

Thermodynamics of ferrotoroidic materials: Toroidocaloric effect

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The three primary ferroics, namely ferromagnets, ferroelectrics, and ferroelastics, exhibit corresponding large (or even giant) magnetocaloric, electrocaloric, and elastocaloric effects when a phase transition is induced by the application of an appropriate external field. Recently the suite of primary ferroics has been extended to include ferrotoroidic materials in which there is an ordering of toroidic moments in the form of magnetic-vortex-like structures, examples being $\text{LiCo}(\text{PO}_4)_3$ and $\text{Ba}_2\text{CoGe}_2\text{O}_7$. In the present work we formulate the thermodynamics of ferrotoroidic materials. Within a Landau free energy framework we calculate the toroidocaloric effect by quantifying isothermal entropy change (or adiabatic temperature change) in the presence of an applied toroidic field when usual magnetization and polarization may also be present simultaneously. We also obtain a nonlinear Clausius-Clapeyron relation for phase coexistence.

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I. INTRODUCTION

Ferroc phenomenon or the presence of switchable domain walls in an external field is a direct consequence of a specific broken symmetry.¹ Loss of spatial inversion symmetry results in ferroelectricity whereas loss of time reversal symmetry results in ferromagnetism. Ferroelasticity is a result of broken rotational symmetry although it remains invariant under both spatial inversion and time reversal symmetries. The fourth possibility corresponds to when both spatial inversion and time reversal symmetries are simultaneously broken. This is the case for recently discovered ferrotoroidic materials² where the long-range order is related to an ordering of magnetic-vortex-like structures characterized by a toroidal dipolar moment. It is important to mention that the ferrotoroidic order is also related to magnetoelectric behavior³ which is one of the main attractions of multiferroics—materials that exhibit two or more ferroic orders simultaneously. This class includes magnetoelastics as well as magnetic shape memory alloys.

In general, both electric and magnetic toroidal moments can be defined within the context of electromagnetism.^{4,5} In the present paper we will exclusively consider the magnetic toroidal moment which is the only one that has the required spatial and time inversion symmetries.⁴ We note that in recent years the study of the unique properties of ferroelectric materials carrying an electric toroidal moment has received considerable attention.^{6,7}

Ferrotoroidic domain walls have been observed in $\text{LiCo}(\text{PO}_4)_3$ using the second harmonic generation technique⁸ and a symmetry classification of such domains has been given recently.⁹ Spontaneous toroidal moments have been attributed to exist in the multiferroic phase of $\text{Ba}_2\text{CoGe}_2\text{O}_7$ (BCG)¹⁰ and may be related to the observed unusual magnetoelectric effects.^{11,12} Single-crystalline thin films of MnTiO_3 with an ilmenite structure also exhibit a ferrotoroidic structure.¹³ Neutron polarimetry indicates that the magnetoelectric MnPS_3 is a viable candidate for ferrotoroidicity.¹⁴ The magnetic phase transition in BiFeO_3 implies the appearance of a toroidal

moment.¹⁵ *Ab initio* calculations suggest that the olivine material $\text{Li}_4\text{MnFeCoNiP}_4\text{O}_{16}$ is possibly ferrotoroidic.¹⁶

A sequence of possibly two ferrotoroidic phase transitions has been considered phenomenologically for Ni-Br boracites.¹⁷ Another physical realization of toroidal order has been considered as an interacting system of disks with a triangle of spins on each disk.¹⁸ Both charge and spin currents can lead to a toroidal state.¹⁹ Recent observation of orbital currents in CuO through resonant x-ray diffraction provides direct evidence of antiferrotoroidic ordering.²⁰ Ferrotoroidic materials exhibit linear magnetoelectric effect; in fact, the toroidal moment is related to an antisymmetric component of the magnetoelectric tensor ($\alpha_{ij} \neq \alpha_{ji}$). Moreover, the toroidal moment can be viewed as a quantum geometric phase.²¹ Beyond the magnetoelectric applications toroidic materials can also act as novel metamaterials.²²

One way of realizing the physical consequences of toroidal moment is to characterize the thermal response of the material to an externally applied field that couples to this moment and gives rise to measurable caloric effects. Actually, caloric effects are inherent to every material and are commonly quantified by the adiabatic temperature change or by the isothermal entropy change that occur when an external field is applied or removed. In the solid state, the most studied caloric effect is the magnetocaloric effect,²³ mainly after the discovery in the mid-nineties of materials displaying a giant magnetocaloric effect in the vicinity of room temperature.²⁴ However, in recent years other caloric effects such as the electrocaloric,²⁵ elastocaloric,²⁶ or barocaloric²⁷ have also received considerable attention.

A crucial feature common to most materials exhibiting a giant caloric effect is the occurrence of a first-order phase transition. The expected large (discontinuous) change of the order parameter at the transition involves a large entropy content (associated with the latent heat) which is at the origin of the giant caloric effect. Moreover, a strong coupling between different degrees of freedom such as structural, magnetic, and

electric enables the transition to be driven by different fields conjugated to such properties. The study of caloric effects is thus a convenient method in order to study the thermodynamics of this class of complex materials. For instance, this should apply to multiferroic materials which are expected to show more than one caloric effect, e.g., simultaneous electrocaloric and magnetocaloric effects, or more precisely a magneto-electrocaloric effect. The latter has not been reported yet. The present paper deals with the thermal response and the associated caloric effects resulting from changes of toroidal order in ferrotoroidic materials (undergoing a paratoroidic to ferrotoroidic transition). These changes are likely to give rise to a toroidocaloric effect in this class of materials. Indeed, the study of toroidocaloric effect is expected to provide new insights into understanding the important problem of switching the toroidal moment.⁷

In this paper we study the thermodynamics of multiferroics and first derive expressions for magnetoelectrocaloric and toroidocaloric equations in Sec. II and Sec. III treating magnetization, polarization, and toroidization as independent order parameters. In Sec. IV we present a Landau free energy for a paratoroidic to ferrotoroidic transition with a specific coupling between toroidization, polarization, and magnetization; derive a phase coexistence (Clausius-Clapeyron) relation; and compute the toroidocaloric effect. Possible experimental implications are discussed in Sec. V in which we also present our main conclusions.

II. CALORIC EFFECTS: GENERAL ASPECTS

Consider a generic thermodynamic system and take temperature (T) and generalized forces or fields ($\{\mathbf{Y}_i\}$) as independent variables. Differential changes of the fields will yield a differential change of entropy [$S = S(T, \{\mathbf{Y}_i\})$] given by

$$\begin{aligned} dS &= \frac{C}{T} dT + \sum_i \left(\frac{\partial S}{\partial \mathbf{Y}_i} \right)_{T, \{\mathbf{Y}_{j \neq i}\}} d\mathbf{Y}_i \\ &= \frac{C}{T} dT + \sum_i \left(\frac{\partial \mathbf{X}_i}{\partial T} \right)_{\{\mathbf{Y}_j\}} d\mathbf{Y}_i, \end{aligned} \quad (1)$$

where $C/T = \left(\frac{\partial S}{\partial T} \right)_{\{\mathbf{Y}_i\}}$ defines the heat capacity at constant fields $\{\mathbf{Y}_i\}$ and we have taken into account the general Maxwell relations:

$$\left(\frac{\partial S}{\partial \mathbf{Y}_i} \right)_{T, \{\mathbf{Y}_{j \neq i}\}} = \left(\frac{\partial \mathbf{X}_i}{\partial T} \right)_{\{\mathbf{Y}_j\}}. \quad (2)$$

Here $\{\mathbf{X}_i\}$ denote generalized displacements thermodynamically conjugated to the fields $\{\mathbf{Y}_i\}$. Any interplay between the different degrees of freedom will be taken into account through the fact that any \mathbf{X}_i is, in principle, a function of all fields. Therefore, the interplay must be introduced through the state equations.

For each generalized displacement a caloric effect will occur when the corresponding conjugated field is varied. Suppose, for instance, that the field \mathbf{Y}_i changes from 0 to \mathbf{Y}_i so that the system passes from a state $(T_i, 0)$ to (T_f, \mathbf{Y}_i) , where T_i and T_f are the temperatures of the initial and final states respectively. The corresponding change of entropy is given by $S(T_f, \mathbf{Y}_i) - S(T_i, 0)$. The two limits of interest that quantify

the caloric effect associated to the property \mathbf{X}_i conjugated to the field \mathbf{Y}_i are the isothermal and the adiabatic limits. In the isothermal case $T_i = T_f = T$ and the thermal response is characterized by a change of entropy given by

$$\begin{aligned} \Delta S(T, 0 \rightarrow \mathbf{Y}) &= S(T, \mathbf{Y}_i) - S(T, 0) \\ &= \int_0^{\mathbf{Y}_i} \left(\frac{\partial \mathbf{X}_i}{\partial T} \right)_{\{\mathbf{Y}_j\}} d\mathbf{Y}_i. \end{aligned} \quad (3)$$

In the adiabatic limit, $\Delta S = 0$, and the thermal response is quantified by the change of temperature given by

$$\begin{aligned} \Delta T(T_i, 0 \rightarrow \mathbf{Y}) &= T_f(\mathbf{Y}_i) - T_i(0) \\ &= - \int_0^{\mathbf{Y}_i} \frac{T}{C} \left(\frac{\partial \mathbf{X}_i}{\partial T} \right)_{\{\mathbf{Y}_j\}} d\mathbf{Y}_i. \end{aligned} \quad (4)$$

Therefore, the caloric response of a material to a given field \mathbf{Y}_j will be given by $\left(\frac{\partial \mathbf{X}_i}{\partial T} \right)_{\{\mathbf{Y}_j\}}$.

Examples

In the case of the magnetocaloric effect the corresponding expression for the isothermal entropy change is

$$\Delta S(T, 0 \rightarrow \mathbf{H}) = \int_0^{\mathbf{H}} \left(\frac{\partial \mathbf{M}}{\partial T} \right)_{\{\mathbf{H}\}} \cdot d\mathbf{H} \quad (5)$$

and for the adiabatic temperature change it is

$$\Delta T(T_i, 0 \rightarrow \mathbf{H}) = - \int_0^{\mathbf{H}} \frac{T}{C} \left(\frac{\partial \mathbf{M}}{\partial T} \right)_{\{\mathbf{H}\}} \cdot d\mathbf{H}, \quad (6)$$

where \mathbf{H} is the magnetic field (strictly we should write $\mu_0 \mathbf{H} = \mathbf{B}$) and \mathbf{M} is the magnetization. Notice that by just replacing \mathbf{H} by the electric field \mathbf{E} and \mathbf{M} by the polarization \mathbf{P} the corresponding changes of entropy and temperature that quantify the electrocaloric effect are obtained. Similarly, by replacing \mathbf{H} by the stress σ and \mathbf{M} by the strain ε we get the corresponding changes of entropy and temperature for the mechanocaloric effect. Therefore, a barocaloric effect (a particular case of mechanocaloric effect) involving pressure p and change in volume ΔV is also expected.

III. MATERIALS WITH TOROIDAL ORDER: THERMODYNAMICS

The three basic moments of the electromagnetic field are electric, magnetic, and toroidal moments. Therefore, we assume that the three ferroic properties are characterized by the corresponding moments per unit volume, polarization (\mathbf{P}), magnetization (\mathbf{M}), and toroidization ($\boldsymbol{\tau}$), that can be assumed as independent (vector) order parameters. Here the toroidization is assumed to originate only from the existence of magnetic toroidal moments. In fact, this appears to be the case for $\text{LiCo}(\text{PO}_4)_3$ ⁸ and $\text{Ba}_2\text{CoGe}_2\text{O}$.^{11,12} The corresponding thermodynamically conjugated fields will be the electric, \mathbf{E} , magnetic, \mathbf{H} , and toroidal, \mathbf{G} , fields. Therefore, the ‘‘thermodynamic identity’’ for such a (closed) system reads

$$dU = T dS + \mathbf{E} \cdot d\mathbf{P} + \mathbf{H} \cdot d\mathbf{M} + \mathbf{G} \cdot d\boldsymbol{\tau}, \quad (7)$$

where U is the internal energy per unit volume, T the temperature, and S the entropy per unit volume. The field \mathbf{G} coupling

to the toroidization is related to the electric and magnetic fields through $\mathbf{G} = \mathbf{E} \times \mathbf{H}$. This choice, however, deserves some discussion. Note that the natural conjugated field of the magnetic toroidal moment is $\nabla \times \mathbf{B}$.⁴ Nevertheless, since we are only considering homogeneous macroscopic bodies in thermodynamic equilibrium, from symmetry considerations we assume that \mathbf{G} is the appropriate macroscopic field that enables external control of the toroidization. This is actually in agreement with Refs. 3 and 4, where it is shown that the free energy of a system with magnetic toroidal moment must include a term proportional to the product $\boldsymbol{\tau} \cdot \mathbf{G}$. It is worth pointing out that the field \mathbf{G} cannot be modified independently of the fields conjugated to polarization and magnetization. From the thermodynamic identity (7), this relationship between \mathbf{G} , \mathbf{E} , and \mathbf{H} requires that

$$\left(\frac{\partial U}{\partial \boldsymbol{\tau}}\right)_{S, \mathbf{P}, \mathbf{M}} = \left(\frac{\partial U}{\partial \mathbf{P}}\right)_{S, \mathbf{M}, \boldsymbol{\tau}} \times \left(\frac{\partial U}{\partial \mathbf{M}}\right)_{S, \mathbf{P}, \boldsymbol{\tau}}. \quad (8)$$

We now define the Gibbs free energy \mathcal{G} through the following Legendre transform:

$$\mathcal{G} = U - TS - \mathbf{E} \cdot \mathbf{P} - \mathbf{M} \cdot \mathbf{H} - \boldsymbol{\tau} \cdot \mathbf{G}. \quad (9)$$

Differentiating this expression and replacing dU in (9), we obtain

$$d\mathcal{G} = -SdT - [\mathbf{P} + (\mathbf{H} \times \boldsymbol{\tau})] \cdot d\mathbf{E} - [\mathbf{M} + (\boldsymbol{\tau} \times \mathbf{E})] \cdot d\mathbf{H}. \quad (10)$$

Taking into account that double differentiation of \mathcal{G} is independent of the order in which it is carried out, we obtain the following Maxwell relations:

$$\left(\frac{\partial S}{\partial \mathbf{E}}\right)_{T, \mathbf{H}} = \left(\frac{\partial \mathbf{P}}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} + \mathbf{H} \times \left(\frac{\partial \boldsymbol{\tau}}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} \quad (11)$$

and

$$\left(\frac{\partial S}{\partial \mathbf{H}}\right)_{T, \mathbf{E}} = \left(\frac{\partial \mathbf{M}}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} + \left(\frac{\partial \boldsymbol{\tau}}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} \times \mathbf{E}. \quad (12)$$

We now take into account that polarization and magnetization can be written as the sum of an intrinsic term originating from (preexisting) free electric and magnetic moments and a contribution arising from the toroidal moments. The toroidal contributions satisfy^{1,3,19}

$$\mathbf{P}_t = -\boldsymbol{\tau} \times \mathbf{H} \quad (13)$$

and

$$\mathbf{M}_t = \boldsymbol{\tau} \times \mathbf{E}. \quad (14)$$

Then, the Maxwell relations (11) and (12) can be written in the form

$$\left(\frac{\partial S}{\partial \mathbf{E}}\right)_{T, \mathbf{H}} = \left(\frac{\partial \mathbf{P}_i}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} + \left(\frac{\partial \mathbf{P}_t}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} = \left(\frac{\partial \mathbf{P}}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} \quad (15)$$

and

$$\left(\frac{\partial S}{\partial \mathbf{H}}\right)_{T, \mathbf{E}} = \left(\frac{\partial \mathbf{M}_i}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} + \left(\frac{\partial \mathbf{M}_t}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} = \left(\frac{\partial \mathbf{M}}{\partial T}\right)_{\mathbf{H}, \mathbf{E}}, \quad (16)$$

where the intrinsic contributions to the polarization and magnetization are related to the total as $\mathbf{P} = \mathbf{P}_i + \mathbf{P}_t$ and $\mathbf{M} = \mathbf{M}_i + \mathbf{M}_t$.

A second set of Maxwell relations are obtained from differentiation with respect to \mathbf{E} and \mathbf{M} . This yields

$$\left(\frac{\partial \mathbf{P}_t}{\partial \mathbf{H}}\right)_{T, \mathbf{E}} = \left(\frac{\partial \mathbf{M}_t}{\partial \mathbf{E}}\right)_{T, \mathbf{H}}, \quad (17)$$

where we have taken into account that the intrinsic components \mathbf{P}_i and \mathbf{M}_i do not depend on \mathbf{H} and \mathbf{E} , respectively. This means that magnetoelectricity in the system originates only from the toroidal order. Notice that Eq. (17) just expresses that the magnetoelectric tensor α_{ij} obeys $P_i = \chi_{ij}^p E_j + \alpha_{ij} H_j$ and $M_i = \alpha_{ij} E_j + \chi_{ij}^m H_j$, where χ_{ij}^p and χ_{ij}^m are dielectric and magnetic susceptibility tensors, respectively. From the $\boldsymbol{\tau} \cdot \mathbf{G}$ term in Eq. (9) it also follows that the components of the toroidal moment obey the proportionality $\tau_1 \sim (\alpha_{23} - \alpha_{32})$, $\tau_2 \sim (\alpha_{31} - \alpha_{13})$, and $\tau_3 \sim (\alpha_{12} - \alpha_{21})$.

An interesting relationship between $\boldsymbol{\tau}$ and \mathbf{P}_t , \mathbf{M}_t can be obtained considering that

$$\begin{aligned} \mathbf{P}_t \times \mathbf{M}_t &= -(\boldsymbol{\tau} \times \mathbf{H}) \times (\boldsymbol{\tau} \times \mathbf{E}) \\ &= (\boldsymbol{\tau} \times \mathbf{E}) \times (\boldsymbol{\tau} \times \mathbf{H}) \\ &= -(\boldsymbol{\tau} \times \mathbf{E}) \times (\mathbf{H} \times \boldsymbol{\tau}) \\ &= -\boldsymbol{\tau} \times (\mathbf{E} \times \mathbf{H}) \times \boldsymbol{\tau} \\ &= -\boldsymbol{\tau} \times \mathbf{G} \times \boldsymbol{\tau}. \end{aligned} \quad (18)$$

Taking into account the general vectorial relation $\mathbf{A} \times \mathbf{B} \times \mathbf{A} = \mathbf{A}(\mathbf{A} \cdot \mathbf{B}) - \frac{1}{2}A^2\mathbf{B}$, we can rewrite the preceding equation as

$$\mathbf{P}_t \times \mathbf{M}_t = \frac{1}{2}\tau^2\mathbf{G} - \boldsymbol{\tau}(\mathbf{G} \cdot \boldsymbol{\tau}), \quad (19)$$

which points out that $\mathbf{P}_t \times \mathbf{M}_t$ is different from zero only under an applied toroidal field \mathbf{G} . Here $\tau = |\boldsymbol{\tau}|$ denotes the magnitude of toroidization.

The toroidocaloric effect

The equation quantifying the toroidocaloric effect under an applied electric or magnetic field is obtained using Maxwell relations (11) and (12). We obtain the following isothermal changes of entropy:

$$\begin{aligned} \Delta S(T, 0 \rightarrow \mathbf{E}) &= \int_0^{\mathbf{E}} \left[\left(\frac{\partial \mathbf{P}_i}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} + \mathbf{H} \times \left(\frac{\partial \boldsymbol{\tau}}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} \right] \cdot d\mathbf{E} \end{aligned} \quad (20)$$

and

$$\begin{aligned} \Delta S(T, 0 \rightarrow \mathbf{H}) &= \int_0^{\mathbf{H}} \left[\left(\frac{\partial \mathbf{M}_i}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} + \left(\frac{\partial \boldsymbol{\tau}}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} \times \mathbf{E} \right] \cdot d\mathbf{H}. \end{aligned} \quad (21)$$

The corresponding equations for the adiabatic change of temperature are

$$\begin{aligned} \Delta T(T_i, 0 \rightarrow \mathbf{E}) &= - \int_0^{\mathbf{E}} \frac{T}{C} \left[\left(\frac{\partial \mathbf{P}_i}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} + \mathbf{H} \times \left(\frac{\partial \boldsymbol{\tau}}{\partial T}\right)_{\mathbf{E}, \mathbf{H}} \right] \cdot d\mathbf{E} \end{aligned} \quad (22)$$

and

$$\begin{aligned} \Delta T(T_i, 0 \rightarrow \mathbf{H}) &= - \int_0^{\mathbf{H}} \frac{T}{C} \left[\left(\frac{\partial \mathbf{M}_i}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} + \left(\frac{\partial \boldsymbol{\tau}}{\partial T}\right)_{\mathbf{H}, \mathbf{E}} \times \mathbf{E} \right] \cdot d\mathbf{H}. \end{aligned} \quad (23)$$

The second term in the square brackets in Eqs. (20)–(23) represents the toroidal contribution. It is interesting to notice that when applying an electric (magnetic) field, no toroidal contribution to the caloric effect will occur if the magnetic (electric) field is zero.

If only toroidal order is present in the system the above equations for isothermal entropy change reduce to

$$\Delta S(T, 0 \rightarrow \mathbf{E}) = \int_0^{\mathbf{E}} \left(\frac{\partial \mathbf{P}_t}{\partial T} \right)_{\mathbf{E}, \mathbf{H}} \cdot d\mathbf{E} \quad (24)$$

and

$$\Delta S(T, 0 \rightarrow \mathbf{H}) = \int_0^{\mathbf{H}} \left(\frac{\partial \mathbf{M}_t}{\partial T} \right)_{\mathbf{H}, \mathbf{E}} \cdot d\mathbf{H}. \quad (25)$$

One finds similar expressions for the adiabatic temperature change $\Delta T(T_i, 0 \rightarrow \mathbf{E})$ and $\Delta T(T_i, 0 \rightarrow \mathbf{H})$.

IV. LANDAU MODEL FOR A MATERIAL UNDERGOING A FERROTOROIDIC TRANSITION

We assume that the toroidization ($\tau = |\boldsymbol{\tau}|$) is the order parameter to describe a paratoroidic to ferrotoroidic transition and propose the following minimal Landau model which includes a coupling between toroidization (τ), magnetization (M), and polarization (P), and the presence of toroidal (G), magnetic (H), and electric (E) fields:

$$\begin{aligned} F(T, \boldsymbol{\tau}, \mathbf{P}, \mathbf{M}) \\ = \frac{1}{2} A_0 (T - T_c^0) \tau^2 + \frac{1}{4} C \tau^4 + \frac{1}{2} \chi_p^{-1} P^2 + \frac{1}{2} \chi_m^{-1} M^2 \\ + \kappa \boldsymbol{\tau} \cdot (\mathbf{P} \times \mathbf{M}) - \mathbf{G} \cdot \boldsymbol{\tau} - \mathbf{H} \cdot \mathbf{M} - \mathbf{E} \cdot \mathbf{P}. \end{aligned} \quad (26)$$

Note that the term κ is the lowest order symmetry allowed term (satisfying space and time reversal symmetry) which provides the coupling between toroidization, polarization, and magnetization (see Ref. 28). Here the inverse toroidic susceptibility $\chi_t^{-1} = A_0(T - T_c^0)$, where A_0 is the ‘‘toroidic stiffness,’’ T_c^0 is the transition temperature, and $C > 0$ is the nonlinear toroidic coefficient. In particular, $\chi_t = \partial \mathbf{P} / \partial \mathbf{H} = \partial \mathbf{M} / \partial \mathbf{E}$. We also note that a Landau theory of ferrotoroidic transitions in boracites¹⁷ and $\text{Ba}_2\text{CoGe}_2\text{O}_7$ (BCG)¹⁰ has been considered previously. However, these studies did not consider any caloric effects.

Minimization with respect to polarization and magnetization gives

$$\frac{\partial F}{\partial \mathbf{P}} = \chi_p^{-1} \mathbf{P} - \mathbf{E} + \kappa (\mathbf{M} \times \boldsymbol{\tau}) = 0 \quad (27)$$

and

$$\frac{\partial F}{\partial \mathbf{M}} = \chi_m^{-1} \mathbf{M} - \mathbf{H} + \kappa (\boldsymbol{\tau} \times \mathbf{P}) = 0. \quad (28)$$

We now solve these two equations assuming (for simplicity) that $\mathbf{E} = (E, 0, 0)$ and $\mathbf{H} = (0, H, 0)$ and therefore $\mathbf{G} = (0, 0, EH)$ and $\boldsymbol{\tau} = (0, 0, \tau)$. For $\mathbf{P} [= (P, 0, 0)]$ and $\mathbf{M} [= (0, M, 0)]$ we obtain

$$P = \chi_p E - \kappa \chi_p \chi_m H \tau + O(\tau^2) \simeq \chi_p E - \alpha H \quad (29)$$

and

$$M = \chi_m H - \kappa \chi_p \chi_m E \tau + O(\tau^2) \simeq \chi_m H - \alpha E, \quad (30)$$

where in the above two equations we have neglected the nonlinear magnetoelectric effects. The magnetoelectric coefficient $\alpha = \kappa \chi_p \chi_m \tau$ is a quadrilinear product of electric susceptibility ($\chi_p = \partial \mathbf{P} / \partial \mathbf{E}$), magnetic susceptibility ($\chi_m = \partial \mathbf{M} / \partial \mathbf{H}$), the coupling constant κ , and the toroidization τ . Thus, either for $\kappa = 0$ or $\tau = 0$ there is no magnetoelectric effect. Substitution of P (29) and M (30) in the free energy (26) gives the following general type of effective free energy:

$$F_e = F_0(E, H) + \frac{1}{2} A \tau^2 + \frac{1}{3} B \tau^3 + \frac{1}{4} C \tau^4 + \lambda \tau, \quad (31)$$

with

$$F_0 = -\frac{1}{2} (\chi_p E^2 + \chi_m H^2), \quad (32)$$

$$\begin{aligned} A &= A_0 (T - T_c^0) - \kappa^2 \chi_p \chi_m [\chi_m H^2 + \chi_p E^2] \\ &= A_0 (T - T_c), \end{aligned} \quad (33)$$

$$T_c = T_c^0 + \frac{\kappa^2}{A_0} \chi_p \chi_m [\chi_m H^2 + \chi_p E^2], \quad (34)$$

$$B = 3\kappa^3 \chi_m^2 \chi_p^2 E H, \quad (35)$$

$$\lambda = (\kappa \chi_m \chi_p - 1) E H. \quad (36)$$

This corresponds to the free energy of a system subjected to an effective external field λ , proportional to the toroidal field $G = EH$. When $G = 0$, and therefore from (35) $B = 0$, the free energy (31) describes a paratoroidal-to-ferrotoroidal second-order phase transition whereas under the application of a toroidal field $G \neq 0$ (and $B \neq 0$), the transition becomes a first-order one. Actually, the physics contained in (31) is very rich since, in addition to λ , the cubic B coefficient also depends on the toroidal field G and the linear $A(T)$ term explicitly depends on the E and H fields. In other words, λ , $A(T)$, and B are not independent. This leads to a competition between B and λ depending on the value of the coupling constant κ (i.e., the choice of the ferrotoroidic material) and to a nonlinear Clausius-Clapeyron equation. It is worth pointing out that the addition of nonlinear terms in Eqs. (29) and (30) would lead to higher order terms in the expansion (31) that go beyond the minimal model. However, within the spirit of the Landau theory, we expect such terms are not essential.

For some purposes, it may be convenient to rescale the free energy according to the definitions proposed in Ref. 29:

$$\begin{aligned} a_0 &= \frac{A_0 C}{B^2}, \\ h &= \frac{\lambda C^2}{|B|^3}, \\ \tau_r &= \frac{C}{|B|} \tau, \\ f_r &= \frac{F_{\text{eff}}}{B^4} C^3, \end{aligned} \quad (37)$$

which yields the following rescaled free energy, valid for $B \neq 0$ only:

$$f_r = f_0 + \frac{1}{2} a \tau_r^2 + \frac{1}{3} \tau_r^3 + \frac{1}{4} \tau_r^4 + h \tau_r. \quad (38)$$

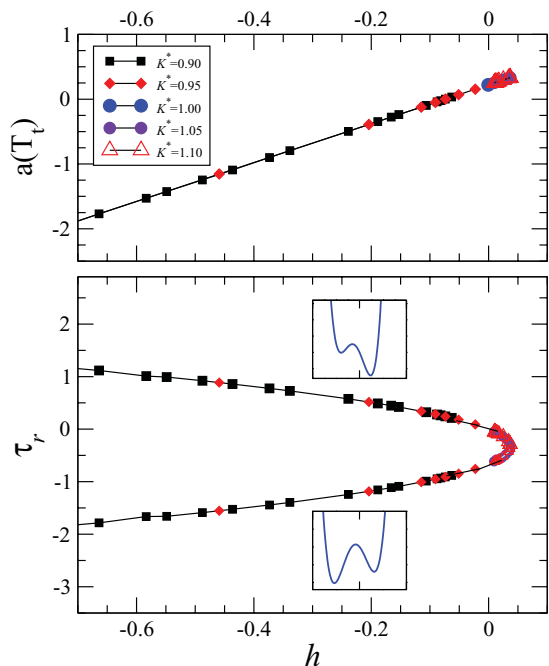


FIG. 1. (Color online) Rescaled phase diagram as a function of the field h for the temperature coefficient $a(T_t)$ (upper panel) and the order parameter τ_r (lower panel). Different symbols denote results obtained for different values of the effective coupling constant $\kappa^* = \kappa \chi_p \chi_m$.

As usual, the linear coefficient a is temperature dependent $a = a_0(T - T_c)$ and provides the temperature scale, while h provides the scale of the external effective field.

A. Phase diagram

Figure 1 shows the phase diagram for the rescaled variables (37) defined above. In the upper panel we have plotted the behavior of h vs $a(T)$ which gives the coexistence line. The region above the line is paratoroidic whereas below it is ferrotoroidic. The coexistence line ends in a critical point that can be calculated from the condition

$$-\frac{\partial h}{\partial \tau} = a + 2\tau + 3\tau^2 = 0. \quad (39)$$

One obtains that the critical point is located at $(h_c, a_c) = (\frac{1}{27}, \frac{1}{3})$. Notice that the field is $h \leq 0$ for $\kappa^* \leq 1$ whereas for $\kappa^* > 1$ we have $h > 0$ but $h < h_c = \frac{1}{27}$. The existence of this critical point is also revealed from the turning point in the behavior of τ_r vs h shown in the lower panel. Below the critical field ($h < h_c$), there are two possible values of τ_r related to the two possible wells in the free energy, as is schematically illustrated in the insets. Different symbols denote that the results have been obtained for different values of the effective coupling parameter $\kappa^* = \kappa \chi_m \chi_p$ by solving numerically the model (31). The subsequent application of scaling relations defined in (37) leads to the curves shown in Fig. 1.

Actually, the unscaled free energy (31) is more suitable for studying independently the effect of the external toroidal field G and the material-dependent coupling parameter κ . For convenience, we set $\chi_p = 1$, $\chi_m = 1$, $C = 1$, $T_c^0 = 1$, and

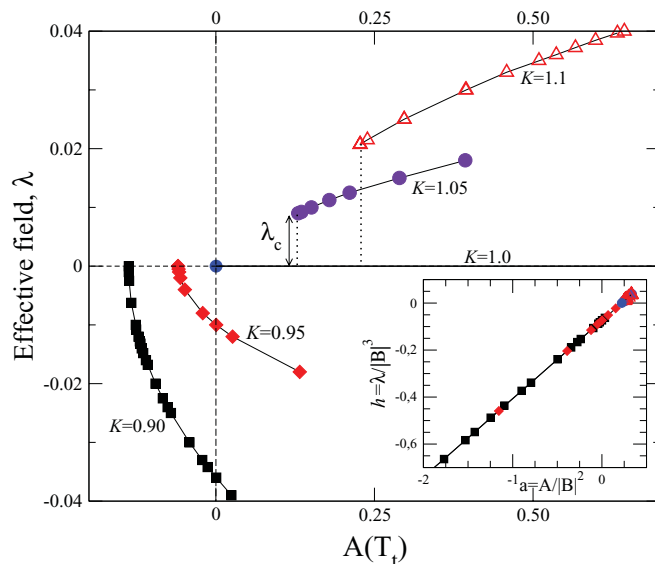


FIG. 2. (Color online) Phase diagram showing the effective field λ as a function of the transition temperature $A(T_t) = T_t - T_c$ for representative values of $\kappa > 1$, $\kappa = 1$, and $\kappa < 1$. The inset shows the coexistence line in rescaled variables. The (blue) dot on the $\lambda = 0$ line corresponds to the case of $B = 0$.

$A_0 = 1$, which renders the following dependence for the model parameters:

$$B = 3\kappa^3 EH = 3\kappa^3 G, \quad (40)$$

$$\lambda = (\kappa - 1)EH = (\kappa - 1)G, \quad (41)$$

$$A(T) = T - T_c, \quad (42)$$

$$T_c = 1 + \kappa^2(E^2 + H^2). \quad (43)$$

The only free parameter is the coupling constant κ . From now on we will restrict ourselves to values of $\kappa > 0$ and consequently to $B \geq 0$. Under these conditions, different situations can be considered:

(1) $B > 0$ and $\lambda = 0$, which corresponds to $\kappa = 1$. In the low-temperature regime the solution corresponds to a minimum located at $\tau < 0$.

(2) $B > 0$ and $\lambda > 0$, which corresponds to $\kappa > 1$. In this case the low-temperature minimum also occurs at $\tau < 0$.

(3) $B > 0$ and $\lambda < 0$, which corresponds to $0 < \kappa < 1$. In that case, competition between $\tau < 0$ and $\tau > 0$ occurs: $\lambda < 0$ favors the minimum to occur at $\tau > 0$ while $B > 0$ favors the minimum to occur at $\tau < 0$.

As a reference case, we also consider the possibility of $G = 0$. In that situation,

(4) $B = 0$ and $\lambda = 0$ for all values of κ . The transition is continuous and occurs at $T_c^0 = 1$. In the low-temperature phase the free energy shows two symmetric minima at $\pm\tau_0$.

The corresponding phase diagram obtained from the unscaled free energy (31) is depicted in Fig. 2. It shows the behavior of the effective field λ as a function of the transition temperature T_t [or $A(T_t) = T_t - T_c$] for the three different regimes of the coupling parameter mentioned above, namely $\kappa > 1$, $\kappa = 1$, and $\kappa < 1$. (i) For $\kappa > 1$ (upper panel) the

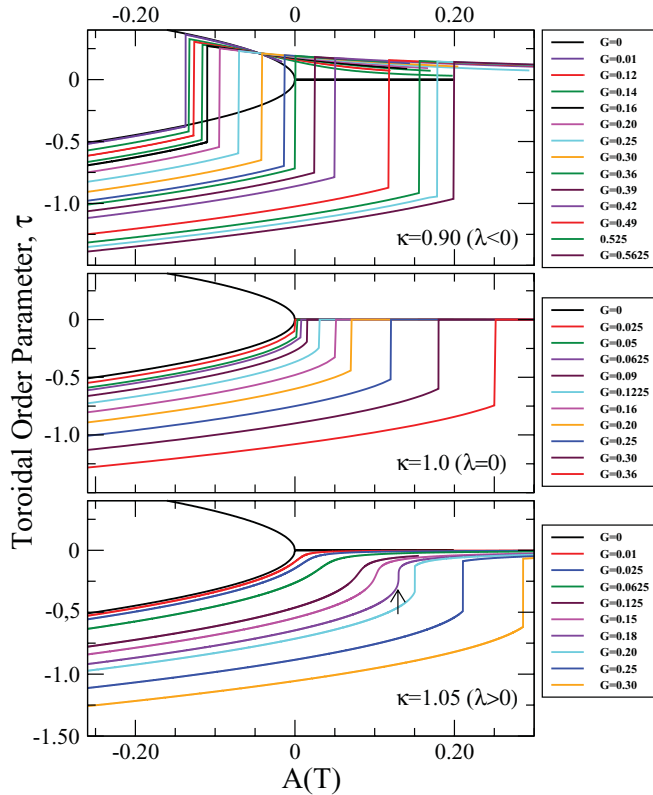


FIG. 3. (Color online) Toroidal order parameter as a function of temperature for $\kappa = 0.90$, $\kappa = 1$, and $\kappa = 1.05$ and selected values of the applied toroidal field G . The arrow in the lower panel indicates the occurrence of the discontinuous transition.

transition exists for values of λ above the critical field $\lambda_c(\kappa) > 0$, which in turn depends on the value of κ . Moreover, T_t increases with λ as can be seen from the representative curves obtained for $\kappa = 1.05$ and 1.10 . (ii) For $\kappa = 1$ the effective field is $\lambda = 0$ and the coexistence line is horizontal starting at the critical point (at the origin) corresponding to the limiting case of $G = 0$ ($B = 0$) and denoted by a blue dot. (iii) Finally, for $\kappa < 1$ one has $\lambda < 0$ and the transition exists for values of λ arbitrarily close to zero at temperatures $T_t < T_c$. For increasing values of G , λ decreases while $A(T_t)$ increases; thus eventually the latter may become positive. We stress that all curves correspond to discontinuous phase transitions except the point located at the origin that corresponds to $B = 0$ and therefore to a continuous phase transition.

Figure 3 shows the temperature behavior of the toroidal order parameter τ for three representative values of the coupling parameter, namely $\kappa = 0.90, 1.0, 1.05$, and different values of the toroidal field $G = EH$ as indicated in the lateral panels. The case $\kappa = 1.05$ (lower panel) nicely illustrates the effect of the field on the ferrotoroidic transition in the region of $\kappa > 1$. For zero field ($G = 0$), the transition is continuous and, indeed, occurs at $T = T_c^0 = 1$ (symmetric curve with double branch). By increasing the field ($G > 0$), the transition first disappears (continuous crossover, no singularity, from $\tau \neq 0$ to $\tau = 0$) and subsequently for higher values of the field a first-order transition occurs at a temperature $T_t > T_c^0$ revealed by a discontinuous jump in τ (indicated by an arrow), whose magnitude increases with G . In the case of $\kappa = 1$ (middle

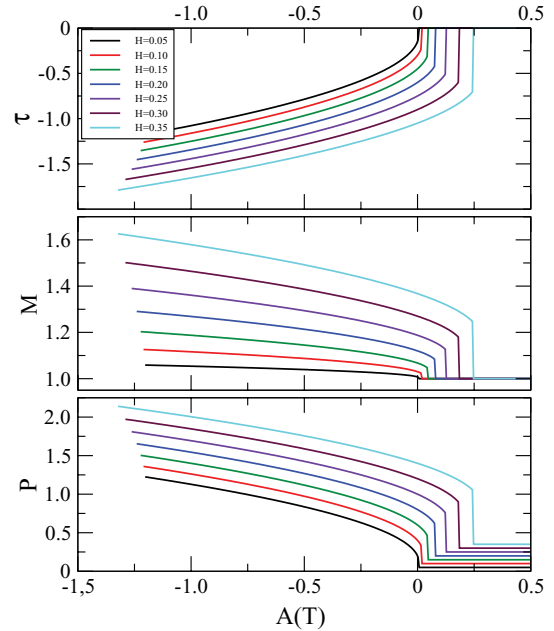


FIG. 4. (Color online) Toroidal order parameter (τ), magnetization (M), and polarization (P) as a function of temperature $A(T) = T - T_c$ for $\kappa = 1.0$. The toroidal field is modified by changing the magnetic field H but keeping constant the value of the electric field $E = 1.0$.

panel), the transition is discontinuous and exists for every value of $G \neq 0$, although it is continuous for $G = 0$. In the case $\kappa < 1$ as soon as the field is applied a first-order transition from $\tau < 0$ to $\tau > 0$ occurs with cooling. For low values of G , the transition takes place at $T_t < T_c$ but with increasing values of G , T_t also increases and the transition takes place above T_c . This behavior results from the competition between B and λ .

The temperature behavior of the polarization P and the magnetization M can then be obtained from the expressions (29) and (30), respectively. The results are shown in Fig. 4 for the case of $\kappa = 1.0$ and different values of $G = EH$ ($E = 1.0$).

B. Nonlinear Clausius-Clapeyron equation

Since the transition predicted by the model is discontinuous, it can be characterized by means of the corresponding Clausius-Clapeyron equation. Such equation relates the slope of the coexistence curve (Fig. 2, inset) to the magnitude of the discontinuities in the order parameter and entropy at the transition temperature. We recall that in the present model, the harmonic [$A(T)$] and cubic (B) coefficients and the effective field (λ) are not independent. As noted below, this will give rise to a Clausius-Clapeyron equation which turns out to be nonlinear in the order parameter discontinuity.

Indeed, at the transition, one can write

$$dF_e^{(I)} = dF_e^{(II)}, \quad (44)$$

where (I) and (II) are the para- and ferrotoroidic phases, respectively. For each phase, the derivative of the effective

free energy can be written as

$$dF_e = \left(\frac{\partial F_e}{\partial T} \right)_\lambda dT + \left(\frac{\partial F_e}{\partial \lambda} \right)_T d\lambda, \quad (45)$$

where $F_e(T, \lambda)$ is the thermodynamic free energy given by the expression (31) with $\tau = \tau(T)$ in equilibrium. The partial derivatives are

$$\left(\frac{\partial F_e}{\partial T} \right)_\lambda = -S = -\frac{A_0}{2} \tau^2, \quad (46)$$

$$\left(\frac{\partial F_e}{\partial \lambda} \right)_T = \frac{1}{E(\kappa - 1)} \left(\frac{\partial F_e}{\partial H} \right)_T, \quad (47)$$

where S is the entropy and the derivative with respect to the field λ is taken at constant E , and

$$\left(\frac{\partial F_e}{\partial H} \right)_T = -H(1 + A_0 \kappa^2 \tau^2) + E(\kappa^3 \tau^3 + \tau(\kappa - 1)). \quad (48)$$

Taking into account (46), (47), and (48), condition (44) reads

$$\begin{aligned} dT(S_{II} - S_I) &= \partial_\lambda(\Delta F_e) d\lambda \\ &= \frac{d\lambda}{E(\kappa - 1)} \left[\left(\frac{\partial F_e}{\partial H} \right)_T^{(II)} - \left(\frac{\partial F_e}{\partial H} \right)_T^{(I)} \right] \end{aligned} \quad (49)$$

with

$$\begin{aligned} &\left(\frac{\partial F_e}{\partial H} \right)_T^{(II)} - \left(\frac{\partial F_e}{\partial H} \right)_T^{(I)} \\ &= [(\tau_{(II)}^3 - \tau_{(I)}^3)E - (\tau_{(II)}^2 - \tau_{(I)}^2)H]\kappa^3 \\ &\quad + (\tau_{(II)} - \tau_{(I)})(\kappa - 1)E. \end{aligned} \quad (50)$$

Finally, the corresponding Clausius-Clapeyron equation takes the form

$$\frac{d\lambda}{dT} = \frac{\Delta S}{\partial_\lambda(\Delta F_e)} = \frac{(S_{II} - S_I)E(\kappa - 1)}{\left(\frac{\partial F_e}{\partial H} \right)_T^{(II)} - \left(\frac{\partial F_e}{\partial H} \right)_T^{(I)}}. \quad (51)$$

Notice that for $\kappa = 1$, the slope of the coexistence curve is zero although there exists a jump in both τ and S at the transition point. In Fig. 5 we have plotted the coexistence line for $\kappa = 1.10$ (black dots) and its numerical derivative (continuous blue line). The squares (full red) are the results of computing the right-hand side of Eq. (51) from the magnitude of the discontinuity of τ and S at the transition temperature. The agreement is very good.

C. Toriodocaloric effect

The toriodocaloric effect can be computed as

$$\begin{aligned} S(T, G = EH) - S(T, G = 0) \\ &= \int_0^{G=EH} \left(\frac{\partial \tau}{\partial T} \right)_G dG \\ &= \frac{1}{2} A_0 [\tau^2(T, G = 0) - \tau^2(T, G = EH)]. \end{aligned} \quad (52)$$

This is an important equation for the isothermal toroidal field-induced entropy change which is analogous to the expression found long ago for the adiabatic electric field-induced temperature change in the case of the electrocaloric effect.³⁰ The isothermal entropy change (ΔS) as a function of temperature for various values of applied toroidal field ($G = EH$) has been plotted in Fig. 6 for the same three

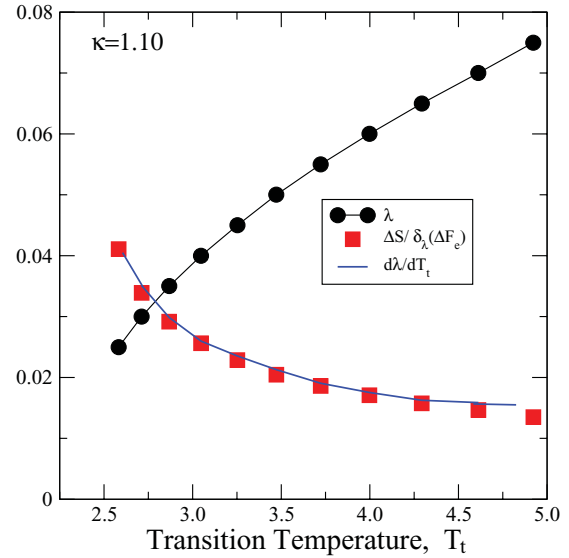


FIG. 5. (Color online) Verification of the Clausius-Clapeyron equation. Coexistence line (black dots) for $\kappa = 1.10$ obtained at constant $E = 1.0$ and its derivative (blue continuous line). Notice that the scale is the same for both curves. Red squares denote the results of computing the right-hand side of Eq. (51) from the discontinuities of τ and S at the transition point.

representative values of κ as in Fig. 3. As can be observed, with increasing field value the jump in ΔS increases.

It is interesting to relate this entropy change characterizing the toriodocaloric effect with the corresponding changes giving the magnetocaloric and electrocaloric effects. This can

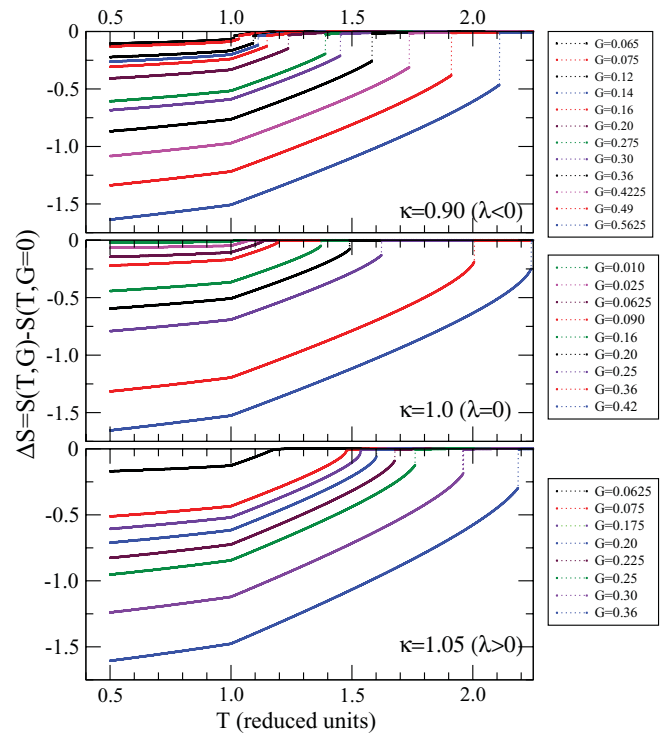


FIG. 6. (Color online) Toriodocaloric effect as a function of temperature and selected values of the applied toroidal field, $\kappa = 0.90, 1.0$, and 1.05 .

be done using Eqs. (29) and (30); a straightforward calculation gives

$$\begin{aligned} \Delta S(T, 0 \rightarrow G = EH) \\ = \frac{1}{\kappa \chi_p \chi_m} [\Delta S_P(T, H, 0 \rightarrow E) + \Delta S_M(T, E, 0 \rightarrow H)], \end{aligned} \quad (53)$$

where ΔS_P and ΔS_M are the entropy changes giving the electrocaloric and the magnetocaloric effects at constant magnetic and electric fields, respectively.

To apply our results to a specific material we need to obtain parameters (e.g., κ) for $\text{LiCo}(\text{PO}_4)_3$ using the data from second harmonic generation⁸ and other thermodynamic measurements, in particular the toroidal susceptibility. The latter is related to the antisymmetric part of the magnetoelectric tensor as discussed in Ref. 15 for BiFeO_3 . It is interesting to point out that Eq. (53) suggests that if the electric and magnetic susceptibilities are known, κ could be estimated from measurements of the entropy changes ΔS , ΔS_P , and ΔS_M .

V. CONCLUSIONS

With the discovery of the fourth kind of primary ferroic materials, namely the ferrotoroidics,^{2,3} it is important to understand the equilibrium thermodynamic properties of such materials. We provided a basic framework to calculate the toroidocaloric effect based on a Landau free energy. Our main finding is the isothermal change in entropy as a function of the applied toroidal field for different values of coupling between toroidization, polarization, and magnetization. The fact that the application of a toroidal field modifies the order of the transition from continuous to first order is very informative regarding caloric effects since larger changes of entropy are expected to be induced thanks to the large entropy content associated with the latent heat of a first-order transition. However, when dealing with real materials, the existence of energy losses arising from hysteresis and domain wall effects^{23,31} (which are intrinsic to first-order transition and are expected to reduce the caloric efficiency) should be taken into account. This important aspect has not been considered in the present paper since strict equilibrium situations are

assumed. In any case, our predictions should be observable in experiments on materials such as $\text{LiCo}(\text{PO}_4)_3$, $\text{Ba}_2\text{CoGe}_2\text{O}_7$ (BCG), MnTiO_3 , MnPS_3 , and some boracites. Below 21.8 K neutron diffraction measurements in $\text{LiCo}(\text{PO}_4)_3$ indicate the simultaneous presence of ferrotoroidic and antiferromagnetic (AFM) order as a result of Co^{2+} ion ordering.⁸

Similarly, in BCG there is a transition at 6.7 K below which there is a coexistence of ferrotoroidic and AFM order again resulting from single-ion effects.¹⁰ In the ilmenite structure MnTiO_3 there is an antiferromagnetic ordering below 63.5 K. At cryogenic temperatures it exhibits ferrotoroidic behavior above 6 T magnetic field due to spin flopping.¹³ These results confirm the existence of a ferrotoroidic phase in a number of materials; however, the measurement of the toroidal moment as a function of temperature and toroidal field has not been undertaken. Therefore, at the present stage it is not possible to contrast our predictions with experimental results. We expect, however, that our results including the nonlinear Clausius-Clapeyron relation will be a motivation for experimentalists to undertake experiments aimed at characterizing the thermodynamic behavior of ferrotoroidic materials in the vicinity of the phase transition.

Using the Landau free energy we can also obtain the profiles of ferrotoroidic domain walls by including a symmetry-allowed gradient term $(\nabla\tau)^2$,¹⁹ i.e., the Ginzburg term. Such domain walls have been observed in $\text{LiCo}(\text{PO}_4)_3$ using optical second harmonic generation techniques.⁸ With doping-induced disorder in such materials we expect that novel phases such as toroidic tweed and toroidic glass should also exist and remain to be observed experimentally. With symmetry-allowed coupling of strain to toroidization, if we apply stress to such a crystal we expect toroidoelastic effects, i.e., a change in toroidization with hydrostatic pressure or shear. These important topics will be explored in the near future.

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