Spontaneous toroidal moment and field-induced magnetotoroidic effects in $Ba_2CoGe_2O_7$

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The unusual magnetoelectric effects observed in the multiferroic phase arising below $T_N = 6.7$ K in $Ba_2CoGe_2O_7$ (BCG) are related to the spontaneous toroidal moment existing in this compound. The transition to the multiferroic state, which involves spontaneous magnetization, polarization, and toroidal moment gives rise to spontaneous toroidic effects. These effects correspond to specific contributions to the induced polarization and magnetization under applied magnetic or electric fields which can be differentiated from standard nonlinear magnetoelectric contributions. The toroidic contribution to the electric polarization in BCG is shown to result from single-ion effects.

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I. INTRODUCTION

The resurgence of interest in multiferroic materials has prompted discussion of the relevance of the concept of magnetic toroidal moment for clarifying the macroscopic and microscopic properties of these systems.[1–14] The existence of a macroscopic moment asymmetric under both time reversal and space inversion long remained elusive[15–18] until the observation of the independent coexistence of ferrotoroidic and antiferromagnetic domains in $LiCoPO_4$.[19] This result provides a motivation for investigating toroidic effects in the ferroelectric phases of multiferroic materials, in which the space-asymmetric electric polarization is induced by a time-asymmetric and space-asymmetric magnetic order. In the absence of well-defined physical properties showing direct experimental evidences of a spontaneous toroidal moment in magnetic systems, one of the important issues is to find a material in which specific magnetoelectric effects[20] would reflect the effective role of the toroidal moment.

Here we analyze theoretically the magnetoelectric effects disclosed in the multiferroic phase of $Ba_2CoGe_2O_7$ (BCG).[21,22] Due to its unique magnetic symmetry, this phase allows existence of spontaneous magnetization, polarization, and toroidal moment, as well as linear and nonlinear magnetoelectric effects. Furthermore, the spontaneous toroidal moment $\vec{T}$ has the same symmetry as the antiferromagnetic order-parameter $\vec{L}$ to which it is bilinearly coupled. This allows interpreting the magnetoelectric effects reported in BCG, as resulting either from higher-order coupling of the polarization to $\vec{L}$ or as field-induced toroidic effects. In this respect, we emphasize that the specific critical behaviors reported for the polarization components under applied magnetic fields[21,22] should allow for distinguishing the respective contributions of the antiferromagnetic and toroidal order parameters. At the microscopic level, the toroidal contribution to the spontaneous polarization is shown to result from single ion effects.

II. PHASE DIAGRAM AND MULTI-DOMAIN PATTERN OF BCG

The $P\bar{4}2_1m1'$ paramagnetic space group of BCG[23] has at the center of the tetragonal Brillouin zone ($\vec{k} = 0$) five irreducible representations (IRs) denoted by τ_1–τ_5.[24] The one-dimensional IR's τ_1–τ_4 induce nonpolar magnetic symmetries $P\bar{4}2_1m$, $P\bar{4}2_1m'$, $P\bar{4}'2_1m$, and $P\bar{4}'2_1m'$, and are not associated with the transition to the ferroelectric phase observed in BCG below $T_N = 6.7$ K. The two-dimensional IR τ_5 spanned by the order-parameter components $\eta_1 = \rho\cos(\theta)$ and $\eta_2 = \rho\sin(\theta)$ is associated with the Landau expansion:

$$F = \frac{\alpha}{2}\rho^2 + \frac{\beta_1}{4}\rho^4 + \frac{\beta_2}{4}\rho^4\cos(4\theta) + \cdots + \frac{\gamma}{8}\rho^8\cos^2(4\theta). \qquad (1)$$

Minimizing F yields three possible magnetically ordered phases below the paramagnetic phase:

(i) Phase I corresponds to $\rho^e = \pm(\frac{\alpha_0(T_N - T)}{\beta_1+\beta_2})^{\frac{1}{2}}$ and $\cos(4\theta) = 1$ ($\theta = n\frac{\pi}{2}$). It has the orthorhombic magnetic space groups $P2_1'2_12'$ ($\eta_1 = \rho^e, \eta_2 = 0$) or $P2_12_1'2'$ ($\eta_1 = 0, \eta_2 = \rho^e$), which form energetically equivalent domains of the same equilibrium phase.

(ii) Phase II has the magnetic symmetry $Cm'a2'$ with $\rho^e = \pm(\frac{\alpha_0(T_N - T)}{\beta_1-\beta_2})^{\frac{1}{2}}$ and $\cos(4\theta) = -1$ ($\theta = (2n+1)\frac{\pi}{4}$), or equivalently $\eta_1 = \pm\eta_2 = \rho^e$. The phase involves a variety of spontaneous physical properties and domains represented in Fig. 1. Denoting $\vec{s_1}$ and $\vec{s_2}$ the magnetic spins associated with the Co^{2+} ions located at (0,0,0) and (0.5,0.5,0) positions,[23] the phase displays four weak ferromagnetic and/or antiferromagnetic domains with a spontaneous unit cell magnetization $\vec{M} = \vec{s_1} + \vec{s_2}$ along the m' plane and unit cell antiferromagnetic vector $\vec{L} = \vec{s_1} - \vec{s_2}$ along the a plane. The polar symmetry of the phase also gives rise to two ferroelectric($\pm P_z$)-ferroelastic($\pm e_{xy}$) domains, and four *ferrotoroidic domains* corresponding here[2] to the spontaneous toroidal moment $\vec{T} = \hat{\nu}(\vec{M} \times \vec{P})$, collinear to $\vec{L}$, where $\hat{\nu}$ is a third rank tensor. $\vec{T}$ and $\vec{L}$ have the same symmetry and are bilinearly coupled.

(iii) Phase III of symmetry $P2'$ is stabilized for $\theta \neq n\frac{\pi}{4}$ and requires an eighth-degree expansion of F, involving eight weak ferromagnetic and/or antiferromagnetic domains and two ferroelectric-ferroelastic domains.

The theoretical phase diagram containing the preceding phases is shown in Fig. 2. Phases II and III allow a spontaneous

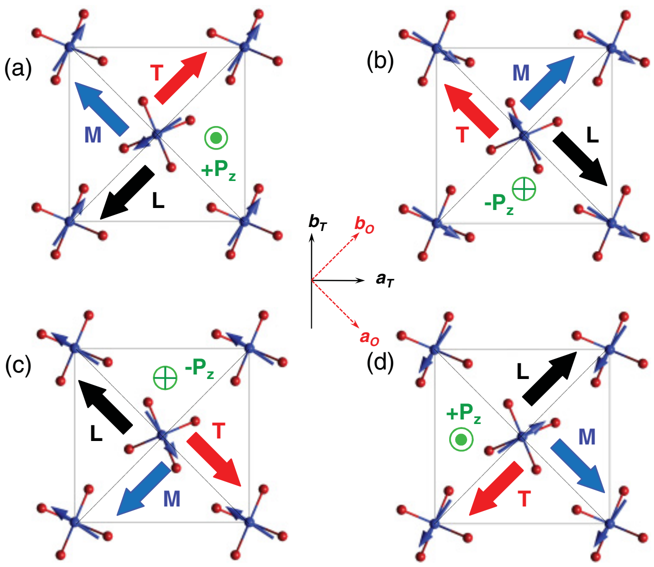

FIG. 1. (Color online) Respective orientations of the magnetization ($\vec{M}$), antiferromagnetic vector ($\vec{L}$), toroidal moment ($\vec{T}$), and polarization ($\vec{P}$) in the four multiferroic domains of BCG. Dark blue thin arrows represent the orientation of the spins $\vec{s}_1$ and $\vec{s}_2$ located in positions (0,0,0) and (0.5,0,5,0) in the tetragonal paramagnetic structure. The central inset shows the tetragonal and orthorhombic settings used in the text.

polarization along z, as observed experimentally in BCG.[21,22] However, only phase II can be reached directly from the paramagnetic phase, whereas a transition to phase III goes across phases I or II, or displays a first-order character. The temperature dependence of the polarization varies continuously at T_N, and the configuration of the spin moments[22] is consistent with the four domains of phase II. Therefore, phase II can unambiguously be identified as the multiferroic phase arising below T_N.

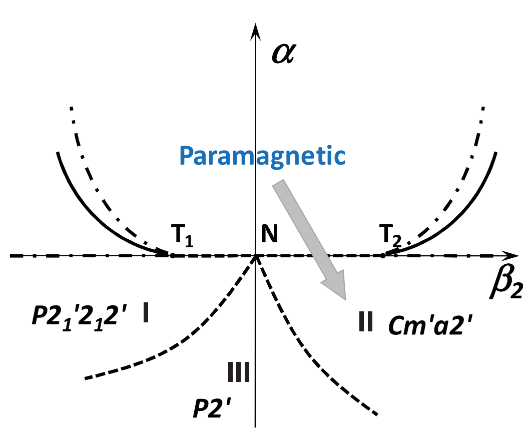

FIG. 2. (Color online) Theoretical phase diagram associated with the free-energy F given by Eq. (2). Solid and hatched curves are first- and second-order transitions lines. Hatched-dotted curves are limits of stability lines. T_1 and T_2 are tricritical points. N is a four-phase point. The arrow represents the thermodynamic path followed in BCG.

III. SPONTANEOUS AND FIELD-INDUCED TOROIDIC EFFECTS

Let us express the effective transition free-energy F_{eff} in the multiferroic phase in terms of the spontaneous measurable variables $\vec{L}=(L_x,L_y),\vec{M}=(M_x,M_y)$, and P_z, taking into account their lowest degree coupling invariants. It reads:

$$\begin{aligned} F_{\text{eff}} &= a_1L^2+a_2L^4+b_1M^2+b_2M^4+c(L_xM_y+L_yM_x)\\ &\quad+\frac{P_z^2}{2\varepsilon_{zz}^0}+\delta_1L_xL_yP_z+\delta_2M_xM_yP_z\\ &\quad+\delta_3(M_xL_y-M_yL_x)P_z \end{aligned} \tag{2}$$

where ε_{zz}^0 is the dielectric permittivity in the paramagnetic phase, and a_i,b_i,c, and δ_i are phenomenological coefficients. Minimizing F_{eff} with respect to P_z yields the equilibrium polarization below T_N:

$$P_z^e=-\varepsilon_{zz}^0[\delta_1L_xL_y+\delta_2M_xM_y+\delta_3(M_xL_y-M_yL_x)]. \tag{3}$$

The two first terms into brackets express the respective contributions of the antiferromagnetic and weak-ferromagnetic order parameters to the polarization, whereas the third term reflects their coupling contribution. Since $|\vec{L}|$ and $|\vec{M}|$ vary below T_N as $\sim(T_N-T)^{\frac{1}{2}}$, P_z^e varies as (T_N-T), consistent with the linear dependence observed for $P_z^e(T)$,[21] corresponding to an improper ferroelectric critical behavior. The dielectric permittivity varies as $\varepsilon_{zz}(T)=\varepsilon_{zz}^0(1+\frac{\varepsilon_{zz}^0\delta_1^2}{2a_2})$ for $T<T_N$, in agreement with the reported upward discontinuity at T_N.[21]

The δ_3 term in Eq. (2) reflects the invariance of the mixed vector product $(\vec{M}\times\vec{L})\cdot\vec{P}$ under the symmetry operations of the paramagnetic phase. Since the toroidal moment $\vec{T}=(T_x,T_y)$ has the same symmetry as the antiferromagnetic vector $\vec{L}$, one has analogously a mixed coupling invariant $(T_xM_y-T_yM_x)P_z$ reflecting the invariance of the mixed products $(\vec{T}\times\vec{M})\cdot\vec{P}$ or $(\vec{T}\times\vec{P})\cdot\vec{M}$ which express the following relationships between the spontaneous macroscopic vectors

$$\vec{P}^s=\hat{\mu}(\vec{T}^s\times\vec{M}^s) \tag{4}$$

and

$$\vec{M}^s=\hat{\lambda}(\vec{T}^s\times\vec{P}^s), \tag{5}$$

where $\hat{\mu}$ and $\hat{\lambda}$ are third rank tensors. Therefore applying electric or magnetic fields the field induced dielectric, magnetic, and toroidal coupling contributions to the free-energy read:

$$F_D=\frac{P^2}{2\varepsilon_0}+\varepsilon\vec{E}\cdot\vec{P}+\alpha\vec{H}\cdot\vec{P}+\sigma^H(\vec{T}\times\vec{H})\cdot\vec{P}, \tag{6}$$

$$F_M=\mu_0\frac{M^2}{2}+\chi\vec{H}\cdot\vec{M}+\beta\vec{E}\cdot\vec{M}+\sigma^E(\vec{T}\times\vec{E})\cdot\vec{M}, \tag{7}$$

$$F_T=\nu_0\frac{T^2}{2}+\kappa_1\vec{E}\cdot\vec{T}+\kappa_2\vec{H}\cdot\vec{T}+\sigma^{EH}(\vec{E}\times\vec{H})\cdot\vec{T}, \tag{8}$$

minimizing Eqs. (6)–(8) with respect to $\vec{P}$, $\vec{M}$, and $\vec{T}$, and taking into account the spontaneous quantities $\vec{P}^s,\vec{M}^s,\vec{T}^s$ existing in the absence of applied fields yields the equations of state for the *total* polarization, magnetization, and toroidal moment

$$\vec{P}=\vec{P}^s+\hat{\varepsilon}\vec{E}+\hat{\alpha}\vec{H}+\hat{\sigma}^H(\vec{T}\times\vec{H}), \tag{9}$$

$$\vec{M} = \vec{M}^s + \hat{\chi}\vec{H} + \hat{\beta}\vec{E} + \hat{\sigma}^E(\vec{T} \times \vec{E}), \quad (10)$$
$$\vec{T} = \vec{T}^s + \hat{\kappa}^E\vec{E} + \hat{\kappa}^H\vec{H} + \hat{\sigma}^{EH}(\vec{E} \times \vec{H}). \quad (11)$$

The $\hat{\epsilon}$,$\hat{\alpha}$,$\hat{\chi}$, and $\hat{\beta}$ terms correspond to linear magnetoelectric effects, whereas the third-rank tensors $\hat{\sigma}^H$ and $\hat{\sigma}^E$ precede additional polarization and magnetization components induced by the coupling of the total toroidal moment $\vec{T}$ to noncollinear $\vec{H}$ or $\vec{E}$ fields. $\hat{\kappa}^E$ and $\hat{\kappa}^H$ are the electrotoroidal and magnetotoroidal tensors. The $\hat{\sigma}^{EH}$ term represents the induced toroidal contribution under noncollinear electric and magnetic fields. One should emphasize that the toroidal contributions to $\vec{P}$ and $\vec{M}$ in Eqs. (9) and (10), which are activated by a single external field noncollinear to $\vec{T}$, differ from the "ferromagnetotoroidic" and "ferroelectrotoroidic" effects[25] implying the application of two distinct noncollinear fields.

IV. MAGNETOELECTRIC EFFECTS

Equations (9)–(11) provide an interpretation of the remarkable magnetoelectric effects reported in BCG[21,22] as resulting from the existence of a spontaneous toroidal moment. Applying H_z field gives rise to a polarization component P_x increasing from 0 to 120 μCm^{-2} for $0 < H_z < 8T$. In the orthorhombic setting, which is turned by 45° with respect to the tetragonal axes (Fig. 1), one gets from Eqs. (9)–(11):

$$P_x(H_z) = \left[\alpha_{13} + T_y^s\left(\chi_{33} + \sigma_{123}^H\right)\right]H_z. \quad (12)$$

Consistent with the linear increase observed for $P_x(H_z)$ with increasing field[21] and with its sign reversal on reversing H_z.[22] The sharp increase of $P_x(T)$ below T_N at constant field,[21] denotes a substantial toroidal contribution, with respect to the linear magnetoelectric contribution $\alpha_{13} \approx (T_N - T)^{\frac{1}{2}}$. The observed increase of $P_z(H_z)$ from -11 μCm^{-2} at $H_z = 0$, to $+80$ μCm^{-2} in 8T is given by:

$$P_z(H_z) = P_z^s + \left(\chi_{23}T_x^s - \chi_{13}T_y^s\right)H_z. \quad (13)$$

The shift of $P_z(H_z)$ to higher temperature under applied field[21] is due to the renormalization of the coefficient $a_1 \approx (T - T_N)$ in Eq. (2), which increases T_N by $T_N(H_z) - T_N(0) \approx \chi_{33}H_z^2$. In order to account for the even dependence of H_z observed for $P_z(H_z)$, one has to consider a higher order contribution, e.g. $\simeq H_z^2$, to $P_z(H_z)$.

Other magnetoelectric effects have been reported[22] under application of H_{xy} and $H_{\bar{x}y}$ fields. P_z *increases* by increasing H_{xy} and *decreases* when increasing $H_{\bar{x}y}$.[22] Projecting Eq. (9) along z, one gets:

$$P_z(H_{xy}) = -P_z(H_{\bar{x}y}) = \tfrac{1}{2}\left(\alpha_{31} + \sigma_{321}^H T_y^s + \sigma_{312}^H T_x^s\right)H_{xy}. \quad (14)$$

Turning the H_{xy} field by 90° transforms a ferroelectric domain into another, changing the sign of P_z.[22] As for $P_z(H_z)$, a shifting of the transition temperature is observed under H_{xy} field,[22] $P_z(T)$ decreasing smoothly down to $T_N = 12$ K for $H_{xy} = 5$ T. These effects occur at low magnetic fields. At higher fields $P_x(H_{xy})$ decreases and changes sign.[22] This behavior, assumed to correspond to a spin-structural change,[22] requires including the higher-order invariant $(\vec{T}^s \times \vec{H}) \cdot (\vec{T}^s \cdot \vec{H}) \approx \frac{K(T_x^s,T_y^s)}{2}H_{xy}^2$ in Eq. (9). For $K < 0$, $P_z(H_{xy})$ decreases above the threshold field $H_{xy}^{\text{th}} = -\frac{\alpha_{31}+A}{4K}$ taking negative values for $H_{xy} > 2H_{xy}^{\text{th}}$.

V. MICROSCOPIC TOROIDIC CONTRIBUTION TO THE POLARIZATION

To gain insight into the nature of the magnetic interactions governing the magnetoelectric and toroidic behaviors of BCG, let us express the order-parameter components in function of the magnetic spins $\vec{s}_1$ and $\vec{s}_2$. Writing $\vec{s}_i = s_i^a\vec{a} + s_i^b\vec{b} + s_i^c\vec{c}$ ($i = 1,2$), where $\vec{a}$,$\vec{b}$,$\vec{c}$ are the tetragonal lattice vectors, the representation Γ transforming the $s_i^{a,b,s}$ components decomposes into $\Gamma = \tau_1 + \tau_2 + 2\tau_5$, i.e., *two order-parameter copies*, denoted (η_1,η_2) and (ζ_1,ζ_2), *are involved in the transition mechanism*. Standard projector techniques[26] give:

$$\eta_1 = s_1^a + s_2^a, \quad \eta_2 = -\left(s_1^b + s_2^b\right),$$
$$\zeta_1 = s_1^b - s_2^b, \quad \zeta_2 = s_1^a - s_2^a. \quad (15)$$

It shows that the two order-parameter copies coincide with the ferromagnetic and antiferromagnetic vectors. On the other hand, projections of Γ on τ_1 and τ_2 lead to $s_1^c - s_2^c = 0$ and $s_1^c + s_2^c = 0$, i.e., $s_1^c = s_2^c = 0$, confirming the in-plane spin ordering in BCG. The equilibrium values of (η_1,η_2) and (ζ_1,ζ_2) in phase II yield the spin configurations for the four magnetic domains represented in Fig. 1, namely: two weak ferromagnetic domains for $s_1^a + s_2^a = \pm(s_1^b + s_2^b)$, and two antiferromagnetic domains for $s_1^b - s_2^b = \pm(s_1^a - s_2^a)$. The spontaneous polarization P_z^e at zero field reads

$$P_z^e = \delta_1'\eta_1\eta_2 + \delta_2'\zeta_1\zeta_2 + \delta_3'(\eta_1\zeta_2 + \eta_2\zeta_1), \quad (16)$$

analogue to Eq. (3). Using Eq. (12) yields

$$\begin{aligned} P_z^e = {} & \delta_1'\left(s_1^a s_1^b + s_1^a s_2^b + s_2^a s_1^b + s_2^a s_2^b\right) \\ & + \delta_2'\left(s_1^a s_1^b - s_1^b s_2^a - s_2^b s_1^a + s_2^a s_2^b\right) \\ & + \delta_3'\left(s_1^{a2} - s_2^{a2} - s_2^{b2} + s_2^{b2}\right). \end{aligned} \quad (17)$$

Equation (17) holds for a pair of antiferromagnetic domains (e.g., $\eta_1^e = \eta_2^e$ and $\zeta_1^e = \zeta_2^e$) whereas $-P_z^e$ coincides with the other pair ($\eta_1^e = -\eta_2^e,\zeta_1^e = -\zeta_2^e$). The δ_1', δ_2', and δ_3' terms represent the respective contributions of the spontaneous ferromagnetic, antiferromagnetic, *and toroidal* contributions to the spontaneous polarization arising in the multiferroic state. The δ_3' term, which is the microscopic analog of the spontaneous toroidic effect given by Eq. (4), reflects *single-ion effects*, while the two other terms contain invariants $s_i^u s_i^v (i = 1,2; u,v = a,b)$, also corresponding to single-ion effects, and $s_i^u s_j^v (i \neq j)$ invariants expressing the symmetric part of the exchange coupling interaction between the two Co spins. These results support the interpretation[21] that the spin-dependent *p-d* hybridization between the transition-metal (Co) and ligand (O) contributes to the ferroelectricity in BCG via the spin-orbit interaction, as well as the proposed mechanism of lattice relaxation induced by exchange striction.[22] Note that the Dzialoshinskii-Moriya (DM) interaction does not contribute directly to the polarization but is responsible of the canting inducing the weak-ferromagnetic moments,[23] which stabilizes the toroidal moment giving rise to the δ_3' term in Eq. (17).

VI. SUMMARY, DISCUSSION, AND CONCLUSION

In summary, our theoretical analysis of the magnetoelectric effects reported in BCG shows that they can be described by the existence in the multiferroic phase of a spontaneous toroidal moment $\vec{T}$ displaying the same symmetry as the antiferromagnetic order-parameter $\vec{L}$. Equations of state relating the total polarization $\vec{P}$ and magnetization $\vec{M}$ to the toroidal moment have been proposed, involving the existence of specific toroidal contributions to $\vec{P}$ and $\vec{M}$ under, respectively, applied magnetic and electric fields. At the microscopic level, the toroidal contribution to the spontaneous polarization has been shown to be due to single-ion effects.

One may question if a toroidal-free approach involving the sole antiferromagnetic order-parameter $\vec{L}$ would also provide a consistent interpretation of the magnetoelectric effects observed in BCG. In order to clarify this point, let us consider, for example, the field dependence of P_x given by Eq. (12), which is a purely magnetic-field induced effect, since P_x has no direct coupling to $\vec{L}$ or $\vec{T}$ but couples to these two order-parameters only via the H_z field. Equation (12) shows that P_x varies linearly with H_z and is formed by the sum of three different terms: (i) $\alpha_{13}H_z$ corresponds to the linear magnetoelectric effect, $\alpha_{13}(T)$ varying critically as $(T_N - T)^{1/2}$; (ii) $\chi_{33}H_z$ is the contribution to the field of the weak magnetization induced by H_z, varying also as $(T_N - T)^{1/2}$; (iii) the toroidal contribution $T_y^s\sigma_{123}^H H_z$ assumed in our description corresponds at constant field to a $(T_N - T)^{3/2}$ power law. At very low field H_z, the observed critical behavior of $P_x(H_z)$ follows an S-shape type[21,22] temperature dependence at constant field, consistent with the $(T_N - T)^{3/2}$ power law typifying the toroidal term. Such critical behavior cannot be due to the higher-order magnetoelectric contribution $(L_x^2 L_y + L_y^2 L_x)P_x H_z$ since $\vec{L}$ also induces the power law $(T_N - T)^{1/2}$ via the linear magnetoelectric effect. Therefore if the critical exponents 1/2 and 3/2 are both related to the same order-parameter $\vec{L}$, the former should be dominating at a second-order transition. Furthermore, at very low field the nonlinear magnetoelectric contribution is negligible with respect to the linear one. Accordingly, the experimentally observed $(T_N - T)^{3/2}$ power law for $P_x(H_z)$ at constant field corresponds indeed to a magneto-toroidic effect. An additional support to this interpretation is the similar power laws found experimentally for $P_z(H_{xy})$ (Eq. (14) and $P_z(H_z)$ (Eq. (13), which can also be related to the corresponding toroidic contributions.

In the absence of measurable physical quantity that would give a direct proof of the presence of the toroidal moment in a multiferroic phase, the coupling of the toroidal moment to the polarization and magnetization can give rise to behaviors reflecting its specific contribution to the magnetic field. This contribution corresponds to higher-order effects which can be differentiated from standard nonlinear magnetoelectric effects. Besides the critical behavior of field-induced components of the polarization the nonlinear H^2 contribution to $\vec{P}$ is observable above and below the transition while the $\vec{T} \times \vec{H}$ contribution would be observable only below T_N. More generally, the symmetries of the third-rank tensors $\hat{\sigma}^H$ and $\hat{\sigma}^E$ are different from the symmetries of the nonlinear magnetic and electric susceptibilities. Therefore, more spectacular toroidic effects, differing from standard nonlinear magnetoelectric effects, should be disclosed in systems exhibiting a spontaneous toroidal moment, involving the orientations of magnetic or electric field-induced polarization and magnetization components and the corresponding domain patterns.

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