Magnetoelectric phenomena in $BaMnF_4$ and $BaMn_{0.99}Co_{0.01}F_4$

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Dielectric behavior near the Néel temperatures of $BaMnF_4$ and $BaMn_{0.99}Co_{0.01}F_4$ has been measured. In accord with earlier measurements by Samara and Richards, pure $BaMnF_4$ displays a decrease in the a-axis dielectric constant for $T < T_N$ which is approximately proportional to the square of the sublattice magnetization. The 1% Co sample exhibits no dielectric anomaly at T_N. Whereas the samples have the same structural symmetry (C_2 point group), the magnetic symmetry of $BaMnF_4$ is $2'$ and that of $BaMn_{0.99}Co_{0.01}F_4$ is 2. For the latter symmetry there is no spin canting. Thus, unlike $BaMnF_4$, $BaMn_{0.99}Co_{0.01}F_4$ is not a ferromagnet. The present observations confirm our earlier hypothesis that the dielectric anomaly at T_N is an effect due entirely to weak ferromagnetism in a low-symmetry ferroelectric. A Landau theory for the magnetic phase of $BaMnF_4$ is presented. A term proportional to $l_z m_x P^2$, where l_z, m_x, P are respectively sublattice magnetization, ferromagnetic moment, and electric polarization, is introduced, and it is shown that the dielectric anomaly $\Delta\epsilon_a(T)$ can have either sign and is proportional to l_z^2, in agreement with experiment. The theory also gives predictions for linear magnetoelectric coefficient and canting angle, and suggests the existence of strong nonlinear magnetoelectric coupling.

I. INTRODUCTION

Since its discovery[1] by Samara and Richards in 1976, the dielectric anomaly at T_N in $BaMnF_4$ has been the subject of several papers.[2–4] The problem of dielectric changes at spin-ordering temperatures is an old one, first examined by Samokhvalov[5] in Cr_2O_3, later confirmed by Fang and Brower[6] and by Lal, Srivastava, and Srivastava.[7] The measurements differ qualitatively from those predicted in Rado's theory,[8] which yields too small an effect and the wrong temperature dependence. A review of the problem is given by O'Dell.[9]

In the special case of $BaMnF_4$, we have argued elsewhere that its weak ferromagnetism could arise in part from its spontaneous electric polarization[10] and the linear magnetoelectric interaction.[11] Furthermore, we have argued[2,3] that this weak ferromagnetism is the cause of the dielectric anomaly below T_N.

In an effort to confirm this explanation as the cause of the a-axis anomaly, ϵ_a was measured in a sample of $BaMnF_4$ doped with 1 at.% cobalt. This concentration of cobalt is known[12] to impose a $BaCoF_4$-type magnetic structure; i.e., the axis of the spins is rotated from b to a. This produces a change in the magnetic symmetry with only minor changes in the other properties of the system.

One would therefore expect, and it was indeed found, that there is no dielectric anomaly in the cobalt-doped material.

Any model for the a-axis dielectric anomaly must account for its disappearance in a cobalt-doped sample of $BaMnF_4$. As noted above, substitution of cobalt for 1% of the manganese atoms changes the axis of the spins; otherwise the magnetic structure is unchanged. In order to determine the effect of this rotation on the magnetic symmetry, it is necessary to know if there is a change in the crystal structure. Since $BaCoF_4$ does not have the cell-doubling incommensurate transition which occurs in $BaMnF_4$, one must ascertain the presence or absence of this transition in the cobalt-doped sample. The dielectric constant of this sample had a λ-shaped peak at 250 K like that observed at the structural phase transition in $BaMnF_4$. In addition, in unpublished Raman work in our laboratory by G. E. Feldkamp and K. Douglas, it has been found that the soft-mode behaviors near T_C in $BaMnF_4$ and $BaMn_{0.99}Co_{0.01}F_4$ are identical. One may conclude that the presence of a small amount of cobalt does not eliminate the structural phase transition, and the low-temperature crystal structure in both samples is the same. The magnetic point group thus changes from $2'$ to 2 on the addition of 1% cobalt.

Magnetic group 2 allows the magnetoelectric effect, but the form of the tensor,

$$\begin{pmatrix} \chi^{11}_{me} & 0 & 0 \\ 0 & \chi^{22}_{me} & \chi^{23}_{me} \\ 0 & \chi^{32}_{me} & \chi^{33}_{me} \end{pmatrix},$$

is complementary to that allowed by 2′. Thus a polarization along the a axis may couple only to an a-axis magnetization in a crystal with magnetic symmetry 2. This suggests the magnetoelectric effect as a possible source of the a-axis dielectric anomaly, and, in particular, that the c-axis magnetization is important.

II. EXPERIMENT

The circuit used to measure the dielectric constant is shown in Fig. 1. The sample, with silver paste electrodes, and the reference capacitor were mounted on a temperature-controlled copper block in a cryostat. Temperatures were measured with platinum and germanium resistance thermometers embedded in the copper block. Other than the nominally symmetric bridge circuit used, no effort was made to reduce the effect of lead capacitance or edge effects, so only changes in the dielectric constant could be determined.

Moreover, because the sample geometries were not identical, the absolute magnitudes of dielectric changes in $BaCo_{0.01}Mn_{0.99}F_4$ and $BaMnF_4$ measured in the present work cannot be compared with each other or with the earlier data of Samara and Richards. The results shown in Fig. 2 for the cobalt-doped sample (upper curve) and a sample of pure $BaMnF_4$ (lower curve) do, however, yield a qualitative comparison. Clearly the change in magnetic symmetry eliminates the anomaly in the dielectric constant. In order to emphasize changes near T_N, a linear temperature dependence has been subtracted from the data. This extrapolation cannot hold down to 0 K

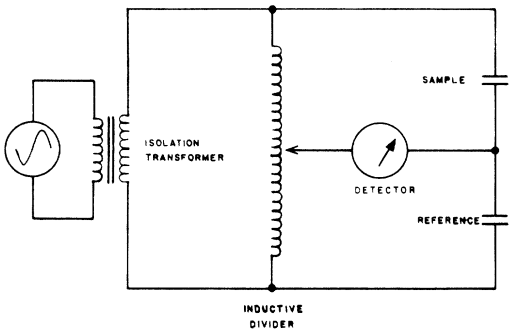

FIG. 1. Diagram of the ac bridge circuit used for dielectric measurements on $BaMnF_4$ and $BaMn_{0.99}Co_{0.01}F_4$.

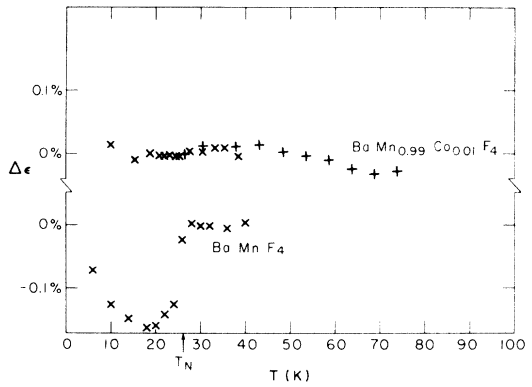

FIG. 2. Dielectric anomaly for ϵ_a in $BaMnF_4$ and $BaMn_{0.99}Co_{0.01}F_4$. The data points show deviations from a linear fit to $\epsilon_a(T)$ from 4 to 40 or 77 K. x = Ge-thermometer data; + = Pt-thermometer data.

$(\partial\epsilon/\partial T$ must be zero at $T=0)$. Its use is responsible for the decrease in the anomaly at low temperature as plotted in Fig. 2. A more exact treatment is given in Sec. III.

III. ANALYSIS OF $\epsilon_a(T)$ DATA IN $BaMnF_4$

In Fig. 3 we reproduce the dielectric data of Ref. 1. In order to analyze the magnetic anomaly near T_N in these a-axis dielectric data, we need first to subtract off the lattice contribution in a very accurate way. Although the linear subtraction performed in Fig. 2 was sufficient to display qualitative differences between $BaMnF_4$ and $BaCo_{0.01}Mn_{0.99}F_4$, it is not sufficient for quantitative analysis. We have employed an expression given in Eq. (1) for the fitting of the ϵ_a

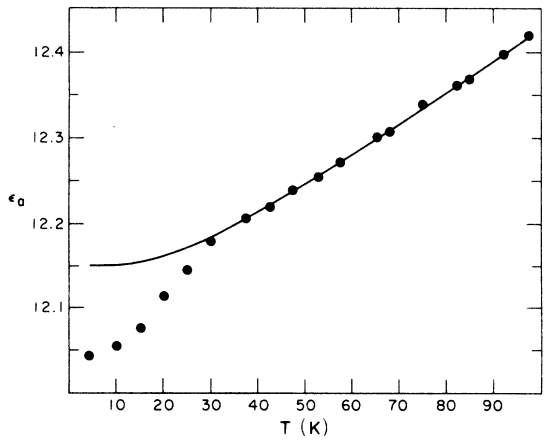

FIG. 3. Dielectric anomaly for ϵ_a in $BaMnF_4$, from Ref. 1; the curve is a fit to Eq. (1).

data of Ref. 1:

$$\epsilon_a(T) = \epsilon_a(0) + C_0[\exp(\hbar\omega_0/k_B T) - 1]^{-1} \quad . \qquad (1)$$

This expression involves three fitting parameters. It is similar to Barrett's expression[13] in that it is a function which satisfies the second law of thermodynamics at $T=0$ and yields a classical form linear in T at higher temperatures. This equation assumes that the soft-mode behavior of the ferroelectric mode is dominated by its coupling to all other transverse optic modes on the same branch. Here C_0 is a coupling constant, and ω_0 is the mean frequency of final states in the soft optic branch.

Our nonlinear least-squares fit of the Ref. 1 $\epsilon_a(T)$ data yielded $\epsilon_a(0) = 12.15 \pm 0.01$, $C_0 = 0.23 \pm 0.02$, and $\omega_0 = 43 \pm 2$ cm^{-1}. This value of ω_0 is in agreement with the experimental $k=0$ value of the soft mode, which is 41 cm^{-1} at low temperatures.[14] These parameters were obtained by fitting the data from 26 to 100 K. The parameters were then used to calculate $\epsilon_a(T)$ below T_N from Eq. (1). In the following section it will be shown that the sign and T dependence of $\Delta\epsilon_a(T)$ below T_N is in complete accord with a mean-field theory.

IV. ANALYSIS OF $\Delta\epsilon_a(T)$

The most direct connection between the electric and magnetic properties of a substance is the magnetoelectric effect. Magnetoelectric measurements have been performed on $BaMnF_4$ and $BaCoF_4$ by Zorin, Al'shin, and Astrov,[15] and Al'shin, Astrov, and Zorin.[16] They measured the magnetic moment perpendicular to the b axis produced by an alternating electric field applied parallel to the b axis. The resulting magnetic moment shows a complicated dependence on the frequency of the applied field. Several large maxima were observed in the region of 5–10 kHz even at temperatures far above the Néel temperature. Zorin *et al.* give a plausible interpretation of these observations in terms of two-dimensional magnetic ordering. For the purpose of this work the important result of the magnetoelectric measurements is at low frequencies. Below 4 kHz the magnetoelectric effect vanishes at all temperatures in $BaCoF_4$, while in $BaMnF_4$ there is a small magnetoelectric effect at 6 K at the lowest frequency, which vanishes at temperatures above the Néel temperature. The conclusion that $BaMnF_4$ has a static magnetoelectric effect while $BaCoF_4$ does not may be viewed as a consequence of the fact that $BaCoF_4$ does not have a cell-doubling phase transition. In both materials the magnetic unit cell is twice the room-temperature chemical cell. Dvorak[17] and Ryan and Scott[14] have shown that, when the magnetic cell is twice the chemical cell, there can be no magnetoelectric effect.

Finally, $BaMnF_4$ is known to be a weak ferromagnet. The importance of this fact to the interaction of electric and magnetic properties is not obvious but will be shown in the next section. Venturini and Morgenthaler[18] observed by antiferromagnetic resonance that the two spin sublattices in $BaMnF_4$ are canted toward the c axis at an angle of 3 mrad at 4.2 K. This corresponds to a magnetization of 1460 A m^{-1} (1.46 emu cm^{-3}) parallel to the c axis. Zorin *et al.*[19] have also reported a c-axis magnetization. Their value of 9 A m^{-1} (0.009 emu cm^{-3}) has probably been reduced by the cancellation of oppositely directed domains.

What follows below is a mean-field theory based upon Dzyaloshinskii's original approach to weak ferromagnetism. The key term responsible for the ϵ_a anomaly at T_N is shown to be of the form $\langle \vec{S}_j \times \vec{S}_{j+1} \rangle P^2$, where S_j is the spin on the jth ion, and P is the electric polarization. This is a coupling of ferroelectric polarization with the usual Dzyaloshinskii-Moriya anisotropic exchange term. It will be shown to yield $\Delta\epsilon_a(T)$ in agreement with experiment.

We begin by forming a free energy based upon an inspection of the magnetic and lattice symmetries.

The projection in the bc plane of the unit cell of $BaMnF_4$ in the antiferromagnetic phase is shown in Fig. 4(a); the spin orientations are consistent with the neutron-diffraction experiments.[20] The exchange

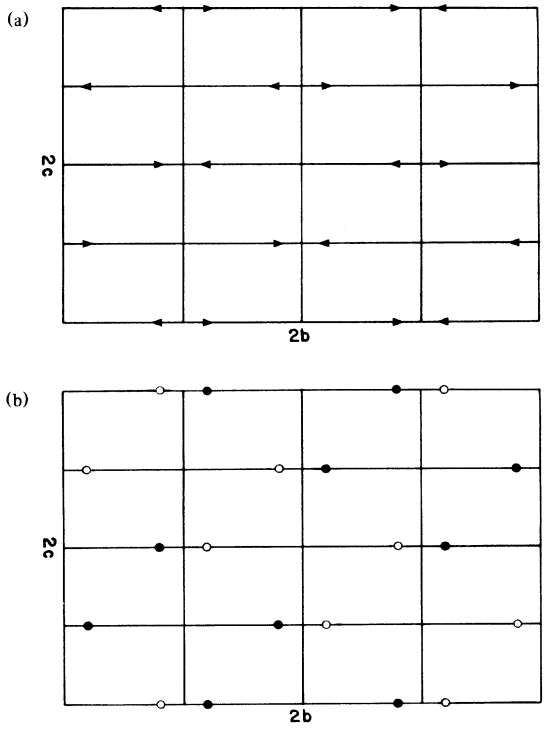

FIG. 4. Spin structures in $BaMF_4$: (a) $BaMnF_4$; (b) $BaMn_{0.99}Co_{0.01}F_4$.

coupling in the b direction is much weaker than in the ac plane, and the magnetic susceptibilities in the neighborhood of the Néel temperature T_N show behavior typical of quasi-two-dimensional systems.[21–23] The anisotropy field H_A maintaining the spin orientation in the b direction is very weak. From the spin-flop critical field $H_{sf}=10.4$ kOe at 1.4 K, Holmes, Eibschütz, and Guggenheim[21] estimate $H_A \simeq 100$ Oe, and suggest that the dipolar contribution to H_A is significant. In fact the substitution of 1% Co is sufficient to cause the spins to align along the a axis [Fig. 4(b)] as in $BaCoF_4$.

The transition to the antiferromagnetic phase does not involve any change in unit-cell dimension; because of the presumed rotation[24,25] of MnF_6 octahedra in the 250-K phase transition, the unit cell already has the dimensions shown in Fig. 4(a) below 250 K.

The point group of the magnetic structure of Fig. 4(a) consists of the identity E and the element $2'$ (180° rotation about the a axis followed by time reversal), whereas the point group of Fig. 4(b) is 2. The former group allows spin canting in the c direction, and indeed $BaMnF_4$ is a weak ferromagnet with a canting angle[18] of approximately 3 mrad at 4.2 K. By contrast, spin canting is not allowed in the structure of Fig. 4(b). The nonzero elements of the magnetoelectric tensor χ_{ij} can be found by noting that $R\chi_{ij}=-\chi_{ij}$, where R is the time-reversal operator, and in 180° rotation $a\rightarrow a$, $b\rightarrow b$, $c\rightarrow -c$. It follows that the $BaMnF_4$ [Fig. 4(a)]

$$\chi_{ij}=\begin{pmatrix} 0 & \chi_{ab} & \chi_{ac} \\ \chi_{ab} & 0 & 0 \\ \chi_{ac} & 0 & 0 \end{pmatrix} \tag{2}$$

while in the Co-doped material [Fig. 4(b)] χ_{ij} has the complementary form, with nonzero elements where the zeros appear in Eq. (2) and vice versa.

We now construct a Landau free-energy expression to describe the antiferromagnetic transition in $BaMnF_4$. As shown in Fig. 4(a), we use axes $x=c$, $y=a$ (polar axis), $z=b$ (sublattice ordering direction). The analysis follows the method used by Dzyaloshinskii[26] in the first investigation of weak ferromagnetism. The variables with which we are concerned are the sublattice magnetization

$$\vec{l}=\tfrac{1}{2}g\mu_B S^{1/2}(S+1)^{1/2}\left\langle \sum_i (\vec{S}_{i\uparrow}-\vec{S}_{i\downarrow})\right\rangle \ \mathrm{Am}^{-1} \ , \tag{3}$$

the weak magnetic moment

$$\vec{m}=g\mu_B S^{1/2}(S+1)^{1/2}\left\langle \sum_i (\vec{S}_{i\uparrow}+\vec{S}_{i\downarrow})\right\rangle \ , \tag{4}$$

and the electric polarization $\vec{P}=(0,P,0)$. In Eqs. (3) and (4) $g=2$ and $S=\frac{5}{2}$ per Mn, μ_B is the Bohr magneton, and the sums are over the unit volume. $\langle\ \rangle$ denotes a thermal average. Note that l vanishes above T_N despite the two-dimensional spin ordering. The constants are inserted so that $\vec{l}$ is the sublattice magnetization and $\vec{m}$ the magnetization, measured in Am^{-1}. Since the unit cell is not doubled in the phase transition, the free energy is constructed from invariants of the high-temperature-phase point group,[26,27] namely $(E, 2)$. The invariants of second order in the magnetic variables are $\vec{l}^2$, $\vec{m}^2$, $\vec{l}\cdot\vec{m}$, l_z^2, m_z^2, $m_x l_z$, $m_z l_x$. The polarization P is separately invariant, so the coefficients of the magnetic invariants can be functions of P. We postulate that the Gibbs-free-energy density has the form

$$\Phi=\tfrac{1}{2}f(l^2,l_z^2)+\tfrac{1}{2}Bm^2+(\beta_0+\beta_1 p+\beta_2 p^2)m_x l_z-\gamma m_z l_x$$
$$+\tfrac{1}{2}D(\vec{l}\cdot\vec{m})^2+\tfrac{1}{2}Kp^2-\vec{P}\cdot\vec{E}-\vec{m}\cdot\vec{H} \ . \tag{5}$$

In writing Eq. (5), we use the fact that for weak ferromagnetism a Landau theory applies over an extended temperature range, since $\vec{m}$ is small at all temperatures.[26] This is particularly important for $BaMnF_4$, since the quasi-two-dimensional character means that fluctuations are large around T_N. The function $f(l^2,l_z^2)$ is assumed to be such that $\vec{l}$ takes its equilibrium value and is directed along z; the simple form is

$$f(l^2,l_z^2)=\tfrac{1}{2}Al^2-\tfrac{1}{2}al_z^2+\tfrac{1}{4}Gl^4 \ , \tag{6}$$

but we do not restrict attention to this form. No term in $\vec{l}\cdot\vec{m}$ appears in Eq. (5); the inclusion of such a term would have the effect of making the order parameter a linear combination of $\vec{l}$ and $\vec{m}$ rather than $\vec{l}$ itself.

The polarization P is written

$$P=P_s+p \ , \tag{7}$$

where P_s is the pyroelectric moment and p an additional part induced by the electric field $\vec{E}$ and by the coupling to the magnetic variables. As mentioned, any of the coefficients of the magnetic terms can in principle be functions of p. However, physical arguments have been used to reduce the possibilities. One mechanism of magnetoelectric coupling is an electric field modulation of the single-ion anisotropy[28] corresponding here to a p dependence of parameter a in Eq. (6), but in view of the very low anisotropy and its possible dipolar origin, this mechanism seems unlikely to contribute. We therefore assume that the coupling is, as shown, via the term $m_x l_z$. We shall be concerned only with linear response functions, and we shall expand all results to second order in the parameters β and γ of Eq. (5). It is then sufficient to write the coefficient of $m_x l_z$ as a quadratic expression in p. The proper independent variables for Φ are E and H; the meaning of Eq. (5) is that one first finds values of $\vec{l}$, $\vec{m}$, and p that minimize Φ, then substitutes these values, expressed in terms of E and

H, back into Φ. To find linear susceptibilities, it is sufficient to evaluate Φ up to terms quadratic in E and H. We shall also reject terms of higher than second order in β. It will emerge that $l_z = O(l)$, $m_x = O(\beta)$ and $p = O(E) + O(\beta H) + O(\beta^2)$. Thus the term $\frac{1}{2}\beta_2 p^2 m_x l_z$ contributes $O(\beta^2 E^2)$, whereas a term in $p^3 m_x l_z$ would contribute only $O(\beta^2 E^3)$, and can be omitted. Similarly, $m_z l_x = O(\beta H^2)$, and the p dependence of γ can be neglected.

The fourth-order term $\frac{1}{2}D(\vec{l}\cdot\vec{m})^2$ in Eq. (5) is included so that the $\beta \to 0$ limits of the magnetic susceptibilities have the usual forms for a two-sublattice antiferromagnet. A possible term $\frac{1}{2}D' l^2 m^2$ is omitted since its effect[29] would be to produce a difference between χ_{aa} and χ_{cc} for $T < T_N$, and this is not seen experimentally.[21]

The equilibrium values of $\vec{l}$, $\vec{m}$, and P and the linear susceptibilities are found from Eq. (5) in the standard way. That is, one solves the seven equations $\partial F/\partial \vec{l} = 0$, $\partial F/\partial \vec{m} = 0$, and $\partial F/\partial p = 0$, where only terms zero order or linear in E and H are retained. The general form of the equations is intractable, but they can be solved by means of expansion in powers of β, and of γ treated as $O(\beta)$. (Borovik-Romanov and Ozhogin[30] used such an expansion in discussing the weak ferromagnet $CoCO_3$, and our results for the magnetic susceptibilities agree with theirs.) To order β^2, the results are as follows: for $T > T_N$,

$$l_z = \beta_0 H_x / B d(0) \quad , \tag{8}$$

$$m_x = [B^{-1} + \beta_0^2 / B^2 d(0)] H_x \quad , \tag{9}$$

$$m_y = H_y / B \quad , \tag{10}$$

$$m_z = (B - \gamma^2 / f_1)^{-1} H_z \quad , \tag{11}$$

$$p = E_y / K \quad ; \tag{12}$$

for $T < T_N$,

$$l_z = l_0 + \beta_0^2 / d'(l_0) - \beta_0 H_x / B l_0 d'(l_0) \quad , \tag{13}$$

$$m_x = -\beta_0 l_0 / B - \beta_1 l_0 E_y / BK + [B^{-1} + \beta_0^2 / B^2 d'(l_0) l_0 + \beta_1^2 l_0^2 / B^2 K] H_x \quad , \tag{14}$$

$$m_y = H_y / B \quad , \tag{15}$$

$$m_z = s H_z / (sr - q^2) \quad , \tag{16}$$

where

$$s = f_1 + D\beta_0^2 l_0^2 / B^2 \quad , \tag{17}$$

$$r = B + D l_0^2 \quad , \tag{18}$$

$$q = \gamma + D\beta_0 l_0^2 / B \quad , \tag{19}$$

$$P = P_s + \beta_0 \beta_1 l_0^2 / BK - \beta_1 l_0 H_x / BK + [K^{-1} + (\beta_1^2 + \beta_0 \beta_2) l_0^2 / BK^2] E_y \quad . \tag{20}$$

In these formulas,

$$f_1 = \partial f / \partial l^2 \tag{21}$$

and

$$d(l_z) = f_1 + \partial f / \partial l_z^2 \quad . \tag{22}$$

so that l_0, the zero-order equilibrium value of l_z, is given by

$$d(l_0) = 0 \quad . \tag{23}$$

This has no solution for $T > T_N$, but note that

$$d(0) \to 0 \quad \text{as} \quad T \to T_N \quad . \tag{24}$$

It may be helpful to note that if $f(l^2, l_z^2)$ has the simple form of Eq. (6), and if in addition

$$a - A = \alpha(T_N - T) \tag{25}$$

then

$$d(0) = \tfrac{1}{2}\alpha(T - T_N) \tag{26}$$

and for $T < T_N$

$$l_0 = \alpha^{1/2}(T_N - T)^{1/2} / G^{1/2} \quad , \tag{27}$$

$$d'(l_0) = G^{1/2} \alpha^{1/2} (T_N - T)^{1/2} \quad . \tag{28}$$

With these forms, the correspondence between the magnetic susceptibilities derived from Eqs. (8) to (19) and previous results for weak ferromagnets[30,31] is readily established. However, we shall not make use of the temperature dependences in Eqs. (25) to (28).

For $T > T_N$, Eqs. (8) to (12) show that there is no coupling between magnetic and electric properties. The result [Eqs. (8)–(11)] shows that the magnetic field induces antiferromagnetic ordering above T_N, with a magnitude diverging as $T \to T_N$.[30] Equations (9) to (11) show an isotropic susceptibility B^{-1} with anisotropic corrections of order β^2. In view of Eq. (24), the onset of weak ferromagnetism is signaled by divergence in order β^2 of the susceptibility χ_{xx}.[30,31] It is not clear to what extent the divergence would be masked by critical fluctuations. The experiments[21] showed isotropic susceptibility above T_N, so presumably β^2 corrections were not detected.

For $T < T_N$, l_z, m_x, and P have nonzero equilibrium values as well as field-induced parts. Combining the equilibrium values of l_z and m_x, we see that the predicted spin-canting angle is

$$\Theta_c = \beta_0 / B \quad , \tag{29}$$

which is a standard result. We emphasize that this applies for an infinite specimen, with no account taken of demagnetization or depolarization effects. Equation (20) shows that the equilibrium polarization is changed in order β^2:

$$p_e = \beta_0 \beta_1 l_0^2 / BK \quad . \tag{30}$$

The magnetic susceptibilities are given by the H-dependent parts of Eqs. (14) to (16). To order 0 in β, they give

$$\chi_{xx}=\chi_{yy}=\chi_{\perp}=B^{-1} \tag{31}$$

and

$$\chi_{zz}=\chi_{\parallel}\neq\chi_{\perp} \tag{32}$$

as in a standard antiferromagnet. The experimental results show $\chi_{xx}=\chi_{yy}$ and $\chi_{zz}\neq\chi_{xx}$, but with a peak around T_N due to the quasi-two-dimensional character of the system which a mean-field theory of the present type cannot predict. To order β^2, χ_{xx} and χ_{yy} differ, and the term $\beta_0^2/B^2d'(l_0)l_0$ in Eq. (14) gives the divergence in χ_{xx} below T_N (Refs. 30,31) corresponding to the one already noted above T_N. Again, this divergence was not detected in experiments.[21]

The magnetoelectric susceptibility is given from Eq. (14) or (20) as

$$\chi_{ac}^{\mathrm{me}}=\chi_{xy}^{\mathrm{me}}=-\beta_1 l_0/BK \tag{33}$$

and in addition

$$\chi_{ab}^{\mathrm{me}}=0 \ . \tag{34}$$

Finally, the dielectric constant follows from Eq. (20):

$$\epsilon=1+\epsilon_0^{-1}K^{-1}+\Delta\epsilon \ , \tag{35}$$

with

$$\Delta\epsilon=(\beta_1^2+\beta_0\beta_2)l_0^2/\epsilon_0 BK^2 \ . \tag{36}$$

Note that, if the quadratic term $\beta_2 p^2$ were omitted in Eq. (5), $\Delta\epsilon$ would necessarily be positive, since B is positive. The fact that a coupling linear in p leads to an increase in ϵ has been proved for a specific model of the coupling[4] and is now known to be generally true.[32] The prediction of an increase in ϵ had been a source of difficulty, since experiments[1,33] show a decrease. The addition of the quadratic term alters the case, because $\beta_0\beta_2$ can have either sign; this comment has already been made by Bonfim and Gehring.[32] A decrease in $\Delta\epsilon$, of course, requires

$$|\beta_0\beta_2|>\beta_1^2 \tag{37}$$

and in that sense the quadratic term has to be large. With use of Eq. (29), the β_2 term of Eq. (36) can be written

$$\Delta\epsilon=\beta_2\langle m_x l_z\rangle K^2 \ , \tag{38}$$

where $\langle\ \rangle$ is the equilibrium value. This result is expected on general grounds.[32]

The canting angle [Eq. (29)], the magnetoelectric susceptibility [Eq. (33)], and the dielectric anomaly [Eq. (36)], are related in that they all arise from the Dzyaloshinskii-Moriya term in Φ. However, since there are three parameters in that term, there is no necessary numerical relationship between the three quantities. Although β_2 appears here only in $\Delta\epsilon$, it will also contribute to a higher-order magnetoelectric susceptibility. Inserting the lowest-order expressions $p=E_y/K$ and $m_x=H_x/B$ in the term $\beta_2 p_y^2 m_x l_z$, we find a contribution to Φ of $\chi_{(2)}^{\mathrm{em}}E_y^2H_x$, where

$$\chi_{(2)}^{\mathrm{em}}=\beta_2 l_0/K^2B \ . \tag{39}$$

This is only one contribution to the nonlinear susceptibility; to find the full expression one would have to retain all terms quadratic in the fields in the equations for minimizing Φ, which we have not attempted to do.

It is instructive to compare the present model with the theory of improper ferroelectrics.[34] In that case one has a two-component order parameter, corresponding to a two-dimensional representation of the high-temperature point group, and the polarization P is coupled to the order parameter. Here, on the other hand, we have a one-component order parameter, l_z, both m_x and P being coupled to l_z. In the improper ferroelectric the coupling leads to a discontinuity in the dielectric constant at the critical temperature T_c. If the coupling is linear in P, then $\epsilon(T<T_c)>\epsilon(T>T_c)$, but, if a P^2 coupling is included, the discontinuity can have either sign.[35,36] P^2 coupling is apparently required in boracites in which ϵ decreases at the phase transition.[37] Here Eq. (38) gives that ϵ is continuous, while $d\epsilon/dT$ is discontinuous at the phase transition. In order for $d\epsilon/dT$ to decrease at T_N, it is necessary to include P^2 coupling.

The present model describes an improper ferroelectric in the sense that, although P is not the order parameter, it changes at T_N as given by Eq. (30). Despite the fact that the order parameter l_0 is one dimensional, the change in p is not proportional to l_0. We therefore believe that this model is a counter example to Levanyuk and Sannikov's[34] assertion that one cannot have a true improper ferroelectric with a one-dimensional order parameter.

V. COMPARISON WITH EXPERIMENT

We make the simplifying assumption that the temperature dependence in the various expressions is due to l_0, and that B, K, and the β parameters are temperature independent. The result of antiferromagnetic-resonance experiments[38] is that l_0 is well fitted by the mean-field curve resulting from the $S=\frac{5}{2}$ Brillouin function. In addition to comparing temperature dependences, we also estimate the values of the various parameters.

The magnetic susceptibility[21] and dielectric constant[1,33] for $T>T_N$ give estimates of B and K, respectively, namely,

$$B=1.37\times10^8\ \mathrm{C^2\,kg^{-1}\,m^{-1}} \ , \tag{40}$$

$$K=1.01\times10^{10}\ \mathrm{C^{-2}\,kg\,m^3\,s^{-2}} \ . \tag{41}$$

The canting angle at 4.2 K is 3 mrad,[25] so from Eqs. (31) and (40)

$$\beta_0 = 4.10 \times 10^5 \, \mathrm{C^2 kg^{-1} m^{-1}} \ . \tag{42}$$

Equation (38) predicts that the dielectric anomaly should vary with temperature as l_0^2. The best least-squares fit to the data was shown in Fig. 3. The comparison between $\Delta\epsilon$ and a $\frac{5}{2}$ Brillouin l_0^2 is shown in Fig. 5. If it is assumed that β_1^2 is negligible compared with $\beta_0\beta_2$, then Eqs. (38), (40)–(42), and Fig. 5 yield

$$\beta_2 = 2.76 \times 10^{11} \, \mathrm{kg^{-1} m^3} \ , \tag{43}$$

where $l_0(T=0)$ has been taken as 95% of full saturation value.

It is seen from Eqs. (35) and (32) that the magnetoelectric coefficient χ_{ac}^{me} and the change in equilibrium polarization p_e are both proportional to β_1. The magnetoelectric data[15,16] are in relative units, and cannot be used to determine β_1. If we take as an upper limit[9] $c\chi^{em} \simeq 10^{-3}$, then the polarization shift at $T=0$ is $p \simeq 5 \times 10^{-7} \, \mathrm{C\,m^{-2}}$. The results of Glass *et al.*[39] are such that the vertical scale is multiplied by 3×10^{-6} to yield[40] P in $\mathrm{C\,m^{-2}}$. Thus the anomaly predicted here is smaller than the experimental value by one or two orders of magnitude, and is therefore most unlikely to be detectable.

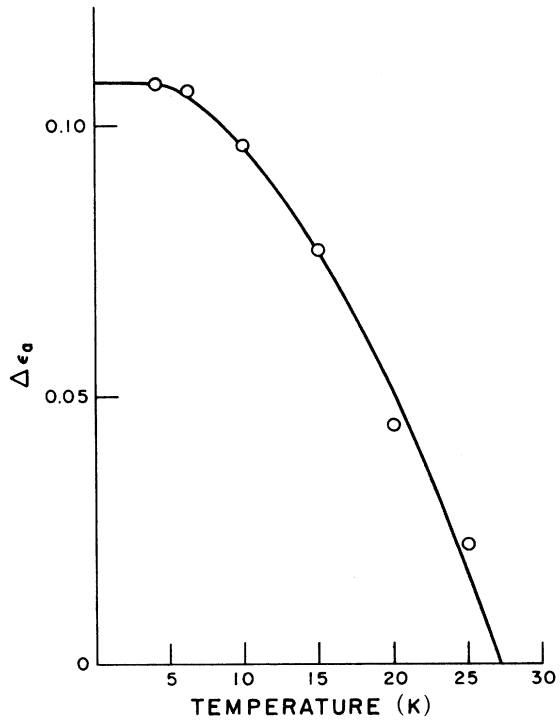

FIG. 5. $\Delta\epsilon_a(T)$ from Fig. 3 compared with $l_0^2(T)$.

VI. COMMENTS AND DISCUSSION

A primary motivation of this work was to understand the a-axis dielectric anomaly in $BaMnF_4$, and also the absence of such an anomaly in the cobalt-doped material. As already mentioned, cobalt doping alters the symmetry of the antiferromagnet phase, so that spin canting is not allowed, and changes the form of the magnetoelectric tensor.

We have argued that the dominant magnetoelectric coupling in $BaMnF_4$ is via modification of the Dzyaloshinskii-Moriya interaction; the dielectric anomaly Eq. (38), the polarization anomaly Eq. (30), and the magnetoelectric coefficient Eq. (33) all depend on the parameters of that interaction. In the Co-doped material a term $\beta\psi(P)m_x l_z$ in Φ is still allowed (the point group above T_N is the same), but l_z no longer has a zero-order value, so the effects of the term are much smaller. One therefore expects for the Co-doped material no dielectric anomaly, no polarization anomaly, and a much weaker magnetoelectric effect than in $BaMnF_4$. There are no experiments with which the latter two predictions can be compared.

A more difficult problem for us to understand is the observed canting angle below T_N. Our earlier analysis[10] predicts a canting induced by magnetoelectric coupling. This is discussed numerically in Appendix A. This canting will be along the $\pm c$ direction in ferroelectric domains having spontaneous electric polarization along $\pm a$. Appendix A shows that the measured magnitude[18] at 4.2 K requires an unusually large magnetoelectric susceptibility if we assume this is the *only* source of spin canting. However, the free energy of Eq. (5) allows a second contribution to spin canting through the ordinary Dzyaloshinskii-Moriya interaction. This canting should be uncorrelated with the magnetoelectrically induced canting, since, in the absence of a magnetoelectric anneal, magnetic and ferroelectric domains should be uncorrelated. Thus, one would expect two different values of canting angle: One in regions where the two effects add, and one where they subtract. This disagrees with experiments.[18] It suggests that the ferroelectric domains are random (since $BaMnF_4$ is ferroelectric and twinned as grown from the melt, it cannot be poled by cooling through T_c in an applied electric field), but that the magnetic and ferroelectric domains are highly correlated. This could arise from the direct magnetoelectric interactions or from strain, i.e., ferroelastic plus magnetoelastic interactions, which minimize total energy for correlated domains. That is, of the two possible combinations of spin-canting angles, one will have a lower total energy. It would be highly desirable, in order to clarify this situation, to extend the work of Ref. 18 by measuring the canting angle from 4 K to T_N. If the usual Dzyaloshinskii-Moriya interaction is dominant, the canting angle $\Theta(T)$ will

be absolutely independent of T right up to T_N whereas, if the magnetoelectric canting is dominant, as suggested by Fox and Scott,[10] $\Theta(T)$ will vary strongly with T as $m(T)$, becoming zero as $T \to T_N$.

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APPENDIX A: DEPOLARIZATION EFFECTS

In order to make comparisons between the Landau theory of Sec. V, which assumes infinite-bulk media, and real experimental values, which are measured on finite specimens of varied geometries, it is necessary to worry about size and shape effects. These effects are independent of the possible different microscopic magnetoelectric mechanisms[28,41,42] (which include spin-orbit effects, Dzyaloshinskii-Moriya anisotropic exchange, electric field dependence of g values, etc.). Thus, a macroscopic, thermodynamic approach is suitable.

For the usual experimental situation where electric fields are produced using electrodes at specified potentials, and magnetic fields are produced by specified currents, the appropriate independent variables are $\vec{E}$ and $\vec{H}$. For dependent variables choose the electric polarization $\vec{P}$ and the magnetization $\vec{M}$. Then, with the assumption that the material is linear, the constitutive relations have the form[43]

$$\vec{P} = \vec{P}_0 + \epsilon_0 \chi_e \vec{E} + \frac{1}{c} \chi_{em} \vec{H} \ , \tag{A1}$$

$$\vec{M} = \epsilon_0 c \, \chi_{me} \vec{E} + \chi_m \vec{H} \ , \tag{A2}$$

where the electric susceptibility χ_e, magnetic susceptibility χ_m, and the magnetoelectric susceptibilities χ_{em} and χ_{me} are all second-rank tensors. A thermodynamic argument may be used to show that $\chi_{me} = \chi_{em}$. The term $\vec{P}_0$ is responsible for the spontaneous polarization in a ferroelectric.

Another relation between $\vec{E}$ and $\vec{P}$ is provided by the field equations through the boundary conditions. For an ellipsoidal sample in a uniform applied field, it takes the form

$$\vec{E} = \vec{E}_a - n \vec{P} / \epsilon_0 \ , \tag{A3}$$

where the depolarization factor n is a second-rank tensor which depends only on the shape of the sample, and E_a is the electric field which would exist in the absence of the sample. Similarly, the boundary condition relating H and M is

$$\vec{H} = \vec{H}_a - n \vec{M} \ . \tag{A4}$$

Eliminating $\vec{E}$ and $\vec{H}$ from these four equations yields

$$(1 + \chi_e n) \vec{P} = \vec{P}_0 + \epsilon_0 \chi_e \vec{E}_a + \frac{1}{c} \chi_{em} \vec{H}_a - \frac{1}{c} \chi_{em} n \vec{M} \tag{A5}$$

and

$$(1 + \chi_m n) \vec{M} = \chi_m \vec{H}_a + c \, \epsilon_0 \chi_{me} \vec{E}_a - c \, \chi_{me} n \vec{P} \ . \tag{A6}$$

Now eliminate $\vec{P}$ with the result

$$\left[1 + \chi_m n - \frac{1}{c^2} \chi_{me} n (1 + \chi_e n)^{-1} \chi_{em} n\right] \vec{M}$$

$$= \chi_m \vec{H}_a + \frac{1}{c} \chi_{me} \vec{E}_a - c \, \chi_{me} n (1 + \chi_e n)^{-1}$$

$$\times (\vec{P}_0 + \epsilon_0 \chi_e E_a + \frac{1}{c} \chi_{em} \vec{H}_a) \ . \tag{A7}$$

This equation shows that, even in the absence of applied fields ($\vec{E}_a = \vec{H}_a = 0$), there exists a nonzero magnetization produced by the spontaneous polarization P_0. This magnetization given by

$$\vec{M} = -\left[1 + \chi_m n - \frac{1}{c^2} n (1 + \chi_e n)^{-1} \chi_{em} n\right]^{-1}$$

$$\times c \, \chi_{me} n (1 + \chi_e n)^{-1} P_0 \ . \tag{A8}$$

In order for this effect to exist, the crystal must have a magnetic point symmetry which permits (1) a spontaneous polarization, (2) a spontaneous magnetization, and (3) a nonzero magnetoelectric effect. Examination of published lists[44] of magnetic groups which permit these effects shows that there are only 13 magnetic groups which permit all three, and they are listed in Table I. The symmetry of the crystal will place constraints on the form of the tensors χ_e, χ_m, and χ_{em}, χ_{me} and thus on the relationship between $\vec{M}$ and $\vec{P}_0$. If the principal axes of the ellipsoidal sample

TABLE I. Magnetic constraints.

Magnetic point group	Constraints on $\vec{P}_0$ and $\vec{M}$
1	none
m'	$\vec{P}_0 \parallel m'$ $\vec{M} \parallel m'$
m	$\vec{P}_0 \parallel m$ $\vec{M} \perp m$
$2'$	$\vec{P}_0 \parallel 2'$ $\vec{M} \perp \vec{P}_0$
$m'm2'$	$\vec{P}_0 \parallel 2'$ $\vec{M} \perp m$
$2.m'm'2$	$\vec{P}_0 \parallel 2$ $\vec{M} \parallel 2$
$3, 3m', 4, 4m'm', 6, 6m'm'$	$\vec{P}_0 \parallel \vec{M} \parallel$ principal axis

are the crystallographic axes, then the tensor n will be diagonal and will not influence the symmetry arguments. Consideration of the form of the susceptibility tensors in each of the 13 magnetic groups shows that tensor coefficient of $\vec{P}_0$ must have the same form as the magnetoelectric tensor χ_{me} (or χ_{em}). The constraints this places on $\vec{P}_0$ and $\vec{M}$ are given in Table I.

Now consider the application of this result to barium manganese fluoride. The crystal structure below 250 K has not been determined, but the spin structure, the room-temperature crystal structure, and the doubling of the unit cell in the bc plane are compatible with only one magnetic point group: $2'$. This group permits the ferroelectrically induced ferromagnetism discussed above. Since the magnitude of the magnetoelectric susceptibility has not been reported, it is not possible to make a complete quantitative comparison of theory with experiment; however, one may assume that the observed weak ferromagnetism is due entirely to this effect and compute the value of χ_{me} from the spontaneous polarization and the magnetization.

This value can then be compared with know values for other manganese compounds.

For magnetic point symmetry $2'$ with the choice of axes used for $BaMnF_4$ (a axis = polar axis), the tensors have the following form

$$\chi_e = \begin{pmatrix} \chi_e^{11} & 0 & 0 \\ 0 & \chi_e^{22} & \chi_e^{23} \\ 0 & \chi_e^{23} & \chi_e^{33} \end{pmatrix}, \quad \chi_m = \begin{pmatrix} \chi_m^{11} & 0 & 0 \\ 0 & \chi_m^{22} & \chi_m^{23} \\ 0 & \chi_m^{23} & \chi_m^{33} \end{pmatrix},$$

$$\chi_{me} = \begin{pmatrix} 0 & \chi_{me}^{12} & \chi_{me}^{13} \\ \chi_{me}^{21} & 0 & 0 \\ \chi_{me}^{31} & 0 & 0 \end{pmatrix}. \tag{A9}$$

The off-diagonal electric and magnetic susceptibilities are not known, but one would expect them to be small, i.e., $\vec{P}$ nearly parallel to $\vec{E}$ and $\vec{M}$ nearly parallel to $\vec{H}$. In what follows they will be neglected. The diagonal magnetic susceptibilities have the following values[21] at 4.2 K (cgs units)

$$\chi_m^{11} = \chi_m^{33} = 4.8 \times 10^{-4} \text{ and } \chi_m^{22} = 5.3 \times 10^{-5},$$

i.e.,

$$\chi_m^{11} = 6.0 \times 10^{-3}, \quad \chi_m^{22} = 6.7 \times 10^{-4}$$

(SI units, dimensionless).

In addition, assume that the sample is an ellipsoid of revolution with the axis of revolution being the a axis. The depolarization tensor n then has the form

$$n = \begin{pmatrix} n_1 & 0 & 0 \\ 0 & n_2 & 0 \\ 0 & 0 & n_2 \end{pmatrix}. \tag{A10}$$

For a sphere $n_1 = n_2 = \frac{1}{3}$. For an oblate spheroid with axes in the ratio 1:10 (as an approximation to a thin disc), $n_1 = 0.86$ and $n_2 = 0.070$.

Nor proceed to substitute these values into the relation between $\vec{M}$ and $\vec{P}_0$. Since the magnetoelectric susceptibility is very small, the first factor on the right-hand side of Eq. (A8) is well approximated by a unit matrix. The equation then becomes

$$M_1 = 0, \tag{A11}$$

$$M_2 = \frac{c\chi_{me}^{21} n_1}{1 + \chi_e^{11} n_1} P_0, \tag{A12}$$

$$M_3 = \frac{c\chi_{me}^{31} n_1}{1 + \chi_e^{11} n_1} P_0. \tag{A13}$$

Inserting the experimental values $M_2 = 0$, $M_3 = 1.460$ Am^{-1} and the spontaneous polarization calculated from the structural model $P_0 = 0.115$ $Cm^{-2} = 3.45 \times 10^4$ esu/cm^2 results in

$$\chi_{me}^{21} = 0 \tag{A14}$$

and

$$\chi_{me}^{31} = \begin{cases} 6.0 \times 10^{-4}, \text{ sphere} & \text{(A15)} \\ 5.2 \times 10^{-4}, \text{ oblate spheroid (SI units)}. & \text{(A16)} \end{cases}$$

These values are compatible with the magnetoelectric susceptibility in the five manganese compounds for which it has been measured. These values are given in Table II.

TABLE II. Magnetoelectric susceptibilities of manganese compounds.

Compound	Maximum magnetoelectric susceptibility
$LiMnPo_4$	3.1×10^{-4} [a]
$MnNb_2O_6$	5.0×10^{-5} [b]
$Ta_2Mn_4O_9$	1.1×10^{-4} [c]
$Nb_2Mn_4O_9$	2.1×10^{-5} [c]
$MnGeO_3$	2.0×10^{-5} [d]

[a] M. Mercier, E. F. Bertaut, G. Quezel, and P. Bauer, Solid State Commun. 7, 149 (1969).
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APPENDIX B: SPIN TRANSFORMATION

We have been intrigued by the fact that the free energy we use in Eq. (5) yields an electric polarization which varies as the *square* of the order parameter l. This is a sufficient condition[45] for a phase transition to be described as "improper". Despite this identification of the Néel temperature as an improper ferroelectric phase transition in $BaMnF_4$, we find, as discussed in Sec. V, that our free energy is not equivalent to that of Levanyuk and Sannikov.[34] In particular, our order parameter $\underset{\sim}{l}$ is not two dimensional. In this Appendix B we intentionally construct a two-dimensional order parameter[46] from spin variables and show that it leads to the free energy of Ref. 34.

Let

$$\eta = S_j^z - iS_{j+1}^x \ , \tag{B1}$$

$$\xi = S_{j+1}^z - iS_j^x \ , \tag{B2}$$

then we have a two-dimensional order parameter with components η and ξ. Here z is the antiferromagnetic spin axis b, and x is the ferromagnetic spin axis c. All expectation values involving S_j^y vanish and so this third coordinate may be ignored. We then treat the dielectric anomaly at T_N as that for an improper ferroelectric phase transition,[45] where the order parameter is related to the magnetization through Eqs. (B1) and (B2). Note that the expectation value $\langle \eta\xi^* + \eta^*\xi \rangle$ is just the magnetic energy $\langle \vec{S}_j \cdot \vec{S}_{j+1} \rangle$ in this description. The important invariant term in the free energy[34] is $(\eta^2 - \xi^2)P^2$, where P is the electric polarization. This is equal to $\langle \vec{S}_j \times \vec{S}_{j+1} P^2 \rangle$ from Eqs. (B1) and (B2). The full expression for the free energy is[34]

$$\Phi = \tfrac{1}{2}\alpha(\eta^2+\xi^2) + \tfrac{1}{4}\beta_1'(2\eta\xi)^2 + \tfrac{1}{4}b(\eta^2+\xi^2)^2 + (\eta^2-\xi^2)(\beta_0+\beta_1 P+\beta_2 P^2) - PE + \tfrac{1}{2}KP^2 \tag{B3}$$

At equilibrium, $\partial\Phi/\partial\eta = \partial\Phi/\partial\xi = \partial\Phi/\partial P = 0$. These relations require that

$$\epsilon(T < T_N) = \epsilon(T > T_N)[1 + 4(\beta_1' K)^{-1}(\beta_1^2 + \beta_0\beta_2)] \ , \tag{B4}$$

where $(\beta_1^2 + \beta_0\beta_2)$ may be negative. Remarkably, this expression for $\Delta\epsilon_a(T_N)$ is almost equivalent to that in Eq. (36). Both are proportional to $(\beta_1^2 + \beta_0\beta_2)$. However, in (B4) (and in Ref. 34) this is a step discontinuity, whereas in Eq. (36) it is smoothed as $m^2(T)/m^2(0)$. The latter agrees with experimental for $BaMnF_4$. The same smoothing of a negative change in ϵ is also observed for the ferroelectric phase transition in nickel iodine boracite[37] and has been attributed in Ref. 34 to fluctuations neglected in mean-field theories. A comparison of Eqs. (36) and (B4) in the present work suggest that, to the contrary, the step-down discontinuity in $\epsilon(T)$ prediced in Ref. 34 is an unphysical artifact of the free energy assumed, and that a free energy for the boracites functionally similar to Eq. (5) would yield a smooth decrease, in agreement with experiment.

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