Spontaneous toroidic effects in Ba$_2$CoGe$_2$O$_7$

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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.$^{1,2}$ The existence of a macroscopic moment asymmetric under both time reversal and space inversion long remained elusive$^{3}$ until the observation of the independent coexistence of ferrotoroidal and antiferromagnetic domains in LiCoPO$_4$. This result provides a motivation for investigating toroidic effects in the ferroelectric phases of magnetic multiferroic materials, in which the space-asymmetric electric polarization is induced by a time-asymmetric and space-asymmetric magnetic order. In absence of well defined physical properties showing direct experimental evidences of a toroidal moment in magnetic systems, one of the important issues is to find a material in which specific magnetoelectric effects$^4$ would reflect indirectly the influence of the toroidal moment. Here we analyze theoretically the magnetoelectric effects disclosed in the multiferroic phase of Ba$_2$CoGe$_2$O$_7$ (BCG)$^{5,6}$ and show that due to its specific magnetic symmetry, the existence of spontaneous polarization and magnetization under applied magnetic or electric fields which provide indirect indications of the existence and role of the toroidal moment in multiferroic materials. The toroidic contribution to the electric polarization in BCG is shown to result from single-ion effects.

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The unusual magnetoelectric effects observed in the multiferroic phase arising below $T_N=6.7$K in Ba$_2$CoGe$_2$O$_7$ (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 produce specific contributions to the spontaneous polarization and magnetization under applied magnetic or electric fields which provide indirect indications of the existence and role of the toroidal moment in multiferroic materials. 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.$^{1,2}$ The existence of a macroscopic moment asymmetric under both time reversal and space inversion long remained elusive$^{3}$ until the observation of the independent coexistence of ferrotoroidal and antiferromagnetic domains in LiCoPO$_4$. This result provides a motivation for investigating toroidic effects in the ferroelectric phases of magnetic multiferroic materials, in which the space-asymmetric electric polarization is induced by a time-asymmetric and space-asymmetric magnetic order. In absence of well defined physical properties showing direct experimental evidences of a toroidal moment in magnetic systems, one of the important issues is to find a material in which specific magnetoelectric effects$^4$ would reflect indirectly the influence of the toroidal moment. Here we analyze theoretically the magnetoelectric effects disclosed in the multiferroic phase of Ba$_2$CoGe$_2$O$_7$ (BCG)$^{5,6}$ and show that due to its specific magnetic symmetry, the existence of spontaneous polarization and magnetization under applied magnetic or electric fields which provide indirect indications of the existence and role of the toroidal moment in multiferroic materials. The toroidic contribution to the electric polarization in BCG is shown to result from single-ion effects.

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\[ \vec{M} = (M_x, M_y), \vec{L} = (L_x, L_y) \text{ and } P_z \text{ as:} \]

\[ F = a_1 L^2 + a_2 L^4 + b_1 M^2 + b_2 M^4 + \]

\[ c(M_x L_x - M_y L_y) + \frac{P_z^2}{2 \varepsilon_{zz}} + \delta_1 L_x L_y P_z + \]

\[ \delta_2 M_x M_y P_z + \delta_3(M_x L_y - M_y L_x)P_z \]  \hspace{1cm} (2)

where \( \varepsilon_{zz}^0 \) is the dielectric permittivity in the paramagnetic phase, and \( a_i, b_i, c \) and \( \delta_i \) are phenomenological coefficients. The equilibrium polarization below \( T_N \) reads:

\[ P_z^c = -\varepsilon_{zz}^0 [\delta_1 L_x L_y + \delta_2 M_x M_y + \delta_3(M_x L_y - M_y L_x)] \hspace{1cm} (3) \]

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 \( \sim (T_N - T)^2 \), \( P_z^c \) varies as \( (T_N - T) \), consistent with the linear dependence observed for \( P_z^c(T) \) corresponding to an improper ferroelectric critical behaviour. The dielectric permittivity varies as \( \varepsilon_{zz}(T) = \varepsilon_{zz}^0 \left( 1 + \frac{\varepsilon_{zz}^0 \delta_1}{2\varepsilon_{zz}} \right) \) for \( T < T_N \), in agreement with the reported upward discontinuity at \( T_N \).

The \( \delta_3 \)-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. Analogously, the existence of the \( (T_x M_y - T_y M_x)P_z \) invariant involving the toroidal moment components \( (T_x, T_y) \), expresses the invariance of the mixed vector products \( (\vec{T} \times \vec{M}) \cdot \vec{P} \) and \( (\vec{T} \times \vec{P}) \cdot \vec{M} \) which yield the following relationships between the spontaneous components:

\[ \vec{P} = \hat{\mu}(\vec{T} \times \vec{M}) \hspace{1cm} \text{(4)} \]

and

\[ \vec{M} = \hat{\lambda}(\vec{T} \times \vec{P}) \hspace{1cm} \text{(5)} \]

where \( \hat{\mu} \) and \( \hat{\lambda} \) are third rank tensors. Applying electric or magnetic fields the existence of a spontaneous toroidal moment \( \vec{T}^s \) gives:

\[ \vec{P} = \vec{P}^s + \hat{\varepsilon} \vec{E} + \hat{\alpha} \vec{H} + \hat{\sigma}^H (\vec{T} \times \vec{H}) \hspace{1cm} \text{(6)} \]

\[ \vec{M} = \vec{M}^s + \hat{\chi} \vec{H} + \hat{\beta} \vec{E} + \hat{\sigma}^E (\vec{T} \times \vec{E}) \hspace{1cm} \text{(7)} \]

\[ \vec{T} = \vec{T}^s + \hat{\kappa}^E \vec{E} + \hat{\kappa}^M \vec{H} + \hat{\sigma}^{EH} (\vec{E} \times \vec{H}) \hspace{1cm} \text{(8)} \]

where 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 non-collinear $\vec{H}$ or $\vec{E}$ fields, $\vec{r}^E$ and $\vec{r}^E$ are the
electrotoroidal and magnetotoroidal tensors. The $\tilde{\sigma}^{EH}$-term
represents the induced toroidal contribution under
non-collinear electric and magnetic fields. One should
emphasize that the toroidal contributions to
collinear electric and magnetic fields. One should em-
curves are first and second-order transitions lines. Hatched
dotted curves are limits of stability lines. $T_1$ and $T_2$ are tri-
critical points. $N$ is a four-phase point. The arrow represents
the thermodynamic path followed in BCG.

FIG. 2: (Color online) Theoretical phase diagram associate-
d 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 tri-
critical points. $N$ is a four-phase point. The arrow represents

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

Other magnetoelectric effects have been reported under
application of $H_{xy}$ and $H_{zy}$ fields. $P_z$ increases
by increasing $H_{xy}$ and decreases when increasing $H_{xy}$.

Projecting Eq. (6) along $z$, one gets:

$$P_z(H_{xy}) = \Delta P_x(H_{xy}) = \frac{1}{2} (\sigma_{31} + \sigma_{31}^H \chi_{xy}^s + \sigma_{31}^H \chi_{xy}^s) H_{xy}$$

(11)

Turning the $H_{xy}$ field by $90^\circ$ transforms a ferroelectric
domain into another, changing the sign of $P_x$.

As for $P_x(H_z)$, a shifting of the transition temperature is ob-
erved under $H_{xy}$ field $P_x(T)$ decreasing smoothly down

$T_N=12K$ for $H_{xy}=5T$, with a $(T_N - T)^{\frac{1}{2}}$ critical
dependence of $A(T_N, T_y) = \sigma_{31}^H T_y^s + \sigma_{31}^H T_y^s T_z^s$. These effects occur at low magnetic fields. At higher fields $P_x(H_{xy})$
decreases and changes sign. This behaviour, assumed to correspond to a spin-structural change, requires in-
cluding the higher-order invariant $(T^z \times \vec{H}) \cdot (T^z \cdot \vec{H}) \approx \frac{\kappa(T^z, T_y)}{2} H_{xy}^2$ in Eq. (6). For $K < 0$, $P_x(H_{xy})$ decreases
above the threshold field $H_{xy}^{th} = -\frac{2\chi_{31} A_4}{4K}$ taking negative values for $H_{xy} > 2H_{xy}^{th}$.

To gain insight into the nature of the magnetic interac-
tions governing the magnetoelectric and toroidal be-
aviours of BCG, let us express the order-parameter components in function of the magnetic spins $s_1^z$ and $s_2^z$. Writing $s_1^z = s_1^a \bar{a} + s_1^b \bar{b} + s_1^c \bar{c}$ ($i = 1, 2$), where $\bar{a}, \bar{b}, \bar{c}$ are the tetragonal lattice vectors, the representa-
tion $\Gamma$ transforming the $s_1^{ab,s}$ components decomposes into
$\Gamma = \tau_1 + \tau_2 + 2\tau_5$, i.e. two order-parameter copies,
denoted $(\eta_1, \eta_2)$ and $(\zeta_1, \zeta_2)$, are involved in the transition
mechanism. Standard projector techniques give:

$$\eta_1 = s_1^a + s_2^a, \eta_2 = -(s_1^b + s_2^b)$$
$$\zeta_1 = s_1^a - s_2^a, \zeta_2 = s_1^a - s_2^a$$

(12)

It shows that the two order-parameter copies coincide with
the ferromagnetic and antiferromagnetic vectors. On the other hand, projections of $\Gamma$ on $\tau_1$ and $\tau_2$ lead to $s_1^z - s_2^z = 0$ and $s_1^z + s_2^z = 0$, i.e. $s_1^z = s_2^z = 0$, confirming
the in-plane spin ordering in BCG. The equilibrium values of $(\eta_1, \eta_2)$ and $(\zeta_1, \zeta_2)$ in phase II yield the spin
configurations for the four magnetic domains represented
in Fig. 1, namely: two weak ferromagnetic domains for
$s_1^a + s_2^a = \pm(s_1^a + s_2^a)$, and two antiferromagnetic domains

$$P_z(H_z) = P_z^s + (\chi_{23} T_z - \chi_{13} T_y^s) H_z$$

(10)

The observed increase of $P_z(H_z)$ from $-11\mu Cm^{-2}$ at $H_z = 0$, to $+80\mu Cm^{-2}$ in 8T is given by:

$$P_z(H_z) = P_z^s + (\chi_{23} T_z - \chi_{13} T_y^s) H_z$$

(10)
for \( s_1^h - s_2^h = \pm (s_1^a - s_2^a) \). The spontaneous polarization \( P_z^e \) at zero field reads:

\[
P_z^e = \delta_1' \eta_1 \eta_2 + \delta_2' \zeta_1 \zeta_2 + \delta_3' (\eta_1 \zeta_2 + \eta_2 \zeta_1) \tag{13}
\]

analogous to Eq. (3). Using Eq. (12) yields:

\[
P_z^e = \delta_1'(s_1^a s_1^b + s_1^a s_2^b + s_2^a s_1^b + s_2^a s_2^b) \\
+ \delta_2'(s_1^b s_1^b - s_1^b s_2^b - s_2^b s_1^b + s_2^b s_2^b) \\
+ \delta_3'(s_1^a - s_2^2 - s_2^b + s_2^2) \tag{14}
\]

Eq. (14) holds for a pair of antiferromagnetic domains (e.g. \( \eta_1' = \eta_2' \) and \( \zeta_1' = \zeta_2' \)) whereas \( -P_z^e \) coincides with the other pair \( (\eta_1' = -\eta_2', \zeta_1' = -\zeta_2') \). The \( \delta_1' \), \( \delta_2' \) and \( \delta_3' \) terms represent the respective contributions of the spontaneous ferromagnetic, antiferromagnetic and toroidal contributions to the spontaneous polarization arising in the multiferroic state. The \( \delta_3' \) term, which is the microscopic analogue of the spontaneous toroid 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 that the spin-dependent \( p-d \) interaction between the transition-metal (Co) and ligand \( (\text{O}) \) contributes to the ferroelectricity in BCG via the spin-orbit interaction, as well as the proposed mechanism of lattice relaxation induced by exchange striction.

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, which stabilize the toroidal moment giving rise to the \( \delta_1' \) term in Eq. (14).

In conclusion, our theoretical analysis shows that in multiferaic compound exhibiting spontaneous magnetization, polarization and toroidal moment, field-induced toroid effects occur, consisting of additional toroidal contributions to the polarization and magnetization. These toroidal effects allow a comprehensive description of the specific magnetoelectric properties observed in BCG, which have been shown to relate to additional toroidal contributions to the polarization, corresponding at the microscopic level to single site magnetic interactions. They should allow clarifying the intrinsic role of the toroidal moment in magnetic multiferroics.

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