in the previous case, the kernel symmetry is $P2'$, and therefore the minimal diffraction symmetry is monoclinic. There are six magnetic orbits but again four independent magnetic moments. A deeper analysis of basis functions shows that magnetic moments at positions #1, #2, #3 and #7, #8, #9, respectively, are related by analogous equations as follows,

$$\mathbf{R}^2\mathbf{M}(\mathbf{r}_1) + \mathbf{R}\mathbf{M}(\mathbf{r}_2) + \mathbf{M}(\mathbf{r}_3) = 0,$$

$$\mathbf{R}^2\mathbf{M}(\mathbf{r}_8) + \mathbf{R}\mathbf{M}(\mathbf{r}_7) + \mathbf{M}(\mathbf{r}_9) = 0,$$

where

$$\mathbf{R} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

is the threefold rotation. These equations follow from the mutual orthogonality conditions between the invariant subspace of the carrier space generated by the selected irrep E_1 and those generated by one-dimensional irreps whose kernels contain the threefold rotation. Those relationships are not involved in the magnetic space group explicitly and therefore the direct use of the 12 basis functions found makes a stronger restriction than would follow from the magnetic space group itself. In order to make both descriptions equivalent we have to include these relationships as additional restrictions in the latter case. This can be expressed in Opechowski's classification as

$$\left[P622;\, P2';\ \begin{array}{r}\mathbf{M}(\mathbf{r}_1), \mathbf{M}(\mathbf{r}_2), \mathbf{M}(\mathbf{r}_3) = -\mathbf{R}^2\mathbf{M}(\mathbf{r}_1) - \mathbf{R}\mathbf{M}(\mathbf{r}_2), \\ \mathbf{M}(\mathbf{r}_7), \mathbf{M}(\mathbf{r}_8), \mathbf{M}(\mathbf{r}_9) = -\mathbf{R}^2\mathbf{M}(\mathbf{r}_8) - \mathbf{R}\mathbf{M}(\mathbf{r}_7)\end{array}\right].$$

Similar restrictions to those stated for $P622$ can be found in other phase transitions driven by higher-dimensional irreps of trigonal, hexagonal or cubic paramagnetic space groups. Such

relationships for the kernel symmetries and their variants appearing for the epikernels will be published separately.

The fact that the magnetic space groups in these cases yield implicit restrictions connected to the selection of certain irreps only confirms that looking for kernels and epikernels is very useful. Magnetic symmetry can serve as a basis for further theoretical considerations about secondary effects induced by coupling of lattice and magnetic moments. The magnetic space group can also be used for finding all compatible possible irreps, when more irreps are to be used to test finer changes induced by the phase transition.

4. Superspace approach to magnetic structures for $\mathbf{k} \neq 0$

4.1. Magnetic diffraction symmetry for $\mathbf{k} \neq 0$

The superspace approach developed by de Wolff *et al.* (1981) makes it possible to describe periodical perturbations, commensurate or incommensurate with the basic three-dimensional translation symmetry. For magnetic modulated structures the magnetization density can be generalized to a higher-dimensional space to recover the translational symmetry. An equation analogous to (3) allows a generalized structure factor to be introduced. In the following we shall confine ourselves to one modulation vector $\mathbf{k}$.

The magnetic moment of the atom ν can be expressed as a Fourier series,

$$\mathbf{M}_\nu(\mathbf{k}\cdot\mathbf{r}_\nu) = \mathbf{M}_{\nu,0} + \sum_m \big[\mathbf{M}_{\nu,ms}\sin(2\pi m\mathbf{k}\cdot\mathbf{r}_\nu) + \mathbf{M}_{\nu,mc}\cos(2\pi m\mathbf{k}\cdot\mathbf{r}_\nu)\big], \quad (10)$$

where $\mathbf{M}_{\nu,0}$, $\mathbf{M}_{\nu,ms}$ and $\mathbf{M}_{\nu,mc}$ are the absolute term, amplitude of the sine term and amplitude of the cosine term, respectively.

The magnetic structure factor derived from the kinematic theory of diffraction leads to sharp diffraction spots localized at diffraction points $\mathbf{H}$ and $\mathbf{Q} = \mathbf{H} \pm m\mathbf{k}$ ($m > 0$),

$$\begin{aligned}\mathbf{F}_{\rm mag}(\mathbf{H}) &= p\sum_{\nu=1}^{N_{\rm mag}} f_\nu(|\mathbf{H}|)\mathbf{M}_{\nu,0}T_\nu(\mathbf{H})\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_\nu),\\ \mathbf{F}_{\rm mag}(\mathbf{H}\pm m\mathbf{k}) &= p\sum_{\nu=1}^{N_{\rm mag}} f_\nu(|\mathbf{H}\pm m\mathbf{k}|)T_\nu(\mathbf{H}\pm m\mathbf{k}) \times \frac{\mathbf{M}_{\nu,mc}\pm i\mathbf{M}_{\nu,ms}}{2}\exp 2\pi i\mathbf{H}\cdot\mathbf{r}_\nu \end{aligned} \quad (11)$$

[for explanation of the symbols see equation (4)].

The formulas (11) do not include secondary modulation effects of atomic positions. For such effects it must be combined with the structure-factor formula of positional modulated structures (see, for example, Perez-Mato *et al.*, 1986; Petříček & Coppens, 1988).

The rotation and translation part of the superspace symmetry operation with respect to the generalized (3+1)-dimensional basis has the following matrix form,

$$\hat{\mathbf{S}} = \left(\begin{bmatrix}\mathbf{R}_{\rm E} & 0\\ \mathbf{R}_{\rm M} & \mathbf{R}_{\rm I}\end{bmatrix}, \theta\middle|\begin{bmatrix}\mathbf{s}_{\rm E}\\ \mathbf{s}_{\rm I}\end{bmatrix}\right), \quad (12)$$

where $\mathbf{R}_{\rm E}$, $\mathbf{R}_{\rm M}$, $\mathbf{R}_{\rm I}$ and $\theta = \pm 1$ are external 3×3, mixed 1×3, internal 1×1 block matrices and the time inversion sign, respectively. The right-upper 3×1 block is just a zero column. The non-zero matrix blocks are related by the additional condition

$$\mathbf{R}_{\rm M} = \mathbf{k}\mathbf{R}_{\rm E} - \mathbf{R}_{\rm I}\mathbf{k}.$$

Then the modulation function of the magnetic moment at the symmetry-related atom $\mathbf{r}_\mu = \hat{\mathbf{S}}\mathbf{r}_\nu = \mathbf{R}_{\rm E}\mathbf{r}_\nu + \mathbf{s}_{\rm E}$ is

$$\mathbf{M}_\mu(x_{4,\mu}) = \mathbf{R}_{\rm mag}\mathbf{M}_{\nu,0} + \mathbf{R}_{\rm mag}\sum_n\big[\mathbf{M}_{\nu,ns}\sin 2\pi n x_{4,\nu} + \mathbf{M}_{\nu,nc}\cos 2\pi n x_{4,\nu}\big], \quad (13)$$

where

$$\begin{aligned}\mathbf{R}_{\rm mag} &= \theta\det(\mathbf{R}_{\rm E})\mathbf{R}_{\rm E},\\ x_{4,\mu} &= \mathbf{k}\cdot\mathbf{r}_\mu,\\ x_{4,\nu} &= \mathbf{k}\cdot\mathbf{r}_\nu + \mathbf{R}_{\rm I}^{-1}(\mathbf{k}\cdot\mathbf{s}_{\rm E} - \mathbf{s}_{\rm I}).\end{aligned}$$

Therefore, the way used to derive diffraction symmetry (8) and extinction conditions (9) for $\mathbf{k} = 0$ can be used for modulated structures too. The only difference is that we are using here the generalized magnetization density and that the diffraction vector is expressed as $\mathbf{Q} = \mathbf{H} \pm m\mathbf{k}$ ($m > 0$). The symmetry of a diffraction pattern of modulated magnetic structures is again equal to the Laue symmetry derived from the magnetic superspace group.

4.2. Representation analysis for $\mathbf{k} \neq 0$

For a modulated structure the representation analysis should start from representations of the paramagnetic space group. All irreps can again be divided into two families. Any irrep of the first one yields symmetry groups containing the symmetry element $\hat{\mathbf{S}} = (\mathbf{E}, -1\,|\,0,0,0,0)$ [now defined in (3+1)-dimensional superspace], and may induce only paramagnetic phases. Irreps of the second family can give rise to, among others, magnetic groups containing the symmetry element $\hat{\mathbf{S}} = (\mathbf{E}, -1\,|\,0,0,0,1/2)$ which has a selective effect to even and odd harmonics in (10). All even-order harmonics and the absolute term become zeros but, on the other hand, the symmetry element has no effect on the odd harmonics. For a polar vector field the effect would be reversed.

In accordance with the notation for grey magnetic groups and for superspace groups as defined in *International Tables for Crystallography*, Vol. C (1999, §9.8.3.3), we can extend symbols of such magnetic groups with the symbol $1'$ combined with 0 or with *s* [*e.g. Pnma*$1'(\alpha00)0sss$].

The problem of equivalence between using linear combinations of basis functions and the magnetic superspace group is analogous to the non-modulated case. For trigonal and hexagonal symmetry some additional conditions are to be added to the magnetic superspace groups to make these descriptions equivalent. The reasons for using magnetic symmetry remain the same too.

4.3. Commensurate case

It has been shown (*e.g.* Ribeiro, 2007) that for coupling of magnetic ordering and ferroelectricity the symmetry of a commensurate structure can play a very important role. The problem of how the incommensurate symmetry is transferred to the supercell has been solved by several authors (*e.g.* Yamamoto & Nakazawa, 1982; Tamazyan *et al.*, 1994). The symmetry operation from the superspace group of a commensurate structure with $\mathbf{k} = (p_1/q,\ p_2/q,\ p_3/q)$ is applicable in the supercell if the expression

$$\mathbf{k} \cdot (\mathbf{s}_\mathrm{E} + \mathbf{l}) - \mathbf{s}_\mathrm{I} + (1 - \mathbf{R}_\mathrm{I})t_0 \qquad (14)$$

has an integer value for at least one lattice vector **l**. The parameter t_0 defines the shift of q commensurate sections of four-dimensional space along the fourth axis. From the form of (14) it is clear that for symmetry operations with $\mathbf{R}_\mathrm{I} = -1$ we can always find a value of t_0 (generally different for each symmetry operation) to fulfil the condition. On the other hand, for the superspace operations with $\mathbf{R}_\mathrm{I} = 1$, the origin shift cannot change their transferability to the supercell.

The condition (14) can be applied to magnetic superspace groups as well. Specifically the symmetry operation $\hat{\mathbf{S}} = (\mathbf{E}, -1|0, 0, 0, 1/2)$ with $\mathbf{k} = (p/q, 0, 0)$ cannot be transferred into the supercell for odd q. On the other hand, for $q = 2n$ we obtain the symmetry operation $\hat{\mathbf{S}}_{3d} = (\mathbf{E}, -1|1/2, 0, 0)$, which means that the magnetic moments have alternating orientations with periodicity $n\mathbf{a}$ when going along the first axis of the commensurate cell. This is in full accordance with the fact that only odd harmonic terms are present in the modulation function (10).

5. Conclusions

It has been shown that in the determination of magnetic structures the use of both magnetic space/superspace groups and representation analysis plays a different, rather complementary, role. While magnetic symmetry operations have a direct impact (which differs for the rotation and the translation parts) on a diffraction pattern of the crystal, the basis functions of the active irrep(s) can be used to find the ordering of magnetic moments. It appears that, at least for the hexagonal family for certain irreps of paramagnetic space groups with $\mathbf{k} = 0$, there exist extra relationships among three magnetic moments where any two determine the third. Such relationships do not have a direct impact on the diffraction symmetry, and therefore magnetic groups must be complemented with specific restrictions on the magnetic moments. Using the full set of restrictions is very important for refinement of magnetic structures because it minimizes correlations between parameters. Calculation is then more stable and reliable. Moreover, using magnetic symmetry helps to understand the formation of magnetic domains.

Combination of representation analysis and the knowledge of the symmetry of the diffraction pattern expressed in the magnetic space/superspace groups seems to be an ideal concept for description and calculation of magnetic structures. This article will serve as a theoretical basis for more practically oriented publications about the implementation of magnetic symmetry combined with representation analysis in the system of programs *Jana2006* (Petříček *et al.*, 2006) and applications of this program to some selected structures (Petříček *et al.*, 2010). It should be noted that practical results have already been obtained using *Jana2006* and that they fully support our conclusions given here.

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