Internal-strain mediated coupling between polar Bi and magnetic Mn ions in the defect-free quadruple-perovskite BiMn$_3$Mn$_4$O$_{12}$

Andrea Gauzzi$^\dagger$ and Gwenaelle Rousse

Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie-Sorbonne Universités and CNRS, 75005 Paris, France

Francesco Mezzadri and Gianluca Calestani

Dipartimento di Chimica - GIAF, Università degli Studi di Parma, 43100 Parma, Italy

Gilles André and Françoise Bourée

Laboratoire Léon Brillouin, CEA-CNRS, 91191 Gif-sur-Yvette, France

Marco Calicchio, Edi Gilioli, Riccardo Cabassi, Fulvio Bolzoni, and Andrea Prodi

Istituto dei Materiali per Elettronica e Magnetismo Consiglio Nazionale delle Ricerche, Area delle Scienze, 43100 Parma, Italy

Pierre Bordet

Institut Néel-CNRS, 25, rue des Martyrs, 38042 Grenoble, France

Massimo Marezio

CRETA-CNRS, 25, rue des Martyrs, 38042 Grenoble, France

(Dated: June 23, 2011)

By means of neutron powder diffraction measurements in the 1.5-300 K range, we investigated the effect of the polar Bi$^{3+}$ ion on the magnetic ordering of the Mn$^{3+}$ ions in BiMn$_3$Mn$_4$O$_{12}$, the counterpart with quadruple perovskite structure of the simple perovskite BiMnO$_3$. At all temperatures, the data are consistent with a noncentrosymmetric spacegroup Im which contrasts the centrosymmetric one 12/m previously reported for the isovalent and isomorphic compound LaMn$_3$Mn$_4$O$_{12}$. This difference gives evidence of a Bi$^{3+}$-induced polarization of the lattice in BiMn$_3$Mn$_4$O$_{12}$. At low temperature, the two Mn$^{3+}$ sublattices of the A' and B sites are found to order antiferromagnetically (AFM) in an independent fashion at 25 and 55 K, respectively, similarly to the case of LaMn$_3$Mn$_4$O$_{12}$. However, both magnetic structures of BiMn$_3$Mn$_4$O$_{12}$ radically differ from those of LaMn$_3$Mn$_4$O$_{12}$. Specifically, in BiMn$_3$Mn$_4$O$_{12}$ the moments $\mathbf{M}_{A'}$ of the A' sites form an anti-body AFM structure, whilst the moments $\mathbf{M}_{B}$ of the B sites result from a large and uniform modulation $\pm \mathbf{M}_{B, b}$ along the b-axis of the moments $\mathbf{M}_{B, ac}$ in the ac-plane of an E-type structure. The modulation is found to be strikingly correlated with the displacements of the Mn$^{3+}$ ions induced by the Bi$^{3+}$ ions. Our symmetry analysis of this correlation unveils a strong magnetoelastic coupling between the internal strain field created by the Bi$^{3+}$ ions and the moment of the Mn$^{3+}$ ions in the $B$ sites. We ascribe this phenomenon to the high symmetry of the oxygen sites and to the absence of oxygen defects, two characteristics of quadruple perovskites not found in simple ones, which prevent the release of the Bi$^{3+}$-induced strain through distortions or disorder. This result demonstrates the possibility of achieving a large magnetoelastic coupling mediated by internal strain in proper ferroelectrics and suggests a novel concept of internal strain engineering for multiferroics design.

PACS numbers: 75.85.+t,75.47.Lx,75.25.-j,75.80.+q

I. INTRODUCTION

The possibility of mutually controlling electric polarization and magnetization in multiferroic materials may lead to new device concepts for electronics. The challenge is to design materials with an effective magnetoelectric coupling suitable for applications. A first strategy is to achieve a coupling between polar and magnetic ions in the same compound. This is typically the case of Bi-based compounds, such as the perovskite system BiBO$_3$, where the 6$s^2$ lone pair of the Bi$^{3+}$ ion forms an electric dipole, while the B site is occupied by a magnetic ion, such as Mn$^{3+}$ or Fe$^{3+}$1–6. Despite intense research, modest magnetoelectric couplings have been hitherto reported in these compounds; this has been explained by the fact that the mere coexistence of polar and magnetic ions does not necessarily lead to their coupling1–3. Indeed, in these compounds, the ferroelectric order develops independent of the magnetic one (proper ferroelectricity). Recently, the focus has thus been moved to improper ferroelectrics, where ferroelectricity is induced by magnetism. Among the manganese oxides relevant here, notable are the $R$MnO$_3$7,8 and $R$Mn$_2$O$_7$9,11 systems ($R$=Y or rare earth), where a sizable tunability of
the polarization by applied fields has been reported\textsuperscript{12,13}. Various magnetoelastic coupling mechanisms have been considered, such as the spin-current interaction in spiral magnetic structures or the exchange striction in frustrated magnets\textsuperscript{14-18}, and the debate has attracted a great deal of interest.

In the absence of a firm theoretical framework, the possibility of a large coupling between polar and magnetic ions remains open and new hints are provided by recent experiments. Notable is a striking enhancement of magnetoelastic response in epitaxial BiFeO\textsubscript{3} films, where strain drives a rhombohedral to pseudo-tetragonal phase transition\textsuperscript{19,20}. Although the mechanism of this enhancement remains unclear, this result suggests that the magnetoelastic coupling in proper ferroelectrics is sensitive to strain and structural distortions\textsuperscript{21}. To clarify this point would be important for multiferroics design. This is a challenging task for the BiBO\textsubscript{3} system owing to the complex structure-property relationships, e.g. polymorphism\textsuperscript{22-24}, modulated structure\textsuperscript{25} and sensitivity to oxygen vacancies\textsuperscript{26-28}.

In this paper, we address the above point in a simpler system. By neutron powder diffraction, we have studied the effect of the polar Bi\textsuperscript{3+} ion on the magnetic ordering in BiMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12} \textsuperscript{29,30}, the counterpart with quadruple perovskite structure of the simple perovskite BiMnO\textsubscript{3}. Quadruple perovskites are described by the general formula $AA'B'_2B_4O_{12}$ \textsuperscript{31-33} and we shall restrict to the single-valent manganese oxides AMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12}, where $A$ is a three-valent ion, such as La\textsuperscript{3+}, Pr\textsuperscript{3+}, Bi\textsuperscript{3+}, Mn\textsuperscript{4+}, and Mn\textsuperscript{3+} occupies both $A'$ and $B$ sites. The structure (see Fig. 1) consists of the same pseudocubic network of corner-sharing BO\textsubscript{6} octahedra characteristic of simple perovskites ABO\textsubscript{3}, such as the aforementioned BiMnO\textsubscript{3} and TbMnO\textsubscript{3} multiferroics. Our motivation is that, in spite of this similarity, quadruple perovskites display a simpler distortion pattern and no oxygen vacancies\textsuperscript{33,34,35,38}. Our results show a striking correlation between the internal strain field induced by the polar Bi\textsuperscript{3+} ions and the magnetic ordering of the Mn\textsuperscript{3+} ions in BiMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12}. This conclusion provides a hint to achieve an effective magnetoelastic coupling between polar and magnetic ions in perovskite-like compounds.

**A. Structural characteristics of quadruple perovskites $A$Mn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12}**

As discussed in previous papers\textsuperscript{33,34}, the above favorable characteristics arise from the following features of quadruple perovskites. 1. Their structure is obtained by doubling the cubic unit cell axis of simple ABO\textsubscript{3} perovskites; the new unit cell therefore contains two distinct $A$ and $A'$ sites at the corners and middle of the cube edges, respectively. This doubling is caused by a large buckling of the BO\textsubscript{6} octahedra driven by the Jahn-Teller (JT) distortion of the $A'$ site. As a result, the Mn-O-Mn bond angle is drastically reduced to $\sim 135^\circ$, an unusually small value as compared to the $\sim 160^\circ$ value of simple perovskites, such as LaMnO\textsubscript{3}, which typically display orthorhombic-type distortions\textsuperscript{39}. 2. The large buckling lowers the coordination number of the $A'$ site from twelve to four, which prevents oxygen vacancies, as these would destabilize the structure. Indeed, no evidence of vacancies has been hitherto reported in any quadruple perovskite\textsuperscript{29,33,34,37,38}. No extra oxygen atoms can be hosted either within the structure owing to its high-density\textsuperscript{35,37}. 3. The simple distortions arise from the high symmetry of the cubic Im\textsubscript{3} phase, where all oxygen atoms occupy a unique high symmetry $m_..$ site, which only permits a rigid tilt of the BO\textsubscript{6} octahedra\textsuperscript{31}. The JT distortion of the octahedra requires a cubic Im\textsubscript{3} to monoclinic $I2/m$ phase transition typically realized at low temperature.

**B. Single-valent Mn$^{3+}$ quadruple perovskites $LaMn_3Mn_4O_{12}$ and BiMn$_3Mn_4O_{12}$**

In view of the above considerations, quadruple perovskites are a model system to investigate the coupling between Bi$^{3+}$ and Mn$^{3+}$ ions and BiMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12} is an obvious choice. It was previously reported\textsuperscript{29,30} that the nuclear structure of this compound is similar to that of the isoivalent LaMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12} \textsuperscript{30}, where La$^{3+}$ instead of Bi$^{3+}$ occupies the $A$ site. A structural study on single crystals\textsuperscript{29} shows that the main difference between the two structures is the center of symmetry breaking in the former, which is described by the $Im$, instead of $I2/m$, space group. This study confirms that this breaking is caused by the polar properties of the Bi$^{3+}$ ion, which

![FIG. 1. (Color online) Nuclear unit cell of the quadruple perovskite structure of BiMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12}. Note that the Mn$^{3+}$ ions occupy two distinct $A'$ and $B$ Jahn-Teller sites with square and octahedral coordination, respectively.](Image)
leads to a sizable spontaneous polarization $\sim 7 \mu C \, \text{cm}^{-2}$ at room temperature. In addition, BiMn$_3$Mn$_4$O$_{12}$ displays an AFM transition at $T_N = 55$ K concomitant to an anomaly of the dielectric constant, which suggests a coupling between AFM order and polarization. Interestingly, LaMn$_3$Mn$_4$O$_{12}$ exhibits a similar AFM transition in the same temperature range $T_N = 78$ K but no dielectric anomaly$^{34,36}$. The above results motivate the present study of the magnetic structure of BiMn$_3$Mn$_4$O$_{12}$.

II. EXPERIMENTAL METHODS

1. High-pressure synthesis of BiMn$_3$Mn$_4$O$_{12}$ powders

Powder samples of single-phase BiMn$_3$Mn$_4$O$_{12}$ were synthesized under high pressure in a multi-anvil apparatus at 4 GPa and 1000 °C for one hour as discussed in detail elsewhere$^{29}$. After the high pressure and high temperature synthesis, the samples were quenched down to room temperature in less than 1 minute in order to stabilize the high pressure phase. In order to check phase purity, the as-prepared samples were first analyzed using a commercial Siemens X-ray powder diffractometer equipped with a Cu K$_\alpha$ radiation.

2. Neutron powder diffraction measurements

The nuclear and magnetic structures were studied at 300 K and in the 1.5-100 K range by means of neutron powder diffraction data collected at the 3T2 and G4-1 diffractometers, respectively, of the Laboratoire Léon Brillouin in Saclay, France. The 3T2 instrument is a high-resolution diffractometer with wavelength $\lambda = 1.225$ Å, whilst G4-1 is a high intensity diffractometer optimized for magnetic structure determination with $\lambda = 2.43$ Å. Both nuclear and magnetic structures were refined using the FullProf Suite package$^{10}$.

III. RESULTS

A. Nuclear structure of BiMn$_3$Mn$_4$O$_{12}$ at room temperature

We first consider the room temperature diffractogram of Fig. 2. The data analysis shows that the as-prepared samples are 96% pure or better with Mn$_3$O$_4$ (haussmannite) as main impurity$^{33}$. In agreement with Ref.$^{29}$, the room temperature structure was successfully refined in the noncentrosymmetric space group $I\bar{m}$, with $a = 7.545(1)$ Å, $b = 7.362(1)$ Å, $c = 7.536(1)$ Å, $\beta = 91.178(2)^\circ$. In Fig. 2, we compare the observed and calculated diffractograms. The refined structural parameters are reported in Table I, where we note a good agreement between observed and calculated intensities, with $R_p = 4.21\%$, $wR_p = 5.57\%$, and $\chi^2 = 3.67$. The salient features of the refined structure are seen by considering the simplified cubic $I\bar{m}$ structure. In this structure, the MnO$_6$ octahedra are regular with the Mn$^{3+}$ ions (B sites) in the center of each octant of the unit cell; the square-coordinated Mn$^{3+}$ ions (A' sites) are located in the middle of the cell axes; the Bi$^{3+}$ ions (A sites) occupy the cell corners and center; all twenty four oxygen atoms occupy the same site with high $m..$ symmetry. In the real $I\bar{m}$ structure of Table I, all sites split into sites with lower symmetry and lower multiplicity. For instance, the centrosymmetric eightfold B site of Mn with cubic $..3.$ symmetry splits into two noncentrosymmetric fourfold sites Mn4 and Mn5 with translational $..1.$ symmetry only. The displacements of the Mn$^{3+}$ and O$^{2-}$ ions allowed by the $I\bar{m}$ symmetry lead to a macroscopic polarization of the crystal, $\mathbf{P}$, approximately oriented along the ac-diagonal, in accord with the quasi isotropic properties of the ac-plane. On the other hand, the local dipoles (or microscopic polarization) of the MnO$_6$ octahedra have no constraints because the symmetry of the Mn4 and Mn5 sites is purely translational. Thus, these dipoles have a non-zero component along the b-axis. In Table II we report an estimate of the dipoles computed using a point-like charge model.

In Table III we report the six Mn-O bond lengths of the MnO$_6$ octahedra and note that they vary within a broad 1.840-2.295 Å range. Hence, the description of the crystal field in terms of $e_g$ $x^2 - y^2$ and $3z^2 - r^2$ orbitals is no longer appropriate, which prevents a straightforward application of the Goodenough-Kanamori-Anderson (GKA) rules$^{42}$ to estimate the sign and the strength of the exchange interaction between neighboring Mn$^{3+}$ ions.

![Fig. 2](image-url)
TABLE I. Refined structural parameters of BiMn$_3$Mn$_4$O$_{12}$ at 300 K within the $Im$ space group. Numbers in parentheses indicate statistical uncertainty. Atomic coordinates $x$, $y$ and $z$ are given in reduced lattice units. Statistical indicators of the refinement are reported at the bottom.

| Atom     | Wyckoff position | Site symmetry | $x$     | $y$     | $z$     | $B_{iso}$ ($\AA^2$) |
|----------|------------------|---------------|---------|---------|---------|---------------------|
| Bi       | 2a               | $m$           | 0.052(3)| 0       | 0.066(3)| 0.18(5)            |
| Mn1($A'$)| 2a               | $m$           | 0       | 0       | 0.5     | 0.18(5)            |
| Mn2($A'$)| 2a               | $m$           | 0.494(4)| 0       | 0.454(3)| 0.18(5)            |
| Mn3($A'$)| 2a               | $m$           | 0.469(3)| 0       | -0.005(4)| 0.18(5)          |
| Mn4(B)   | 4b               | 1             | 0.237(3)| 0.737(2)| 0.256(3)| 0.18(5)            |
| Mn5(B)   | 4b               | 1             | 0.236(3)| 0.762(2)| 0.747(3)| 0.18(5)            |
| O1       | 2a               | $m$           | 0.326(3)| 0.5     | 0.178(3)| 0.3(1)             |
| O2       | 2a               | $m$           | 0.177(3)| 0       | 0.664(3)| 1.0(1)             |
| O3       | 2a               | $m$           | 0.165(4)| 0       | 0.286(3)| 0.5(1)             |
| O4       | 2a               | $m$           | 0.800(4)| 0       | 0.301(4)| 0.8(1)             |
| O5       | 4b               | 1             | 0.477(3)| 0.818(2)| 0.315(4)| 0.9(1)             |
| O6       | 2a               | 0.298(3)| 0.833(2)| -0.026(3)| 1.0(1)       |
| O7       | 4b               | 0.298(3)| 0.833(2)| -0.026(3)| 1.0(1)       |
| O8       | 4b               | 1             | 0.665(3)| 0.193(2)| 0.001(3)| 0.8(1)             |

Reliability factors with all non-excluded points for pattern:

- $R$-factors (not corrected for background): $R_p=4.21$, $wR_p=5.57$, $R_{exp}=2.93$, $\chi^2=3.62$
- Conventional Rietveld $R$-factors for pattern: $R_p=16.2$, $wR_p=16.2$, $R_{exp}=8.50$, $\chi^2=3.62$
- Global user-weighted $\chi^2$ (Bragg contribution)=3.67

TABLE II. Components along the $a$-, $b$- and $c$-axis of the local electric dipole $\mathbf{d}$ on the MnO$_6$ octahedra estimated using a point-like charge model for the Mn$^{3+}$ and O$^{2-}$ ions. Units are $q_e\AA$, where $q_e$ denotes the electron charge.

| Mn site | $d_a$ | $d_b$ | $d_c$ |
|---------|-------|-------|-------|
| Mn4     | -0.072| 0.399 | 0.453 |
| Mn5     | -0.018| -0.207| 0.246 |

TABLE III. Mn-O distances in $\AA$ for the octahedral Mn$^{3+}$ B sites. Numbers in parentheses indicate statistical uncertainty.

| Mn site | O site | Mn-O distance |
|---------|--------|---------------|
| Mn4     | O1     | 1.96(2)       |
| Mn4     | O7     | 1.88(3)       |
| Mn4     | O8     | 1.96(3)       |
| Mn4     | O6     | 2.29(3)       |
| Mn4     | O5     | 1.95(3)       |
| Mn4     | O3     | 2.02(2)       |
| Mn5     | O8     | 1.98(3)       |
| Mn5     | O6     | 1.84(3)       |
| Mn5     | O2     | 1.91(2)       |
| Mn5     | O4     | 2.03(2)       |
| Mn5     | O5     | 2.11(3)       |
| Mn5     | O7     | 2.21(3)       |

Another reason of inapplicability is the large buckling of the MnO$_6$ octahedra. Indeed, the Mn-O-Mn bond angle of $\sim 135^\circ$ falls in between the opposite limits of $90^\circ$ and $180^\circ$ considered by the above rules.

B. Low-temperature diffraction data: magnetic orderings of BiMn$_3$Mn$_4$O$_{12}$

We now consider the evolution of the diffraction data in the 1.5-100 K range (see Fig. 3). These data indicate that the symmetry of the nuclear structure is $Im$ at all temperatures. At 55 and 25 K, two new sets of diffraction peaks show up, which are attributed to the two AFM orderings probed by previous magnetization measurements. The indexing of the two sets is consistent with two distinct $k_1=(1/2,0,1/2)$ and $k_2=(0,0,0)$ propagation vectors, respectively. This is similar to the case of the isovalent LaMn$_3$Mn$_4$O$_{12}$, which exhibits an independent AFM ordering of the Mn$^{3+}$ and A' sublattices at comparable temperatures $T_{N,A}=78$ K and $T_{N,A'}=21$ K, respectively. Since the exchange interaction between Mn$^{3+}$ ions is expected to be similar in BiMn$_3$Mn$_4$O$_{12}$, for BiMn$_3$Mn$_4$O$_{12}$ as well we propose the same scenario of two independent AFM orderings for the $B$ and $A'$ sublattices, with $T_{N,B}=55$ K and $T_{N,A'}=25$ K. The question of the absence of coupling between the two magnetic sublattices in quadruple perovskites has been discussed elsewhere.22,38

Fig. 3 shows that the AFM transition at 55 K is characterized by an unusual feature. The appearance of the magnetic peaks indexed by $k_1$ is followed at slightly lower temperature (50 K) by a sudden increase of intensity of certain Bragg peaks. Since the magnetic response of the system is AFM, this increase indicates that the AFM structure of the $B$ sublattice contains a uniform component described by the $k_2$ propagation vector. On the other hand, the AFM ordering of the $A'$ sublattice is
completely described by \( k_2 \) and corresponds to the loss of the I centering (anti-body centering) of the lattice.

C. Refinement of the magnetic structure of BiMn₃Mn₄O₁₂

To solve the magnetic structures of both sublattices, we determined the basis functions of the irreducible representations of the \( \text{Im} \) space group for the relevant propagation vectors and Wyckoff sites of the Mn\(^{3+} \) ions (see Table IV). The \( \Gamma_{\text{mag}} = 3\Gamma_1 \oplus 3\Gamma_2 \) decomposition into irreducible representations is obtained for the two Mn4 and Mn5 sites of the \( B \) sublattice and for both \( k_1 \) and \( k_2 \) vectors, whilst the \( \Gamma_{\text{mag}} = \Gamma_1 \oplus 2\Gamma_2 \) decomposition is obtained for the three Mn1, Mn2 and Mn3 sites of the \( A' \) sublattice and for the only relevant \( k_2 \) vector. Thanks to the above analysis, we performed simulated annealing refinement of the diffraction data with the following constraints: 1. the total magnetic moment has been set to zero for both \( A' \) and \( B \) sublattices, as the magnetization data of Ref. give evidence of an AFM response; 2. we have assumed that the candidate structures follow the \( \Gamma_1 \) or \( \Gamma_2 \) representation, not an admixture of the two. For the refinements, the two 1.5 and 35 K data set were used in order to solve separately the structures of the \( A' \) and \( B \) sublattices. Indeed, the ordering of the \( B \) sublattice is complete at 35 K, as apparent from the temperature dependence of the magnetic peak intensities in Fig. 3 and of the lattice parameters in Fig. 5. Also, 35 K is sufficiently higher than the ordering temperature \( T_{N,A'} = 25 \) K of the \( A' \) sublattice, so the structure of the latter can be neglected.

1. Magnetic structure of the \( B \)-sublattice

As to the \( B \) sublattice, the magnetic structural models described by \( \Gamma_1 \) yielded the best statistical results. The result of the refinement is shown in Fig. 4 and Table V, whilst the structure is illustrated in Fig. 5. We outline the characteristics of this structure by analyzing separately the two \( k_1 \)- and \( k_2 \)-components with moments parallel and perpendicular to the \( ac \)-plane, respectively. The \( k_1 \)-component consists of an \( E \)-type AFM structure with moments in the \( ac \) plane \( M_{B,ac} = 1.37 \) \( \mu_B \). This structure can be viewed as zig-zag chains along the \( a \)- and \( c \)-axis with alternate antiparallel and parallel moments. We recall that LaMn₃Mn₄O₁₂ displays a different \( C \)-type structure made of ferromagnetically (FM) coupled AFM \( ac \)-planes. It is remarkable that two compounds with similar nuclear structures and isoelectronic properties exhibit radically different magnetic orders. This is a first indication of the role played by the polar Bi\(^{3+} \) ion on the magnetic ordering. As to the magnetic structure of the \( k_2 \)-component, Table V and Fig. 5 show that the moments are oriented along the \( b \)-axis and that they are as large as \( M_{B,b} = 1 \mu_B \). In view of the discussion below, it is noted that the orientation depends on the crystallographic site, i.e. the moments of the Mn4 (Mn5) sites are parallel (antiparallel) to the \( b \)-axis. In summary, the moments \( M_B \) of the \( B \) sites result from an unusual superposition of two components \( M_{B,ac} \) and \( M_{B,b} \) with dis-

### Table IV. Basis functions, \( \psi_i \), for the axial vectors associated with the irreducible representations \( \Gamma_1 \) and \( \Gamma_2 \) for the two different \( B \) and \( A' \) sites of the magnetic Mn\(^{3+} \) ions and for the two different propagation vectors \( k_1 \) and \( k_2 \) that describe the magnetic structure of BiMn₃Mn₄O₁₂.

| Wyckoff Site | Basis Functions | \( \psi_1 \) | \( \psi_2 \) | \( \psi_3 \) |
|-------------|----------------|-------------|-------------|-------------|
| 4b Wyckoff site (octahedral \( B \) site), \( k_1=(1/2 \ 0 \ 1/2) \) | \( \Gamma_1 \) \((x \ y \ z) = (x - y \ z) \) | \( \psi_1 \) | \( \psi_2 \) | \( \psi_3 \) |
| 4b Wyckoff site (octahedral \( B \) site), \( k_2=(0 \ 0 \ 0) \) | \( \Gamma_2 \) \((x \ y \ z) = (x + y \ z) \) | \( \psi_1 \) | \( \psi_2 \) | \( \psi_3 \) |
| 2a Wyckoff site (square-coordinated \( A' \) site), \( k_2=(0 \ 0 \ 0) \) | \( \psi_2 \) | \( \psi_3 \) | \( \psi_3 \) |

![FIG. 3. Temperature dependence of the powder neutron diffraction patterns of BiMn₃Mn₄O₁₂. The wavelength used is \( \lambda=2.43 \) \( \AA \). Three magnetic transitions are visible at 55 (\( \bullet \)), 50 (\( \bigcirc \)) and 25 K (\( \triangledown \)). The first two ones refer to the ordering of the magnetic \( B \)-sublattice, whilst the third one refers to the \( A' \)-sublattice. The (\( \bigcirc \)) symbol labels the peaks associated with the \( k_1=(1/2 \ 0 \ 1/2) \) propagation vector, whilst the (\( \bullet \)) symbol labels the Bragg peaks whose intensities exhibit a jump at 50 K and are therefore associated with the \( k_2=(0,0,0) \) propagation vector. The (\( * \)) symbol labels the peaks of the antiferromagnetic transition of the Mn₂O₄ impurity. Inset: detail of the behavior of the (101) and (110)-(101) doublet Bragg peaks and of the (100) ± \( k_1 \)-\( (001) \) ± \( k_1 \) magnetic doublet peak.](image-url)
tinct \( \mathbf{k}_1 \) and \( \mathbf{k}_2 \) propagation vectors. Hence, the magnetic structure can be viewed as a large and uniform modulation ±\( \mathbf{M}_{B,b} \) of an \( E \)-type structure. The total moment resulting from this superposition is \( M_B = 1.70 \mu_B \), a much smaller value than the value of 4.0 \( \mu_B \) expected for the high spin state (\( S=2 \)) of the \( \text{Mn}^{3+} \) ion. This discrepancy was reported for \( \text{LaMn}_3\text{Mn}_4\text{O}_{12} \), as well\(^{34} \), thus confirming the inadequacy of a purely ionic model for the electronic states of manganese oxides with quadruple perovskite structure.

2. Magnetic structure of the \( A' \)-sublattice

Also in the case of the AFM structure of the \( A' \) sublattice, the best structural model is described by the \( \Gamma_1 \) representation. The magnetic moments and the structural model are reported in Table V and Fig. 6, respectively. The structure consists of an anti-body centered AFM ordering with a moment \( M_{A'} = 1.22 \mu_B \) per site. The structure turns out to be identical to that of \( \text{NaMn}_3\text{Mn}_4\text{O}_{12} \)\(^{33} \) but different from that of \( \text{LaMn}_3\text{Mn}_4\text{O}_{12} \). This confirms the key role played by \( \text{Bi}^{3+} \) in altering the stability of competing magnetic orderings in these two isoelectronic and almost isostructural compounds. Similarly to the previous case of the \( B \)-site, also the moment per \( A' \) site turns out to be much smaller than that expected according to a purely ionic model.

IV. CORRELATION BETWEEN LATTICE POLARIZATION AND MAGNETIC ORDERING

We should now provide a physical interpretation of the magnetic orderings observed. Our point concerns the symmetry properties of the \( \text{Bi}^{3+} \)-induced lattice polarization and of the AFM structure of the \( \text{Mn}^{3+} \) \( B \)-sublattice.
TABLE V. Magnetic structures of the $B$ and $A'$ sublattices of BiMn$_3$Mn$_4$O$_{12}$ at 1.5 K. The structures are obtained after refinement of the diffraction data of Figure 4. The nuclear unit cell parameters are: $a=7.537(1)$ Å; $b=7.354(1)$ Å; $c=7.534(1)$ Å; $\alpha, \gamma=90^\circ$; $\beta=91.213(1)^\circ$. Magnetic moments are given in Cartesian coordinates and in Bohr magneton $\mu_B$ units. Numbers in parentheses indicate statistical uncertainty. Approximate atom coordinates are given. The magnetic structure of both sublattices is described by the $\Gamma_1$ representation, i.e. the moments $(M_x,M_y,M_z)$ transform as $(-M_x,M_y,-M_z)$ upon application of the mirror operation $(x,y,z) \rightarrow (x,-y,z)$ on atom coordinates (see text and Table IV).

| Atom coordinates | $M_x$ | $M_y$ | $M_z$ |
|------------------|-------|-------|-------|
| Mn4 (1/4 3/4 1/4) | 1.37(1) | −1.22(4) | 0 |
| Mn4 (3/4 1/4 3/4) | 1.37(1) | −1.22(4) | 0 |
| Mn5 (1/4 3/4 3/4) | 1.37(1) | 1.22(4) | 0 |
| Mn5 (3/4 1/4 1/4) | 1.37(1) | −1.22(4) | 0 |

| Mn$^{3+}$ B-sublattice ($T_{N,B}=55$ K); propagation vector $k_1=(1/2 0 1/2)$ |
|------------------|-------|-------|-------|
| Mn4 (1/4 3/4 1/4) | 0.99(2) | 0 | 0.99(2) |
| Mn4 (3/4 1/4 3/4) | 0.99(2) | 0 | 0.99(2) |
| Mn5 (1/4 3/4 3/4) | 0.99(2) | −0.99(2) | 0 |
| Mn5 (3/4 1/4 1/4) | 0.99(2) | −0.99(2) | 0 |

| Mn$^{3+}$ A′-sublattice ($T_{N,A'}=25$ K); propagation vector $k_2=(0 0 0)$ |
|------------------|-------|-------|-------|
| Mn1 (0 0 1/2) | 1.22(1) | 0 | 1.22(1) |
| Mn1 (1/2 1/2 0) | 1.22(1) | 0 | −1.22(1) |
| Mn2 (1/2 0 1/2) | 1.22(1) | 0 | −1.22(1) |
| Mn2 (0 1/2 0) | 1.22(1) | 0 | 1.22(1) |
| Mn3 (1/2 0 0) | 1.22(1) | 0 | 1.22(1) |
| Mn3 (0 1/2 1/2) | 1.22(1) | 0 | −1.22(1) |

The above considerations also account qualitatively for

FIG. 6. The same as in the preceding Figure for the Mn$^{3+}$ $A'$-sublattice.
the stability of the $M_b$ structure. Indeed, the moments are bound to be parallel along the $b$-axis because of the $\Gamma_1$ symmetry of the strain field. In addition, the moments on the Mn4 and Mn5 sites tend to be antiparallel as the exchange interaction is predominantly AFM within the $ac$-plane. Both characteristics are indeed found in our experiment. A quantitative account of the stability of the $M_b$ structure goes beyond the scope of this work; it may be provided by ab initio calculations in the local spin density approximation that include the on-site repulsion between $d$-electrons or ad hoc Hamiltonians that include the charge, orbital and spin degrees of freedom. These methods have been applied to LaMn$_3$Mn$_4$O$_{12}$, $R$MnO$_3$, and $R$Mn$_2$O$_5$ among others, and an application may be envisaged in our case as well.

Our picture of magnetoelastic coupling along the $b$-axis also accounts for the temperature-dependence of the unit cell parameters reported in Fig. 7. One notes that the AFM ordering of the $B$ sites at 55 K is accompanied by a sizable expansion of both $a$- and $c$-axes, whilst the $b$-axis displays no anomaly. This indicates a magnetostriction only in the $ac$-plane, which is explained as follows. The variations of the unit cell parameters reflect the external strain induced by the macroscopic polarization, $P$. As mentioned before, in BiMn$_3$Mn$_4$O$_{12}$, $P$ is approximately oriented along the $ac$ diagonal, while its $b$-component is identically zero. Therefore, we expect a magnetostriction only along this diagonal, in agreement with Fig. 7. Similar arguments account for the absence of magnetostriction at the AFM transition of the Mn$^{3+}$ ions at the $A'$ sites at $T_{N,A'}=25$ K. Indeed, the $b$-component of the dipole at this site is identically zero because of the $m$ symmetry of these sites. Thus, the only symmetric internal strain mode $\Gamma_1$ available for the magnetoelastic coupling vanishes in this case.

**V. CONCLUSIONS**

In conclusion, we found that the magnetic order of the Mn$^{3+}$ ions in the quadruple perovskite BiMn$_3$Mn$_4$O$_{12}$ is strongly modulated by the internal strain field induced by the polar Bi$^{3+}$ ion. This observation suggests a mechanism of magnetoelectric coupling between Bi$^{3+}$ and Mn$^{3+}$ ions driven by the magnetoelastic coupling due to the internal strain field, in agreement with a previous observation of giant magnetoelastic effect in the multiferroic $R$MnO$_3$ system$^{22}$. Our analysis indicates that this mechanism is effective in BiMn$_3$Mn$_4$O$_{12}$ thanks to two features of quadruple perovskites: a) the high symmetry of the oxygen atoms surrounding the Bi$^{3+}$ ion, which limits structural distortions, thus preventing the release of the strain; b) the absence of oxygen disorder. Further experimental and theoretical work is needed to test the tunability of the magnetic order of BiMn$_3$Mn$_4$O$_{12}$ by an electric field, a prerequisite for applications.

In the light of the above considerations, our result demonstrates that a large magnetoelectric coupling between magnetic and polar ions can be achieved in proper ferroelectrics. The coupling mechanism which accounts for our result suggests that site symmetry is an effective control parameter of the internal strain responsible for the coupling. This conclusion suggests a novel concept of internal strain engineering for the effective design of multiferroics.
