On the symmetry of incommensurate magnetic phases and its applications

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Although superspace formalism has become the standard approach for the analysis of structurally modulated crystals, it has remained during the last thirty years almost unexplored as a practical tool to deal with magnetic incommensurate structures. This situation has recently changed with the development of new computer tools for magnetic phases based on this formalism. In this context we show here that, as in the case of non-magnetic incommensurate systems, the concept of superspace symmetry provides a simple, efficient and systematic way to characterize the symmetry and rationalize the structural and physical properties of incommensurate magnetic materials. The method introduces significant advantages over the most commonly employed method of representation analysis for the description of the magnetic structure of a crystal. But, more importantly, in contrast with that method, it consistently yields and classifies all degrees of freedom of the system. The knowledge of the superspace group of an incommensurate magnetic material allows to predict its crystal tensor properties and to rationalize its phase diagram, previous to any appeal to microscopic models or mechanisms. This is especially relevant when the properties of incommensurate multiferroics are being studied. We present first a summary of the superspace method under a very practical viewpoint particularized to magnetic modulations. Its relation with the usual representation analysis is then analyzed in detail, with the derivation of important general rules for magnetic modulations with a single propagation vector. The power and efficiency of the formalism is illustrated with various selected examples, including some multiferroic materials.

61.44.Fw, 61.50.Ah, 75.85.+t

I. INTRODUCTION

The use of the superspace formalism for the description of modulated magnetic structures was proposed at the early stages of its development, more than thirty years ago [1]. However, although this theory has become the standard approach for the analysis of incommensurate and commensurate non-magnetic modulated crystals[2,3,4], it has remained essentially unexplored as a practical approach to deal with magnetic incommensurate structures except for some testimonial works [5]. This situation has recently changed with the extension of the refinement program JANA2006 to magnetic structures[6,7,8]. This program can now deal with the refinement of modulated (commensurate or incommensurate) magnetic structures by using refinement parameters and symmetry constraints consistent with any magnetic superspace group.

In contrast with incommensurate structural modulations, in the case of incommensurate magnetic structures the need of the superspace formalism was not compelling because the representation analysis method developed by Bertaut [9,10], which decomposes the magnetic configuration space into basis modes transforming according to different physically irreducible representations (irreps) of the paramagnetic space group, can be used for the description of magnetic modulations, independently of their propagation vector being commensurate or incommensurate. Since long ago the programs commonly employed for the refinement of incommensurate magnetic structures, such as FullProf [11], use this approach. The recent upsurge of research work on multiferroic materials, where the spin-lattice coupling is an essential part of their structural properties, has evidenced however the limits of the representation method. In this approach, the magnetic point group that underlies the magnetoelectric properties of the system is generally neither known nor controlled, and may be inadvertently changed during the refinement, depending on the

restrictions introduced on the basis functions during the refinement process. In this context, the symmetry and in particular, the point group symmetry of incommensurate magnetic structures when described in terms of irrep modes, has been the subject of discussion (see for instance references [12,13,14]). These studies have analysed the role of space inversion in incommensurate modulations described by irrep modes, and have independently rediscovered concepts that are intrinsic of the superspace formalism.

While the relation between the description of non-magnetic incommensurate structures using either irrep modes or superspace formalism has been studied in detail [15,16,17,18,19,20] (with clear advantage for the superspace approach), the analogous relation for incommensurate magnetic structures has never been discussed in a general context. It is the purpose of this article to fill this gap and show the comparative advantages of the superspace formalism for the analysis of incommensurate magnetic structures.

In the case of a non-magnetic incommensurate structure, it is well known that the modulation can be described within a certain approximation by the basis functions associated with one or a few irreps. However, it is the symmetry given by a superspace group that determines all the possible irreps that can be present in the distortion, whatever small. If the distorted phase originates in a Landau-type order parameter transforming according to a single irrep, the possible superspace groups of the resulting distorted phase can be determined in a straightforward manner. In the simplest cases, if the irrep is only bidimensional, with two arms in its k-vector star (k and $-k$), there is a one to one correspondence between an irrep and a superspace group symmetry. But even in this case, there is an essential difference between the use of an irrep label or the use of the corresponding superspace group to characterize the symmetry of the structure. Namely, the superspace group defines not only the symmetry restrictions present in the first harmonic of the modulation, corresponding to this specific irrep, but it also automatically includes all

symmetry restrictions that are present in any other possible induced secondary distortions, such as higher harmonics in the modulated distortion. We will show that this important difference between the use of irreps and superspace symmetry applies also to the case of magnetic incommensurate structures. Magnetic modulated structures are often purely sinusoidal within experimental resolution, and can have a negligible coupling with the lattice, but in the important cases where this coupling is specially significant (as in multiferroics) and/or the cases where the magnetic modulation becomes anharmonic, the use of the superspace symmetry allows to consider in a systematic way all possible degrees of freedom that, due to the symmetry break, are unclenched.

In the case of irreps with dimension larger than two the superspace group of the structure depends on the direction taken by the order parameter within the irrep space [17, 18]. In these cases the association of an irrep with the modulation is in general not sufficient to define all the constraints that the configuration has, due to the symmetry of the phase. We will show that the same applies for incommensurate magnetic structures.

It must be mentioned that a similar difference exists in commensurate magnetic structures between the representation analysis and the use of Shubnikov magnetic space groups. It is remarkable that the intense discussion arisen in the late sixties [9, 21] about the use of the representation analysis as alternative to Shubnikov magnetic space groups somewhat missed this important point. The two methods were only considered and discussed as alternative approaches for describing and restricting the parameterization of magnetic structures, disregarding the additional role of the magnetic space group as the simplest method to articulate the restrictions imposed by the magnetic ordering on all degrees of freedom and properties of the phase. The two methods are in fact complementary. The description of a commensurate magnetic structure in terms irrep modes is somewhat incomplete if the magnetic space group associated with the

corresponding spin configuration is not explicitly given. It is this magnetic symmetry that expresses in the most economical way all possible symmetry-forced constraints of the phase. For instance, crystal tensor properties, including magnetic, electric, elastic and all their crossed responses, will be constrained by the magnetic point group corresponding to this magnetic space group. Analogously, the tensor properties of an incommensurate magnetic phase are in general constrained by the point group associated with its superspace group. The knowledge of the superspace group of an incommensurate magnetic phase and its corresponding point group is then a fundamental step to rationalize its crystal tensor properties, as for instance its magnetoelastic and magnetoelectric responses.

Therefore, as proposed in Ref. 7, the most efficient approach to the full characterization of incommensurate magnetic structures should then be a combined use of both tools, namely the assignment of a superspace group to describe all symmetry constraints on the structure and symmetry properties of the phase, and a hierarchical decomposition of the structural degrees of freedom into modulations described by irrep modes compatible with the postulated superspace symmetry. Along this line, Ref. 22 reported in detail one example where the relation between superpace symmetry and the representation analysis was discussed and exploited to characterize the symmetry constraints on the magnetoelectric properties in a family of multiferroics.

In this article we pretend to give a comprehensive view of the application of superspace symmetry concepts to the analysis of magnetic incommensurate structures and their properties. After a brief summary of the superspace method and its relation with the usual representation analysis, the power and efficiency of the superspace description will be shown by means of a detailed discussion of various examples, including several multiferroic materials.

II. SUPERSPACE SYMMETRY AND MAGNETIC MODULATIONS

We briefly summarize here the properties of a superspace group defining the symmetry of an incommensurate phase, valid for magnetic or non-magnetic ordered structures. A more complete and detailed introduction to these concepts can be found in the general references[2,3,4]. Here only the main results are summarized, but taking care that the arguments and the expressions include explicitly the case of magnetic structures. For the sake of simplicity, and also because it is the most common case in modulated magnetic structures, we restrict the definitions to systems with one-dimensional modulations, i.e. with a single propagation vector, for which the superspace has (3+1) dimensions.

A. Basic concepts

A modulated magnetic structure with a single incommensurate propagation vector $\boldsymbol{k}$ is described within the superspace formalism by a normal periodic structure (the so-called basic structure) with its symmetry given by a conventional magnetic space group (let us call it Ω_b) plus a set of atomic modulation functions defining the deviations from this basic periodicity of each atom in each unit cell, in what concerns their positions, their magnetic moments and/or their occupation probability, etc. The value of a certain atomic property A_μ of an atom μ in the unit cell of the basic structure (as for instance its occupation probability, its static displacement, its magnetic moment, its thermal displacement tensor, etc.) varies from one cell to another according to a modulation function $A_\mu(x_4)$ of period one, such that its value $A_{l\mu}$ for the atom μ at the unit cell $\boldsymbol{l}$, with basic position $\boldsymbol{r}_{l\mu} = \boldsymbol{l} + \boldsymbol{r}_\mu$ ($\boldsymbol{l}$ being a lattice translation of the basic structure) is given by the value of the function $A_\mu(x_4)$ at $x_4 = \boldsymbol{k}.\,\boldsymbol{r}_{l\mu}$:

$$A_{l\mu} = A_{\mu}\left(x_4 = \boldsymbol{k}.\,\boldsymbol{r}_{l\mu}\right) \tag{1}$$

Thus, a basic conventional periodic structure, a modulation wave vector $\boldsymbol{k}$ and a set of periodic atomic modulations $A_{\mu}\left(x_4\right)$ for each atom in its unit cell describe completely the aperiodic crystal, as they determine the aperiodic values of the local atomic quantities of any atom in any unit cell of the basic structure. These modulation functions, being periodic with period 1, can be expressed as Fourier series of type:

$$A_{\mu}(x_4) = A_{\mu,0} + \sum_{n=1,\ldots} [A_{\mu,ns} \sin(2\pi n x_4) + A_{\mu,nc} \cos(2\pi n x_4)] \tag{2}$$

Considering the definition of x_4, this description does not apparently differ much from the usual approach of using basis functions (waves) transforming according to irreps of the paramagnetic space group[11]. However, fundamental differences appear when the symmetry properties are defined. It is important at this point to stress that the magnetic space group Ω_b of the basic structure, is not necessarily the one associated with the paramagnetic phase, but it can be in general a subgroup.

By definition, any operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ of the magnetic space group Ω_b of the basic structure (with $\boldsymbol{R}$ being a point-group operation, θ being -1 or +1 depending if the operation includes time reversal or not, and $\boldsymbol{t}$ a translation in 3d real space) transforms the incommensurately modulated structure into a distinguishable incommensurate modulated structure, but with the same basic structure and with all its modulation functions only differing from those of the original structure by a common translation of the internal coordinate x_4, such that the new modulation functions $A'_{\mu}\left(x_4\right)$ of the $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$-transformed structure satisfy

$$A'_{\mu}\left(x_4\right) = A_{\mu}\left(x_4 + \tau\right), \tag{3}$$

where τ depends on each specific operation. In other words, the modulated structure obtained by the transformation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ only differs from the original one by a global phase translation $-\tau$ of the whole modulation of the system. The original configuration can be then recuperated by an additional translation τ along the so-called internal coordinate, i.e. the phase of the modulation functions, and one can speak of $(\boldsymbol{R},\theta\,|\,\boldsymbol{t},\tau)$ as a symmetry operation of the system defined in a four-dimensional mathematical space where the fourth dimension corresponds to the continuous argument of the periodic modulation functions.

The addition of the global phase translation of the modulation as a fourth dimension allowing an additional type of transformations of the structure is enabled by the fact that a phase translation of the modulation in an incommensurate phase (corresponding to the well-known phason excitations characteristic of incommensurate structures) keeps the energy invariant, in the same way that rotations, roto-inversions, translations, and time reversal do. Thus, the superspace symmetry group is the subgroup of all types of transformations, including global phase shifts of the modulation, that keep the energy invariant and the system undistinguishable after the transformation. This energy invariance of the added phase translations ensures the robustness of the superspace symmetry concept for characterizing the symmetry restrictions associated with an incommensurate phase [23]. The symmetry, so defined, is a feature valid within the whole range of a thermodynamic phase and cannot be broken except by a phase transition.

If $(\boldsymbol{R},\theta\,|\,\boldsymbol{t},\tau)$ belongs to the (3+1)dim superspace group of an incommensurate magnetic phase, the action of $\boldsymbol{R}$ on its propagation vector $\boldsymbol{k}$ necessarily transforms it into a vector equivalent to either $\boldsymbol{k}$ or $-\boldsymbol{k}$. This means:

$$\boldsymbol{k}.\,\boldsymbol{R} = R_I\boldsymbol{k} + \boldsymbol{H}_R\ , \tag{4}$$

where R_I is either +1 or -1 and $\boldsymbol{H_R}$ is a reciprocal lattice vector of the basic structure that depends on the operation $\boldsymbol{R}$. The vectors $\boldsymbol{H_R}$ can only be different from zero if the propagation vector $\boldsymbol{k}$ includes a commensurate component [2].

The restrictions in the form of the atomic modulation functions resulting from a superspace group operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t},\tau)$ can be derived from the definitions above. They can be summarized as follows: if in the basic structure an atom μ is related with an atom ν by the operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ such that $(\boldsymbol{R}\,|\,\boldsymbol{t})\boldsymbol{r}_\nu = \boldsymbol{r}_\mu + \boldsymbol{l}$, then their atomic modulation functions are not independent and relate as:

$$A_\mu\left(R_I x_4 + \tau_o + \boldsymbol{H_R}.\,\boldsymbol{r}_\mu\right) = Transf(\boldsymbol{R},\theta)A_\nu\left(x_4\right), \tag{5}$$

where $\tau_o = \tau + \boldsymbol{k}.\,\boldsymbol{t}$ and $Transf(\boldsymbol{R},\theta)$ is the operator associated with the transformation of the local quantity A_μ by the action of the point-group operation $(\boldsymbol{R},\theta)$. Thus, Eq. (5) introduces a relation between the modulation functions of the magnetic moments of the two atoms of the form:

$$\boldsymbol{M}_\mu\left(R_I x_4 + \tau_o + \boldsymbol{H_R}.\,\boldsymbol{r}_\nu\right) = \theta\det(\boldsymbol{R})\boldsymbol{R}.\;\boldsymbol{M}_\nu\left(x_4\right), \tag{6}$$

while the atomic modulation functions $\boldsymbol{u}_\mu(x_4)$, $\boldsymbol{u}_\nu(x_4)$ defining the atomic displacements in each basic cell with respect to the basic positions $\boldsymbol{r}_{l\mu}$ and $\boldsymbol{r}_{l\nu}$ relate as:

$$\boldsymbol{u}_\mu\left(R_I x_4 + \tau_o + \boldsymbol{H_R}.\;\boldsymbol{r}_\nu\right) = \boldsymbol{R}.\;\boldsymbol{u}_\nu\left(x_4\right) \tag{7}$$

This means that only the modulation functions for the set of atoms in the asymmetric unit of the basic structure are necessary to define the whole structure. Notice that equations (6) and (7) imply specific restrictions on the possible forms of the modulation functions of

atoms that occupy positions in the basic structure that are left invariant ($\mu = \nu$) by some symmetry operations of Ω_b.

According to the above definitions, all translations of the basic lattice combined with conveniently chosen phase shifts, namely the operations $(\boldsymbol{1},+1\,|\,\boldsymbol{t},-\boldsymbol{k}.\boldsymbol{t})$ (here, $\boldsymbol{1}$ represents the identity matrix), belong to the superspace group of the structure, forming its (3+1)-dim lattice. If $\boldsymbol{k} = (k_x, k_y, k_z)$ is expressed in the reciprocal basis of the basic space group Ω_b, then the four elementary translations $(\boldsymbol{1},+1\,|\,1\,0\,0,-k_x)$, $(\boldsymbol{1},+1\,|\,0\,1\,0,-k_y)$, $(\boldsymbol{1},+1\,|\,0\,0\,1,-k_z)$ and $(\boldsymbol{1},+1\,|\,0\,0\,0,1)$ generate this lattice and define a unit cell in the (3+1)-dim superspace. In the basis formed by these superspace unit cell translations, the symmetry operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t},\tau)$ can be expressed in the standard form of a space group operation in a 4-dim space, $(\boldsymbol{R}_s,\theta\,|\,\boldsymbol{t}_s)$, where $\boldsymbol{t}_s$ is a four dimensional translation and $\boldsymbol{R}_s$ a 4×4 integer matrix defining the transformation of a generic point (x_1, x_2, x_3, x_4):

$$\boldsymbol{R}_S = \begin{pmatrix} \mathrm{R}_{11} & \mathrm{R}_{12} & \mathrm{R}_{13} & 0 \\ \mathrm{R}_{21} & \mathrm{R}_{22} & \mathrm{R}_{23} & 0 \\ \mathrm{R}_{31} & \mathrm{R}_{32} & \mathrm{R}_{33} & 0 \\ \mathrm{H}_{\boldsymbol{R}1} & \mathrm{H}_{\boldsymbol{R}2} & \mathrm{H}_{\boldsymbol{R}3} & \mathrm{R}_{\mathrm{I}} \end{pmatrix} \tag{8}$$

Here, the R_{ij} are the matrix coefficients of the rotational 3-dim operation $\boldsymbol{R}$ of the space group operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ belonging to Ω_b (expressed in the basis of the basic unit cell), (H_{R1}, H_{R2}, H_{R3}) the components (in the corresponding reciprocal basis) of the vector $\boldsymbol{H_R}$ defined in Eq. (4), and R_I is +1 or -1, according to Eq. (4). The superspace translation $\boldsymbol{t}_s$ in the 4-dim basis is given by (t_1, t_2, t_3, τ_0), where t_i are the three components of $\boldsymbol{t}$ in the basis of the basic unit cell and $\tau_o = \tau + \boldsymbol{k}.\boldsymbol{t}$, as in Eq. (5). The value of τ_0 does not depend

on the specific value of the irrational component(s) of the incommensurate wave vector $\boldsymbol{k}$. The group composition law is then a trivial extension of the one for (3dim)- space groups:

$$\left(\boldsymbol{R}_{s1},\theta_1 \,|\, \boldsymbol{t}_{s1}\right)\left(\boldsymbol{R}_{s2},\theta_2 \,|\, \boldsymbol{t}_{s2}\right)=\left(\boldsymbol{R}_{s1}.\ \boldsymbol{R}_{s2},\ \theta_1\theta_2 \,|\, \boldsymbol{R}_{s1}.\ \boldsymbol{t}_{s2}+\boldsymbol{t}_{s1}\right) \tag{9}$$

Superspace groups can therefore be defined with symmetry cards analogous to those of normal space groups, as done in JANA2006 [6].

A superspace group operation $\left(\boldsymbol{R}_s,\theta \,|\, \boldsymbol{t}_s\right)$ can be symbolically expressed in the simpler form $\{\boldsymbol{R},\theta \,|\, \boldsymbol{t}_s\}$, with $\boldsymbol{t}_s=(t_1,t_2,t_3,\tau_0)$, knowing that the 4×4 matrix $\boldsymbol{R}_s$ depends on $\boldsymbol{R}$ as given by Eq. (8), while keeping the translational part expressed in the superspace unit cell basis. We will use the keys { } to distinguish this form of expressing the superspace symmetry operations, which obviates the ever present $-\boldsymbol{k}.\boldsymbol{t}$ internal translation along x_4. In the following, we will use when appropriate one or the other notation, and their equivalence $\left(\boldsymbol{R},\theta \,|\, t_1\, t_2\, t_3,\tau\right)=\{\boldsymbol{R},\theta \,|\, t_1\, t_2\, t_3\ \tau_o\}$ with ($\tau_o=\tau+\boldsymbol{k}.\,\boldsymbol{t}$), should be kept in mind.

Summarizing, an incommensurate magnetic structure can be fully described by specifying: *i*) the magnetic superspace group (as in normal crystallography, this symmetry group can be unambiguously given by listing its symmetry operations); *ii*) the conventional periodic basic structure (usually non-magnetic), with a symmetry given by a normal magnetic space group; and *iii*) a set of periodic atomic modulation functions (period 1) defining, according to Eq. (1), the spin modulations for the atoms of the asymmetric unit of the basic structure.

If, besides the magnetic modulation, there exist additional structural modulations (as, for instance, when the spin-lattice coupling causes induced lattice distortions), these will be given by the corresponding modulation functions defined for the atoms of the same asymmetric unit, and the superspace symmetry group of the system constrains both magnetic and non-magnetic modulation functions. It is important to stress that the

magnetic point group of the system is given by the set of point-group operations present in the operations belonging to the superspace group. The simplicity, lack of ambiguity and generality of this description that includes in an automatic way the point group symmetry of the system, will become patent in the discussion of the examples below.

B. Diffraction symmetry and extinction rules

The diffraction pattern of a single-k incommensurately modulated structure (magnetic or not) can be indexed with four indices, using the incommensurate wave vector $\boldsymbol{k}$ as a fourth basis vector in addition to the reciprocal unit cell vectors $\{\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*\}$ of the basic structure. More concretely, the diffraction vector $\boldsymbol{H}$ of any Bragg reflection can be indexed as a four dimensional vector with four integers $(hklm)$ satisfying:

$$\boldsymbol{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\boldsymbol{k} \tag{10}$$

The existence of a superspace group operation $\{\boldsymbol{R},\theta|\boldsymbol{t}_s\}$ in the incommensurate system is reflected both in the non-magnetic structure factor $\boldsymbol{F}(\boldsymbol{H})$ and in the magnetic structure factor $\boldsymbol{F}_M(\boldsymbol{H})$, which must satisfy the relations

$$\boldsymbol{F}(\boldsymbol{H}) = e^{i2\pi \boldsymbol{H}.\boldsymbol{t}_s}\boldsymbol{F}(\boldsymbol{H}.\boldsymbol{R}_S) \tag{11}$$

$$\boldsymbol{F}_M(\boldsymbol{H}) = e^{i2\pi \boldsymbol{H}.\boldsymbol{t}_s}\theta\, det(\boldsymbol{R})\boldsymbol{R}.\boldsymbol{F}_M(\boldsymbol{H}.\boldsymbol{R}_S), \tag{12}$$

where $\boldsymbol{H}.\boldsymbol{t}_s$ represents $ht_1 + kt_2 + lt_3 + m\tau_o$ and $\boldsymbol{H}.\boldsymbol{R}_S$ stands for $(hklm).\boldsymbol{R}_S$, with the matrix 4×4 matrix $\boldsymbol{R}_s$ acting on the diffraction vector $\boldsymbol{H}$ as a four-component row vector. Note that by definition, $\boldsymbol{H}.\boldsymbol{R}_S$ yields the four-index representation of the rotated diffraction vector $\boldsymbol{H}.\boldsymbol{R}$, defined in real space. Equations (11) and (12) ensure that both the magnetic and non-magnetic diffraction properties comply with the point group

symmetry associated with the superspace group, the diffracted intensities being equal for any pair of diffraction vectors $\boldsymbol{H}$ and $\boldsymbol{H}.\boldsymbol{R}$, related by a point-group operation $\boldsymbol{R}$ present in the superspace group. Equations (11) and (12) can also be used to derive any extinction rule that may be forced by a superspace symmetry operation for diffraction vectors such that $\boldsymbol{H}.\boldsymbol{R}_S = \boldsymbol{H}$. For such type of diffraction vectors, these equations reduce to:

$$F(\boldsymbol{H}) = e^{i2\pi \boldsymbol{H}.\boldsymbol{t}_s} F(\boldsymbol{H}) \tag{13}$$

$$\boldsymbol{F}_M(\boldsymbol{H}) = e^{i2\pi \boldsymbol{H}.\boldsymbol{t}_s} \theta \, det(\boldsymbol{R}) \boldsymbol{R}.\boldsymbol{F}_M(\boldsymbol{H}) \tag{14}$$

In the case of non-magnetic diffraction, the structure factor should then vanish and extinction happens for $\boldsymbol{H}.\boldsymbol{t}_s \neq$ integer. For magnetic diffraction, the structure factor is an axial vector and Eq. (14) only forces, in general, a certain restriction on its direction depending on the value of $\boldsymbol{H}.\boldsymbol{t}_s$. This restriction results in an extinction rule for non-polarized magnetic neutron diffraction if the restricted direction is the one of the diffraction vector [7].

In addition to extinction rules associated with specific operations of the superspace group, Eq. (13) and Eq. (14) explain rather general ones, showing that they can also be traced back to the superspace symmetry of the system. Below, we list a few examples [henceforth, when indicating concrete operations and not generic operations as above, we drop the index θ and indicate the inclusion of time reversal by adopting the usual convention of adding a prime to the point-group operation symbol (1', m_x', 2_y', ...)].

a) Non-magnetic incommensurate structures. The corresponding magnetic superspace group necessarily includes the time reversal operation $\{1'|0000\}$. Eq. (13) is trivially

fulfilled for this operation, but Eq. (14) becomes $\boldsymbol{F}_M(\boldsymbol{H}) = -\boldsymbol{F}_M(\boldsymbol{H})$, implying the trivial result that the magnetic structure factor is zero for any $\boldsymbol{H}$.

b) Single-k incommensurate magnetic structures. The magnetic superspace group necessarily includes the time reversal operation $\{1'|000\frac{1}{2}\}$ (see next Section). This implies that for any diffraction vector $F(\boldsymbol{H}) = e^{i\pi m} F(\boldsymbol{H})$ and $\boldsymbol{F}_M(\boldsymbol{H}) = -e^{i\pi m}\boldsymbol{F}_M(\boldsymbol{H})$. Therefore, magnetic diffraction is restricted to satellites with *m* odd, while non-magnetic diffraction is responsible of main reflections (*m=0*) and possible satellites with *m* even. Thus, the separation of magnetic and non-magnetic diffractions, and the restriction of magnetic diffraction to odd-order satellites in many incommensurate magnetic structures can be traced back to the presence of the superspace symmetry operation $\{1'|000\frac{1}{2}\}$.

c) Operation $\{2_x|\frac{1}{2}00\frac{1}{2}\}$ in an incommensurate magnetic modulation with $\boldsymbol{k} = (\alpha 00)$. For $\boldsymbol{H} = (h00m)$, non-magnetic diffraction is forbidden for $h + m = odd$, while the magnetic structure factor must satisfy $\boldsymbol{F}_M(h00m) = e^{i\pi(h+m)}\, \boldsymbol{2_x}\cdot \boldsymbol{F}_M(h00m)$, which implies that $\boldsymbol{F}_M(h00m)$ is of type $(F_x,0,0)$ for *h+m= even*, and $(0,F_y,F_z)$ for *h+m=odd*. As only the component of the magnetic structure factor perpendicular to the diffraction vector is observed in non-polarized magnetic diffraction, a systematic absence of magnetic diffraction occurs for *h+m= even*. Here again, extinction rules for magnetic and non-magnetic diffraction are complementary. If the symmetry operation $\{1'|000\frac{1}{2}\}$ is also present, these extinction rules reduce to the presence of both magnetic and non-magnetic satellite reflections around the non-extinct main reflections (*h000*) (with *h even*) as *odd* and *even* satellites, respectively.

Reversely, if instead, the symmetry operation is $\{2_x|\frac{1}{2}000\}$, non-magnetic and magnetic extinction will occur for diffraction vectors (*h00m*) with *h* odd and *h* even, respectively. Hence, magnetic reflections only appear around the extinct main reflections with *h* odd,

while eventual satellites caused by possible structural modulations are restricted to appear around the non-extinct main reflections with *h* even.

d) Operation $\{2_z|0000\}$ *in an incommensurate magnetic modulation with* $\boldsymbol{k}=(00\gamma)$. For $\boldsymbol{H}=(00lm)$, non-magnetic diffraction has no extinctions, while the magnetic structure factor must satisfy $\boldsymbol{F}_M(00lm)=\boldsymbol{2}_z.\boldsymbol{F}_M(00lm)$, which implies that $\boldsymbol{F}_M(00lm)$ is always of the type $(0,0,F_z)$, and therefore non-polarized neutron magnetic diffraction will be absent for diffraction vectors (*00lm*). This means that, in contrast with non-magnetic diffraction, non-screw rotational operations yield extinction rules, and they can be even more restrictive than those for screw operations.

e) Operation $\{4_z|0000\}$ *in an incommensurate magnetic modulation with* $\boldsymbol{k}=(00\gamma)$. For diffraction vectors of the type $(00lm)$, this operation implies that $\boldsymbol{F}_M(00lm)=\boldsymbol{4}_z.\boldsymbol{F}_M(00lm)$. This means that $\boldsymbol{F}_M(00lm)$ must be of the type $(0,0,F_z)$ and, therefore, non-polarized neutron diffraction will be absent for any value of *l* and *m*. On the other hand, if the operation is $(4_z|000\,{}^1\!/_4)$, the symmetry condition becomes $\boldsymbol{F}_M(00lm)=e^{i\pi m/2}\boldsymbol{4}_z.\boldsymbol{F}_M(00lm)$, and $\boldsymbol{F}_M(00lm)$ is of the type $(0,0,F_z)$ for *m* even. Therefore, non-polarized magnetic diffraction is extinct for *m* even, while for *m* odd $\boldsymbol{F}_M(00lm)$ is of the type $(F_x,-iF_x,0)$ for *m=4n+1* and of the type $(F_x,iF_x,0)$ for *m=4n+3*, and non-polarized magnetic diffraction is allowed.

From these examples one can see that for non-polarized neutron magnetic diffraction the extinction conditions associated with specific symmetry operations are quite limited, and do not reach the resolving power of those present in non-magnetic diffraction of structural incommensurate structures, for determining the symmetry of the system. Mirror planes do not yield any kind of extinction, and those resulting from screw rotations can be rather uninformative. Nevertheless, it is important to be aware of the existence of these

symmetry-forced systematic absences. In some cases, their observation can bring very valuable information to identify the phase symmetry. In addition, we have seen above that the simple rules generally applied on an empirical basis (odd satellites for magnetic diffraction, even satellites for non-magnetic, etc.) can be assigned to the presence of the superspace symmetry operation $\{1'|000\frac{1}{2}\}$. One can then foresee and rationalize their breaking in more complex scenarios where this symmetry operation may disappear.

It is important to stress that the extinction rules discussed above are general. They only depend on the presence or absence of a certain symmetry operation in the global superspace group of the system. But, as it happens in non-magnetic diffraction, additional more restrictive extinction conditions can result from the limitation of the magnetic diffraction to some ions at some particular Wyckoff orbit(s) with higher symmetry (the so-called non-characteristic orbits). These extra extinction rules can be relevant in many cases, as the number of magnetic atoms are usually quite limited and are usually located at high-symmetry sites. These additional extinctions can be analytically derived following the same procedure as above, but considering the higher magnetic superspace symmetry of a virtual structure formed only by the magnetic ions.

III. MAGNETIC SUPERSPACE GROUPS AND IRREDUCIBLE REPRESENTATIONS

In accordance with Landau theory, magnetic ordering is a symmetry-breaking process that can be described by an appropriate order parameter. Quite commonly, the transformation properties of this order parameter correspond to those of a single irreducible representation (irrep) of the *magnetic* grey space group associated with the paramagnetic phase. The frequent limitation of the magnetic modulation to a single propagation vector is often a consequence of this restriction to a single primary irrep. In more general cases,

magnetic configurations with a single propagation vector can be decomposed into several magnetic modes transforming according to different irreps that share the same propagation vector. This is the basis for the representation analysis method developed by Bertaut [9,10], which is nowadays the most popular method to describe and determine magnetic structures. The possible magnetic orderings are parameterized using a complete set of basis modes transforming according to the irreps of the paramagnetic space group associated with the observed propagation vector. The magnetic configuration is then determined by using, if possible, the basis modes corresponding to a single irrep, or if necessary, a set of basis modes restricted to a set of irreps as small as possible.

It is important to establish in detail the relationship between the symmetry constraints imposed by the assignment of a certain irrep to the magnetic order parameter and those resulting from ascribing a magnetic superspace group to the magnetic phase. As we will see below, these two sets of constraints are closely related, but superspace symmetry is in general more restrictive and has a comprehensive character for all the degrees of freedom.

The order parameter components can be considered as the amplitudes of a set of static spin waves with propagation vectors $\{\boldsymbol{k}_1,....,\boldsymbol{k}_n\}$ (the so-called star of the irrep) that transform among them when an operation of the symmetry group of the paramagnetic phase is applied. If N is the number of independent spin waves for the propagation vector $\boldsymbol{k}_1$ (i.e., the dimension of the so called small representation), then there exist an equal number for all other wave vectors in the irrep star, and the dimension of the irrep is $n \times N$. In general, an incommensurate magnetic ordering with a single propagation vector and transforming according to a single irrep T can give rise to different superspace group symmetries depending on the *direction* taken by the irrep order parameter in this $n \times N$ space. It should be stressed at this point that the term *irreducible representation* or irrep is used here as equivalent to *physically irreducible representation* because we are interested

in the transformation properties of real physical magnitudes such as the magnetic moments. Therefore, in some cases, these irreps are actually the direct sum of two complex conjugate irreducible representations. This implies that the irrep star is necessarily formed by pairs of wave vectors $\boldsymbol{k}_i$ and $-\boldsymbol{k}_i$.

Independently of the number of arms of the irrep star, the possible directions for the order parameter that yield a magnetic ordering with a single propagation vector, and therefore a symmetry described by a (3+1)-dim superspace group, are necessarily limited to those where only a single wave vector $\boldsymbol{k}$ (and its opposite, $-\boldsymbol{k}$) of the irrep star is involved. We can then constrain the order parameter to a *2N*-dim subspace within the irrep space. The magnetic moment $M(\mu,\boldsymbol{l})$ of any atom $(\mu,\boldsymbol{l})$ in the structure can then be expressed as:

$$M(\mu,\boldsymbol{l}) = \sum_{i=1,\ldots,N} S_i(\boldsymbol{k})\sigma_i(\mu)e^{-i2\pi\boldsymbol{k}.(\boldsymbol{l}+r_\mu)} + S_i(-\boldsymbol{k})\sigma_i^*(\mu)e^{i2\pi\boldsymbol{k}.(\boldsymbol{l}+r_\mu)} \qquad (15)$$

Here, $S_i(\boldsymbol{k})$ and $S_i(-\boldsymbol{k})$ are global complex components of the order parameter, (with $S_i(-\boldsymbol{k}) = S_i^*(\boldsymbol{k})$, $i = 1,\ldots,N$) and $\sigma_i(\mu)$ is the *polarization vector* that defines the internal structure (i.e. the correlation between the atomic magnetic moments in a unit cell) of each of the *N* spin waves. We stress the choice of sign of the exponents in Eq. (15) to keep the convention of a positive phase shift $e^{i2\pi\boldsymbol{k}.\boldsymbol{t}}$ for the action of a translation $(1|\boldsymbol{t})$ on the spin wave amplitude $S_i(\boldsymbol{k})$ (see Eq. (17) below). Of course, the magnetic moments $\sigma_i(\mu)$ in (15) of non-magnetic atoms μ are trivially zero, while for the magnetic ones they will have correlations described by $\sigma_i(\mu)$, according to the requirements of the transformation properties of the relevant irrep.

By definition, an operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ of the paramagnetic symmetry group with $\boldsymbol{R}$ such that $\boldsymbol{k}\cdot\boldsymbol{R}$ is equivalent either to $\boldsymbol{k}$ or to $-\boldsymbol{k}$, transforms any magnetic ordered configuration described by Eq. (15) with a set of amplitudes $\{S_i(\boldsymbol{k}),S_i(-\boldsymbol{k})\}$ into a new one, described by the same equation and polarization vectors $\sigma_i(\mu)$ but with new transformed amplitudes $\{S'_i(\boldsymbol{k}),S'_i(-\boldsymbol{k})\}$ given by:

$$\begin{pmatrix} S'_1(\boldsymbol{k}) \\ \dots \\ S'_N(\boldsymbol{k}) \\ S'_1(-\boldsymbol{k}) \\ \dots \\ S'_N(-\boldsymbol{k}) \end{pmatrix} = \boldsymbol{T}(\boldsymbol{R},\theta\,|\,\boldsymbol{t}) \begin{pmatrix} S_1(\boldsymbol{k}) \\ \dots \\ S_N(\boldsymbol{k}) \\ S_1(-\boldsymbol{k}) \\ \dots \\ S_N(-\boldsymbol{k}) \end{pmatrix}, \tag{16}$$

where $\boldsymbol{T}(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ is a $2N\times 2N$ matrix describing the operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ within the $\{\boldsymbol{k},-\boldsymbol{k}\}$ subspace of the irrep *T*. For instance, in the simple case of a lattice translation $(1\,|\,\boldsymbol{t})$, the matrix $\boldsymbol{T}$ will be of the form:

$$\boldsymbol{T}(1\,|\,\boldsymbol{t}) = \begin{pmatrix} \boldsymbol{1}\cdot e^{i2\pi\boldsymbol{k}\cdot\boldsymbol{t}} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{1}\cdot e^{-i2\pi\boldsymbol{k}\cdot\boldsymbol{t}} \end{pmatrix}, \tag{17}$$

where $\boldsymbol{1}$ and $\boldsymbol{0}$ represent the N-dimensional identity and null matrices, respectively. According to the definition of superspace symmetry introduced in Section II (see Eq. 4), only the operations that keep the order parameter within this limited subspace of two opposite vectors ($\boldsymbol{k}$ and $-\boldsymbol{k}$) may be part of the superspace group. They form, in general, a subgroup of the paramagnetic grey space group that we shall call *extended* little group of $\boldsymbol{k}$, $\Omega_{p,k,-k}$. If the paramagnetic grey space group is non-polar, the extended little group $\Omega_{p,\boldsymbol{k},-\boldsymbol{k}}$ can always be decomposed into two cosets:

$$\Omega_{p,\boldsymbol{k},-\boldsymbol{k}} = \Omega_{p,\boldsymbol{k}} + g_{-\boldsymbol{k}}\Omega_{p,\boldsymbol{k}}, \tag{18}$$

with $\Omega_{p,\boldsymbol{k}}$ being the so-called little group that includes all operations keeping $\boldsymbol{k}$ invariant (up to a reciprocal lattice translation), while the coset $g_{-\boldsymbol{k}}\Omega_{p,\boldsymbol{k}}$ includes an equal number of operations transforming $\boldsymbol{k}$ into $-\boldsymbol{k}$. If the grey group is a polar group, the second coset may not exist and the extended little group coincides in this case with the little group $\Omega_{p,\boldsymbol{k}}$. A phase shift α of the spin wave, of the type discussed in Section II, is given by a simple phase factor for the amplitudes $\{S_i(\boldsymbol{k}), S_i(-\boldsymbol{k})\}$ so that they become $\{e^{i\alpha}S_i(\boldsymbol{k}), e^{-i\alpha}S_i(-\boldsymbol{k})\}$. Therefore, a superspace operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t},\tau)$ exists for a spin configuration {$S_i(\boldsymbol{k})$, $S_i(\boldsymbol{-k})$} described by Eq. (15), if a real value τ can be found such that:

$$\begin{pmatrix} \boldsymbol{S}(\boldsymbol{k}) \\ \boldsymbol{S}(-\boldsymbol{k}) \end{pmatrix} = \begin{pmatrix} \boldsymbol{1}\cdot e^{i2\pi\tau} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{1}\cdot e^{-i2\pi\tau} \end{pmatrix} \cdot T(\boldsymbol{R},\theta\,|\,\boldsymbol{t}) \cdot \begin{pmatrix} \boldsymbol{S}(\boldsymbol{k}) \\ \boldsymbol{S}(-\boldsymbol{k}) \end{pmatrix} \tag{19}$$

Here $\boldsymbol{S}(\boldsymbol{k})$ and $\boldsymbol{S}(\boldsymbol{-k})$ represent the ordered set of complex amplitudes $\{S_1(\boldsymbol{k}),....,S_N(\boldsymbol{k})\}$ and their complex conjugate $\{S_1(-\boldsymbol{k}),....,S_N(-\boldsymbol{k})\}$. This means that the transformation of the spin configuration by the operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ is compensated by a phase shift τ such that the spin configuration is kept invariant.

The invariance equation (19) can be used to derive all possible different superspace symmetries resulting from the condensation of all possible types of single-k magnetic orderings described by a single irrep. For the case of non-magnetic distortions this problem was discussed in [15,16,17,18]. In Ref. 18, the set of all possible superspace groups with a single independent incommensurate modulation wave vector and resulting from a single active irrep were calculated. These superspace groups are obtained as so-called *isotropy subgroups* of the continuous symmetry group associated with the parent structure by adding to the conventional space group operations the continuous set of global phase shifts of the modulation. A complete list of these *isotropy* superspace groups can be found in the ISOTROPY webpage [24]. The generalization of this list to the case of a magnetic

order parameter is straightforward. The possible (3+1)-dim magnetic superspace groups resulting from a magnetic ordering with symmetry properties given by a single irrep can be easily derived from those already listed in Ref. 24, as will be shown below.

In the magnetic case the essential difference is that for each space group operation $(\boldsymbol{R}\,|\,\boldsymbol{t})$, we have to consider two distinct operations $(\boldsymbol{R},-1\,|\,\boldsymbol{t})$ and $(\boldsymbol{R},+1\,|\,\boldsymbol{t})$, distinguishing if the operation includes time reversal or not. The symmetry operations of the paramagnetic phase are thus trivially doubled, with its magnetic space group Ω_p being given by:

$$\Omega_p = G_p + (1'|0\ 0\ 0)G_p\ , \tag{20}$$

where G_p is the ordinary space group of this phase, with operations of type $(\boldsymbol{R},+1\,|\,\boldsymbol{t})$, while the coset $(1'|0\ 0\ 0)G_p$ is constituted by an equal number of operations $(\boldsymbol{R},-1\,|\,\boldsymbol{t})$. It is important to note that the antiunitary properties of the operations in this second coset [25] are irrelevant when working with real quantities such as the atomic magnetic moments. For our purposes, we can then consider ordinary physically irreducible representations (irreps) of the group Ω_p to describe the transformation properties of a configuration of magnetic moments or of atomic displacements. The irreps of Ω_p are trivially related with those of G_p: for each irrep of G_p two irreps of Ω_p exist, one associating the identity matrix $\boldsymbol{1}$ to time reversal, and the other the matrix $-\boldsymbol{1}$. As, by definition, time reversal changes the sign of a magnetic moment, the irreps describing the transformation properties of a spin configuration must correspond to this second type. Therefore, given an irrep T of the paramagnetic space group G_p, it is important to distinguish the two corresponding irreps of Ω_p, depending on being even or odd for time reversal. In the following, we shall call them non-magnetic and magnetic irreps, with explicit generic labels T and mT, following the

notation employed in ISODISTORT [26]. For a magnetic irrep, the matrices in Eq. (19) for the operations $(\boldsymbol{R},-1\,|\,\boldsymbol{t})$ and $(\boldsymbol{R},+1\,|\,\boldsymbol{t})$ are trivially related by inversion, $m\boldsymbol{T}(\boldsymbol{R},-1\,|\,\boldsymbol{t})=-m\boldsymbol{T}(\boldsymbol{R},+1\,|\,\boldsymbol{t})$, while they are equal for the corresponding non-magnetic irrep. This implies that the possible magnetic isotropy superspace groups resulting from a magnetic ordering transforming according to a certain magnetic irrep can be readily derived from the non-magnetic isotropy superspace groups associated with the corresponding non-magnetic irrep (see next Section).

For a magnetic irrep *mT*, the matrix $m\boldsymbol{T}(\boldsymbol{R})$ in Eq. (19) that is associated with the operation $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ belonging to $\Omega_{p,\boldsymbol{k}}$ can be expressed as:

$$\begin{pmatrix} \theta\ \boldsymbol{D}_T(\boldsymbol{R})e^{i2\pi\boldsymbol{k}.\boldsymbol{t}} & \boldsymbol{0} \\ \boldsymbol{0} & \theta\ \boldsymbol{D}_T^*(\boldsymbol{R})\exp^{-i2\pi\boldsymbol{k}.\boldsymbol{t}} \end{pmatrix} \tag{21}$$

with $\boldsymbol{D}_T(\boldsymbol{R})$ denoting a $N\times N$ matrix associated with $\boldsymbol{R}$. The operation $\boldsymbol{R}$ belongs to the so-called little co-group, a point group formed by all point-group operations present in the elements of the little group $\Omega_{p,\boldsymbol{k}}$. The matrices $\boldsymbol{D}_T(\boldsymbol{R})$ form, in general, a *projective* irreducible representation of the little co-group [27], which fully determines both irreps *T* and *mT*. The $N\times N$ matrices $\theta\ \boldsymbol{D}_T(\boldsymbol{R})e^{i2\pi\boldsymbol{k}.\boldsymbol{t}}$ form an irrep of the little group $\Omega_{p,\boldsymbol{k}}$ (*small irrep*), which is sufficient to generate the full irrep *mT*. Except for incommensurate wave vectors at the border of the Brillouin zone in non-symmorphic space groups, the representation $\boldsymbol{D}_T(\boldsymbol{R})$ is an ordinary irreducible representation of the little co-group [27]. The magnetic character of the irrep *mT* is taken into account by the factor θ multiplying the matrix $D_T(\boldsymbol{R})$ in Eq.(21), so that the matrices of the operations that include time reversal are just the opposite of the corresponding operation without time reversal. The first diagonal matrix block in Eq.(21) acts on the amplitudes $\{S_i(\boldsymbol{k})\}$, while the second

matrix block acts on their complex conjugates $\{S_i(-\boldsymbol{k})\}$. The two blocks are, by definition, related by complex conjugation.

In the case of the operations $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ that belong to the coset $g_{-\boldsymbol{k}}\Omega_{p,\boldsymbol{k}}$, the irrep matrices $m\boldsymbol{T}(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ are given by:

$$\begin{pmatrix} \boldsymbol{0} & \theta\ \boldsymbol{D}_T(\boldsymbol{R}')e^{i2\pi\boldsymbol{k}.\boldsymbol{t}} \\ \theta\ \boldsymbol{D}_T^*(\boldsymbol{R}')e^{-i2\pi\boldsymbol{k}.\boldsymbol{t}} & \boldsymbol{0} \end{pmatrix}, \tag{22}$$

where $\boldsymbol{D}_T(\boldsymbol{R}')$ is the $N\times N$ matrix associated by the projective irreducible representation $\boldsymbol{D}_T$ to the operation $\boldsymbol{R}'$ of the little co-group. The operation $\boldsymbol{R}'$ is defined as $\boldsymbol{R}\boldsymbol{R}_{-\boldsymbol{k}}^{-1}$, with $\boldsymbol{R}_{-\boldsymbol{k}}$ being the rotational part of the operation $g_{-\boldsymbol{k}}$ defined in Eq.18, such that for $(\boldsymbol{R},\theta\,|\,\boldsymbol{t}) = g_{-\boldsymbol{k}}$ the element $\boldsymbol{R}'$ is the identity[27]. The operation $g_{-\boldsymbol{k}}$ can be chosen in such a way that the matrices (22) are expressed in a basis that keeps the set $\{S_1(-\boldsymbol{k}),....,S_N(-\boldsymbol{k})\}$ as amplitudes in the $-\boldsymbol{k}$ subspace, with the same order as the one used in the $\boldsymbol{k}$ subspace.

For multidimensional small irreps ($N>1$), the solution of Eq. (19) depends in general on the specific direction taken by the N-dimensional vector $\{S_1(\boldsymbol{k}),....,S_N(\boldsymbol{k})\}$. Therefore, several different superspace symmetry groups are in principle possible for the same irrep. Each complex component of the vector $\{S_1(\boldsymbol{k}),....,S_N(\boldsymbol{k})\}$ has its own phase, while there is only a single global shift τ in Eq. (19) to play with. In general, not all operations of the extended little group $\Omega_{p,\boldsymbol{k},-\boldsymbol{k}}$ are maintained in the superspace group and each case has to be considered separately. Therefore, as we will see in the examples below, the specification of a given irrep, if its small irrep is not one-dimensional, is clearly insufficient to specify the symmetry of the incommensurate phase and the limitations of a representation analysis without additional symmetry considerations become evident.

On the other hand, for irreps with one-dimensional small irreps ($N=1$), there is a one-to-one relationship between a given irrep of the paramagnetic space group and a superspace group. For *N*=1, the matrices (21) and (22) are two dimensional and the spin wave amplitudes reduce to two complex conjugated components $\{S(\boldsymbol{k}), S(-\boldsymbol{k})\}$. In this case the values of $\boldsymbol{D}_T(\boldsymbol{R})$ in (21) are either +1 or -1 (note that we are considering physically irreducible representations), and therefore Eq. (19) is fulfilled for all operations $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ of $\Omega_{p,\boldsymbol{k}}$, with a phase shift $\tau=-\boldsymbol{k}\cdot\boldsymbol{t}$ if $\theta\cdot\boldsymbol{D}_T(\boldsymbol{R})=+1$ or $\tau=-\boldsymbol{k}\cdot\boldsymbol{t}+\frac{1}{2}$ if $\theta\cdot\boldsymbol{D}_T(\boldsymbol{R})=-1$. Hence, considering that $\tau_0=\tau+\boldsymbol{k}\cdot\boldsymbol{t}$, all the operations $(\boldsymbol{R},\theta\,|\,\boldsymbol{t})$ of $\Omega_{\mathrm{p,k}}$ will become part of the superspace group of the system, either as operations $\{\boldsymbol{R},\theta\,|\,\boldsymbol{t}\ 0\}$ or $\{\boldsymbol{R},\theta\,|\,\boldsymbol{t}\ \frac{1}{2}\}$. Similarly, the operations that transform $\boldsymbol{k}$ into $-\boldsymbol{k}$ (the coset $g_{-\boldsymbol{k}}\Omega_{p,\boldsymbol{k}}$) will also satisfy Eq. (19). This can be shown by considering the coset representative $g_{-\boldsymbol{k}}=(\boldsymbol{R}_{-\boldsymbol{k}},+1\,|\,\boldsymbol{t})$, for which $\boldsymbol{D}_T(\boldsymbol{R}')=1$ in Eq. (22). In this case, it is obvious that Eq. (19) is satisfied if $\tau=-\boldsymbol{k}\cdot\boldsymbol{t}+2\phi$, where ϕ is the phase of the complex amplitude $S(\boldsymbol{k})$. Hence, $\{\boldsymbol{R}_{-\boldsymbol{k}},+1\,|\,\boldsymbol{t}\ 2\phi\}$ is a superspace group operation of the system. Consequently, the group structure and the decomposition (18) guarantee that all elements of $g_{-\boldsymbol{k}}\Omega_{p,\boldsymbol{k}}$ will be maintained as elements of the isotropy superspace group. For instance, if $g_{-\boldsymbol{k}}$ is the space inversion $(\bar{1}\,|\,0\ 0\ 0)$, the corresponding superspace operation will be $\{\bar{1}\,|\,0\ 0\ 0\ 2\phi\}$.

For an incommensurate propagation vector $\boldsymbol{k}$ the phase ϕ of $S(\boldsymbol{k})$ is arbitrary and can always be chosen as zero by a convenient choice along the internal space x_4. With such a choice, the operation $\{\boldsymbol{R}_{-\boldsymbol{k}},+1\,|\,\boldsymbol{t}\ 2\phi\}$ becomes $\{\boldsymbol{R}_{-\boldsymbol{k}},+1\,|\,\boldsymbol{t}\ 0\}$. This result has an important consequence for the case of multiferroics. It implies that an incommensurate irrep with a one-dimensional small irrep will never break the magnetic point group associated with the extended little group of $\boldsymbol{k}$, $\Omega_{p,\boldsymbol{k},-\boldsymbol{k}}$. If the paramagnetic space group contains the space

inversion, this symmetry operation will necessarily be maintained by the magnetic ordering, if this is described by a single propagation vector and an irrep with a 1-dim small representation. More generally, if the paramagnetic phase is non-polar, then such a magnetic ordering can never yield a polar phase.

Even in the simple case of 2-dim irreps where, as shown above, a one-to-one correspondence exists between irreps and superspace groups, there are fundamental differences between representation and superspace symmetry analyses. These differences stem essentially from the fact that conventional representation analysis only takes into account the small irreps, and is therefore limited to the symmetry operations that belong to the little group $\Omega_{p,\boldsymbol{k}}$, [11]. However, all the symmetry operations of the extended little group $\Omega_{p,\boldsymbol{k},-\boldsymbol{k}}$ are relevant and induce restrictions upon the magnetic ordering. This means that a fully consistent description in terms of irrep basis modes would require to account for the symmetry constraints that originate in the operations of the coset $g_{-\boldsymbol{k}}\Omega_{p,\boldsymbol{k}}$, a point that has been usually overlooked, except in some recent publications[12,13,14,28]. The extension of the usual representation method in these works was mainly motivated by the need to rationalize the symmetry properties of multiferroic materials. However, this type of extension is relevant for all incommensurate magnetic structures.

IV. SYMMETRY FOR TIME REVERSAL COMBINED WITH A PHASE SHIFT OF THE MODULATION

Knowing that any magnetic irrep associates the inversion matrix $-\boldsymbol{1}$ to the time reversal operation $(1'|0\ 0\ 0)$, it is obvious from Eq. (19) that the operation $(1'|000,\frac{1}{2})$ will necessarily belong to the superspace group of a single-k incommensurate magnetic modulation. This general and rather trivial result is a simple consequence of the sinusoidal

character of any magnetic arrangement with a single propagation vector, and transforming according to a single irrep of any dimension. It is clear that for a sinusoidal wave, a phase shift of π changes the sign of all local magnetic moments. Therefore, the combined operation of this phase shift with time reversal necessarily keeps the system invariant. Despite the simplicity of this result, it has important consequences. It implies that the possible superspace group Ω^s of the system can be expressed as:

$$\Omega^s = G^s + \left(1'|\, 000, \tfrac{1}{2}\right) G^s \,, \tag{23}$$

where G^s is a superspace group formed by all the operations $(\boldsymbol{R}, +1\,|\,\boldsymbol{t}, \tau)$ that satisfy the invariance equation (19). The possible superspace groups G^s in Eq. (23) are those calculated in Ref.18 and listed in Ref. 24 for non-magnetic irreps. From Eq. (23), their magnetic counterparts can be trivially derived.

The consequences of the ubiquitous presence of the operation $\left(1'|\, 000, \tfrac{1}{2}\right)$ in the superspace symmetry of any single-k sinusoidal magnetic incommensurate phase are simple, and very restrictive. As seen from Eq. (5) and Eq.(6), such an operation implies that the spin modulations are constrained to odd order Fourier terms, while structural modulations are limited to terms of even order, consistently with the extinction rules discussed in Section IIB. This implies that, if the magnetic modulation becomes anharmonic within the same phase, only odd magnetic harmonics should appear (otherwise the symmetry will be further broken), while the coupling with the lattice can only produce structural modulations with even terms, i.e. with $2\boldsymbol{k}$ as primary modulation vector. This is a rather well known property of many incommensurate magnetic modulations (see the example of chromium below), whose origin and validity limits are fully grasped when derived from the superspace symmetry properties of the modulation.

The symmetry operation $(1'|000,\frac{1}{2})$ also implies that the magnetic point group of the phase includes the time reversal operation. Therefore, single-k incommensurate phases originated from a single irrep can never be ferromagnetic (or ferrotoroidic) , i.e. no magnetization (or ferrotoroidal moment) can appear as an induced secondary weak effect. This result, which can be considered part of the above mentioned restriction of the magnetic configuration to odd-harmonics, illustrate a fundamental advantage of using superspace symmetry concepts. Assigning a superspace symmetry for the magnetic structure not only defines the symmetry constraints existing in the first harmonic of the magnetic modulation, but also consistently introduces all the constraints existing for any other degree of freedom of the system.

There has been in the previous literature on magnetic superspace groups [1,5,8] some confusion about the significance of the operation $(1'|000,\frac{1}{2})$. The observed magnetic modulation is often limited to a single harmonic, and its coupling with the lattice can be neglected. In such a case, one can reduce the description of the magnetic arrangement to a sinusoidal magnetic spin wave, which trivially complies with the constraints imposed by the operation $(1'|000,\frac{1}{2})$. Therefore, when the model is limited to the first harmonic, one can be tempted to consider that the transformation $(1'|000,0)$ is equivalent to the transformation $(1|000,\frac{1}{2})$. Under this viewpoint, the superspace groups $Pn'2_1m'(0\beta0)$ and $Pn2_1m(0\beta0)s0s$ were considered in Ref.5 equally valid to describe the symmetry of a particular incommensurate magnetic phase with a sinusoidal modulation, because operations such as $(m'_z|000,0)$ and $(m_z|000,\frac{1}{2})$ were considered undistinguishable. However, these two symmetries are not equivalent when taken as comprehensive symmetry elements of the system, because they imply quite different constraints upon other degrees of freedom. For instance, crystal tensor properties related with magnetism

would be quite different. In the first case, with the magnetic point group $m'2m'$, a ferromagnetic component along *y* would be allowed, while it would be forbidden for the second symmetry (with the point group $m2m$). The correct approach is therefore to consider the two operations as distinct members of the superspace group of the system. The correct superspace group is therefore $Pn2_1m1'(0\beta0)s0ss$ which, in terms of a coset expansion can be expressed as:

$$Pn2_1m1'(0,\beta,0)s0ss = Pn2_1m(0,\beta,0)s0s \; + \; (1'|000,\tfrac{1}{2})Pn2_1m(0,\beta,0)s0s, \qquad (24)$$

in agreement with the general expression (23). The magnetic point group of the system is therefore *m2m1´*, a symmetry that forbids ferromagnetism. Notice that although a standard notation for magnetic superspace groups does not exist, the notation adopted here is a natural extension of the well-established rules for non-magnetic superspace groups[3, 29].

V. SOME ILLUSTRATIVE EXAMPLES

A. The simplest case: a centrosymmetric incommensurate modulation

Let us consider a paramagnetic phase with space group $P\bar{1}$, so that its magnetic group is $P\bar{1}1'$. Let us suppose that the system transforms into a magnetic phase with an incommensurate propagation vector (α,β,γ) along an arbitrary direction and is driven by a single active irrep. The little group $\Omega_{p,k}$ is limited to $P11'$, and therefore only one magnetic small irrep exists, with character +1 and -1 for the identity and time reversal, respectively. According to the general rules discussed above, the inversion centre will be maintained in the incommensurate structure and its superspace group can be labelled as $P\bar{1}1'(\alpha\beta\gamma)0s$, its representative operations being (besides the 4-dim lattice translations)

$\{1|0000\}$, $\{\bar{1}|0000\}$, $\{1'|000\frac{1}{2}\}$ and $\{\bar{1}'|000\frac{1}{2}\}$, which in the notation of the symmetry cards used in JANA2006 (Ref.6) can be expressed as (x_1 x_2 x_3 x_4 m), (-x_1 -x_2 -x_3 -x_4 m), (x_1 x_2 x_3 x_4+½ -m) and (-x_1 -x_2 -x_3 -x_4+½ -m). This is an obvious notation indicating unambiguously the linear transformations in the four-dimensional basis explained in Section II.

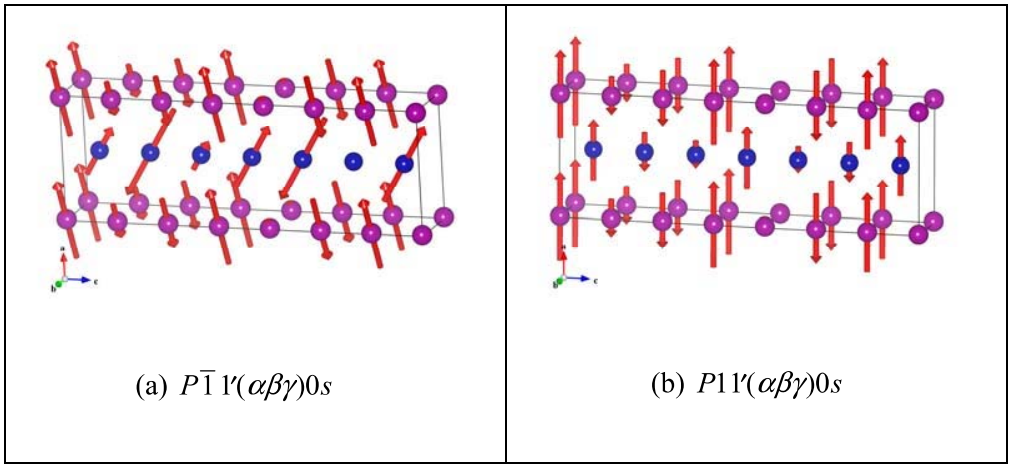
The spin modulations $\boldsymbol{M}_{\mu}(x_4)$ of all magnetic atoms are restricted to odd Fourier terms due to the operation $\{1'|000\frac{1}{2}\}$, while any possible spin-lattice coupling can only induce structural modulations $\boldsymbol{u}_{\mu}(x_4)$ with even Fourier terms. The inversion operation $\{\bar{1}|0000\}$ restricts further the modulations of those atoms lying on special positions of the paramagnetic structure. According to Eq. (5) and Eq.(6), the Fourier series (see Eq. (2)) describing the spin modulations for atomic sites with inversion symmetry (Wyckoff positions 1a, 1b,…, 1h) can only have cosine terms, while the Fourier series of the induced structural modulations can only include sine terms. In addition, the modulation functions for an atom in a general position (*x,y,z*), say atom 1, determines the modulation of its symmetry related (-*x,-y,-z*), say atom 2, according to the relations:

$$\boldsymbol{M}_2(-x_4) = \boldsymbol{M}_1(x_4) \tag{25}$$

$$\boldsymbol{u}_2(-x_4) = -\boldsymbol{u}_1(x_4) \tag{26}$$

This implies that the corresponding Fourier components (see Eq. 2) must be related in the form $M_{2,ns} = -M_{1,ns}$, $M_{2,nc} = M_{1,nc}$ (n-odd) and $u_{2,ns} = u_{1,ns}$, $u_{2,cs} = -u_{1,nc}$ (n-even), the sub-indexes *s* and *c* indicating the sine and cosine Fourier amplitudes, respectively.

As the global phase of the modulation in an incommensurate phase is arbitrary, the above discussion restricting the modulations of atoms at centrosymmetric sites to cosine or sine terms may be misleading. In fact, we have made a specific choice for this arbitrary phase,



(a) $P\bar{1}\,1'(\alpha\beta\gamma)0s$ (b) $P1\,1'(\alpha\beta\gamma)0s$

FIG 1. Examples of magnetic structures keeping (a) and breaking (b) centrosymmetry, showing that collinearity of all spin waves is not necessary for keeping the inversion centre. A triclinic $P\bar{1}$ structure with different magnetic atoms at sites (000) and $(½½½)$ and propagation vector (0 0 0.32) is considered in both cases. In case (a), the spin modulations in both atoms are in phase and the superspace group maintains the space inversion operation. In case (b), despite being collinear, the magnetic modulation of both atoms are phase shifted and the inversion symmetry is broken. The labels of the superspace symmetries corresponding to each case are indicated.

by choosing the origin along the internal coordinate x_4 in such a way that the internal translation τ of the operation $\{\bar{1}\,|\,0000\}$ is zero (see Section III). This simplifies the modulation functions to cosine or sine terms and Eq. (25) and (26) also become simpler. The modulation feature that is independent of the origin choice is the fact that the modulation functions for all atoms at special positions must be in phase (see FIG. 1), and that the possible induced structural modulations (only even Fourier terms) are necessarily shifted by $\frac{\pi}{2}$ or $-\frac{\pi}{2}$ with respect to the magnetic modulation.

As shown in FIG. 1, the breaking of space inversion by an incommensurate modulation is sometimes difficult to visualize. If, for example, the system has several independent magnetic atomic sites in the paramagnetic phase, the restrictions that keep the inversion

symmetry do not necessarily imply a collinear magnetic ordering. Superspace formalism automatically clarifies all the structural details of this type.

It is illustrative to compare the superspace description of this simple example with the one derived from a standard representation analysis, as done for instance, via the computer tool BasiReps in FullProf [11], or other similar programs [30, 31]. These programs would introduce for this case no constraint on the possible magnetic sinusoidal modulations of atoms at special positions, and propose independent modulations for any pair of atoms related by inversion, so that the inversion symmetry is in general broken. Therefore, a general modulation, without any symmetry, is considered as default basis for the description of the magnetic configuration. This basis obviously does not have the transformation properties for space inversion demanded for a modulation fully symmetry-adapted to the irrep. This is due to the fact that this type of programs only considers the little group of $\boldsymbol{k}$, i.e. the operations that keep invariant the wave vector, and not those interchanging $\boldsymbol{k}$ and $-\boldsymbol{k}$. But, in this example, the only symmetry condition forced on the modulation comes from this second type of symmetry operation.

The disregard of the symmetry operations interchanging $\boldsymbol{k}$ and $-\boldsymbol{k}$ is a general flaw of the representation analysis methodology, as it is nowadays being used for the case of incommensurate structures. Atoms belonging to the same Wyckoff orbit in the paraelectric phase, but only related by operations that transform $\boldsymbol{k}$ into $-\boldsymbol{k}$ are considered to be splitted into independent orbits in the magnetic phase even if the magnetic mode corresponds to a single irrep. This assumption is in general not correct and is presently a practical limitation of these programs, which could be easily avoided if their symmetry-adapting process of the basis functions were extended to include the operations interchanging the two opposite wave vectors. If superspace symmetry is used, as this example shows, all symmetry conditions on the magnetic modulation coming from the

irrep are taken into account automatically. The resulting symmetry constraints on the structure become obvious.

In this example there is only one possible irrep. Therefore, any spin configuration for a given propagation vector will be described in general as a sum of spin waves transforming according to the same unique irrep. This seems somewhat paradoxical with the fact discussed above that a modulation transforming according to this irrep includes some restrictions on its form. This paradox is solve by the fact that a spin wave of arbitrary form without any symmetry restriction requires the simultaneous presence of at least two spin modulations with the same irrep symmetry but having some relative arbitrary phase shift. For a magnetic modulation transforming according to a single irrep, the operation $\{\bar{1}\,|\,0000\}$ will be part of the superspace group once the origin along the internal space is conveniently chosen, but a second spin wave will in general be phase shifted, say by ϕ, and therefore, for the same x_4 origin, its inversion symmetry operator will be $\{\bar{1}\,|\,000\ 2\phi\}$. Hence, the global configuration that includes both spin waves necessarily loses inversion symmetry, maintaining however the operation $\{1'|000\tfrac{1}{2}\}$. The resulting symmetry can therefore be labelled as $P11'(\alpha\beta\gamma)0s$, and no restriction on the global form of the spin wave will exist, except the restriction to odd Fourier terms. This scenario corresponds to the condensation in the magnetic phase of two distinct and independent magnetic order parameters, associated with two spin waves with the same propagation vector and the same irrep.

This simple example seems to be realized in the compound $FeVO_4$, [32]. This material has a paramagnetic phase with space group $P\bar{1}$, and exhibits at low temperatures two subsequent incommensurate magnetic phases with a propagation vector along an arbitrary direction. The first phase is non-polar, while the second one exhibits some spontaneous electric polarization. This would correspond to a transition sequence:

$$P\bar{1}\,1' \;\rightarrow\; P\bar{1}\,1'(\alpha,\beta,\gamma)0s \;\rightarrow\; P1\,1'(\alpha,\beta,\gamma)0s$$

where the inversion centre is lost and the appearance of ferroelectricity happens in the second transition, with the condensation of a second magnetic order parameter. In Ref. 32, the intermediate phase was reported as having a magnetic configuration without inversion symmetry (despite exhibiting no induced polarization), but it seems that the phase relations between the inversion-related Fe atoms that were used to check the presence of inversion symmetry were not those explained above [33]. Therefore the most reasonable scenario remains the chain of symmetry breaks depicted above with the inversion centre of the magnetic point group being broken in the second transition.

B. The incommensurate phase of $CaFe_4As_3$

This metallic compound is orthorhombic with symmetry *Pnma* at room temperature [34]. Two magnetic phases at low temperature have been reported [35]. A first phase below 90 K (phase ICM) is incommensurate with $\boldsymbol{k} = (0\beta0)$ with $0.375 < \beta < 0.39$, while below 26 K the propagation vector locks into the commensurate value $\beta = 3/8 = 0.375$ (phase CM). The first transition has been identified with the condensation of a magnetic mode with symmetry given by the irrep $m\Delta_1$, and a centrosymmetric magnetic point group has been assigned to the ordered phase [35]. The star of this irrep has two wave vectors. Its corresponding small irrep is 1-dim and is defined by the irrep of the little co-group having characters equal to +1 for all its operations without time reversal (and -1 for time reversal). According to the rules explained in Sections III and IV, a magnetic ordering according to this irrep implies a superspace symmetry that can be labelled as $Pnma1'(0\beta0)000s$, and is described in detail in Table I. The paramagnetic structure of $CaFe_4As_3$ has four independent Fe atoms at Wyckoff positions 4c (x ¼ z). These sites are invariant by the

TABLE I. Representative operations of superspace group $Pnma1'(0\beta0)000s$ described by using the generalized Seitz type symbol explained in the text (left column) and symmetry cards of the type used in the program JANA2006 (Ref.6). The operations with time reversal are obtained by multiplying the first eight operations by $\{1'|000\frac{1}{2}\}$, as indicated symbolically in the last row.

$\{1\|0000\}$	x_1	x_2	x_3	x_4	$+m$
$\{2_x\|\frac{1}{2}\frac{1}{2}\frac{1}{2}0\}$	$x_1+½$	$-x_2+½$	$-x_3+½$	$-x_4$	$+m$
$\{2_y\|0\frac{1}{2}00\}$	$-x_1$	$x_2+½$	$-x_3$	x_4	$+m$
$\{2_z\|\frac{1}{2}0\frac{1}{2}0\}$	$-x_1$+½	$-x_2$	$x_3+½$	$-x_4$	$+m$
$\{\bar{1}\|0000\}$	$-x_1$	$-x_2$	$-x_3$	$-x_4$	$+m$
$\{m_x\|\frac{1}{2}\frac{1}{2}\frac{1}{2}0\}$	$-x_1+½$	$x_2+½$	$x_3+½$	x_4	$+m$
$\{m_y\|0\frac{1}{2}00\}$	x_1	$-x_2+½$	x_3	$-x_4$	$+m$
$\{m_z\|\frac{1}{2}0\frac{1}{2}0\}$	$x_1+½$	x_2	$-x_3+½$	x_4	$+m$
$\{1'\|000\frac{1}{2}\}$	x_1	x_2	x_3	$x_4+½$	$-m$
	... $\times\{1'\|000\frac{1}{2}\}$				

operation $(m_y|0\frac{1}{2}0)$. By considering Eq. (5) for the case of the superspace operation $\{m_y|0\frac{1}{2}00\}$, one can then conclude that the magnetic modulation functions of the four Fe independent atoms are forced to satisfy:

$$M_x(-x_4)=-M_x(x_4),\ M_y(-x_4)=M_y(x_4),\ M_z(-x_4)=-M_z(x_4) \qquad (27)$$

This means that components x and z of the modulation can only have sine terms in their Fourier series, while only cosine terms are allowed for the y component. According to the experiments, the magnetic modes are aligned along the y-axis. Consequently, assuming only a *single* magnetic spin wave corresponding to the irrep $m\Delta_1$, the modulation functions $(M_x(x_4),M_y(x_4),M_z(x_4))$ for the four independent Fe-atoms should be of the form $\left(0,M^i_{y,1c}\cos(2\pi x_4),0\right)$, with i=1,2,3,4 labelling the four independent atoms. Only four

parameters are therefore necessary to describe the magnetic structure. As in the previous case, the fundamental symmetry constraint is not the limitation to cosine functions of the spin modulation, which is due to a convenient choice of the global arbitrary phase of the magnetic modulation, but the fact that the modulation functions of the four Fe atoms should be in phase. An arbitrary phase shift between these atoms would mean to add four independent $m\Delta_1$ modes, their sum having transformation properties different from those of a single irrep $m\Delta_1$.

Eq. (5) also determines for each of the four Wyckoff orbits the modulation functions of the symmetry related atoms. This is summarized in Table II. The modulation functions for the atoms related by either the glide plane perpendicular to the x direction or the z direction have opposite modulation functions, while the atoms related by the screw binary axis along y have the same modulation function.

It is once again illustrative to compare this result with the one coming from the conventional representation analysis, as implemented in [11,30,31]. The last column in Table II indicates the restrictions of the spin modulations for any of the four independent Wyckoff orbits of Fe atoms introduced in Ref. 35 as allegedly adapted to a magnetic spin wave induced by a single irrep $m\Delta_1$. The appearance in the mode description of the phase shift $\frac{\beta}{2}$ for the atoms having different positions along the y direction is only a minor nuisance caused by the different parameterization of the modulations, which uses the argument $\boldsymbol{k}\cdot\boldsymbol{l}$ instead of the argument $\boldsymbol{k}\cdot(\boldsymbol{l}+\boldsymbol{r}_\mu)$ adopted in the superspace formalism (see Section II). If this latter were used, this phase shift would disappear and, more importantly, the definition of the modulation functions would become independent of the choice of the "zero" cell. However, the real important difference between the two descriptions resides in the free relative phases Φ_i between the modulations of the four independent Fe atoms that are

included in this standard representation mode description. This would imply the need of seven parameters for describing the structure: four real amplitudes for the four independent Fe sites, and three phases, as one of them could be arbitrarily chosen to be zero. In contrast, as shown in Table II, the superspace analysis shows that the number of free parameters is only four, namely the amplitudes of the four independent modulation functions, since the four modulations of the four Wyckoff orbits are constrained to be in phase. Again, as in the previous example, this difference occurs because the conventional representation analysis method disregards the irrep transformation property associated with the operations interchanging $\boldsymbol{k}$ and $-\boldsymbol{k}$. In the present case, the Fe sites are invariant for one of these operations, namely $\{m_y|0\tfrac{1}{2}00\}$, which forces their modulations to be in phase. Therefore, the model for the magnetic structure refined in Ref. 35 does not include any symmetry restriction coming from the mirror plane m_y. This forces the actual magnetic point group of the reported refined model to be $m2m1'$, i.e. a polar symmetry along *y*, rather than the $mmm1'$ point group symmetry that was assumed in the theoretical considerations of that article. The superspace group encompassing the symmetry properties of the magnetic structure reported in that article is, in fact, $Pn2_1a1'(0\beta0)000s$.

Therefore, inadvertently, the magnetic structural model proposed in Ref. 35 for the incommensurate phase of $CaFe_4As_3$ is a non-centrosymmetric one. It is interesting to see then how large are the deviations of the refined model from the actual symmetry constraints of a *single* $m\Delta_1$ mode structure or, equivalently, the centrosymmetric superspace group symmetry $Pnma1'(0\beta0)000s$. The reported refined phases are $\Phi_2 = 0.14(3)$, $\Phi_3 = 0.45(3)$, $\Phi_4 = 0.01(4)$, with the choice $\Phi_1 = 0$. As seen, the deviations from the "symmetric" values 0 or ½ are very small in all cases, close to their standard deviations, except for phase Φ_2.

TABLE II. Relation among the modulation functions $M_y(x_4)$ of the magnetic moments along the y direction for the atoms of a Wyckoff orbit *4c* within the superspace group $Pnma1'(0\beta0)000s$. In the fourth column, the modulation functions considered in Ref.35 are shown for comparison. β is the y-component of the incommensurate propagation vector $\boldsymbol{k} = (0\beta0)$ and $\boldsymbol{l}$ stands for a lattice vector of the basic structure that labels a particular unit cell.

Superspace operation	*Position in the basic structure*	$M_y(x_4)$	$M_y(\boldsymbol{k}\cdot\boldsymbol{l})$
$\{1\|0000\}$	*atom 1*: x, ¼, z	$M^i_{y,1c}\cos(2\pi x_4)$	$M_i\cos[2\pi(\boldsymbol{k}\cdot\boldsymbol{l}+\Phi_i)]$
$\{2_y\|0\frac{1}{2}00\}$	*atom 2*: -x, ¾, -z	$M^i_{y,1c}\cos(2\pi x_4)$	$M_i\cos[2\pi(\boldsymbol{k}\cdot\boldsymbol{l}+\Phi_i+\frac{\beta}{2})]$
$\{m_z\|\frac{1}{2}0\frac{1}{2}0\}$	*atom 3*: $x+$½, ¼, -z+½	$-M^i_{y,1c}\cos(2\pi x_4)$	$-M_i\cos[2\pi(\boldsymbol{k}\cdot\boldsymbol{l}+\Phi_i)]$
$\{m_x\|\frac{1}{2}\frac{1}{2}\frac{1}{2}0\}$	*atom 4*: -x+½, ¾, z+½	$-M^i_{y,1c}\cos(2\pi x_4)$	$-M_i\cos[2\pi(\boldsymbol{k}\cdot\boldsymbol{l}+\Phi_i+\frac{\beta}{2})]$

This example corresponds to a 1-dim small irrep for the magnetic order parameter. As stressed above, in these cases there is a one-to-one correspondence between the irrep and the superspace group. The two methods would be equivalent for describing a sinusoidal magnetic modulation, if the representation analysis method were fully applied with the inclusion of the operations transforming $\boldsymbol{k}$ into $-\boldsymbol{k}$. In the case of multidimensional small irreps, however, the two approaches have much more fundamental differences, since the one-to-one correspondence between irreps and superspace groups disappears. Below we consider one simple example.

C. The modulated phases of Chromium

At high temperature, Chromium has a bcc structure with a space group $Im\bar{3}m$, and exhibits two distinct incommensurate modulated magnetic phases at lower temperatures (see [36, 37] and references therein). Below $T_{c1} \approx 311\,\mathrm{K}$, its magnetic moments become ordered (phase I) according to a transversal modulation with a propagation vector (00γ), and with γ decreasing smoothly from ≈ 0.96 to ≈ 0.95. The transversal modulation is

stable down to $T_{c2} \approx 122$ K, where the spin modulation, while keeping the direction of the propagation vector, becomes longitudinal (phase II). We shall discuss here the possible magnetic symmetries of these two incommensurate magnetic phases of Cr, and the constraints imposed upon their physical and structural properties.

Following the usual method of representation analysis [9,10,11], we first determine the magnetic irreps that can be involved in any magnetic configuration with a propagation vector (00γ) lying in the DT line of the Brillouin zone [38]. This implies to decompose the 3-dim magnetic representation T_M of the little group $I4mm1'$ of this wave vector into magnetic irreps of this space group. This decomposition leads to:

$$T_M = mDT4 + mDT5 \quad , \tag{28}$$

with the small irreps $mDT4$ and $mDT5$ having one and two dimensions, respectively. For reference, these irreps are defined in Table III with the irrep notation of ISOTROPY [24]. The irrep $mDT4$ describes the transformation properties of spin waves with spins oriented along *z*, i.e. longitudinal waves, while $mDT5$ describes transversal spin waves in the *xy* plane. Therefore $mDT4$ must be the active irrep for phase II, while phase I must be associated with irrep $mDT5$. We can determine the possible superspace symmetries associated with the condensation of each of these irreps, following the rules explained in the preceding sections. The little group of the propagation wave vector $\boldsymbol{k} = (00\gamma)$ is the subgroup $I4mm1'$ (of $Im\bar{3}m1'$). The irrep star has 6 arms, but we are only interested in single-k modulations, i.e. in (3+1)-dim isotropy superspace subgroups. In the present case, the extended little group $\Omega_{p,k,-k}$ is :

$$I4/mmm1' = I4mm1' + (\bar{1}\,|\,000)\, I4mm1' \tag{29}$$

TABLE III. Irreducible representations of the little co-group $4mm1'$, defining the two possible small magnetic irreps with a wave vector (00γ) of the magnetic space group $Im\bar{3}m1'$ (little group $I4mm1'$). As there is a one to one correspondence between them, for simplicity, we use the same label for the irreps of the little co-group, the corresponding small irreps of the little group, the irrep of the extended little group and the full irrep of the whole group.

	E	2_z	4_z	4_z^{-1}	m_x	m_y	m_{xy}	m_{-xy}	$1'$
$mDT4$	1	1	1	1	-1	-1	-1	-1	-1
$mDT5$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}-i&0\\0&i\end{pmatrix}$	$\begin{pmatrix}i&0\\0&-i\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&i\\-i&0\end{pmatrix}$	$\begin{pmatrix}0&-i\\i&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$

i) Phase II

Let us start with the simpler case of phase II, where the active irrep is the 2-dim irrep $mDT4$. According to the rules discussed in Section III, the determination of the corresponding superspace group is straightforward: all operations of $I4/mmm1'$, with the addition of a phase shift 0 or ½ along the internal space, are included in the superspace group. The shift ½ in the internal space will be necessary for the operations of the little group having character -1 for the irrep $mDT4$, plus their counterparts in the coset $(\bar{1}|000)\,I4mm1'$. Thus, the superspace group corresponding to the irrep $mDT4$ is $I4/mmm1'(00\gamma)00sss$, its generators being listed in Table IV. This result differs from the one that can be found in Ref.1, where it was also discussed as an example. The symmetry proposed there must be corrected. As mentioned in Section IV, this early work did not include the effect of the symmetry operation $\{1'|000\frac{1}{2}\}$.

The restrictions of the magnetic superspace symmetry corresponding to $mDT4$, both on the magnetic and positional structure of the compound, can be easily derived from Eq. (5). In the paramagnetic phase, the single atom per primitive cell is located at the origin and

according to Eq. (4), the modulation of its magnetic moment $\boldsymbol{M}(x_4) = (M_x(x_4), M_y(x_4), M_z(x_4))$ must satisfy the following relations:

$$\begin{aligned}
&(M_x(x_4), M_y(x_4), M_z(x_4)) = (-M_x(x_4), M_y(x_4), M_z(x_4)) \\
&(M_x(x_4 + ½), M_y(x_4 + ½), M_z(x_4 + ½)) = (M_x(x_4), -M_y(x_4), -M_z(x_4)) \\
&(M_x(-x_4), M_y(-x_4), M_z(-x_4)) = (M_x(x_4), M_y(x_4), M_z(x_4)) \\
&(M_x(x_4 + ½), M_y(x_4 + ½), M_z(x_4 + ½)) = (-M_x(x_4), -M_y(x_4), -M_z(x_4))
\end{aligned} \tag{30}$$

These four relations characterize the transformation properties of the spin wave under the action of each of the four generators of the group $\{4_z|0000\}, \{m_x|000\tfrac{1}{2}\}$, $\{\bar{1}|0000\}$ and $\{1'|000\tfrac{1}{2}\}$, respectively. They imply that the x and y components should vanish in all Fourier harmonics, while the z component is bounded to include in its Fourier decomposition just cosine odd terms:

$$M_z(x_4) = \sum_{n=odd} M_{zn} \cos(2\pi n x_4) \tag{31}$$

The modulation related to this superspace symmetry is therefore longitudinal, as expected from conventional representation analysis. But here we have obtained the additional information that additional odd-harmonics, with propagation vectors $n\boldsymbol{k}$ (n odd), are allowed as secondary induced spin waves, as long as they are in phase with the primary longitudinal spin wave of propagation vector $\boldsymbol{k} = (00\gamma)$. The modulation can therefore become anharmonic within phase II, but the symmetry constrains this anharmonicity to odd and in-phase harmonics. Third order magnetic satellites have been indeed observed in the magnetic phases of Cr, [36, 37, 39], indicating the existence of a significant third order harmonic in the spin modulation. Its existence can be understood as the result of symmetry-allowed energetic terms of type:

$$S^n(\boldsymbol{k})S(-n\boldsymbol{k}) + S^n(-\boldsymbol{k})S(n\boldsymbol{k}) \quad (n \text{ odd}), \tag{32}$$

which induce in equilibrium a non-zero amplitude of the n^{th} harmonic, $S(n\boldsymbol{k})$, proportional to the n^{th} power of the primary order parameter:

$$S(n\boldsymbol{k}) \propto S^n(\boldsymbol{k}) \quad (n \text{ odd}). \tag{33}$$

Eq. (33) also implies that the secondary anharmonic modulations must be in phase with the primary harmonic (see also Eq. (31)). Hence, the physical constraints on the possible anharmonic components of the spin modulation are automatically introduced by the assignment of the superspace group $I4/mmm1'(00\gamma)00sss$.

Similarly, one can obtain the possible form of the structural modulations induced through spin-lattice coupling. The displacive modulation $\boldsymbol{u}(x_4)$ of the atomic positions is restricted by the superspace symmetry to be along z with only even sine terms:

$$u_z(x_4) = \sum_{n=even} u_n^z \sin(2\pi n x_4) \tag{34}$$

Moreover, as this displacive modulation does not include a homogeneous term, the average position of the Cr atoms cannot change with respect to the paramagnetic phase. Indeed, second and fourth order satellites have been observed in the two magnetic phases of chromium [36, 37, 39], and ascribed to strain modulation produced by longitudinal atomic displacements. As in the previous case, they result from symmetry allowed linear couplings with powers of the primary harmonic order parameter. In this case, due to the requirement of time reversal invariance, these powers are restricted to even values, that is, only even harmonics in the modulation can be induced. Given that the global phase of the modulation is arbitrary, the restriction of the Fourier series (34) to sine functions should be considered in relation with Eq. (31). Together, the two equations express a constraint on

the relative phase shift between the displacive and the magnetic modulations: the induced displacive modulation must be shifted by $\frac{\pi}{2}$ or $-\frac{\pi}{2}$ with respect to the magnetic modulation. It is interesting to see in detail the physical origin of this phase shift that the superspace group introduces automatically. We can express a displacive modulation along z of the chromium atoms with wave vector $n\boldsymbol{k}$ (n even) in the form:

$$\mathbf{u}_n(\boldsymbol{l}) = Q(n\boldsymbol{k})\boldsymbol{e}_z e^{-i2\pi n\boldsymbol{k}.\boldsymbol{l}} + Q(-n\boldsymbol{k})\boldsymbol{e}_z e^{i2\pi n\boldsymbol{k}.\boldsymbol{l}} \quad (n \text{ even}), \tag{35}$$

where $\mathbf{u}_n(\boldsymbol{l})$ denotes the displacement of the Cr atom at the $\boldsymbol{l}^{th}$ unit cell, $\boldsymbol{e}_z$ a normalized displacement vector along z and $Q(-n\boldsymbol{k}) = Q(n\boldsymbol{k})^*$ the complex conjugate amplitudes of the n^{th} harmonic of the displacive modulation. These complex amplitudes $\left(Q(n\boldsymbol{k}),\ Q(-n\boldsymbol{k})\right)$ transform according to irrep DT1, with the inversion operation transforming it into $\left(-Q(-n\boldsymbol{k}),\ -Q(n\boldsymbol{k})\right)$. Irrep DT1 also describes the transformation properties of $(S^n(\boldsymbol{k}),\ S^n(-\boldsymbol{k}))$ for n-even (although in a different basis) such that the inversion operation transforms it into $(S^n(-\boldsymbol{k}),\ S^n(\boldsymbol{k}))$. Therefore, the following energy coupling term is symmetry allowed in the energy potential:

$$i\left(S^n(\boldsymbol{k})\,Q(-n\boldsymbol{k}) - S^n(-\boldsymbol{k})\,Q(n\boldsymbol{k})\right) \qquad (n \text{ even}), \tag{36}$$

This coupling implies a non-zero equilibrium value for $\left(Q(n\boldsymbol{k}),Q(-n\boldsymbol{k})\right)$ of the form:

$$Q(n\boldsymbol{k}) \propto i\,S^n(\boldsymbol{k}) \quad (n \text{ even}) \tag{37}$$

Therefore, for a primary magnetic modulation with zero initial phase (Eq. 31), the displacive modulation will be $u_{nz}(\boldsymbol{l}) = |Q(n\boldsymbol{k})|\sin(2\pi n\boldsymbol{k}.\ \boldsymbol{l})$, in accordance with Eq. (34). Note that even if Eq. (37) is an approximation, the predicted relative phase shift is symmetry forced and has general validity.

Let us consider other examples of how superspace symmetry automatically encompasses secondary degrees of freedom that can be present in the incommensurate magnetic phase. Equation (5) can be used to elucidate how the symmetry constrains a scalar modulation such as a charge or an occupational modulation. As can be readily derived, the superspace symmetry $I4/mmm1'(00\gamma)00ss$ restricts the Fourier series of these scalar fields to include only even cosine terms. Also, the assignment of the superspace group $I4/mmm1'(00\gamma)00sss$ to phase II of Cr implies establishing symmetry constraints to the crystal tensor properties, either magnetic or non-magnetic. In this case, as the point group symmetry corresponds to the centrosymmetric grey group $4/mmm1'$, ferromagnetism and linear magnetoelasticity and linear magnetoelectricity are forbidden.

ii) Phase I

We consider now the case of phase I, with the transversal spin modulation transforming according to $mDT5$. This irrep is four dimensional, and therefore gives freedom to define, according to Eq. (19), different directions in the irrep space and different superspace symmetries. The problem can be dealt with in mathematical terms, without the need to assign any specific microscopic meaning to the four components of the order parameter $(S_1(\boldsymbol{k}), S_2(\boldsymbol{k}), S_1(-\boldsymbol{k}), S_2(-\boldsymbol{k}))$. According to Eq. (21), the transformation properties of these components under an operation $(\boldsymbol{R},\theta|\boldsymbol{t})$ of the little group $I4mm1'$ are given by 4×4 matrices $T(\boldsymbol{R},\theta|\boldsymbol{t})$ of type:

$$\begin{pmatrix} T_{sm} & 0 \\ 0 & T_{sm}^{*} \end{pmatrix}, \tag{38}$$

where T_{sm} is the 2×2 matrix corresponding to the small irrep of mDT5 that is listed in Table III. The matrices associated to the operations of the coset $(\bar{1}|000)\,I4mm1'$ of the

extended little group can be readily obtained. Applying the rule of Eq. (22) to $g_{-\boldsymbol{k}} = \{2_y \mid 0000\}$, taken as coset representative, gives the following DT5 matrix:

$$T(2_y \mid 000) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \tag{39}$$

The matrices corresponding to the other operations transforming $\boldsymbol{k}$ into $-\boldsymbol{k}$ can be readily derived by multiplying the matrix (39) with the matrix of type (38) of the relevant operation in $I4mm1'$.

As the amplitudes for $\boldsymbol{k}$ and $-\boldsymbol{k}$ are related by complex conjugation, the order parameter is fully defined by the complex amplitudes for $\boldsymbol{k}$, $(S_1(\boldsymbol{k}), S_2(\boldsymbol{k})) = \left(S_1 e^{i2\pi\phi_1},\ S_2 e^{i2\pi\phi_2}\right)$. Knowing the transformation properties of these two complex amplitudes for an operation of the extended little group group $4/mmm1'$, the fulfilment of Eq. (19) for a certain τ can be verified. Let us analyse some examples.

We will consider only operations without time reversal, since the extension to the operations with time reversal is straightforward, as explained in Section III. The operation $(2_z \mid 000)$ transforms $\left(S_1 e^{i2\pi\phi_1},\ S_2 e^{i2\pi\phi_2}\right)$ into $\left(-S_1 e^{i2\pi\phi_1},\ -S_2 e^{i2\pi\phi_2}\right)$. This means that the superspace operation $\{2_z \mid 000\frac{1}{2}\}$ is present for any values of the two complex amplitudes of the order parameter. The operation $(4_z \mid 000)$ yields $\left(-iS_1 e^{i2\pi\phi_1},\ iS_2 e^{i2\pi\phi_2}\right)$, implying that the superspace symmetry operation $\{4_z \mid 000\frac{1}{4}\}$ will be present for configurations of type $\left(S_1 e^{i2\pi\phi_1},\ 0\right)$ (or similarly, operation $\{4_z \mid 000\frac{3}{4}\}$ for $\left(0,\ S_2 e^{i2\pi\phi_2}\right)$). The inversion $(\bar{1} \mid 000)$, as it transforms the order parameter into $\left(S_2 e^{-i2\pi\phi_2},\ S_1 e^{-i2\pi\phi_1}\right)$, will give rise to a superspace symmetry operation $\{\bar{1} \mid 000\ \ \phi_1 + \phi_2\}$ only for configurations of the type $\left(Se^{i2\pi\phi_1},\ Se^{i2\pi\phi_2}\right)$.

TABLE IV: Possible superspace symmetries of incommensurate spin arrangements in a $\mathrm{Im}\bar{3}m$ structure with propagation vector $\boldsymbol{k} = (00\gamma)$, and transforming according to either irrep $mDT4$ (first row) or $mDT5$ (rest). The restrictions on the form of the order parameter required for each specific symmetry are indicated in the second column. In general, only one direction of the order parameter is shown from the set of equivalent ones corresponding to different domains. Only in the case that the symmetry of different equivalent domains corresponds to different enantiomorphic groups, both are explicitly listed. The choice done of the arbitrary global phase of the spin modulation is shown in the 4th column.

Irrep	Order parameter	Superspace group	Phase	Generators (and $\{1'\|000\frac{1}{2}\}$)
$mDT4$	$Se^{i2\pi\phi}$	$I4/mmm1'(00\gamma)00sss$	$\phi = 0$	$\{4_z\|0000\}$ $\{m_x\|000\frac{1}{2}\}$ $\{\bar{1}\|0000\}$
$mDT5$	$\left(Se^{i2\pi\phi},\ 0\right)$	$I4221'(00\gamma)q00s$	$\phi = 0$	$\{4_z\|000\frac{1}{4}\}$ $\{2_y\|0000\}$
	$\left(0,\ Se^{i2\pi\phi}\right)$	$I4221'(00\gamma)\bar{q}00s$	$\phi = 0$	$\{4_z\|000\frac{3}{4}\}$ $\{2_y\|0000\}$
$mDT5$	$\left(Se^{i2\pi\phi}, Se^{i2\pi\phi}\right)$	$Immm1'(00\gamma)s00s$	$\phi = 0$	$\{2_z\|000\frac{1}{2}\}$ $\{\bar{1}\|0000\}$ $\{m_x\|000\frac{1}{2}\}$
$mDT5$	$\left(Se^{i2\pi\phi}, Se^{i2\pi(\phi+\frac{1}{2})}\right)$	$Fmmm1'(00\gamma)s00s$	$\phi = -\frac{1}{4}$	$\{2_z\|000\frac{1}{2}\}$ $\{\bar{1}\|0000\}$ $\{m_{xy}\|000\frac{1}{2}\}$
$mDT5$	$\left(Se^{i2\pi\phi_1}, Se^{i2\pi\phi_2}\right)$	$I112/m1'(00\gamma)s0s$	$\phi_1 = -\phi_2$	$\{2_z\|000\frac{1}{2}\}$ $\{\bar{1}\|0000\}$
$mDT5$	$\left(S_1e^{i2\pi\phi}, S_2e^{i2\pi\phi}\right)$	$I2221'(00\gamma)00ss$	$\phi = 0$	$\{2_z\|000\frac{1}{2}\}$ $\{2_y\|0000\}$
$mDT5$	$\left(S_1e^{i2\pi\phi}, S_2e^{i2\pi(\phi-1/2)}\right)$	$F2221'(00\gamma)00ss$	$\phi = \frac{1}{8}$	$\{2_z\|000\frac{1}{2}\}$ $\{2_{xy}\|0000\}$
$mDT5$	$\left(S_1e^{i2\pi\phi_1}, S_2e^{i2\pi\phi_2}\right)$	$I1121'(00\gamma)ss$	-----	$\{2_z\|000\frac{1}{2}\}$

In this way, all special directions in the order parameter space can be explored and their isotropy superspace subgroups derived. Table IV lists the results. This type of calculations is presented here in detail to illustrate the method, but it should be stressed that programs such as ISODISTORT and/or JANA2006 can provide automatically such type of results for any irrep.

According to Table IV, a $mDT5$ magnetic ordering can produce seven different magnetic symmetries, depending on the direction of the order parameter. The groups $I4221'(00\gamma)q00s$ and $I4221'(00\gamma)\bar{q}00s$ in the list are associated with physically equivalent enantiomorphic spin configurations [40]; they can therefore be considered, for our purposes, as a unique symmetry. As in the case of phase II, the restrictions on the Cr modulations for all the possible alternative symmetries of Table IV can be derived by using the equations discussed in Section II (see Table V).

Figure 2 depicts schematically the form of the magnetic configurations for some symmetries. As seen, the constraints of the tetragonal superspace groups force the spin wave to adopt helical configurations. This can be easily checked, as illustrated in the following. Let us consider for concreteness the group $I4221'(00\gamma)q00s$. According to Eq. (6), and due to the operation $\{4_z \mid 000\frac{1}{4}\}$, the magnetic modulation of the chromium atom at the origin must verify the condition:

$$\boldsymbol{M}\left(x_4+\tfrac{1}{4}\right)=4_z^+.\ \boldsymbol{M}\left(x_4\right) \tag{40}$$

This constraint implies that the modulations of the *x* and *y* components of the spins should be in right-handed quadrature. Furthermore, Eq. (40) combined with the relation $\boldsymbol{M}\left(x_4+\tfrac{1}{2}\right)=-\boldsymbol{M}\left(x_4\right)$ that is forced by the operation $\{1'\mid 000\tfrac{1}{2}\}$, implies that the *z*-component of the magnetic modulation must be zero. This means that the symmetry only allows transversal modulations. In addition, the operation $\{2_y \mid 0000\}$ forces

$$\boldsymbol{M}\left(-x_4\right)=2_y.\ \boldsymbol{M}\left(x_4\right), \tag{41}$$

which, together with Eq. (40), imply that the first harmonic of $\boldsymbol{M}\left(x_4\right)$ must be of the form:

$$\left(M_x^1\left(x_4\right),\ M_y^1\left(x_4\right)\right)=\left(M_1\sin(2\pi x_4),\ -M_1\cos(2\pi x_4)\right) \tag{42}$$

Note that there is only the single free parameter, M_1, to be determined. Similarly, if a third harmonic exists, it must be of the form:

$$\left(M_x^3(x_4),\, M_y^3(x_4)\right) = \left(M_3 \sin(2\pi x_4),\, M_3 \cos(2\pi x_4)\right), \tag{43}$$

with opposite sign correlation of the two components. These relations are then repeated for higher harmonics depending on their parity. The first harmonic is therefore a helical arrangement along *z* axis, with the spins rotating in the xy plane (see Figure 2). According to Eq. (1), the pitch angle of the helix (rotation angle of the magnetic moments between consecutive cells along the *z*-axis) is $2\pi\gamma$, where γ is the modulus of the propagation wave vector. Note that this pitch angle, along with the constancy of the modulus of the local magnetic moments, are not forced by symmetry and can vary if higher harmonics exist in the magnetic modulation.

The superspace symmetry $I4221'(00\gamma)q00s$ (or $I4221'(00\gamma)\bar{q}00s$) implies a point group $4221'$ and the loss of inversion for the helical arrangement. However, the structure remains non-polar because of the conservation of the binary axes in the plane *xy*.

There are group-subgroup relations among some of the possible symmetries, such that some of the constraints are common to all cases, while others disappear as the symmetry is lowered. One can see in Table V and FIG. 2 that the superspace symmetries that keep the inversion centre correspond necessarily to collinear arrangements. The inversion operation $\{\bar{1}\,|\,0000\}$ implies for an atom at the origin that $\boldsymbol{M}(-x_4) = \boldsymbol{M}(x_4)$, which reduces the Fourier series of the spin wave to cosine terms, forcing the collinearity. On the other hand, the operation $\{2_z\,|\,000\tfrac{1}{2}\}$, common to all of the groups, implies that the magnetic modulation function of an atom at the origin must satisfy the condition $\boldsymbol{M}(x_4+\tfrac{1}{2}) = 2_z.\,\boldsymbol{M}(x_4)$, which together with the condition $\boldsymbol{M}(x_4+\tfrac{1}{2}) = -\boldsymbol{M}(x_4)$ resulting from the operation $\{1'\,|\,000\tfrac{1}{2}\}$, restricts the modulations to be transversal even if

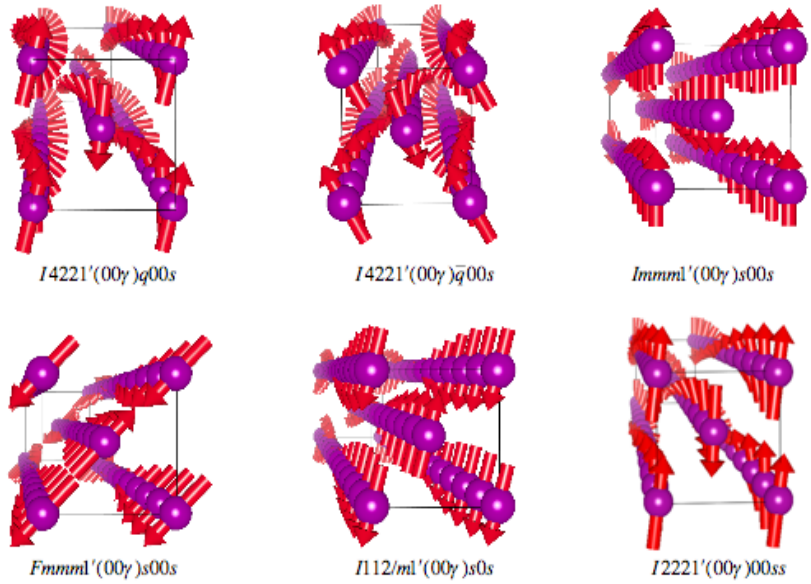


FIG. 2. Scheme of possible magnetic modes of different superspace symmetry for a bcc structure, with a propagation wave vector (0 0 ~0.96) and irrep *m*DT5. The corresponding superspace group is indicated below (see TABLE IV). The figures depict about half wavelength of the incommensurate frozen spin wave. The mode observed in phase I of chromium is the one with superspace group $Immm1'(00\gamma)s00s$.

higher order harmonics are present (which must necessarily be of odd order). The non-centrosymmetric orthorhombic symmetries produce elliptical rotations of the magnetic moments along the propagation direction, with the axes of the elliptical orbit fixed along the *x* and *y* directions (for the $I2221'(00\gamma)00ss$ symmetry) or the oblique directions (1 1 0) and (-1 1 0) (for the case of $F2221'(00\gamma)00ss$). It is remarkable that only in the case of a fully arbitrary modulation of the magnetic moments in the *xy* plane, the *m*DT5 mode produces a polar symmetry. Note that if the symmetry of the paraelectric phase were reduced to I4/m, the helical magnetic ordering would yield in this case a phase with superspace symmetry $I41'(00\gamma)qs$ or $I41'(00\gamma)\bar{q}s$, i.e. a phase with polar symmetry.

It is also illustrative to see in detail how the possible induced displacive structural modulations are constrained by the superspace symmetry. In this case the operation $\{1'|000\frac{1}{2}\}$ implies subperiodicity of half a period, $\boldsymbol{u}\left(x_4+\frac{1}{2}\right)=\boldsymbol{u}\left(x_4\right)$. This property, together with the one resulting from operation $\{2_z|000\frac{1}{2}\}$ common to all possible order parameter orientations, limits the possible displacive modulations to a longitudinal polarization. In the case of all higher symmetry groups, the additional symmetry operations constrains further the modulation to sine Fourier terms, while in the case of the tetragonal superspace groups, an equation analogous to eq. (40) forces the relation $\boldsymbol{u}\left(x_4+\frac{1}{4}\right)=\boldsymbol{u}\left(x_4\right)$ and a displacive modulation is restricted to 4n harmonics:

$$u_z(x_4) = \sum_n u_n^z \sin(8\pi n x_4) \tag{44}$$

An analogous restriction can be derived for any possible scalar (charge, occupation, etc.) modulation. A full summary of all these conditions for the different possible symmetries can be found in Table V.

Similarly to the case of phase II, the symmetry restrictions both in the direction, phase, and the possible harmonics of the structural modulations can be traced back to the symmetry constraints on the spin-lattice couplings. If we denote $Q(2\boldsymbol{k})$ the complex amplitude of a longitudinal displacive modulation with wave vector $2\boldsymbol{k}$ (see Eq. (35)), then its lowest order coupling to the order parameter $(S_1(\boldsymbol{k}),S_2(\boldsymbol{k}))$ is given by the symmetry invariant:

$$i\left(S_1(\boldsymbol{k})S_2(\boldsymbol{k})\,Q(-2\boldsymbol{k}) - S_1(-\boldsymbol{k})S_2(-\boldsymbol{k})\,Q(2\boldsymbol{k})\right) \tag{45}$$

This coupling is similar to the one found in phase II for an order parameter of symmetry *m*DT4 (see eq. (36)). The difference here is that this coupling is inactive for the special

directions of the order parameter corresponding to helical configurations, where either $S_1(\boldsymbol{k})$ or $S_2(\boldsymbol{k})$ are zero. According to eq. (45), the amplitude of the induced second harmonic longitudinal modulation is given at first approximation by $Q(2\boldsymbol{k}) \propto i\, S_1(\boldsymbol{k}) S_2(\boldsymbol{k})$ and therefore this modulation will be zero in an helical phase, in agreement with Eq. (44), derived directly from the superspace symmetry. The advantages of the use of superspace symmetry concepts become then obvious: all the physical constraints in the magnetic and lattice modulations of the system, for a given thermodynamic phase, are automatically introduced at any level of approximation in the description of the structure.

The modulated magnetic moments of phase I have been reported to be along either the *x* or *y* direction, with coexistence of both orientations as domains[36]. According to Tables IV and V, the symmetry of this arrangement is given by the orthorhombic group $Immm1'(00\gamma)s00s$. As it is usual in Landau type phase transitions, the symmetry realized in the distorted phase corresponds to a high symmetry direction in the order parameter space. The tetragonal helical arrangement was also proposed in some early works [41], but was later discarded. Nevertheless, the distinction between a collinear modulation with equilibrated domain populations and a helical arrangement may be difficult, and the possibility of a helical arrangement in Cr has persisted in the literature [42, 43]. However, according to the symmetry analysis presented above (Table V), the helical arrangement, having tetragonal superspace symmetry, can be directly discarded by the experimental observation of an induced non-magnetic modulation with wave vector $2\boldsymbol{k}$. This non-magnetic modulation, which has been confirmed by different diffraction studies [37,39,36], is incompatible with the superspace magnetic symmetry of a circular helical spin wave, and therefore cannot be induced by it. As shown above, this incompatibility can be derived from physical arguments, and it has been occasionally pointed out under particular physical models of the system[44, 42]. A comparison of the derivation of this incompatibility

TABLE V. Symmetry restrictions on the Fourier series describing the modulations of one atom at the origin for the each of the possible isotropy magnetic superspace groups listed in TABLE IV. Components not explicit listed are zero. The cross relations between the amplitudes of sine and cosine terms are indicated symbolically. If the modulations are restricted to sine or cosine terms, a parenthesis with the word is added. If necessary, the restriction in the order-type of the harmonics is also indicated. The general restriction caused by the symmetry operation $\{1'|000\frac{1}{2}\}$ is given in the second row.

Superspace group	Magnetic $\boldsymbol{M}(x_4)$	Displacive $u_z(x_4)$	Charge/Occupation $\rho(x_4)$
	$\boldsymbol{M}(x_4+\frac{1}{2})=-\boldsymbol{M}(x_4)$ odd harmonics	$\boldsymbol{u}(x_4+\frac{1}{2})=\boldsymbol{u}(x_4)$ even harmonics	$\rho(x_4+\frac{1}{2})=\rho(x_4)$ even harmonics
$I4/mmm1'(00\gamma)00sss$	$M_z(\cos)$	$u_z(\sin)$	$\rho(\cos)$
$I4221'(00\gamma)q00s$	$M_x(\sin/4n+1)=-M_y(\cos/4n+1)$ $M_x(\sin/4n+3)=M_y(\cos/4n+3)$	$u_z(\sin/4n)$	$\rho(\sin/4n)$
$I4221'(00\gamma)\bar{q}00s$	$M_x(\sin/4n+1)=M_y(\cos/4n+1)$ $M_x(\sin/4n+3)=-M_y(\cos/4n+3)$	$u_z(\sin/4n)$	$\rho(\sin/4n)$
$Immm1'(00\gamma)s00s$	$M_x=0$ $M_y(\cos)$	$u_z(\sin)$	$\rho(\cos)$
$Fmmm1'(00\gamma)s00s$	$M_x(\cos)=M_y(\cos)$	$u_z(\sin)$	$\rho(\cos)$
$I112/m1'(00\gamma)s0s$	$M_x(\cos)$ $M_y(\cos)$	$u_z(\sin)$	$\rho(\cos)$
$I2221'(00\gamma)00ss$	$M_x(\sin)$ $M_y(\cos)$	$u_z(\sin)$	$\rho(\cos)$
$F2221'(00\gamma)00ss$	$M_x(\sin)=-M_y(\sin)$ $M_x(\cos)=M_y(\cos)$	$u_z(\sin)$	$\rho(\cos)$
$I1121'(00\gamma)ss$	$M_x(x_4), M_y(x_4)$	$u_z(x_4)$	ρ , no condition

in Ref. 44 with the one above is a vivid illustration of the power and simplicity of superspace formalism to extract the maximum information from the experimental data in a straightforward manner.

A comment on the observed behaviour of the neutron diffraction magnetic reflections of type (*0 0 l m*) is in order. These reflections along the direction of the propagation vector can be detected in phase I, and disappear in phase II [36]. In a simple monatomic structure, as that of chromium, this behaviour can be directly taken as the signature of the change of the magnetic moments of the Cr atoms from a transversal to a longitudinal geometry. But the extinction of the magnetic reflections (*0 0 l m*) in phase II can be more fundamentally explained within the frame of the preceding symmetry analysis. The symmetry change between phase I and phase II is $I4/mmm1'(00\gamma)00sss \rightarrow Immm1'(00\gamma)s00s$. This means that the symmetry operation $\{2_z|000\frac{1}{2}\}$ in phase I becomes $\{2_z|0000\}$ in phase II. While the first operation does not give rise to any extinction the second, as seen in Section II, explains the absence of all reflections of type $(00lm)$. The change in this symmetry operation is of course also directly correlated with the change from a transversal to a longitudinal spin wave, and the extinction can be directly related with the longitudinal character of the spin wave in phase II. But this simple correlation would disappear in a more complex structure having off-centre magnetic atoms with the same symmetry change. In such a case, the existence of either $\{2_z|000\frac{1}{2}\}$ or $\{2_z|0000\}$ would no longer force the spin configuration to be longitudinal or transversal, but the switching off of the $(00lm)$ reflection would still be a signature of the transformation of $\{2_z|000\frac{1}{2}\}$ into $\{2_z|0000\}$.

It has been argued that the assignment of an irrep to the magnetic distortion is more restrictive or informative than the assumption of a specific magnetic symmetry [45]. This is certainly not true for incommensurate structures. As shown in the above examples, even in the simplest case of a one-dimensional small irrep, the superspace symmetry introduces

either deeper or equivalent restrictions, depending respectively on the use of the conventional representation analysis or the conventional analysis modified to include all the symmetry operations of the extended little group. But in the case of multi-dimensional small irreps, the assignment of a superspace group implies the choice of a particular subspace within the space of magnetic basis modes corresponding to a given irrep, and this is outside the scope of representation analysis, as it is being presently used.

In the example of chromium, the assignment of the irrep $mDT5$ for the magnetic ordering only means to restrict the spin modulation of the atoms to transversal sinusoidal modulations, while the choice of the superspace group further restricts this first harmonic of the modulation. Obviously an extended representation method that would include the restrictions on the symmetry adapted functions corresponding to the required special directions in representation space for each of the superspace groups would become equivalent for the restrictions on the first harmonic modulation. But this methodology is unnecessarily complicated, as the most general form of the modulation for each possible symmetry, including magnetic and structural waves, and any harmonic, can be directly obtained from an unambiguous definition of the superspace group through its generators. The power of the superspace approach is that, once a possible magnetic superspace symmetry is assigned to the system under study (either derived for a certain irrep, or from inspection of the properties of the experimental data) representation analysis and group theory are no longer needed to describe the structure. The constraints on the magnetic modulations and on any structural degree of freedom can be directly derived from the assigned superspace group in a standard, crystallographic form. There is no need of building up basis modes, as done in the standard representation method, or to appeal either to the underlying irrep properties of the magnetic ordering, or to representation theory. Superspace symmetry operations are defined in a standard unambiguous form, analogous

to space group operations, and the resulting symmetry restrictions on the spin and non-magnetic modulations for any harmonic can be directly derived (the program JANA2006 does it automatically). Then, both the magnetic and the atomic structure can be described and refined using crystallographic methods with the characterization of the atomic positions and modulation functions of an asymmetric unit of the relevant superspace group.

The very particular features of helical structures and other highly regular spin arrangements in incommensurate magnetic phases are usually introduced *ad-hoc* when trying to fit the diffraction data of phases with higher superspace symmetry within the set of possible ones originated by a single active irrep. The example of chromium shows that the regular features of these arrangements can be rationalized as corresponding to different superspace groups, and their parameterization systematized following the rules of superspace formalism. These rules are robust in the sense that their breaking necessarily implies a thermodynamic phase transition.

D. Incommensurate magnetic phases with two primary irreps: the $RMnO_3$ compounds

In the previous examples, we have essentially considered possible superspace symmetries of single-k magnetic phases with a unique primary irrep magnetic mode. The term *primary* is used here in the sense that the presence of other (*secondary*) modes within the same phase is explained just as induced or secondary effects. This implies, in particular, that the symmetry associated with secondary modes must be, by definition, fully compatible with the symmetry dictated by the primary mode. Then, the intersection of the superspace groups associated with the different superposed modes trivially coincides with the one imposed by the single primary mode. In the cases discussed above, for example, higher harmonics of the magnetic modulation transforming according to different irreps may

occur, but they do not break further the symmetry of the phase, which is solely dictated by the primary mode.

However, magnetic phases may also result from the condensation of several primary irrep modes. The characterization of the possible symmetries that can arise in these cases is therefore an important issue. This is particularly true in the case of multiferroics and/or magnetoelectric compounds, where phenomena like ferroelectricity or the linear magnetoelectric effect often originate from complex magnetic orders that involve several primary irreps. In this fourth example, we show that the symmetry of these more general single-k magnetic configurations can be straightforwardly derived by considering the intersection of the superspace groups that would result from each of the primary irrep modes, taken separately. For an experimental example where this type of symmetry analysis has been applied, see Ref. 46.

Let us then consider a phase that results from the superposition of two irrep primary modes. We will assume that these two modes share a common propagation vector, so that the resulting phase is a single-k magnetic phases describable by a (3+1)-dim superspace group. From the above definition of primary mode, the superspace groups that may arise from these two modes, taken separately, are not group-subgroup related, and their intersection depends, in general, on the relative phases of the corresponding modulations. As seen in Section III, in the case of the symmetry operations transforming $\boldsymbol{k}$ into $-\boldsymbol{k}$, the translational part along the coordinate x_4 depends on the choice of the origin in the internal space, i.e. it depends on the global phase associated with the modulation. In order to derive the symmetry of the superposition of two active irrep modes, one must then explicitly consider this dependence. When there is a single irrep incommensurate modulation, one is always allowed to choose this phase as zero. However, if two primary irrep modulations are superposed, only one of the modulation phases can be arbitrarily

chosen by fixing an origin, and the relative phase difference between the two modulations becomes physically relevant. Consequently, the global superspace symmetry depends in general on the relative phase shift of the two irrep magnetic modulations.

If an incommensurate system has a generic symmetry operation $\{\boldsymbol{R},\theta\,|\,\boldsymbol{t}\ \ \tau_o\}$, a shift of the global phase of the modulation by a quantity ϕ (in 2π units), is equivalent to a translation of the origin of the internal coordinate x_4 by $-\phi$. Under this origin shift, the above symmetry operation becomes $\{\boldsymbol{R},\theta\,|\,\boldsymbol{t}\ \ \tau_o - R_I\phi + \phi\}$, where R_I is defined in eq. (4). This means that the operations that keep $\boldsymbol{k}$ invariant do not change, while those transforming $\boldsymbol{k}$ into $-\boldsymbol{k}$ transform into $\{\boldsymbol{R},\theta\,|\,\boldsymbol{t}\ \ \tau_o + 2\phi\}$. The intersection of the symmetry groups for the different primary irrep modes will then depend on their global phases through their presence in these operations. Let us consider for instance the case of two irrep modes that keep inversion $\{\bar{1}\,|0000\}$ in their respective isotropy superspace groups. The translation along the internal space is zero in the two groups, because the global phase of each irrep magnetic mode has been chosen conveniently. However, if the global phases (in 2π units) of the two modes are ϕ_1 and ϕ_2 (with respect to the position of the inversion centre along the internal space), the corresponding inversion symmetry operations are $\{\bar{1}\,|000\ 2\phi_1\}$ and $\{\bar{1}\,|000\ 2\phi_2\}$, respectively. Hence, a superposition of the two modes will maintain inversion only if $\phi_2 - \phi_1 = n/2$. Similarly, if two irrep modes with a common $\boldsymbol{k} = (0\beta 0)$ are superposed, a first one having a symmetry $\{2_z\,|00\tfrac{1}{2}0\}$ (that is, $\{2_z\,|00\tfrac{1}{2}\ 2\phi_1\}$ for an arbitrary origin in the internal space) and a second one the symmetry $\{2_z\,|00\tfrac{1}{2}\tfrac{1}{2}\}$ ($\{2_z\,|00\tfrac{1}{2}\ \tfrac{1}{2}+2\phi_2\}$, for the same generic origin), then their combined effect will maintain the common two-fold axis only if $\phi_2 - \phi_1 = \tfrac{1}{4} + \tfrac{n}{2}$. We have then the ingredients to derive in a straightforward form the symmetry breaking produced by the action of two irrep modes with the same propagation vector, depending on their relative phases.

As mentioned above, the knowledge of the symmetry that results from the presence of several active irreps is especially important for the analysis of possible multiferroic orderings. We have seen, for instance in section III, that a single 2-dim incommensurate irrep magnetic mode cannot break space inversion, and therefore, cannot induce improper ferroelectricity. However, the action of two 2-dim magnetic irreps can break the centrosymmetry of a paramagnetic phase and induce a secondary spontaneous polarization, with ferroelectric properties. Let us consider, as a concrete working example, the possible irrep magnetic orderings with propagation vector $\boldsymbol{k} = \beta \boldsymbol{b}^*$ in a paramagnetic phase of symmetry $Pbnm1'$ (standard setting $Pnma1'$), These symmetry conditions correspond to the case of the orthorhombic rare-earth manganites of type $RMnO_3$ (R being a rare earth element) [47], which exhibit at low temperatures several modulated magnetic structures with different types of polar behaviour, some of them with two primary irrep modes [48, 49, 50 ,51].

TABLE VI. Irreps of the little co-group *m2m1'* of the Δ-line in the Brillouin zone, which define the four possible magnetic irreps of the magnetic space group *Pbnm1'*. In the last two columns the resulting superspace group is indicated by its label and the set of generators. The generators: $\{1'|000\frac{1}{2}\}$ and $\{\bar{1}|0000\}$, common to the four groups, are not listed.

irrep	1	m_x	2_y	m_z	1′	Superpace group	Generators
$m\Delta_1$	1	1	1	1	-1	$Pbnm1'(0\beta0)000s$	$\{m_x\|\frac{1}{2}0\frac{1}{2}0\},\{m_z\|00\frac{1}{2}0\}$
$m\Delta_2$	1	-1	1	-1	-1	$Pbnm1'(0\beta0)s0ss$	$\{m_x\|\frac{1}{2}0\frac{1}{2}\frac{1}{2}\},\{m_z\|00\frac{1}{2}\frac{1}{2}\}$
$m\Delta_3$	1	-1	-1	1	-1	$Pbnm1'(0\beta0)s00s$	$\{m_x\|\frac{1}{2}0\frac{1}{2}\frac{1}{2}\},\{m_z\|00\frac{1}{2}0\}$
$m\Delta_4$	1	1	-1	-1	-1	$Pbnm1'(0\beta0)00ss$	$\{m_x\|\frac{1}{2}0\frac{1}{2}0\},\{m_z\|00\frac{1}{2}\frac{1}{2}\}$

TABLE VII. Magnetic superspace groups resulting from the superposition of two primary magnetic irreps with different relative phase shifts, for a paramagnetic space group $Pbnm1'$ and a common propagation wave vector $\boldsymbol{k} = (0\beta 0)$. The superspace groups determine in particular the point group symmetry and the ferroic properties of a phase (see also the TABLE II of Ref. 12 for comparison)

		$m\Delta_1$	$m\Delta_2$	$m\Delta_3$	$m\Delta_4$
$\Delta\Phi = \frac{1}{4} + \frac{n}{2}$ (Mod. 2π)	$m\Delta_1$	$Pb2_1m1'(0\beta0)000s$			
	$m\Delta_2$	$P2_12_12_11'(0\beta0)000s$	$Pb2_1m1'(0\beta0)s0ss$		
	$m\Delta_3$	$P2_1nm1'(0\beta0)000s$	$Pbn2_11'(0\beta0)s00s$	$Pb2_1m1'(0\beta0)ss0s$	
	$m\Delta_4$	$Pbn2_11'(0\beta0)000s$	$P2_1nm1'(0\beta0)00ss$	$P2_12_12_11'(0\beta0)0s0s$	$Pb2_1m1'(0\beta0)0sss$
$\Delta\Phi = \frac{n}{2}$ (Mod. 2π)	$m\Delta_1$	$Pbnm1'(0\beta0)000s$			
	$m\Delta_2$	$P2_1/n1'(0\beta0)00s$	$Pbnm1'(0\beta0)s0ss$		
	$m\Delta_3$	$P2_1/m1'(0\beta0)00s$	$P2_1/b1'(0\beta0)0ss$	$Pbnm1'(0\beta0)s00s$	
	$m\Delta_4$	$P2_1/b1'(0\beta0)00s$	$P2_1/m1'(0\beta0)0ss$	$P2_1/n1'(0\beta0)s0s$	$Pbnm1'(0\beta0)00ss$
$\Delta\Phi$ (arbitrary)	$m\Delta_1$	$Pb2_1m1'(0\beta0)000s$			
	$m\Delta_2$	$P12_111'(0\beta0)0s$	$Pb2_1m1'(0\beta0)s0ss$		
	$m\Delta_3$	$P11m1'(0\beta0)0s$	$Pb111'(0\beta0)ss$	$Pb2_1m1'(0\beta0)ss0s$	
	$m\Delta_4$	$Pb111'(0\beta0)0s$	$P11m1'(0\beta0)ss$	$P12_111'(0\beta0)ss$	$Pb2_1m1'(0\beta0)0sss$

Table VI defines the four different possible magnetic irreps for this propagation vector and their corresponding superspace groups, according to the general rules explained in the preceding sections. It is then straightforward to obtain the possible superspace groups for magnetic configurations originating in the superposition of two primary modes (i.e. configurations of type $m\Delta_i + m\Delta_j$), with different relative phase shifts. For the case under consideration, the possible superspace groups are listed in Table VII. This Table can be

compared with Table II of Ref. 12, where the non-magnetic point groups of the nuclear structure were listed for the case of two magnetic irreps combined in quadrature. Once taken into account the different setting used, the point groups listed there agree with those extracted from Table VII. The list of Ref. 12 was derived using a so-called "non-conventional application of corepresentation analysis", a method involving a non-standard interpretation of the concept of corepresentations. Here, we show that these point groups can be straightforwardly obtained from the superspace symmetries associated with *ordinary irreps* of the paramagnetic grey group. Moreover, by following the superspace formalism, one obtains not only the point groups to be assigned to the structures disregarding the magnetic moments, but also the full magnetic symmetry that dictates the restrictions imposed upon any degree of freedom and any tensor property of the system.

The possible ferroic properties of a magnetic phase, in particular, are unambiguously defined by the knowledge of the superspace group of that phase. In the examples summarized in Tables VI and VII, which apply to the $RMnO_3$ multiferroic compounds, several conclusions can be directly obtained. Firstly, the symmetry operation $\{1'|000\frac{1}{2}\}$ is always maintained for phases with two primary irreps. Therefore, ferromagnetism, ferrotoroidicity and linear magnetoelastic or magnetoelectric effects are symmetry forbidden in this type of phases. A second general conclusion is that the superposition of two primary irrep modes that are either in phase or in anti-phase can never induce improper ferroelectricity, because all possible point groups include space inversion. Reversely, space inversion is always broken if the two modes are in quadrature ($\Delta\Phi = \frac{1}{4} + \frac{n}{2}$), but that does not guarantee the onset of ferroelectricity. As seen in Table VII, the combinations in quadrature $m\Delta_1 + m\Delta_2$ and $m\Delta_3 + m\Delta_4$ give rise to the non-polar and non-centrosymmetric point group *222*. For the remaining combinations of modes in quadrature, the resulting point groups are polar, and therefore the presence of an induced

ferroelectric polarization is to be expected. The direction of this spontaneous electric polarization depends on the specific combination of irreps. For the combination of distinct irreps, the electric polarization is necessarily oriented along one of the two crystallographic directions perpendicular to the wave vector. This corresponds to the case of the cycloidal spin arrangements observed in the $RMnO_3$ compounds [50,51]. But a polarization parallel to the wave vector is expected for two irrep modes with same symmetry and different global phases. Notice that only when the two superposed primary irreps have arbitrary phase shifts it is possible a polarization in a crystallographic plane. But, even in this case where the polarization may rotate in the plane as function of temperature or the external magnetic field, a linear magnetoelectric response remains symmetry forbidden, due to the presence of the symmetry operation $\{1'|000\frac{1}{2}\}$.

It is interesting to consider, within the framework given by the Tables VI and VII, the properties of the different phases reported for $TbMnO_3$, a most studied representative member of the $RMnO_3$ family. This compound displays a first magnetic phase transition at $T_N \approx 41K$, driven by an active irrep of symmetry $m\Delta_3$. At lower temperatures, $T_C \approx 28K$, a second transition leads to a magnetic phase with a superposition in quadrature $m\Delta_3 + m\Delta_2$ [51]. According to Tables VI and VII, these two consecutive transitions correspond to the a symmetry breaking sequence:

$$Pbnm1'-^{(T_N)} \rightarrow Pbnm1'(0\beta 0)s00s-^{(T_C)} \rightarrow Pbn2_11'(0\beta 0)s00s \ .$$

The point group of the first magnetic phase is therefore *mmm1'*, and all possible induced structural distortions (restricted to even harmonics) keep space inversion. In the second transition the point group is reduced to *mm21'*, and one should expect an induced secondary polar structural distortion with an electric polarization oriented along *z*. The assigned superspace symmetries not only rationalize the crystal tensor properties of these

two phases but, when applied on the possible form of the magnetic modulation, also introduce simple relations between the amplitudes and phases of the spin waves of the symmetry-related mangetic atoms in the basic unit cell. As some of Tb atoms are only related by operations that exchange $\boldsymbol{k}$ and $-\boldsymbol{k}$, the symmetry relation between their spin waves cannot be accounted for by the usual representation analysis. It is remarkable that sometimes they have been added with *ad-hoc* arguments, at least partially. For instance, the amplitudes of the two split Tb orbits were forced to be identical in Ref. 51, but their relative phase was refined, when in fact also this phase is symmetry forced.

In the lower temperature magnetic phase of $TbMnO_3$, the magnetic modulation must comply with the superspace group $Pbn2_11'(0\beta0)s00s$; if the magnetic modulation is further restricted to be compatible with A-type local arrangements [50], then the reported dominant cycloidal form of the spin modulation [51] is directly obtained from the symmetry conditions of the mentioned superspace group. However, this superspace group also allows the presence of magnetic modulations of type C, F and G. These other types of modulations are therefore expected to be present, as they are permitted by symmetry. They introduce in the magnetic modulation complex features beyond the simple cycloidal model and they are indeed observed experimentally, although with weak amplitudes [50,52].

Under the application of a magnetic field in the yz plane, $TbMnO_3$ undergoes a phase transition in which the polarization rotates from the *z*- to the *x*-axis. According to Ref. 53, this transition corresponds to a rotation of the plane of the dominant A-type cycloid. In terms of active irreps, this rotation of 90º of the cycloid plane implies a change of the primary magnetic ordering to a superposition in quadrature of type $m\Delta_3 + m\Delta_1$. As seen in Table VII, this scenario is entirely consistent with the observed flip of the polarization. If this field induced phase corresponds to a quadrature superposition of $m\Delta_3 + m\Delta_1$, then its

symmetry is given by the superspace group $P2_1nm1'(0\beta0)000s$, i.e. a phase polar along x, with magnetic point group *2mm1'*.

The ferroelectricity in some of the phases of $TbMnO_3$ has been explained as due to the so-called inverse Dzyaloshinskii-Moriya mechanism. The above discussion shows that the presence of a spontaneous electric polarization and its orientation, can directly be predicted by symmetry arguments, independently of the microscopic mechanism at work.

VI. CONCLUSION

The extension of the superspace formalism to magnetic structures allows a systematic description and application of the symmetry present in incommensurate magnetic phases. Its relation with the usual representation analysis method has been analysed showing the advantages of a combined use of both approaches. The magnetic ordering and possible induced structural distortions in an incommensurate magnetic phase are restricted by its superspace symmetry group, and this property is in general more restrictive than the mere description of the magnetic modulation in terms of basis functions for one or several irreps. A consistent comprehensive account of the symmetry properties of single-k magnetic modulations must include its transformation properties for operations changing k into -k, and this is done automatically by superspace symmetry.

We have shown that single-k incommensurate magnetic modulations have the symmetry operation $\{1'|000\frac{1}{2}\}$, combining time reversal and a semi-period phase shift of the modulation. This ubiquitous simple symmetry operation implies important general properties of these systems, as the grey character of their magnetic point groups or the restriction to odd and even harmonics of the magnetic and structural modulations, respectively. To our knowledge, these general symmetry-forced features of single-k

magnetic phases, although rather familiar for many experimentalists, seem to have never been formulated in a general context, and one can still find studies, which seem to ignore their general validity (see for instance Ref. 54).

An efficient approach to the determination and description of an incommensurate magnetic structure and to the classification of its properties can be achieved by systematically exploring the possible superspace groups associated with one or more irreps, crosschecking successively their adequacy to the experimental data. Extinction rules associated with some superspace symmetry operations can be helpful in this process. Recent developments in the programs JANA2006, [6] and ISODISTORT, [23] allow the automatic calculation of the possible magnetic superspace symmetries for any paramagnetic space group, any propagation wave vector, and any irrep. This should allow a rapid and systematic exploration in experimental studies of all possible spin configurations, from the highest to the lowest possible symmetries.

The symmetry of commensurate magnetic modulations corresponding to the lock-in of the propagation vector into simple rational values (described by conventional Shubnikov space groups) can be directly related with the superspace symmetry of virtual or real neighboring incommensurate phases with irrational propagation vectors. This relation of extreme utility is well known in the study of non-magnetic structural modulations. We have not treated here this subtopic, which is left for a next publication, but some specific examples of its application can be found in Ref. 22. There it can be seen that, similar to the case of a structural modulation, the magnetic symmetry of a commensurate lock-in magnetic phase depends on the parity of the numerator and denominator of the fraction describing the commensurate wave vector, and well-defined parity rules exist concerning for instance the presence of improper (induced) ferroelectricity. The application of these

rules is especially useful to evaluate complex phase diagrams with multiple commensurate and incommensurate phases.

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