Nature of the induced ferroelectric phases in TbMn$_2$O$_5$

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The magnetostructural transitions and magnetoelectric effects reported in TbMn$_2$O$_5$ are described theoretically and shown to correspond to two essentially different mechanisms for the induced ferroelectricity. The incommensurate and commensurate phases observed between 38 K and 24 K exhibit a hybrid pseudo-proper ferroelectric nature resulting from an effective bilinear coupling of the polarization with the antiferromagnetic order-parameter. This explains the high sensitivity of the dielectric properties of the material under applied magnetic field. Below 24 K the incommensurate phase shows a standard improper ferroelectric character induced by the coupling of two distinct magnetic order-parameters. The complex dielectric behavior observed in the material reflects the crossover from one to the other transition regime. The temperature dependences of the pertinent physical quantities are worked out and previous theoretical models are discussed.

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I. INTRODUCTION

It was recently observed\cite{1,2} that an electric polarization can emerge at a magnetic transition if the magnetic spins order in non-collinear spiral structures. This new type of magnetostructural transition was reported in various classes of multiferroic materials\cite{3,4}, such as the rare-earth manganites RMnO$_2$\cite{5,6} and RMn$_2$O$_5$\cite{7,8,9,10,11,12,13}, Ni$_3$V$_2$O$_{10}$, MnWO$_4$\cite{14}, CoCr$_2$\cite{15} or Cr$_2$BeO$_4$\cite{16}. In these compounds the correlation between spins and electric dipoles gives rise to remarkable magnetoelectric effects, indicating a strong sensitivity to an applied magnetic field, such as reversals or flops of the polarization, and a strong enhancement of the dielectric permittivity. In the aforementioned materials the ferroelectric phases appear below an intermediate non-polar magnetic phase, i.e. the breaking of inversion symmetry, which allows emergence of ferroelectric properties, does not occur simultaneously with the breaking of time reversal symmetry.

Theoretical arguments have been raised\cite{17,18,19,20} to justify the observation of magnetoelectric effects in spiral magnets. However, a comprehensive theoretical description of the experimental results disclosed in multiferroic materials could not be achieved because the actual symmetries of the primary (magnetic) and secondary (structural) order-parameters have not been related organically to the thermodynamic functions which provide the relevant phase diagrams. Here, we give a unifying theoretical description of the magnetostructural transitions found in the manganite TbMn$_2$O$_5$\cite{7,8,9,10} in the framework of the Landau theory of magnetic phase transitions\cite{21,22}. It reveals that the transitions observed in this compound at 38 K and 24 K correspond to essentially different mechanisms for the induced ferroelectricity. The 38 K transition involves an effective bilinear coupling of the polarization with a single magnetic order-parameter. It results in a pseudo-proper ferroelectric nature for the phases stable between 38 K and 24 K. By contrast, the 24 K transition exhibits an improper ferroelectric behavior corresponding to a linear-quadratic coupling of the polarization with two distinct magnetic order-parameters.

On cooling below the paramagnetic Pbam1’ (P) structure, TbMn$_2$O$_5$ undergoes five phase transitions\cite{8,9} taking place successively at $T_1 = 43$ K, $T_2 = 38$ K, $T_3 = 33$ K, $T_4 = 24$ K and $T_5 = 10$ K, the corresponding phases being denoted I to V. The paper is organized as follows: In Sec. II the P→I → II → III sequence of transitions giving rise at $T_1$, $T_2$ and $T_3$, to the incommensurate phases I and II, and commensurate phase III\cite{8,9}, is described theoretically. The remarkable magnetoelectric effects occurring at the III→IV → V transitions, taking place at $T_4$ and $T_5$, are analyzed in Sec. III. In Sec. IV our results are summarized and compared to the results obtained in previous theoretical works on TbMn$_2$O$_5$\cite{24,25}. Adaption of our description to other RMn$_2$O$_5$ compounds\cite{24,25} is outlined.

II. THE P→I → II → III TRANSITIONS

The wave-vector associated with the incommensurate antiferromagnetic phase I and ferroelectric phase II is $\vec{k} = (1/2, 0, k_z)$, with $k_z$ decreasing from about 0.30 to 0.25. It is associated with a 4-dimensional irreducible corepresentation (IC) of Pbam1’, denoted $G_1$, whose generators are given in Table I. The complex amplitudes $S_1 = \rho_1 e^{i\theta_1}$, $S_1^* = \rho_1 e^{-i\theta_1}$, $S_2 = \rho_2 e^{i\theta_2}$, $S_2^* = \rho_2 e^{-i\theta_2}$ of the magnetic waves transforming according to $G_1$, form the symmetry-breaking order-parameter for the P→I → II transitions, giving rise to the invariants $J_1 = \rho_1^2 + \rho_2^2$, $J_2 = \rho_1^2 \rho_2^2$, and $J_3 = \rho_1^2 \rho_2^2 \cos 2\theta$, with $\theta = \theta_1 - \theta_2$. 

In Sec. IV our results are summarized and compared to the results obtained in previous theoretical works on TbMn$_2$O$_5$\cite{24,25}. Adaption of our description to other RMn$_2$O$_5$ compounds\cite{24,25} is outlined.
Therefore the homogeneous part of the free-energy density reads:

\[
\Phi_1(\rho_1, \rho_2, \theta) = \sum_{i} \left( a_1 \mathbf{J}_1 + a_2 \mathbf{J}_2 + b_1 \mathbf{J}_3 + b_2 \mathbf{J}_4 + c_1 \mathbf{J}_5 + c_2 \mathbf{J}_6 + \cdots \right)
\]

An eighth degree expansion is required in order to account for the full set of stable phases resulting from the minimization of \(\Phi_1\) and for disclosing the magnetoelectric properties observed in TbMnO\(_2\) \cite{37}. It stems from the following rule demonstrated in Ref. \cite{37}. If \(n\) is the highest degree of the basic order-parameter invariants (here \(n=4\) for the \(J_2\) and \(J_3\) invariants), the free energy has to be truncated at not less than the degree \(2n\) (here \(2n=8\)) for ensuring the stability of all phases involved in the phase diagram. However, one can neglect most of the non-independent invariants of degrees lower or equal to eight (as for example \(J_1^3, J_2^4, J_1 J_2, J_2 J_3\)) which can be shown to have no influence on the stability of the phases, but only modify secondary features of the phase diagram, as for example the shape of the transition lines separating the stable phases. In contrast the invariant \(J_1 J_3\) has to be taken into account for stabilizing "asymmetric" phases with \(\rho_1 \neq \rho_2\). Note that the fourth-degree invariants \(\rho_1^2 \rho_2^2\) and \(\rho_1^2 \rho_2^2 \cos 2\theta\) express at a phenomenological level the exchange striction interactions and anisotropic exchange forces, respectively. Minimizing \(\Phi_1\) with respect to \(\theta\) yields the following equation of state:

\[
\rho_1^2 \rho_2^2 \sin 2\theta \left[ c_1 + d_1 (\rho_1^2 + \rho_2^2) + 2c_2 \rho_1^2 \rho_2^2 \cos 2\theta \right] = 0
\]

Eq. (2) and the equations minimizing \(\Phi_1\) with respect to \(\rho_1, \rho_2\) show that seven phases, labeled 1-7, can be stabilized below the P phase for different equilibrium values of \(\rho_1, \rho_2\) and \(\theta\). Fig. 1 summarizes the equilibrium properties of each phase and their magnetic point-group symmetries. One can verify that the phases denoted 2, 4, 6 and 7 display a ferroelectric polarization along \(y\) and that all phases correspond to an antiferromagnetic ordering except phases 5 and 7 which show a non-zero magnetization along \(x\). The respective location of the phases is indicated in the theoretical phase diagrams shown in Fig. 2, in the space \((a_1, b_1, c_1)\) (Fig. 2(a)) and plane \((b_1, c_1)\) (Fig. 2(b)) of the phenomenological coefficients, and in the orbit space \((J_1, J_2, J_3)\) (Fig. 2(c)). It allows to determine the possible sequences of phases separated by second-order transitions as \(P \rightarrow 1 \rightarrow 6 \rightarrow 7\) or \(P \rightarrow 3 \rightarrow 4 \rightarrow 7\). Dielectric and magnetic properties of the phases are deduced from the coupling of the order-parameter with the polarization \((\vec{P})\) and magnetization \((\vec{M})\) components, which are \(J_4 = \rho_1 \rho_2 P_y \sin \theta\), \(J_5 = (\rho_1^2 - \rho_2^2) M_y M_x\) and \(J_6 = \rho_1 \rho_2 M_x M_y \cos \theta\).

The preceding results allow a consistent interpretation of the \(P \rightarrow I \rightarrow II\) sequence of phases reported in TbMnO\(_2\). Phase 1 observed between \(T_1\) and \(T_2\), corresponds to phase 1 (\(\rho_1 \neq 0, \rho_2 = 0\)) in Fig. 1. It displays the m\(\mu\)m symmetry with antiferromagnetic order in the \((x, y)\) plane \((J_5 = \rho_1^2 M_x M_y)\), a doubling of the lattice parameter \(a\) and an incommensurate modulation along \(c\), expressed by the Lifshitz invariant \(\rho_1^2 \partial^2 \rho_{2y}/\partial z^2\). Figs. 1 and 2 show that
second-order plane and 3 can be reached directly from the P-phase across the transition surfaces, which become curves in (b). Phases 1, 2 (2, 3) and (4, 5, 6) correspond, respectively, to curves and (b) the (|\rho_{1}|ρ_{2}) space, instead of an incommensurate phase III, which involves a fourfold multiplication of the c-lattice parameter, instead of an incommensurate modulation along z. The wave-vector \( \mathbf{k} = (k_x, 0, k_z) \approx (0.48, 0, 0.32) \) associated with the III\( \rightarrow \)IV commensurate-incommensurate transition.
associated with 2 point-groups are.

Fig. 3: (a) Least squares fits for the squared polarization (phase III). (d) Dielectric permittivity (1 non-polar $\Xi$ for order-parameters spanning the two IC's can be written

$$\Phi_2(\rho_i, \Psi_i) = \sum_{i=1}^{5} (\alpha_i \mathcal{J}_i + \beta_i \mathcal{J}_i^2)$$

Minimization of $\Phi_2$ shows that not less than 15 distinct phases can be stabilized for different equilibrium values of $\rho_1$ and $\Psi_i$. 6 of these phases display a ferroelectric polarization component $P_y$, resulting from the mixed coupling invariant: $\mathcal{J}_6 = \bar{P}_y (\rho_1 \rho_2 \sin \Psi_1 + \rho_2 \rho_4 \sin \Psi_2)$. For $\rho_1 = \rho_2 = \rho_3 = \rho_4$, $\Psi_1 = (2n + 1) \Delta$ or (and) $\Psi_2 = n \Delta$, the phases have the structural symmetry m2m. For $\rho_1 \neq 0, \rho_3 \neq 0, \rho_2 = \rho_4 = 0$ or $\rho_1 = \rho_3 = 0, \rho_2 \neq 0, \rho_4 \neq 0$ or $\rho_1 \neq \rho_2, \rho_3 \neq \rho_4$ with $\Psi_1$ or $\Psi_2 = (2n + 1) \Delta$ and $\Psi_1$ or $\Psi_2$ arbitrary, or $\Psi_1$ and $\Psi_2$ arbitrary, the structural symmetry is lowered to $2_y$. The magnetic order in the different phases is expressed by the coupling invariants $\mathcal{J}_7 = M_x M_y (\rho_1 \rho_3 \cos \Psi_1 + \rho_2 \rho_4 \cos \Psi_2)$ and $\mathcal{J}_8 = M_y M_z (\rho_1 \rho_2 \cos \Psi_1 - \rho_2 \rho_4 \cos \Psi_2)$.

The experimental results reported for the magnetic structure of phase IV of TbMnO$_2$ are consistent with a structural symmetry m2m. One can assume, without loss of generality, that the corresponding equilibrium values of the order-parameters in phase IV are $\rho_1 = \rho_2, \rho_3 = \rho_4, \Psi_1 = (2n + 1) \Delta$, $\Psi_2 = 2n \pi$. Therefore the dielectric contribution to the free-energy at the III→IV transition is:

$$P_y^c = \pm \delta_1 \rho_1 \rho_3 P_y + \frac{\rho_1^2 \rho_4^2}{\epsilon_y}$$

Since both order-parameters $\rho_1$ and $\rho_3$ contribute to the symmetry-breaking mechanism at $T_4$, they both vary as $\propto (T_4 - T)^{1/2}$ for $T < T_4$. Therefore $P_y^c$ varies linearly as $(T_4 - T)$, which expresses a typical improper ferroelectric behaviour for the III→IV transition. The dielectric permittivity is given by $\epsilon_{yy} = \epsilon_{yy}^0 (1 - \delta_2 \frac{\rho_1 \rho_3}{\epsilon_y})$, where $\epsilon_y$ is the applied electric field. It yields $\epsilon_{yy} = \epsilon_{yy}^0$ for $T > T_4$, and is approximated by $\epsilon_{yy} \approx \frac{\epsilon_{yy}^0}{1 + \frac{\rho_1 \rho_3}{\epsilon_y}}$ for $T < T_4$, where $f(\beta_i, \alpha_5)$ represents a combination of phenomenological coefficients of $\Phi_2$ with $0 < f(\beta_i, \alpha_5) < 1$. Accordingly, $\epsilon_{yy}(T)$ undergoes an upward step at $T_4$ (Fig. 3(d)), as observed experimentally. Note that the change in the order-parameter symmetry imposes a first-order character to the III→IV transition, consistent with the lattice anomalies observed at 24 K.

The preceding description allows a straightforward explanation of the observed decrease of the equilibrium polarization $P_y^c$ at zero magnetic field which is starting at about 26 K. Below $T_4$, $P_y^c$ is the sum of two distinct contributions given by Eqs. (13) and (15).

$$P_y^c = \pm \epsilon_{yy}^0 [\delta_1 \rho_1 (T_2 - T)/2 + \delta_2 (T_4 - T)]$$

where $\rho_1 \propto (T_1 - T_2)^{1/2}$. Assuming $\delta_1 > 0$ and $\delta_2 < 0$, one can verify that $P_y^c$ decreases for $T \leq T_{\text{max}} = T_2 - \frac{\delta_2 (T_1 - T_2)}{4 \delta_1^2}$. This explanation confirms the conjec-
ture by Hur, et al\(^\text{1}\) that the total polarization is composed by positive and negative components, which appear at \(T_2\) and \(T_4\), respectively. The opposite signs of \(P_y^e\) in Eq. (6) correspond to the opposite ferroelectric domains disclosed by the preceding authors under opposite electric fields. The strong increase of \(P_y^e\) observed below \(T_5\) reflects the positive contribution of phase II to the total polarization. The absence of dielectric anomalies at \(T_5\) suggests that the m\(2\)m symmetry of phase IV remains unchanged in phase V with an eventual change in the respective values of \(\Psi_1\) or (and) \(\Psi_2\).

It remains to understand why the decrease of \(P_y\) is enhanced by application of a magnetic field \(H_x\), leading to a change in sign of \(P_y\) above a threshold field \(H_x^{\text{th}}\). This can be explained by considering the magnetic and magnetoelectric contributions to the free-energy under \(H_x\) field in phase IV: \(\Phi^M_x = \mu_0 M_x^2 - H_x M_x\) and \(\Phi^{ME}_x = \nu \rho_1 \rho_3 P_y M_x^2\). It yields for the field dependent spontaneous polarization in phase IV:

\[
P_y^IV(H_x) = \pm \epsilon_{yy}^0 \rho_1 \rho_3 (\delta_2 + \nu \mu_0^{-1} H_x^2) \quad (7)
\]

For \(\nu < 0\) the application of an \(H_x\) field enhances the negative contribution \(P_y^IV\) to the temperature dependence of the total polarization leading to:

\[
P_y^e(T, H_x) = \\
\pm \epsilon_{yy}^0 \delta_1 (T_1 - T_2)^{1/2}(T_2 - T)^{1/2} + (\delta_2 + \nu \mu_0^{-1} H_x^2(T_4 - T))
\]

Accordingly \(P_y^e(T, H_x)\) changes sign for the temperature dependent threshold field:

\[
H_x^e(T)^2 = \frac{\delta_1 \mu_0(T_1 - T_2)^{1/2}(T_2 - T)^{1/2}}{|\delta_2 \mu_0 + \nu|(T_4 - T)} \quad (9)
\]

From Eqs. (8) and (9) one can verify that with increasing applied field, \(P_y^e(T, H_x)\) decreases more sharply and changes sign at higher temperature (Fig.4), as was actually observed by Hur et al\(^\text{1}\).

**IV. SUMMARY AND DISCUSSION**

In summary, it has been shown that two distinct symmetry breaking ordering parameters are involved in the sequence of five magnetic phases found in TbMn\(_2\)O\(_5\) below:

1) a single four-component order-parameter is associated with the \(\text{P} \rightarrow \text{I} \rightarrow \text{II} \rightarrow \text{III}\) transitions. Two among the components \((S_1, S_1^*)\) give rise at \(T_1\) to the antiferromagnetic phase I, whereas the two others \((S_2, S_2^*)\) are activated at \(T_2\), at the onset of the ferroelectric phase II. \((S_1, S_1^*)\) being frozen at the I II transition. It results in a hybrid pseudo-proper ferroelectric behavior for this transition, which displays critical dielectric anomalies typical of proper ferroelectric transitions, although the magnitude of the induced polarization in phase II is of the order found in improper ferroelectrics. At the II--III transition the translational symmetry along \(z\) becomes commensurate, modifying in a minor way the ferroelectric properties of the material. The theoretical phase diagram showing the location of the phases stabilized in \((\text{TbMn}_2\text{O}_5,\text{as well as the other five phases induced by the} (S_1, S_1^*)\text{ order-parameter, has been worked-out, and the magnetic point-groups of the different phases have been given.}

2) At the commensurate-incommensurate III--IV transition the \((S_1, S_1^*)\) order-parameter splits into two distinct four-component order-parameters \((\eta_i)\) and \((\varsigma_i)\), which couple for inducing the ferroelectric phases IV and V. The III--IV transition shows a standard improper ferroelectric behavior. The absence of noticeable anomaly for the dielectric permittivity at the IV--V transition suggests that the structural symmetry of phase IV remains unchanged in phase V. However, the spontaneous polarization in phase V contributes positively to the observed total polarization \(P_y^e\), whereas phase IV exhibits a negative contribution to \(P_y^e\). Opposite signs of the spontaneous electric polarizations in phases IV and V provide a consistent interpretation of the non-monotonous temperature dependence of \(P_y^e(T)\) across the II--III--IV--V sequence of induced ferroelectric transitions. Application of an \(H_x\) magnetic field modifies the preceding behavior, via the magnetoelectric coupling between \(P_y\) and the induced magnetization \(M_x\), which contributes negatively to the total polarization, explaining the observed change of sign of \(P_y^e(T, H_x)\).

A number of previous studies\(^{24-30}\) proposed a theoretical description of the dielectric and magnetoelectric properties of TbMn\(_2\)O\(_5\). However, none of these studies took fully into account the order-parameter symmetries associated with the different phases. Therefore, the relevant free-energies, expanded to the necessary degrees, and the related coupling terms, could not be disclosed,
and the proper phase diagrams could not be derived. As a consequence, a consistent interpretation of the dielectric behavior at zero magnetic field, or under applied $H_x$ field, could not be given explicitly. In contrast to our phenomenological description, based on the symmetry and thermodynamic considerations underlying the Landau theory of magnetic phase transition, which is free from any microscopic model, the previous works, using different group-theoretical procedures, attempted to deduce the magnetoelectric properties of the material from its complex magnetic structures and related magnetic interactions. For example, Radaelli and Chapon limit their group-theoretical analysis to the irreducible corepresentations of the little group. It does not allow determination of the transition free-energy and of the coupling relating the polarization to the magnetic order-parameter, which they deduce from microscopic coupling mechanisms. The complex procedure proposed by Harris for determining the transition order-parameter from the spin configuration of TbMn$_2$O$_5$ does not provide the relevant order-parameter symmetry, and is not related organically with the different effective free-energies used by Harris et al. for describing the ferroelectric transitions in this material. It leads to oversimplified phase diagrams and to a speculative interpretation of the observed dielectric and magnetoelectric properties. Besides, the critical wave vector assumed by Harris et al. for phases I and II of TbMn$_2$O$_5$ corresponds actually to phases IV and V, which are not described by these authors. The Landau model used by Kadomtseva et al. provides an insight into the exchange and relativistic magnetic contributions to the free-energy and induced polarization involved in RMn$_2$O$_5$ compounds. However, the dimensionality of the irreducible representation and order-parameter assumed in their model (2-dimension instead of two coupled 4-dimensional order-parameters required for ErMn$_2$O$_5$ and YMn$_2$O$_5$) and the fact that two successive and distinct order-parameters are needed for describing the full sequence of observed phases, do not allow these authors to describe consistently the observed dielectric properties and magnetoelectric effects. Along another line, the model proposed by Sushkov et al. gives an interesting analysis of the underlying magnetic forces explaining the induced dielectric properties in the RMn$_2$O$_5$ family, but a detailed description of the observed phase sequences and magnetoelectric effects, that would require considering the actual order-parameter symmetries, is missing.

Similar sequences of ferroelectric phases are found in other RMn$_2$O$_5$ compounds where $R = Bi,Y$ or a rare-earth heavier than Nd. In these compounds, with the exception of BiMn$_2$O$_5$, the first ferroelectric phase does not appear directly below the paramagnetic phase, but below an intermediate non-polar antiferromagnetic phase. Therefore the induced electric polarization results from the coupling of two distinct magnetic order-parameters, one of which having been already activated in the intermediate phase. As a consequence a pseudo-proper coupling is created, which gives rise to the typical critical behavior of a proper ferroelectric transition. In TbMn$_2$O$_5$ the first ferroelectric transition corresponds to $k = (\frac{1}{2},0,k_z)$ and to a single 4-component order-parameter, the pseudo-proper coupling occurring between distinct components of the same order-parameter. A different situation is found in the other RMn$_2$O$_5$ compounds, in which the first transitions correspond to $k = (k_x,0,k_z)$, i.e. the pseudo-proper coupling occurs between two distinct 4-component order-parameters having the symmetries of the $(\eta_i)$ and $(\zeta_i)$ order-parameters, which are associated in the present work to the lower temperature transition sequence of TbMn$_2$O$_5$. The order-parameters involved in the RMn$_2$O$_5$ family correspond in most cases to the symmetries disclosed in the present work for $R = Tb$, i.e. to $k = (\frac{1}{2},0,k_z)$, $(k_x,0,k_z)$ and $(\frac{1}{2},0,\frac{1}{2})$. Two exceptions are presently known, which are:

1) The lower temperature phase of DyMn$_2$O$_5$ induced by bidimensional order-parameters corresponding to the wave-vector $(\frac{1}{2},0,0)$, and
2) The single ferroelectric phase of BiMn$_2$O$_5$ induced by bidimensional IC’s at $k = (\frac{1}{2},0,\frac{1}{2})$.

Accordingly, despite the apparent variety of behaviors found for the dielectric properties and field effects a unifying theoretical framework can be proposed for the RMn$_2$O$_5$ manganites, which can be deduced from the description given in the present work, by interchanging the order-parameters in the observed transition sequences.

V. CONCLUSIONS

In conclusion, the order-parameter symmetries associated with the magnetostructural transitions observed in TbMn$_2$O$_5$ clarify the nature of the ferroelectric phases and permit a consistent description of the magnetoelectric effects observed in this material. In a more general way, our phenomenological approach illustrates the necessity of taking into account the actual order-parameter symmetries and phase diagrams associated with the phase sequences reported in multiferroic compounds. It can be used for analyzing the complex microscopic mechanisms and interactions involved in magnetostructural transitions, which have not been discussed in the present work.

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