Incommensurate magnetic structures of multiferroic $MnWO_4$ studied within the superspace formalism

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The magnetic structures of the incommensurate phases of the prototypic multiferroic $MnWO_4$ are analyzed using superspace symmetry formalism. This approach shows in a very simple way the relation between the magnetic symmetry of the incommensurate phases and any tensorial property, such as ferroelectricity. The magnetic structures have been redetermined by single-crystal neutron diffraction experiments, which revealed fine details of the AF3 and AF2 magnetic structures. The spin modulations of the two manganese ions of the basic unit cell are symmetry-related in the paraelectric incommensurate-magnetic structure (AF3)—they are not forced to be collinear but they must have opposite chirality—while in the multiferroic phase (AF2) they become symmetry independent. It is due to this symmetry break that the electric polarization arises along the *b* axis.

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I. INTRODUCTION

Incommensurate magnetic structures have been traditionally described by the representation analysis method developed by Bertaut.[1,2] In this analysis the magnetic point group associated with the incommensurate magnetic ordering is generally unknown. This is a drawback, especially in the field of multiferroics, since the tensor properties (and, therefore, the ferroic properties) are defined by this magnetic point group. Alternatively, superspace formalism provides this information in a very simple way,[3–7] and is therefore a valuable tool to understand and predict the ferroic properties induced by incommensurate magnetic order. Although this formalism has been known for the last thirty years,[8] it has remained essentially unused in the field of magnetic structures. But the recent extension of the refinement program JANA2006[9] to magnetic diffraction now permits us to analyze quantitatively incommensurate magnetic structures using their superspace symmetry properties.[10–12] This allows us to rationalize the physical properties induced by the incommensurate magnetic order in the framework of a symmetry break. In this article we analyze the incommensurate magnetic phases of $MnWO_4$ within this approach.

$MnWO_4$ is a multiferroic material in which the magnetic order of one of its magnetic phases induces ferroelectricity.[13–15] The crystal structure of the paramagnetic phase has the symmetry $P2/c$ (No. 13, *b*-unique axis, standard setting), and consists of edge-sharing oxygen octahedra that make zig-zag chains along the *c* axis, with the Mn atoms located inside the distorted octahedra and the W atoms located between the chains.[16] Below the Néel temperature ($\approx$13.5 K), the system exhibits three successive phases with different long range magnetic orders, the so-called AF3, AF2, and AF1. According to Lautenschläger *et al.*,[16] for decreasing temperatures, the first magnetic phase, AF3, is an incommensurate magnetic structure where the magnetic moments are oriented along a fixed oblique direction $\hat{u}$ in the *ac* plane, with amplitudes that are sinusoidally modulated. Below 12.5 K, this frozen magnetic wave acquires an additional phase-shifted component along the *b* axis, giving rise to a helical spin structure. These two phases have approximately the same propagation vector $\mathbf{k} = (-0.214, \frac{1}{2}, 0.457)$. By further decreasing the temperature below 6.5 K, the AF1 structure is stabilized. The AF1 magnetic structure is a commensurate collinear structure with $\mathbf{k} = (\pm\frac{1}{4}, \frac{1}{2}, \frac{1}{2})$, where the moments lie in the *ac* plane along

the $\hat{u}$ direction in a $++--$ like configuration. Among these magnetic phases, only the AF2 phase is multiferroic, with an electrical polarization directed along the b monoclinic axis. This orientation is expected from the relation $\mathbf{P} \sim [\mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)]$, and is perpendicular to the spin chirality $(\mathbf{S}_i \times \mathbf{S}_j)$ and the vector $\mathbf{r}_{ij}$ that connects $\mathbf{S}_i$ and $\mathbf{S}_j$.[17,18] The microscopic mechanism that gives rise to the ferroelectricity in these type of materials is still unclear. On one hand, the inverse Dzyaloshinskii-Moriya model predicts for cycloidal magnetic structures net atomic displacements parallel to $\mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$ induced by the exchange striction.[17] Unfortunately, these displacements are expected to be too small[19] to be easily resolved, since in general macroscopic ferroelectricity is the only evidence for their existence. On the other hand, the spin current model proposed by Katusura, Nagaosa, and Balatsky[18] suggests that changes in the electronic density break the inversion symmetry of the charge distribution and are sufficient to explain the ferroelectricity.

The magnetic structures of multiferroic $MnWO_4$ and the magnetic and electric effects that are related to the observed phase transitions have been previously analyzed by using the representation analysis method[16] and the Landau theory of phase transitions.[20,21] In this work, we determine the incommensurate structures of $MnWO_4$, ascribing to each phase its corresponding superspace group. We show how the use of superspace formalism provides, in a simple manner, not only the symmetry of the magnetic structures and their intrinsic restrictions, but also information about the tensor properties of each incommensurate phase, such as ferroelectricity or magnetostructural properties.

II. EXPERIMENTS

Single crystals of $MnWO_4$ were grown by a floating zone method using light heating. The crystal growth was performed in an air atmosphere at a linear speed of 8–10 mm/h with a counter-rotation of crystal and feed rod $\sim$20 min^{-1}. Finally, the crystal was annealed at $T = 1100\,^{\circ}\text{C}$.[22]

Neutron diffraction experiments were performed on the CEA-CRG single-crystal diffractometer D23 at the Institut Laue Langevin (Grenoble, France), using $\lambda = 1.286$ Å wavelength in normal-beam geometry. A set of 166 and 246 magnetic reflections were measured at 13 and 9 K, for phases AF3 and AF2, respectively. All these reflections were first-order magnetic satellites, with diffraction vectors $\mathbf{G} + m\mathbf{k}$, where $\mathbf{G}$ is a reciprocal lattice vector of the nuclear structure, and $\mathbf{k}$ is the wave vector of the magnetic modulation. The reflections were therefore indexed by four integer numbers $(hklm)$, with m being $+1$ or -1. The neutron absorption in the sample ($\mu = 0.033$ mm^{-1}) was corrected using the Cambrigde Crystallography Subroutine Library,[23] and the refinements were done based on the structure factors using JANA2006. Nuclear refinements were also done to obtain an absolute scale factor for the magnetic reflections. Figures of magnetic structures were produced using the program VESTA.[24]

III. SYMMETRY ANALYSIS

Since only first-order magnetic reflections have been observed, one can describe the magnetic modulation with a single harmonic. Hence, the magnetic moments of a magnetic atom μ in the position $\mathbf{r}_\mu$, inside the cell $\mathbf{l}$ of the crystal, can be expressed as follows:

$$\mathbf{M}_{\mu,l} = \mathbf{M}_\mu e^{-2\pi i \mathbf{k}\cdot(\mathbf{l}+\mathbf{r}_\mu)} + \mathbf{M}_\mu^* e^{2\pi i \mathbf{k}\cdot(\mathbf{l}+\mathbf{r}_\mu)} \quad (1)$$

In this context, the introduction of the superspace formalism essentially reduces to the following steps.

(i) The introduction of a modulation function for each magnetic atom μ, defined along a continuous coordinate x_4, which is directly related to the previous expression,

$$\mathbf{M}_\mu(x_4) = \mathbf{M}_\mu e^{-2\pi i x_4} + \mathbf{M}_\mu^* e^{2\pi i x_4}. \quad (2)$$

This simply states that the value of the magnetic moment $\mathbf{M}_{\mu,l}$ of the atom μ at any unit cell $\mathbf{l}$ is given by the value of the corresponding $\mathbf{M}_\mu(x_4)$ modulation function for $x_4 = \mathbf{k}\cdot(\mathbf{l} + \mathbf{r}_\mu)$.

(ii) The definition of a set of symmetry operations (the superspace group) that in general constrain the possible form of these modulation functions and correlate the modulation functions of symmetry-related atoms within the unit cell, such that only some of them are independent. In this way, an asymmetric unit for both atomic positions and modulation functions can be defined. The symmetry operations $\{\mathbf{R},\theta|\mathbf{t},\tau\}$ of the relevant superspace group ($\theta = -1$ or $+1$ labels the inclusion or not of time reversal) are ordinary space group operations $\{\mathbf{R},\theta|\mathbf{t}\}$ belonging to the grey space group of the paramagnetic phase, but followed by some specific translation related with τ along the internal coordinate x_4 of all atomic modulation functions.

In the simplest case of a purely incommensurate propagation vector (see Ref. 5 for the general expressions), the symmetry relation between the magnetic modulation functions of two atoms related by a superspace symmetry operation $\{\mathbf{R},\theta|\mathbf{t},\tau\}$ is given by

$$\mathbf{M}_\mu(R_I x_4 + \tau) = \theta\ det(\mathbf{R})\mathbf{R}\cdot\mathbf{M}_\nu(x_4) \quad (3)$$

with the average position of atom μ being related to that of atom ν by the space group operation $\{\mathbf{R}|\mathbf{t}\} : \{\mathbf{R}|\mathbf{t}\}\mathbf{r}_\nu = \mathbf{r}_\mu + \mathbf{l}$. Here, R_I is $+1$ or -1 if $\mathbf{R}$ keeps $\mathbf{k}$ invariant or transforms $\mathbf{k}$ into $-\mathbf{k}$, respectively. For $\mu = \nu$, Eq. (3) defines a constraint on the form of the modulation. Note that the symmetry relations defined in the superspace formalism, in contrast with the traditional Bertaut representation method, include in general rotational or roto-inversion transformations that change the sign of the propagation vector. These symmetry transformations have been previously treated using a so-called nonconventional use of the co-representations[25] or within the frame of Landau theory.[20,21] As explained in Ref. 5, the use of the superspace formalism introduces automatically and in a simple form the symmetry constraints associated with these operations, not only for the order parameter, but for any degree of freedom of the structure, including nonmagnetic secondary ones (see Sec. IV C).

The space group of the paramagnetic phase of $MnWO_4$ is $P2/c$. In the crystallographic unit cell there is one independent manganese atom located at the $2f$ Wyckoff position: Mn_1 at $(\frac{1}{2}, y, \frac{1}{4})$ with $y = 0.6849(6)$. The symmetry related atom Mn_2 within the unit cell is at $(\frac{1}{2}, -y+1, \frac{3}{4})$ (see Table I for a description of the complete crystal structure refined). In general, for the symmetry analysis of a magnetic structure, the

TABLE I. The crystal structure parameters of $MnWO_4$, from refinement of 154 reflections collected at 9 K (phase AF2). The space group is $P2/c$. Debye-Waller factors (Å^2) and agreement factors are also included. The refinement at 13 K (phase AF3) gave the same result within experimental resolution. Rel. fac. stands for reliability factors.

Cell parameters:		$a = 4.8237(7)$ Å, $b = 5.7552(2)$ Å, $c = 5.0019(2)$ Å, $\beta = 91.0838(7)^\circ$		
Atoms	x	y	z	B_{eq}
Mn	$\frac{1}{2}$	0.6849(6)	$\frac{1}{4}$	0.3(1)
W	0	0.1798(5)	$\frac{1}{4}$	0.2(1)
O1	0.2105(3)	0.1024(2)	0.9412(7)	0.2(1)
O2	0.2503(4)	0.3744(2)	0.3938(6)	0.2(1)
Rel. fac. $R_F = 2.8$, $R_{F^2} = 4.8$, $R_{F^2w} = 5.4\%$				

parent symmetry has to be taken into account, which in this case corresponds to the grey magnetic space group $P2/c1'$ of the paramagnetic phase, where $1'$ refers to the time inversion operation. This space group consists of all the symmetry operations of the ordinary $P2/c$ space group, plus an equal number of operations obtained by multiplying all of them by time reversal $\{1'|0\,0\,0\,0\}$ (which is also a symmetry operation of the paramagnetic phase). The incommensurate propagation vector, $\mathbf{k} = (-0.214, \frac{1}{2}, 0.457)$, lies on the symmetry line G $(\alpha\ \frac{1}{2}\ \gamma)$ of the Brillouin zone.[26] The corresponding little group, formed by the symmetry operators that leave $\mathbf{k}$ invariant, is $Pm1'$. There are two possible magnetic (odd for time reversal) irreducible representations (irreps) of this little group. They are both one-dimensional and are defined by the corresponding irreps of the little cogroup $m1'$ (see Table II).

As explained in Ref. 5, if the magnetic order is realized according to a single one-dimensional small irrep, a unique superspace group can be assigned to the resulting magnetic structure. All the operations of the little group are kept in this superspace group, but a $(0\ 0\ 0\ \frac{1}{2})$ translation (along the internal space) has to be added to those operators that have -1 character. In addition, all operations transforming $\mathbf{k}$ into $-\mathbf{k}$ are also maintained: its chosen representative (for instance the space inversion) can be chosen with zero translation along the internal space by a convenient choice of the phase of the magnetic modulation, while the remaining operations can be obtained from the application of the internal product of the group. Following these rules, the two possible superspace groups corresponding to the two possible active irreps at the G line can be derived (the program JANA2006[9] has also an option to derive them automatically). According to the notation usually employed, they can be labeled as $P2/c1'(\alpha\frac{1}{2}\gamma)00s$ and $P2/c1'(\alpha\frac{1}{2}\gamma)0ss$, and their generators are listed in Table II. It is important to stress that these superspace groups include operations that transform $\mathbf{k}$ into $-\mathbf{k}$. In both cases, the corresponding magnetic point group is $2/m1'$, which implies the absence in such phases of any induced ferroelectricity and of any linear magnetoelectric response. It is also worth mentioning that the magnetic superspace groups associated to magnetic irreps can also be obtained using the program ISODISTORT[27] (method 2), but in this case the symmetries are given in standard settings, which are not the settings used here.

Centered unit cells are used to simplify the description of crystal symmetry in standard crystallography. This can also be done in the case of incommensurate superspace symmetry. The propagation vector $(\alpha\ \frac{1}{2}\ \beta)$ is not purely incommensurate, as it includes a component $\frac{1}{2}$ along y. Because of this commensurate component, the symmetry relations and constraints of the modulations are given by an equation more complex than Eq. (3).[5] This complication can however be avoided, and Eq. (3) can be applied, by using a unit cell doubled along y, so that the propagation vector in its reciprocal basis becomes $\mathbf{k}' = (\alpha\ 0\ \beta)$. The effect of the $(0\ \frac{1}{2}\ 0)$ component of the modulation propagation vector is maintained by the introduction of an appropriate centering translation in superspace. More specifically, one considers a cell $a, 2b, c$ such that now there are four Mn atoms per unit cell. The $(0\ \frac{1}{2}\ 0)$ component of the original modulation only means that the atoms within this unit cell related by a translation b have modulations with a π phase shift. This is ensured by including in the superspace group a centering translation $(0\ \frac{1}{2}\ 0\ \frac{1}{2})$. Indeed, according to Eq. (3), if the atoms in the doubled cell are labeled $\mathrm{Mn}_1 = (\frac{1}{2}, \frac{y_1}{2}, \frac{1}{4})$, $\mathrm{Mn}_2 = (\frac{1}{2}, \frac{-y_1+1}{2}, \frac{3}{4})$, $\mathrm{Mn}_{11} = (\frac{1}{2}, \frac{y_1+1}{2}, \frac{1}{4})$, and $\mathrm{Mn}_{22} = (\frac{1}{2}, \frac{-y_1+2}{2}, \frac{3}{4})$, the modulations of the atoms Mn_{11} and Mn_{22} are $\frac{1}{2}$ shifted with respect to those of the other two atoms:

$$\begin{aligned} \mathbf{M}_{\mathrm{Mn}_{11}}(x_4) &= \mathbf{M}_{\mathrm{Mn}_1}(x_4 + \tfrac{1}{2}), \\ \mathbf{M}_{\mathrm{Mn}_{22}}(x_4) &= \mathbf{M}_{\mathrm{Mn}_2}(x_4 + \tfrac{1}{2}). \end{aligned} \tag{4}$$

The description of a superspace group with these optional centered unit cells is usually indicated in the superspace group label by means of an "X". Thus $P2/c1'(\alpha\frac{1}{2}\gamma)0ss$ becomes $X2/c1'(\alpha0\gamma)0ss$ and $P2/c1'(\alpha\frac{1}{2}\gamma)00s$ becomes $X2/c1'(\alpha0\gamma)00s$. The symmetry operations of the former are described in detail in Table III. The apparent new reflections introduced by the duplication of the basic unit cell are canceled out due to the centering $(0\ \frac{1}{2}\ 0\ \frac{1}{2})$, as depicted in Fig. 1. In the following, we will use this X-centered description of any relevant superspace group.

A magnetic phase can result from the activation of several primary irrep modes. In this case, if the propagation vector is incommensurate, its superspace symmetry is described by the intersection of the superspace groups associated with each individual irrep. This intersection depends on the relative

TABLE II. Irreps of the little cogroup, $m1'$, which define the two possible magnetic irreps of the paramagnetic group $P2/c1'$ with $\mathbf{k} = (\alpha\ \frac{1}{2}\ \gamma)$. The label of the resulting superspace group as well as its generators are provided in each case.

Irrep	1	m	$1'$	Superspace group	Generators
mG_1	1	1	-1	$P2/c1'(\alpha\frac{1}{2}\gamma)00s$	$\{m_y\|0\,0\,\frac{1}{2}\,0\}$, $\{\bar{1}\|0\,0\,0\,0\}$, $\{1'\|0\,0\,0\,\frac{1}{2}\}$
mG_2	1	-1	-1	$P2/c1'(\alpha\frac{1}{2}\gamma)0ss$	$\{m_y\|0\,0\,\frac{1}{2}\,\frac{1}{2}\}$, $\{\bar{1}\|0\,0\,0\,0\}$, $\{1'\|0\,0\,0\,\frac{1}{2}\}$

TABLE III. Representative operations of the space group $P2/c1'(\alpha\frac{1}{2}\gamma)0ss$ described in primitive setting and in the X-centered one. Both generalized Seitz-type notation (left column) and symmetry cards as used in JANA2006 are listed. The labels $-m$ or m indicate whether the operation includes the time inversion ($-m$) or not (m). The remaining operations are obtained by the internal product of the group.

$P2/c1'(\alpha\frac{1}{2}\gamma)0ss$					
$\{1\|0000\}$	x_1	x_2	x_3	x_4	m
$\{2_y\|00\frac{1}{2}\frac{1}{2}\}$	$-x_1$	x_2	$-x_3+\frac{1}{2}$	$x_2-x_4+\frac{1}{2}$	m
$\{\bar{1}\|0000\}$	$-x_1$	$-x_2$	$-x_3$	$-x_4$	m
$\{m_y\|00\frac{1}{2}\frac{1}{2}\}$	x_1	$-x_2$	$x_3+\frac{1}{2}$	$-x_2+x_4+\frac{1}{2}$	m
$\{1'\|000\frac{1}{2}\}$	x_1	x_2	x_3	$x_4+\frac{1}{2}$	$-m$
$X2/c1'(\alpha0\gamma)0ss$					
$\{1\|0000\}$	x_1	x_2	x_3	x_4	m
$\{2_y\|00\frac{1}{2}\frac{1}{2}\}$	$-x_1$	x_2	$-x_3+\frac{1}{2}$	$-x_4+\frac{1}{2}$	m
$\{\bar{1}\|0000\}$	$-x_1$	$-x_2$	$-x_3$	$-x_4$	m
$\{m_y\|00\frac{1}{2}\frac{1}{2}\}$	x_1	$-x_2$	$x_3+\frac{1}{2}$	$x_4+\frac{1}{2}$	m
$\{1'\|000\frac{1}{2}\}$	x_1	x_2	x_3	$x_4+\frac{1}{2}$	$-m$
$\{1\|0\frac{1}{2}0\frac{1}{2}\}$	x_1	$x_2+\frac{1}{2}$	x_3	$x_4+\frac{1}{2}$	m

phases of the corresponding modulations. In what follows we discuss the symmetry resulting from two primary modes. When two primary incommensurate irrep modulations are superposed, only one of the two modulation phases can be arbitrarily chosen. This is done by associating to a representative operation of its superspace group transforming $\mathbf{k}$ into $-\mathbf{k}$ a null translation along the internal space. For the calculation of the intersection of the superspace groups associated with different irrep modulations, one has to consider that if a magnetic modulation is phase shifted by a quantity ϕ the symmetry operators of its superspace group that leave invariant $\mathbf{k}$ do not change, whereas the operations that transform $\mathbf{k}$ into $-\mathbf{k}$ acquire an additional $(0\ 0\ 0\ 2\phi)$ translation along the internal space.[5] If we consider the superposition of two primary modes transforming according to any of the two possible mG_1 and mG_2 irreps, taking into account all possible relative phase shifts, several different superspace groups are possible and can be readily calculated following these rules. They are listed in Table IV. One can see therein that the superposition of two modes mG_1 or two modes mG_2 reduce the magnetic point group symmetry to $m1'$, i.e., a polar group that allows a spontaneous electric polarization on the ac plane, while the superposition in quadrature of a mode mG_1 and a mode mG_2 implies a $21'$ point group symmetry, i.e., a polar symmetry that allows the buildup of electrical polarization along b.

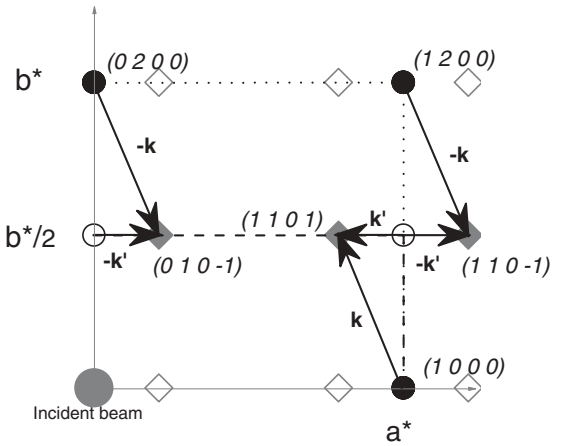

FIG. 1. Scheme of the indexing $(hklm)$ of diffraction peaks according to an a, $2b$, c supercell and a propagation vector $\mathbf{k}' = (\alpha\ 0\ \beta)$ together with a $(0\ \frac{1}{2}\ 0\ \frac{1}{2})$ centering translation (X centering). Full circles and grey rhombuses correspond to nuclear and magnetic reflections, respectively. Magnetic reflections are projected on the plane $(hk0)$. Empty circles and empty rhombuses represent systematic extinctions caused by the X centering, which forces both magnetic and nuclear reflections to obey the $k+m=2n$ reflection condition.

IV. RESULTS AND DISCUSSION

A. Paraelectric AF3 magnetic phase

If we assume that the paraelectric magnetic structure of the AF3 phase corresponds to a single active irrep modulation,

TABLE IV. Superspace groups resulting from the superposition of two irrep magnetic modulations with a phase shift $\Delta\phi$ between them. The magnetic point group of each superspace group is in the last column.

$\Delta\phi = 0, \frac{1}{2}$	$mG_1 + mG_1$	$X2/c1'(\alpha0\gamma)00s$	$2/m1'$
	$mG_2 + mG_2$	$X2/c1'(\alpha0\gamma)0ss$	$2/m1'$
	$mG_1 + mG_2$	$X\bar{1}1'(\alpha0\gamma)0s$	$-11'$
$\Delta\phi = \frac{1}{4}, \frac{3}{4}$	$mG_1 + mG_1$	$Xc1'(\alpha0\gamma)0s$	$m1'$
	$mG_2 + mG_2$	$Xc1'(\alpha0\gamma)ss$	$m1'$
	$mG_1 + mG_2$	$X21'(\alpha0\gamma)0s$	$21'$
$\Delta\phi =$ arbitrary	$mG_1 + mG_1$	$Xc1'(\alpha0\gamma)0s$	$m1'$
	$mG_2 + mG_2$	$Xc1'(\alpha0\gamma)ss$	$m1'$
	$mG_1 + mG_2$	$X11'(\alpha0\gamma)0s$	$11'$

described in Table II, its magnetic symmetry should be described by either the $X2/c1'(\alpha 0\gamma)00s$ or $X2/c1'(\alpha 0\gamma)0ss$ superspace group. Both symmetries include the inversion operation $\{\bar{1}|0\frac{1}{2}0\frac{1}{2}\}$ that relates atoms Mn_1 and Mn_2. According to Eq. (3) this means that the magnetic modulations of both atoms are in both cases related in the form

$$\mathbf{M}_{\mathrm{Mn}_2}\left(-x_4+\tfrac{1}{2}\right)=\mathbf{M}_{\mathrm{Mn}_1}(x_4). \tag{5}$$

This implies that only the modulation of one atom, say Mn_1, is independent, while the two atoms Mn_2 and Mn_1 have, in both superspace groups, identical modulations but with opposite chirality. The distinction between the two possible symmetries comes from the operation $\{2_y|00\frac{1}{2}\tau\}$, which keeps atom Mn_1 invariant and therefore constrains the form of its modulation. According to Eq. (3),

$$\mathbf{M}_{\mathrm{Mn}_1}(-x_4+\tau)=2_y\cdot\mathbf{M}_{\mathrm{Mn}_1}(x_4). \tag{6}$$

If we call $(M_{1x}(x_4), M_{1y}(x_4), M_{1z}(x_4))$ the three components of the magnetic modulation function of Mn_1 along the three crystallographic directions, in the first superspace group $\tau=0$, according to Eq. (6), the modulation of the x, z components of the magnetic moment should be sine-like, while the y component should be cosine-like. On the other hand, for $X2/c1'(\alpha 0\gamma)0ss$, $\tau=\frac{1}{2}$ and the constraint of sine and cosine forms are exchanged, so that

$$M_\alpha(x_4)=M_\alpha^c\cos(2\pi x_4)\quad(\alpha=x,z), \tag{7}$$

$$M_y(x_4)=M_y^s\sin(2\pi x_4), \tag{8}$$

while according to Eq. (5) the spin modulation of atom Mn_2 is given by cosine functions with opposite amplitudes for components x and z, and a sine function of the same amplitude for the y component. Thus, the real amplitudes M_x^c, M_y^s, and M_z^c fully describe the magnetic structure.

It is important to stress that, even if the modulation of Mn_1 were reduced to the plane ac, the choice of cosine or sine functions for its description does not represent a mere phase shift in the global spin wave, because Eq. (5) is also included in the model, and it implies a completely different choice for the correlation with the spins of Mn_2 atoms, if one or the other superspace group is chosen. In both alternative symmetries three parameters are required to describe the magnetic structure.

It is worth to compare here with the usual representation approach. As it is usually used, the representation analysis only introduces the irrep restrictions corresponding to the symmetry operations of the little group, which keeps **k** invariant. Atoms Mn_1 and Mn_2 in the unit cell are related in the paramagnetic phase by the space group operation $\{m_y|01\frac{1}{2}\}$, belonging to the little group. Thus, the representation method introduces a relation between the spin modulations of the two Mn atoms corresponding to this symmetry operation. This relation is equivalent to the one resulting from the superspace operation $\{m_y|0\frac{1}{2}\frac{1}{2},\frac{1}{2}+\tau\}$ (X setting) with $\tau=0$ for mG_1 and $\tau=\frac{1}{2}$ for mG_2, which is present in their respective superspace group. However, no restriction equivalent to the one of Eq. (6) is considered, and therefore, in the representation approach, the spin modulation of one of the atoms is fully free.[16] This means that the relative phases between the modulations of the three spin components are free parameters. As in an incommensurate modulation, one of the phases can be fixed arbitrarily, the number of refinable parameters of the model is five, compared with only three parameters when using the superspace group description. In fact, the model considered in Ref. 16, applying the standard representation analysis method, yields the same result as using the minimal superspace groups $Xc1'(\alpha 0\gamma)0s$ or $Xc1'(\alpha 0\gamma)ss$ corresponding to the superposition of at least two phase-shifted irrep modes of the same irrep symmetry (see Table IV). Note that this model for the magnetic structure would imply a magnetic point group $m1'$, and therefore polarity within the xz plane. As in many other studies, the additional restrictions necessary to increase the symmetry of the model and to reduce the modulations to a single irrep mode were subsequently introduced in Ref. 16 by means of intuitive arguments based on the search for simple modulations (collinear, spiral, etc.). In general, the structures described applying the representation approach (as normally used) are compatible with those obtained using the superspace formalism, but fewer constraints are introduced, and they are less symmetric.

Both superspace groups, $X2/c1'(\alpha 0\gamma)00s$ and $X2/c1'(\alpha 0\gamma)0ss$, were tried alternatively in the refinement of the structure. The 166 observed magnetic reflections resulted after averaging into 66 independent ones with $R_{int}=8.67$. From the refinement it can be clearly concluded that the magnetic symmetry of the paraelectric AF3 phase is $X2/c1'(\alpha 0\gamma)0ss$. The parameters that describe the magnetic structure as well as the agreement factors are given in Table V and the structure is depicted in Fig. 2. The refined value of the amplitude M_y^s describing the symmetry-allowed sine modulation along the y direction is very small, although larger

TABLE V. Refined parameters that describe the magnetic structure of $MnWO_4$ at 13 K with constrains imposed by the $X2/c1'(\alpha 0\gamma)0ss$ superspace group, including and not including a y component in the magnetic modulation. Maximum and minimum values of the ordered moments are given in the last two columns, i.e., the semi-major and semi-minor axes of the helix in the first model and the amplitude of the modulation in the second model. Parameters are defined in the text.

M_x^s	M_y^s	M_z^s	M_x^c	M_y^c	M_z^c	$\lvert m_{\max}\rvert$	$\lvert m_{\min}\rvert$
0.000[a]	0.05(3)	0.000[a]	1.46(3)	0.000[a]	1.18(2)	1.88(4)	0.05(3)
$R_F(\mathrm{obs})=7.15$, $wR_F(\mathrm{obs})=5.51$, $wR_{F^2}(\mathrm{obs})=10.59$							
0.000[a]	0.00[b]	0.000[a]	1.47(2)	0.000[b]	1.17(2)	1.88(3)	
$R_F(\mathrm{obs})=7.23$, $wR_F(\mathrm{obs})=5.63$, $wR_{F^2}(\mathrm{obs})=10.86$							

[a]Constrained by symmetry.
[b]Fixed manually.

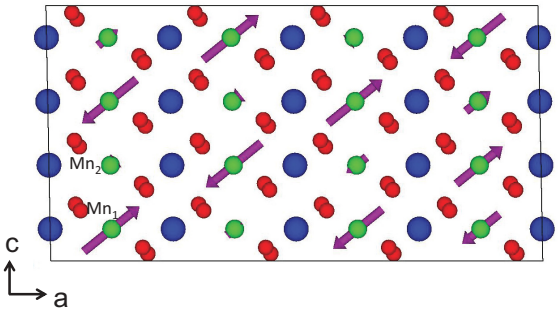

FIG. 2. (Color online) Projection along the b axis of the AF3 phase of $MnWO_4$ at 13 K (Table V). Only the nonperiodic modulation within a region $4a \times 2b \times 2c$ is represented.

than its standard deviation. It was then fixed to zero, and Table V also shows the result of this second refinement. This latter refinement, with the weak M_y^s component neglected, reduces the model to a sinusoidally modulated collinear magnetic modulation in the ac plane, with the direction of the moments (the so-called $\hat{u}$ direction) making approximately a 39(1)° angle with the a axis and $1.88(4)\mu_B$ amplitude. This approximate model is directly comparable and agrees with the magnetic structure proposed in Ref. 16, where the amplitude is $2.1\mu_B$ and the angle is 35°.

It is important to stress that the structure of the AF3 phase is not forced by symmetry to be collinear. A Hamilton test[28] indicates that the weak nonzero value of the amplitude M_y^s is statistically significant. This nonzero modulation for the y spin component makes the spin waves helical, but of opposite chiralities in the two Mn atoms. This situation is represented in Fig. 3, where for clarity an artificially large component M_y^s has been introduced in the model. The two modulations are related by space inversion [see Eq. (5)], which forbids any induced net electric polarization.

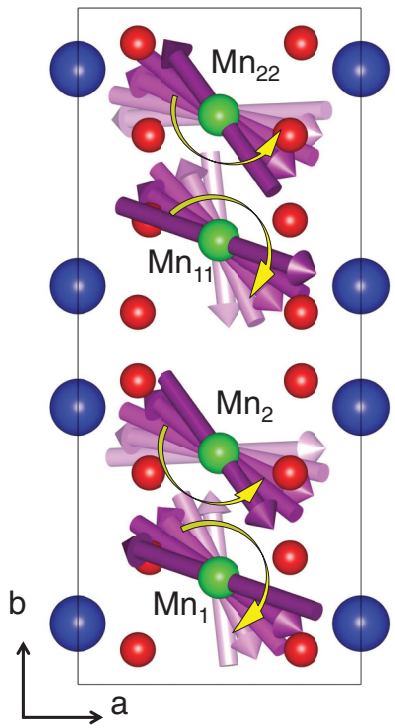

FIG. 3. (Color online) Projection along the c axis of the AF3 phase with an arbitrarily large amplitude of the symmetry-allowed y component of the magnetic modulations. The symmetry of the AF3 phase (a single mG_2 irrep mode) allows a cycloidal component in the Mn modulations but of opposite chirality for Mn_1 and Mn_2.

B. AF2 multiferroic phase

The propagation vector $\mathbf{k} = (\alpha, \frac{1}{2}, \gamma)$ does not change at the transition from the AF3 phase to the multiferroic AF2 phase. The same values $\alpha = -0.214$ and $\gamma = 0.457$ were experimentally observed as a clear signature that the additional symmetry breaking leading to the AF2 phase with spontaneous polarization is "commensurate" with respect to the modulations in the paraelectric AF3 phase. In the simplest scenario, one can consider that this symmetry breaking is due to the activation of an additional irrep magnetic mode. Table IV contains all possible superspace groups that can result from the superposition of two primary irrep magnetic modes. One can see that there are three magnetic symmetries in the table that could in principle describe a multiferroic structure, as their magnetic point groups are $21'$, $m1'$, and $11'$. Those point groups allow the appearance of electric polarization along the b axis, in the xz plane, or along an arbitrary direction, respectively. It is known that the polarization in $MnWO_4$ arises along the b axis.[13–15] Hence, according to Table IV the superspace group symmetry that must correspond to phase AF2 is $X21'(\alpha 0\gamma)0s$ (see Table VI). The inversion and the glide plane that relate Mn_1 and Mn_2 in the AF3 phase are therefore lost at the transition, and these two manganese atoms become symmetry independent. The symmetry $X21'(\alpha 0\gamma)0s$ keeps, however, the operation $\{2_y|00\frac{1}{2}\frac{1}{2}\}$.[29] This means that the spin modulations of both atoms Mn_1 and Mn_2 maintain the symmetry constraints imposed by Eqs. (7) and (8), but with amplitudes that are no longer symmetry related. There are therefore six parameters to refine, three for each manganese atom.

TABLE VI. Representative operations of the space group $P21'(\alpha\frac{1}{2}\gamma)0s$ described in primitive setting and in the X-centered one. Both generalized Seitz-type notation (left column) and symmetry cards as used in JANA2006 are listed. The labels $-m$ or m indicate whether the operation includes the time inversion ($-m$) or not (m). The remaining operations are obtained by the internal product of the group.

$P21'(\alpha\frac{1}{2}\gamma)0s$					
$\{1\|0000\}$	x_1	x_2	x_3	x_4	m
$\{2_y\|00\frac{1}{2}\frac{1}{2}\}$	$-x_1$	x_2	$-x_3+\frac{1}{2}$	$x_2-x_4+\frac{1}{2}$	m
$\{1'\|000\frac{1}{2}\}$	x_1	x_2	x_3	$x_4+\frac{1}{2}$	$-m$
$X21'(\alpha 0\gamma)0s$					
$\{1\|0000\}$	x_1	x_2	x_3	x_4	m
$\{2_y\|00\frac{1}{2}\frac{1}{2}\}$	$-x_1$	x_2	$-x_3+\frac{1}{2}$	$-x_4+\frac{1}{2}$	m
$\{1'\|000\frac{1}{2}\}$	x_1	x_2	x_3	$x_4+\frac{1}{2}$	$-m$
$\{1\|0\frac{1}{2}0\frac{1}{2}\}$	x_1	$x_2+\frac{1}{2}$	x_3	$x_4+\frac{1}{2}$	m

TABLE VII. Refined parameters of the magnetic modulations of the multiferroic phase of pure $MnWO_4$ (9 K) in the superspace group $X21'(\alpha 0\gamma)0s$. The results of constrained refinement forcing the two symmetry-independent atoms to have equal spiral modulation is also included. Maximum and minimum values of the ordered moments are given in the last two columns, i.e., the semi-major and semi-minor axes of the helixes.

Mn_i	M_x^s	M_y^s	M_z^s	M_x^c	M_y^c	M_z^c	$\lvert m_{\max}\rvert$	$\lvert m_{\min}\rvert$
$i=1$	0.0[a]	3.26(7)	0.0[a]	3.28(8)	0.0[a]	2.49(6)	4.1(1)	3.26(7)
$i=2$	0.0[a]	−2.97(6)	0.0[a]	−3.11(8)	0.0[a]	−1.78(6)	3.6(1)	2.97(6)
$R_F(\text{obs})=3.54$, $wR_F(\text{obs})=3.45$, $wR_{F^2}(\text{obs})=6.20$								
$i=1$	0.0[a]	3.14(3)	0.0[a]	3.21(4)	0.0[a]	2.14(5)	3.86(8)	3.14(3)
$i=2$	0.0[a]	−3.14[b]	0.0[a]	−3.21[b]	0.0[a]	−2.14[b]	3.86(8)	3.14(3)
$R_F(\text{obs})=3.94$, $wR_F(\text{obs})=3.75$, $wR_{F^2}(\text{obs})=6.71$								

[a]Constrained by symmetry.
[b]Fixed manually.

The refinement done from 162 independent magnetic reflections (averaged from 246 reflections collected at 9 K with $R_{int}=2.50$) confirmed the superspace symmetry $X21'(\alpha 0\gamma)0s$ for the AF2 phase, and therefore a spin modulation according to a superposition in quadrature of $mG2$ and $mG1$ modes. The refined parameters are listed in Table VII and a scheme of the magnetic structure is plotted in Fig. 4. The moments rotate according to an ellipse in the ub plane, where $\hat{u}$ is the easy direction in the ac plane. In this case, in contrast with the AF3 phase, the chirality of the two Mn_1 and Mn_2 spin chains is the same, see Fig. 4 (a), giving rise to a net electrical polarization by some mechanism such as the spin-orbit driven inverse Dzyaloshinskii-Moriya effect. Note that, although in Fig. 4 (a) the projection of the modulation is done perpendicular to c, the propagation direction of these spirals also has a component parallel to the a axis [$x_4=(\alpha 0\gamma)\cdot(\mathbf{l}+\mathbf{r}_\mu)$ in Eqs. (7) and (8)]. As can be seen in Table VII the deviation from a circular spiral of the modulations of both Mn atoms is very significant. The elliptical orbits have semi-axes (in Bohr magnetons) of [4.1(1), 3.26(7)] and [3.6(1), 2.97(6)], for Mn_1 and Mn_2 respectively. The direction $\hat{u}$ of the magnetic moments also differs between the two atoms, forming an angle with the a axis of about 37(2)° for Mn_1 and of 30(2)° for Mn_2. These differences between the two modulations are basically due to the strong difference of the modulation amplitude along the z axis (see Table VII). While the x and y modulation amplitudes have similar magnitude for both atoms, the amplitude along z differs substantially, and changes both the spiral plane and the elliptical orbit of the magnetic moments.

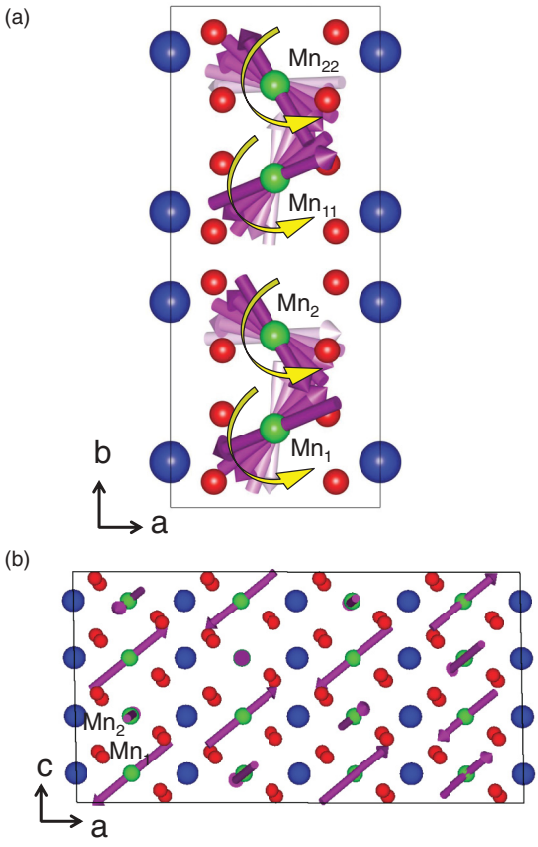

FIG. 4. (Color online) AF2 multiferroic magnetic structure of $MnWO_4$ at 9 K. (a) Projection along the c axis showing the chirality of the structure. (b) Projection along the b axis. Only the nonperiodic modulation within a region $4a\times 2b\times 2c$ is represented.

Table VII also shows the results of a refinement where the amplitudes of the modulations along the three crystallographic directions of the two atoms were forced to be, respectively, of equal magnitude but with opposite sign. These restrictions makes equal the elliptical helix modulations of the two atoms, except for a π phase shift, and reduces the number of refinable parameters to three. This is the model of phase AF2 that was proposed in Ref. 16. In this constrained refinement, the obtained elliptical helix, forced to be common to both atoms, has 3.86(5) μ_B and 3.14(3) μ_B as semi-axes and its plane forms an angle of 34(2)° with the a axis, in agreement with the values reported in Ref. 16. In this constrained model the two superposed magnetic modes are such that the $mG2$ mode is restricted to the plane xz, while the $mG1$ mode is limited to the y direction. In this way, the sign correlation of neighboring spins is the same for the two modes, which will have then the same exchange energy terms. This model therefore neglects those degrees of freedom in the spin arrangement that, although allowed by symmetry, have sign correlations of neighboring spins which are not favored by the exchange coupling.

The simplification included in the model proposed in Ref. 16 is consistent with the prevailing role of the isotropic exchange energy, but the better results of the refinement of

a nonconstrained model, only restricted by the superspace symmetry of the phase, demonstrates that the modulations of the two Mn atoms have significant differences, due to some non-negligible contribution of spin mode components with unfavorable exchange energies. Anisotropic effects beyond the exchange interaction, although weak, are an essential ingredient of multiferroics, and this feature of the magnetic structure of the AF2 phase, demonstrated by the present study, can be considered one of them. This is similar to what happens in weak ferromagnets, where the magnetic ordering exhibits ferromagnetic correlations along some directions, despite being unfavorable from the viewpoint of exchange energy. They appear as secondary effects because they are permitted by symmetry. The application of superspace symmetry allows us to predict similar effects in incommensurate magnetic phases, distinguishing the rigorous restrictions coming from symmetry from those that are only approximate and are associated with the overwhelming role of the isotropic exchange interactions.

C. Atomic modulations

Apart from the constraints on the magnetic modulations, the superspace symmetry of an incommensurate magnetic phase also provides information on the possible displacement modulations of the atoms positions.

Although the structural modulations induced by magnetostructural coupling are in general very weak, and have not been considered in the measurements reported here, it is important to have in mind their possible existence and their expected characteristics. The ferroelectric behavior observed in $MnWO_4$ is in fact part of this induced structural distortion resulting from the magnetic symmetry break, and corresponds to a $\mathbf{k} = 0$ polar structural modulation. In this section we present the symmetry constraints of the atomic (positional) structures of the AF3 and AF2 magnetic phases.

The structural distortions resulting from magnetostructural coupling with the magnetic ordering are subject to the same symmetry than the actual magnetic ordering. This means that the atomic positions can in principle become modulated, but their modulations will be restricted by the same superspace group operations as the magnetic modulations. Their effect is, however, different due to the invariance of the structural modulation for time reversal. Thus, the symmetry operation $\{1'|000\frac{1}{2}\}$, common to both phases, force the possible displacive modulations of any atom to the condition

$$\mathbf{u}_i\left(x_4+\tfrac{1}{2}\right)=\mathbf{u}_i(x_4). \tag{9}$$

This means that any possible induced structural modulation is limited to even harmonics. This is a quite general feature of single-**k** incommensurate magnetic phases (see Ref. 5), restricting possible satellite structural diffraction peaks to even m indices, while magnetic ones are necessarily odd ones if the modulation becomes anharmonic. Second-order satellites due to induced structural modulations, although weak, are indeed quite common,[30–33] and they have been also found in $MnWO_4$ by synchrotron x-ray diffraction.[30]

Note that Eq. (9) implies that the nonmagnetic atomic modulations of Mn_1 and Mn_{11} (as those of Mn_2 and Mn_{22}), related by the centering X, are identical. In principle, provided that second-order satellites are strong enough to be measurable, the atomic modulated structure could be determined separately from the magnetic one using the nonmagnetic superspace group (with modulation wave vector $2\mathbf{k}$), resulting from substituting the operation $\{1'|000\frac{1}{2}\}$ by $\{1|000\frac{1}{2}\}$, and applying then the usual procedures that have become standard for nonmagnetic incommensurate structures. This is, however, not necessary and could be misleading, because magnetic superspace symmetry provides an unified framework that constrains all degrees of freedom, and clarifies the correlation between the constraints imposed upon magnetic and nonmagnetic degrees of freedom.

The Mn and W atoms are kept invariant by the symmetry operation $\{2_y|00\frac{1}{2}\frac{1}{2}\}$, which is common both to AF3 and AF2 phases, and this implies, according to the analog of Eq. (3) that their displacive modulations must satisfy

$$\mathbf{u}_i\left(-x_4+\tfrac{1}{2}\right)=2_y\cdot\mathbf{u}_i(x_4), \tag{10}$$

where i is any Mn or W atom in the paramagnetic unit cell.

Hence, the x and z components of these modulations are restricted to sine terms while the y component can only contain cosine terms:

$$\mathbf{u}_{i\alpha}(x_4)=\mathbf{u}^1_{i\alpha}\sin(4\pi x_4)\quad(\alpha=x,z), \tag{11}$$

$$\mathbf{u}_{iy}(x_4)=\mathbf{u}^0_{iy}+\mathbf{u}^1_{iy}\cos(4\pi x_4), \tag{12}$$

where i = Mn, W.

The displacive modulations that can happen in W and Mn atoms by any kind of magnetostructural coupling are therefore $\frac{\pi}{2}$ shifted with respect to the magnetic modulation of the Mn atoms, independently of the specific atomistic mechanism at work.

In the AF3 phase, any pair of atoms $i = 1,2$, related by $\{\bar{1}|0\frac{1}{2}0\frac{1}{2}\}$, as Mn_1 and Mn_2, have their structural modulations related by

$$\mathbf{u}_2\left(-x_4+\tfrac{1}{2}\right)=-\mathbf{u}_1(x_4) \tag{13}$$

which according to Eqs. (11) and (12) implies equal amplitudes for the x, z sine terms, and opposite ones for the y amplitudes. Mn and W are allowed to have homogeneous ($\mathbf{k} = 0$) displacements along y [see Eq. (12)], but Eq. (13) implies that in the AF3 phase each pair of atoms related by inversion will have opposite homogeneous displacements, consistently with the centrosymmetric point group symmetry $2/m$ of this phase. Something similar happens for the more general modulations of the oxygen atoms in general positions that can have an homogeneous components along the three crystallographic directions. In contrast, in the AF2 phase, as the inversion symmetry operation is no longer valid, the constraint limiting the homogeneous displacements along y of inversion-related atoms to opposite values disappears and a polar distortion mode is allowed.

Summarizing, both AF3 and AF2 phases may exhibit a magnetic induced structural modulation with $2\mathbf{k}$ as primary modulation wave vector. In the AF3 phase this structural modulation maintains an average structure with $P2/c$ symmetry, i.e., the same space group as in the paramagnetic phase, while the structural modulation in the AF2 phases looses some of its constraints and has only as symmetry for the average structure the space group $P2$.

The symmetry constraints on magnetically induced structural distortions have their ultimate origin in the properties of any possible magnetostructural mechanism. Superspace symmetry is a convenient and efficient method to automatically derive these constraints, but one can always trace them back, through a proper Landau theory analysis, to the restrictions on the allowed magnetostructural couplings of the system. An extended discussion of the relation of the general symmetry constraints of magnetically induced structural distortions with the restrictions on the possible magnetostructural coupling terms can be found in Ref. 5.

V. CONCLUSIONS

The two incommensurate magnetic phases of the multiferroic $MnWO_4$ have been analyzed using the superspace formalism. The superspace group corresponding to each phase has been identified, and the structures have been redetermined under these symmetries, using single-crystal nonpolarized neutron diffraction data. The spin modulations of the Mn atoms have been fully determined, distinguishing those features forced by symmetry and fulfilled exactly from those only approximate and essentially caused by the strong weight of the isotropic exchange interaction. The study shows that, in the paraelectric antiferromagnetic phase AF3, the modulations of the two Mn atoms in the unit cell can have a (small) cycloidal component, exactly equal but with opposite chiralities in the two atoms, such that their effects cancel and they cannot induce any electric polarization. In contrast, in the AF2 phase, the addition of a second magnetic mode to the spin modulations breaks the symmetry relation between the two manganese atoms, the two modulations have then chiralities of the same sign, and their effect add up in the buildup of an electric macroscopic polarization.

The superspace group of each phase also determines the magnetic point group governing its crystal tensor properties. The ferroic properties of the multiferroic AF2 phase can then be characterized by the point-group symmetry break $2/m1' \rightarrow 21'$, i.e., by the ferroic species $2/m1'F21'$.[34] This ferroic species implies that there can only be two types of ferroic domains in the AF2 phase, related by the space inversion lost in the symmetry break (or equivalently by the mirror plane). Thus, the correlated switching properties of electric polarization and magnetic modulations in phase AF2 can be readily predicted: space inversion switches polarization, while it keeps invariant the (real) amplitude the $mG2$ irrep mode and changes sign of the (imaginary) amplitude of the $mG1$ irrep modulation. This means that the two domains with opposite polarization have also spin modulations of opposite chirality (related by inversion).

The application of superspace formalism to the quantitative experimental analysis of incommensurate magnetic phases is a promising new development with yet few examples in the literature. We explained here with much detail its application, in order to show this methodology at work in a practical simple case, and demonstrated its prospect as a powerful tool to describe and use systematically the symmetry properties of incommensurate magnetic structures.

As supplemental material,[35] files with complete information of the magnetic refinements, including the experimental data used, have been deposited.

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