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Frequency dependence of magnetoelectric phenomena in $BaMnF_4$

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Equations of motion of the Landau-Lifshitz type are used together with the free-energy expression of an earlier publication [D. L. Fox *et al.*, Phys. Rev. B 21, 2926 (1980)] to derive expressions for dynamic phenomena in the low-temperature phase of $BaMnF_4$. The magnon frequency decreases and the optical-phonon frequency increases with the strength of the magnetoelectric coupling. Three susceptibilities, magnetic, magnetoelectric, and dielectric, are found; all three have poles at both the magnon and the phonon frequency.

I. INTRODUCTION

The various phase transitions occurring in $BaMnF_4$ have been under investigation for nearly a decade, but they are still by no means completely understood. The literature up to about 1978 has been comprehensively reviewed.[1] At about 247 K $BaMnF_4$, which is pyroelectric at room temperature, undergoes a second-order or nearly second-order transition into an incommensurate antiferroelectric phase. The exact nature of this phase transition is still not clear, despite considerable recent activity.[2–10]

In common with other $BaMF_4$ compounds (M = Fe, Ni, or Co), $BaMnF_4$ shows two-dimensional antiferromagnetic ordering below about 70 K. Associated with this ordering is a broad anomaly in the b axis dielectric constant ϵ_b;[11,12] it has been shown[13,14] that the magnitude of the anomaly is proportional to the nearest-neighbor average $\langle S_i^z S_{i+1}^z \rangle$.

At the Néel temperature $T_N = 27$ K magnetic susceptibility measurements[15] show the onset of three-dimensional antiferromagnetic ordering. More precisely, the low-temperature phase is a spin-canted weak ferromagnet, the canting angle being 3 mrad at 4.2 K.[16] The point group of the low-temperature phase[17–19] is $2'$. This point group allows a linear magnetoelectric effect, and indeed a magnetoelectric response has been observed.[20] In the low-temperature phase, then, $BaMnF_4$ has a pyroelectric moment $\vec{P}$ directed along the crystallographic a axis and antiferromagnetic ordering along the b axis, with spin canting producing a weak ferromagnetic moment $\vec{M}$ along the c axis. These relationships are summarized in Fig. 1, which also shows the axis labels to be used.

Below the Néel temperature the a axis dielectric constant ϵ_a shows an anomalous decrease[11,21] $\Delta\epsilon_a$; it has been shown[21] that $-\Delta\epsilon_a \propto L_0^2$, where L_0 is the sublattice magnetization. The close link between the magnetic and dielectric properties is emphasized by the absence of an anomaly $\Delta\epsilon_a$ in $BaMn_{0.99}Co_{0.01}F_4$.[21] The addition of 1% cobalt changes the antiferromagnetic axis from b to a without significantly altering the Néel temperature.[22] It is worth mentioning that the resulting point group 2 does not allow spin canting, although it does allow a linear magnetoelectric effect.

The first attempt[12] to explain the anomaly $\Delta\epsilon_a$ proposed that it resulted from a bilinear coupling between the long-wavelength magnon operator a and the long-wavelength optical-phonon operator b, the model Hamiltonian being

$$\mathscr{H} = \omega_m a^\dagger a + \omega_p b^\dagger b + c_0(ab^\dagger + a^\dagger b) \ . \tag{1}$$

However, it was later shown[23] that Eq. (1) predicts

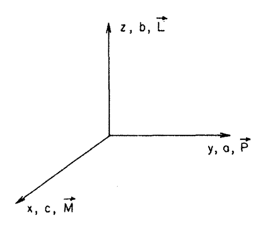

FIG. 1. Notation used in this paper. $\vec{P}$ is the pyroelectric moment, $\vec{L}$ the sublattice magnetization, and $\vec{M}$ the weak ferromagnetic moment.

an increase in ϵ_a, so that Eq. (1) is not a basis for explaining the experimental results. The increase is a consequence of the transfer of oscillator strength from the phonon to the magnon mode as the coupling constant c_0 increases. Besides the variation with c_0 of the zero-frequency dielectric anomaly $\Delta\epsilon_a$, Ref. 23 gave results for the dependence on c_0 of the mode energies and for the frequency dependence of $\Delta\epsilon_a$. A consequence of the transfer of oscillator strength is that $\Delta\epsilon_a$ develops a pole at ω_m, and the residue at this pole increases with c_0. The calculations of Ref. 23 can be readily extended to give the frequency dependence of the magnetic susceptibility and the magnetoelectric susceptibility; what is required, in the notation of Ref. 23, is a calculation of the Green's functions $G_\omega(a\,|\,a^\dagger)$ and $G_\omega(a\,|\,b^\dagger)$.

The calculation in Ref. 23 suffers from a number of shortcomings, apart from the obvious one that since $\Delta\epsilon_a$ disagrees with the experimental result some crucial feature of the magnetic-electric coupling has been omitted. First, the calculation is very schematic, and in particular Eq. (1) is not properly adapted to the symmetry of the system. Second, there is no easy way to extend the calculation to predict temperature dependences.

In Ref. 21 we tried to improve upon Ref. 23 by giving a Landau-type mean-field theory for the low-temperature phase. It was pointed out in particular that a term $\beta_2 P^2 M_x L_z$ in the free energy is allowed by symmetry, and that despite its nonlinearity this term contributes to the linear dielectric constant. It was shown that the inclusion of this term allows $\Delta\epsilon_a$ to have either sign, and that the temperature dependence is $|\Delta\epsilon_a| \propto L_0^2$, in agreement with experiment.

Although Ref. 21 was an improvement on Ref. 23 in that it took proper account of the symmetry, gave a result for $\Delta\epsilon_a$ in agreement with experiment, and predicted temperature dependences, it was restricted to static susceptibilities and related quantities. The purpose of this paper is to extend Ref. 21 by using equations of motion to find expressions for the normal mode frequencies and the frequency dependences of the susceptibilities. The equations of motion are of the type originally proposed by Landau and Lifshitz[24] for magnetic systems and by Landau and Khalatnikov[25] for relaxational systems. The application to ferroelectrics with the inclusion of inertial or kinetic energy terms was pioneered by Tani[26] and is reviewed by Blinc and Zeks.[27]

The plan of the paper is as follows. In Sec. II we set out the free-energy expression Φ used before.[21] It is pointed out that the uniaxial antiferromagnet and a weak ferromagnet are described by special cases of the free-energy expression. Comparison of the static magnetic susceptibilities of the antiferromagnet derived from the free energy with conventional expressions enables us to express some of the parameters of the free energy in terms of the more usual anisotropy and exchange fields. The equations of motion are postulated, and equations giving the linear response of the system to rf driving fields $\vec{H}$ and $\vec{E}$ are derived. Section III is devoted to the resonance frequencies, which are found essentially from the conditions for singularity of the response functions of Sec. II. For the antiferromagnet there are two degenerate modes at the usual antiferromagnetic resonance frequency ω_{AF}. In the magnetoelectric, one of these modes persists at ω_{AF}, while the other couples to the optical phonon with a consequent frequency shift. In Sec. IV we find the rf susceptibilities from the linear response equations of Sec. II. The magnetoelectric susceptibility has poles at both the magnetic resonance frequency and the optical phonon frequency. As at zero frequency,[21] it is found that the dielectric anomaly $\Delta\epsilon_a$ is a sum of two terms, one of which is essentially positive and the other of which can have either sign at zero frequency. The first of these terms, however, has a pole at ω_{AF}, while the second does not. Conclusions are presented in Sec. V.

II. FREE ENERGY AND EQUATIONS OF MOTION

$BaMnF_4$ is a two-sublattice antiferromagnet, and we use variables

$$\vec{L}=\vec{M}_1-\vec{M}_2\,, \tag{2}$$

$$\vec{M}=\vec{M}_1+\vec{M}_2\,, \tag{3}$$

where $\vec{M}_1$ and $\vec{M}_2$ are the sublattice magnetizations. We write the free-energy density in the form[21]

$$\begin{aligned}\Phi = {} & \tfrac{1}{2}(A+a)L^2-\tfrac{1}{2}aL_z^2+\tfrac{1}{4}GL^4+\tfrac{1}{2}BM^2 \\ & +\tfrac{1}{2}D(\vec{L}\cdot\vec{M})^2+(\beta_0+\beta_1 p+\beta_2 p^2)M_xL_z \\ & -\gamma M_zL_x+\tfrac{1}{2}Kp^2-\vec{p}\cdot\vec{E}-\vec{M}\cdot\vec{H}\,,\end{aligned} \tag{4}$$

where the polarization $\vec{P}$ is

$$\vec{P}=\vec{P}_s+\vec{p}\,, \tag{5}$$

with $\vec{P}_s$ the pyroelectric moment. $\vec{E}$ and $\vec{H}$ are external fields which in Ref. 21 were taken as static fields since we calculated static susceptibilities; later in this paper we take them as rf fields for the calculation of rf susceptibilities. Φ is not the most general form allowed by symmetry; some possible terms are omitted on grounds of physical implausibility.[21] In particular, a possible p dependence of the anisotropy parameter a is omitted.

Here and later in looking at the implications of Eq. (4) it is helpful to consider two special cases. If $\beta_0=\beta_1=\beta_2=\gamma=0$, $a>0$, and terms in p are omitted, Eq. (4) describes a uniaxial antiferromagnet. The equilibrium configuration in zero applied field is given by the solution of $\partial\Phi/\partial\vec{L}=\partial\Phi/\partial\vec{M}=0$, namely

$$\vec{L}=(0,0,L_0)\ , \tag{6}$$

$$\vec{M}=0\ , \tag{7}$$

with

$$L_0^2=-A/G\ . \tag{8}$$

In a simple version of the theory, one would set $A=A_0(T-T_N)$, but as before[21] we take the view that the aim of the theory is to express other quantities in terms of L_0. With a static field H reinstated in Eq. (4) the static magnetic susceptibilities $\chi_{\|}=\chi_{zz}$ and $\chi_{\perp}=\chi_{xx}=\chi_{yy}$ of the antiferromagnet can be calculated. Comparison of the expressions[28] with those found in the conventional way[29] gives the identifications

$$aL_0=H_A\ , \tag{9}$$

$$BL_0=2H_E+H_A\ , \tag{10}$$

between parameters of this theory and the exchange and anisotropy fields H_E and H_A which are normally used.

If $\beta_1=\beta_2=0$, $\beta_0=\gamma$, $a>0$, and terms in p are omitted, Eq. (4) describes a weak ferromagnet with equilibrium configuration

$$\vec{L}=(0,0,L_0)\ , \tag{11}$$

$$\vec{M}=(-\beta_0L_0/B,0,0)\ , \tag{12}$$

so that the spin-canting angle is $\theta_c=\beta_0/B$.

In their full form the equations for the equilibrium configuration and static susceptibilities derived from Eq. (4) appear to be intractable. They have been solved[21] by power series expansion up to quadratic terms in the parameters β_0, β_1, β_2, and γ. To that order, $\vec{L}$ remains in the z direction but an additional term of order β^2 is added to L_0, while $\vec{M}$ retains the value in Eq. (12). The static magnetoelectric susceptibility $\chi_{xy}^{em}(0)$ and the static dielectric susceptibility $\chi_{yy}^{ee}(0)$ are

$$\chi_{xy}^{em}(0)=-\beta_1L_0/BK \tag{13}$$

and

$$\chi_{yy}^{ee}(0)=1/K+(\beta_1^2+\beta_0\beta_2)L_0^2/BK^2\ . \tag{14}$$

It is seen from Eq. (14) that the dielectric anomaly is proportional to L_0^2 and can have either sign, as already mentioned.

In order to find resonance frequencies and rf susceptibilities we postulate[24–27] that the mean fields on the sublattices and on the polarization are $-\partial\Phi/\partial M_{1,2}$ and $-\partial\Phi/\partial p$, so as to write equations of motion

$$\frac{1}{\gamma_0}\frac{\partial\vec{M}_i}{\partial t}=-\vec{M}_i\times\frac{\partial\Phi}{\partial\vec{M}_i}+\mathscr{D},\quad i=1,2 \tag{15}$$

$$\mu\frac{\partial^2p}{\partial t^2}+b\frac{\partial p}{\partial t}=-\frac{\partial\Phi}{\partial p}\ . \tag{16}$$

Here γ_0 (taken negative) is the gyromagnetic ratio, $\mathscr{D}$ represents damping, μ is the optical-phonon effective mass, and b a phonon damping parameter. It is essential to include damping in the equations of motion for the longitudinal components M_{iz}. If it were not included, Eq. (15) would give a zero value for the static longitudinal susceptibility, in contradiction to the nonzero value found directly from Eq. (4) and to the experimental results. As can be done for magnetic resonance,[30] we overcome this formal difficulty by assuming that M_{iz} relax towards the values that would be determined by the instantaneous value of the rf field. This is equivalent to using the "modified Bloch equations"[31,32] instead of the usual Bloch equations. It is less essential to include damping in the equations of motion for the transverse magnetization components and for p, but it appears in Eqs. (15) and (16) for completeness. Detailed forms of the damping terms in Eq. (15) will be given below.

In order to apply Eq. (15) to Eq. (4), we use Eqs. (2) and (3) to convert (15) to equations for $\vec{L}$ and $\vec{M}$:

$$\frac{1}{\gamma_0}\frac{\partial\vec{M}}{\partial t}=-\vec{M}\times\frac{\partial\Phi}{\partial\vec{M}}-\vec{L}\times\frac{\partial\Phi}{\partial\vec{L}}+\mathscr{D}\ , \tag{17}$$

$$\frac{1}{\gamma_0}\frac{\partial\vec{L}}{\partial t}=-\vec{L}\times\frac{\partial\Phi}{\partial\vec{M}}-\vec{M}\times\frac{\partial\Phi}{\partial\vec{L}}+\mathscr{D}\ . \tag{18}$$

$\vec{H}$ and $\vec{E}$ are taken as rf fields:

$$\vec{H}=\vec{H}\exp(-i\omega t)\ , \tag{19}$$

$$\vec{E}=\vec{E}\exp(-i\omega t)\ , \tag{20}$$

and $\vec{L}$ and $\vec{M}$ are written in the form

$$\vec{L}=(l_x,l_y,L_0+l_z)\ , \tag{21}$$

$$\vec{M}=(-\beta_0 L_0/B+m_x,m_y,m_z)\ , \tag{22}$$

so that $\vec{l}$ and $\vec{m}$ are the linear response of $\vec{L}$ and $\vec{M}$ to $\vec{H}$ and $\vec{E}$. Equations (16)–(18) are linearized in $\vec{l}$, $\vec{m}$, $\vec{H}$, and $\vec{E}$; with the replacement $\partial/\partial t \rightarrow -i\omega$ they take the form

$$-i\omega m_x/\gamma_0=L_0\Phi_{ly}+m_x/T_2\ , \tag{23}$$

$$-i\omega m_y/\gamma_0=-\beta_0 L_0(\Phi_{mz}-H_z)/B-L_0\Phi_{lx}+m_y/T_2\ , \tag{24}$$

$$-i\omega m_z/\gamma_0=\beta_0 L_0(\Phi_{my}-H_y)/B+m_z/T_1-\chi_0 H_z/T_1\ , \tag{25}$$

$$-i\omega l_x/\gamma_0=L_0(\Phi_{my}-H_y)+l_x/T_2\ , \tag{26}$$

$$-i\omega l_y/\gamma_0=-L_0(\Phi_{mx}-H_x)-\beta_0 L_0\Phi_{lz}/B+l_y/T_2\ , \tag{27}$$

$$-i\omega l_z/\gamma_0=\beta_0 L_0\Phi_{ly}/B+l_z/T_1-\chi_{l0}H_x/T_1\ , \tag{28}$$

$$-(\mu\omega^2+ib\omega)p=-\Phi_p+E\ . \tag{29}$$

The notation for derivatives is

$$\Phi_{ly}=\frac{\partial\Phi}{\partial L_y} \tag{30}$$

and so on. Transverse and longitudinal relaxation times T_1 and T_2 have been introduced. As explained, as $\omega\rightarrow 0$, Eqs. (25) and (28) allow m_z and l_z to relax to the static values $\chi_0 H_z$ and $\chi_{l0}H_x$. Here χ_0 is the relatively complicated form of the static susceptibility χ_{zz}^{mm} given in Ref. 21, Eq. (16), and

$$\chi_{l0}=-\beta_0/2BGL_0^2\ , \tag{31}$$

this being introduced because l_z has a static response to H_x, as is seen from Ref. 21, Eq. (13). Purely for simplicity, no static fields have been included in Eqs. (23)–(29); there would be no difficulty in including them if necessary.

When explicit expressions for the derivatives Φ_{ly} etc. are substituted, it is found that the general structure of Eqs. (23)–(29) is as follows. Equations (23), (27), (28), and (29) are coupled, and give the response of (m_x,l_y,l_z,p) to (H_x,E). Equations (24)–(26) are coupled and give the response of (m_y,m_z,l_x) to (h_y,h_z). Of these two sets of equations, the former are the more interesting, because they describe coupled magnetic-electric behavior. It can also be seen from the explicit form of the equations that in the limit $\omega\rightarrow 0$ the static susceptibilities derived previously[21] are again found.

III. RESONANCE FREQUENCIES

In order to find the resonance frequencies, Eqs. (23)–(29) are solved with the driving fields $\vec{H}$ and $\vec{E}$ omitted. As is clear from the comment at the end of Sec. II, Eqs. (23), (27), (28), and (29) are then coupled homogeneous equations for (m_x,l_y,l_z,p), while Eqs. (24)–(26) are coupled homogeneous equations for (m_y,m_z,l_x). Rather than consider the general case immediately, it is helpful to start with the special case of the antiferromagnet and the weak ferromagnet.

For the antiferromagnet, the longitudinal components m_z and l_z are decoupled from the transverse components and have a purely relaxational behavior

$$i\omega m_z=\Gamma_1 m_z\ , \tag{32}$$

with a similar equation for l_z, where

$$\Gamma_1=-\gamma_0/T_1\ . \tag{33}$$

The equations for m_x and l_y are

$$i\omega m_x=-\gamma_0 H_A l_y+\Gamma_2 m_x\ , \tag{34}$$

$$i\omega l_y=\gamma_0(2H_E+H_A)m_x+\Gamma_2 l_y\ , \tag{35}$$

with

$$\Gamma_2=-\gamma_0/T_2\ , \tag{36}$$

where Eqs. (9) and (10) have been used. The equations for m_y and l_x take the same form, so that the (m_x,l_y) and (m_y,l_x) modes are degenerate. Without damping, $\Gamma_2=0$, the resonance frequency, as is well known, is

$$\omega^2=\omega_{\mathrm{AF}}^2=\gamma_0^2 aBL_0^2=\gamma_0^2(2H_E H_A+H_A^2)\ . \tag{37}$$

For the weak ferromagnet, the equations of motion for m_y and l_x are identical in form to Eqs. (34) and (35), so that the resonance frequency for that mode is still given by Eq. (37). The only difference from the antiferromagnet is that m_z now follws m_y:

$$-\left[\frac{i\omega}{\gamma_0}+\frac{1}{T_1}\right]m_z=\beta_0 L_0 m_y\ . \tag{38}$$

The (m_x,l_y) mode is shifted up in frequency; in the absence of damping the resonance frequency is

$$\omega^2=\omega_{\rm WF}^2=\gamma_0^2(a+\beta_0^2/B)(B+\beta_0^2/B)L_0^2 + (\gamma_0^2\beta_0^2 a/B)(1+2GL_0^2/B)L_0^2 \ . \tag{39}$$

In this mode, l_z follows l_y:

$$-\left[\frac{i\omega}{\gamma_0}+\frac{1}{T_1}\right]l_z=\frac{\beta_0 a}{B}L_0 l_y \ . \tag{40}$$

Equation (39) is exact; for comparison with the full magnetoelectric equations, which we expand to order β^2, note that the shift of $\omega_{\rm WF}$ from $\omega_{\rm AF}$ is second order in β_0.

For both the anitferromagnet and the weak ferromagnet the optical phonon is not coupled to the magnetic resonance modes, as is obvious on general grounds. In the absence of damping, Eq. (29) gives the usual result for the optical-phonon frequency:

$$\omega_{\rm TO}^2=K/\mu \ . \tag{41}$$

After these preliminaries we turn to the magnetoelectric, for which the resonance modes are those given by the full set of equations (23)–(29) with rf fields omitted. If $\gamma=\beta_0$, the (m_y,m_z,l_x) mode still has frequency $\omega_{\rm AF}$ given by Eq. (37); if $\gamma\neq\beta_0$ the frequency is shifted. The (m_x,l_y,l_z) mode is now coupled to the p mode, and both the magnon and phonon frequencies are shifted. It is notable that the coupling between the modes involves only the parameter β_1. The full expressions for the frequencies, involving the solution of a 3×3 secular determinant [l_z can be eliminated by Eq. (40)] are complicated, and it is helpful to expand the shifted mode frequencies in powers of β_1. To order β_1^2, they are

$$\omega_m=\omega_{\rm WF}+\delta\omega_m \ , \tag{42}$$

$$\omega_T=\omega_{\rm TO}+\delta\omega_T \ , \tag{43}$$

with

$$\delta\omega_m=-\frac{\gamma_0^2\beta_1^2 a L_0^4}{2\mu\omega_{\rm WF}(\omega_{\rm TO}^2-\omega_{\rm WF}^2)} \ , \tag{44}$$

$$\delta\omega_T=\frac{\gamma_0^2\beta_1^2 a L_0^4}{2\mu\omega_{\rm TO}(\omega_{\rm TO}^2-\omega_{\rm WF}^2)} \ . \tag{45}$$

The zero-temperature forms of Eqs. (44) and (45) may be compared with the results of Ref. 23. They are consistent in that ω_m goes down and ω_T goes up, the shift in both being proportional to β_1^2. However, there is a significant difference because in Ref. 23 $|\delta\omega_m|=|\delta\omega_T|$, whereas here we have rather $\delta(\omega_m^2)=\delta(\omega_T^2)$. Since the zero-temperature values are $\omega_m=3$ cm^{-1} and $\omega_{\rm TO}=40$ cm^{-1},[12] this is a substantial numerical difference.

Equations (44) and (45) predict the temperature dependences of the frequency shifts. Equation (39) shows that $\omega_{\rm WF}^2\propto L_0^2$; using this and the numerical values just quoted one finds

$$\frac{\omega_{\rm TO}^2-\omega_{\rm WF}^2(T=0)}{\omega_{\rm TO}^2-\omega_{\rm WF}^2(T=T_N)}=0.994 \ . \tag{46}$$

To better than 1%, therefore, the contributions of the corresponding terms in Eqs. (44) and (45) may be disregarded, and the temperature dependences reduce to

$$\frac{\delta\omega_m(T)}{\delta\omega_m(0)}=\frac{L_0^3(T)}{L_0^3(0)} \tag{46}$$

and

$$\frac{\delta\omega_T(T)}{\delta\omega_T(0)}=\frac{L_0^4(T)}{L_0^4(0)} \ . \tag{47}$$

The temperature dependence of $L_0(T)$ in $BaMnF_4$ follows a Brillouin $\frac{5}{2}$ function,[33] and a plot of $L_0^2(T)$ versus T is given in Ref. 21, Fig. 5.

The results of this section are summarized in Fig. 2, which shows a "thought experiment" in which an antiferromagnet is turned first into a weak ferromagnet then into a magnetoelectric with an increasing value of β_1. In the first stage the degeneracy of the two antiferromagnetic modes is lifted, and of course the frequency of the phonon mode is unaltered. In the second stage the coupling between the (m_x,l_y,l_z) and p modes means that the corresponding frequencies move apart, while the (m_y,m_z,l_x) mode continues unperturbed

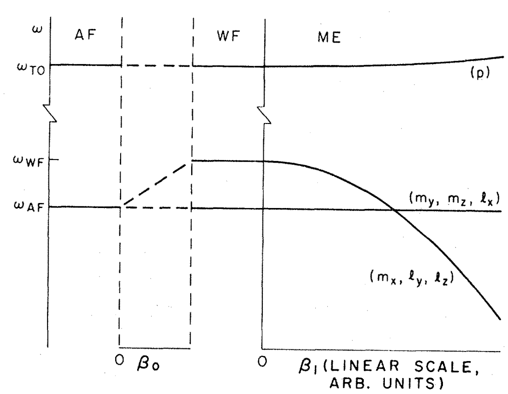

FIG. 2. Summary of the results of Sec. III. The changes in mode frequencies are shown as an antiferromagnet is changed first into a weak ferromagnet, then into a magnetoelectric.

at frequency ω_{AF}. (It is assumed that $\gamma=\beta_0$.) The right-hand side of Fig. 2 may be compared with Fig. 1 of Ref. 23, in which frequencies are plotted against the coupling constant c_0 of the Hamiltonian (1). As mentioned, in Ref. 23 $|\delta\omega_m| = |\delta\omega_T|$, whereas the present result is $\omega_m |\delta\omega_m| = \omega_T |\delta\omega_T|$. The difference between these forms is seen in the relatively small increase of the p-mode frequency in Fig. 2.

IV. SUSCEPTIBILITIES

The susceptibilities are given by the solutions of Eqs. (23)–(29) for the linear response to the rf driving fields. Equations (24)–(26) give a response of (m_y,m_z,l_x) to (h_y,h_z) which for $\beta_0=\gamma$ is the same as that of an antiferromagnet. We therefore concentrate on the solutions of Eqs. (23), (27), (28), and (29). As for the static susceptibilities[21] an exact explicit solution has not been found, and instead we give the result of a power series expansion in the parameters β_i and γ. The susceptibilities of most interest are defined by

$$m_x = \chi_{xx}^{mm} H_x + \chi_{xy}^{em} E \ , \tag{48}$$

$$p = \chi_{xy}^{em} H_x + \chi_{yy}^{ee} E \ . \tag{49}$$

The symmetry by which χ_{xy}^{em} occurs in both off-diagonal positions emerges from the detailed solutions as well as being required on general grounds.

To order β^2, the susceptibilities are

$$\chi_{xx}^{mm} = (aL_0^2 + f_2c_2 + aL_0d_2)(f_2^2 + aBL_0^2)^{-1} \ , \tag{50}$$

$$\chi_{xy}^{em} = -(\beta_1 aL_0^3/\mu)(\omega_{\rm TO}^2 - i\omega\Gamma - \omega^2)^{-1}(f_2^2 + aBL_0^2)^{-1} \ , \tag{51}$$

$$\chi_{yy}^{ee} = \mu^{-1}(\omega_{\rm TO}^2 - i\omega\Gamma - \omega^2)^{-1} + (\beta_1^2 aL_0^4/\mu^2)(\omega_{\rm TO}^2 - i\omega\Gamma - \omega^2)^{-2}(f_2^2 + aBL_0^2)^{-1} + (\beta_0\beta_2 L_0^2/B\mu^2)(\omega_{\rm TO}^2 - i\omega\Gamma - \omega^2)^{-2} \ . \tag{52}$$

The auxiliary notation is

$$c_2 = (\beta_0^2 L_0^2 f_2/B)(f_2^2 + aBL_0^2)^{-1} \ , \tag{53}$$

$$d_2 = -(\beta_0^2 aL_0^3/B)(f_2^2 + aBL_0^2)^{-1} - (\beta_0^2 af_2L_0^3/Bf_1)(1 + 2GL_0^2/B)(f_2^2 + aBL_0^2)^{-1} - \beta_0 L_0 \chi_{l0}(1 + 2GL_0^2/B)/f_1T_1 + (\beta_1^2 aL_0^5/\mu)(\omega_{\rm TO}^2 - i\omega\Gamma - \omega^2)^{-1}(f_2^2 + aBL_0^2)^{-1} \ , \tag{54}$$

$$f_1 = i\omega/\gamma_0 + 1/T_1 \ , \tag{55}$$

$$f_2 = i\omega/\gamma_0 + 1/T_2 \ . \tag{56}$$

χ_{l0} is given in Eq. (31), and the phonon-damping parameter Γ is defined by

$$\mu(\omega_{\rm TO}^2 - i\omega\Gamma - \omega^2) = K - i\omega b - \mu\omega^2 \ . \tag{57}$$

In the absence of damping, $T_2^{-1}=0$,

$$f_2^2 + aBL_0^2 = -\omega^2 + \omega_{\rm AF}^2 \ , \tag{58}$$

where $\omega_{\rm AF}$ is the antiferromagnetic resonance frequency of Eq. (37). It is seen, therefore, that the susceptibilities of Eqs. (50)–(52) have poles at the unshifted magnetic resonance and optical-phonon frequencies. This, and the fact that some of the singularities are double poles, are artifacts introduced by the use of a perturbation expansion. The basic response equations are linear, and the resonance frequencies (42) and (43) are given by the condition that the matrix multiplying the vector (m_x,l_y,p) is singular. In an exact solution, therefore, the susceptibilities would have single poles at the exact resonance frequencies.

In the limit of zero frequency and zero damping, $\omega, T_1^{-1}, T_2^{-1}, \Gamma \to 0$, Eqs. (50)–(52) reduce to the static expressions derived previously.[21] In checking this limit it must be borne in mind that according to Eq. (55), $f_1T_1 \to 1$.

The singularities in Eqs. (50)–(52) occur in different orders in the expansion parameters β_i. χ_{xx}^{mm} has a pole of zero order at $\omega=\omega_{\rm AF}$ and a pole of second order at $\omega=\omega_{\rm TO}$. χ_{xy}^{em} has first-order poles at $\omega_{\rm AF}$ and at $\omega_{\rm TO}$. χ_{yy}^{ee} has a second-order pole at $\omega_{\rm AF}$ and a zero-order pole at $\omega_{\rm TO}$. Since χ_{xx}^{mm} is primarily a magnetic response function, χ_{yy}^{ee} primarily a dielectric response function, and χ_{xy}^{em} a mixed response function, these properties are not surprising.

With damping neglected, χ_{xy}^{em} may be written in the alternative form

$$\chi_{xy}^{em}=(\beta_1 a L_0^3/\mu)(\omega_{\mathrm{TO}}^2-\omega_{\mathrm{AF}}^2)^{-1}\times[(\omega_{\mathrm{TO}}^2-\omega^2)^{-1}-(\omega_{\mathrm{AF}}^2-\omega^2)^{-1}] ,$$

which brings out clearly the relationship between the two poles. The frequency dependence of χ_{xy}^{em} is shown for $T=0$ and for $T=0.71T_N$ in Fig. 3. The reason for choosing the latter value is that it gives a value of L_0^2 equal to half the zero-temperature value.

The terms of order β^2 in χ_{yy}^{ee} may be written as a frequency-dependent dielectric anomaly; with damping again neglected it takes the form

$$\Delta\epsilon=(L_0^2/\epsilon_0 B\mu^2)(\omega_{\mathrm{TO}}^2-\omega^2)^{-2}\times[\beta_1^2\omega_{\mathrm{AF}}^2(\omega_{\mathrm{AF}}^2-\omega^2)^{-1}+\beta_0\beta_2] . \tag{60}$$

The zero-frequency value, given by the second term in Eq. (14), is

$$\Delta\epsilon(\omega=0)=(L_0^2/\epsilon_0 BK^2)(\beta_1^2+\beta_0\beta_2) . \tag{61}$$

When only the static result, Eq. (61), was available we pointed out[21] that the sign of $\Delta\epsilon$ depends on the numerical balance between the contributions β_1^2 and $\beta_0\beta_2$. A negative value of $\Delta\epsilon$, as observed experimentally, requires $\beta_0\beta_2<-\beta_1^2$. It is now seen from Eq. (60) that whereas the two contributions to $\Delta\epsilon$ appear on equal footings at zero frequency, they have quite different frequency dependences. In particular, the β_1^2 term has a pole at $\omega=\omega_{\mathrm{AF}}$ which the other term lacks. Both terms have a singularity at $\omega=\omega_{\mathrm{TO}}$, but as we have pointed out the fact that this is a double pole rather than a single one stems from the use of an expansion in β, and the exact solution cannot have a double pole.

The dependence of $\Delta\epsilon$ on frequency and temperature is illustrated in Fig. 4. In order to draw such a figure one requires separate estimates of β_1^2 and $\beta_0\beta_2$. These cannot be found from the available experimental data, so we have arbitrarily assumed $\beta_0\beta_2=-3\beta_1^2$. Figure 4(a) is dominated by the double pole at $\omega=\omega_{\mathrm{TO}}$, but as explained in Eq. (60) is not accurate in the neighborhood of ω_{TO}. More interest, therefore, attaches to Fig. 4(b),

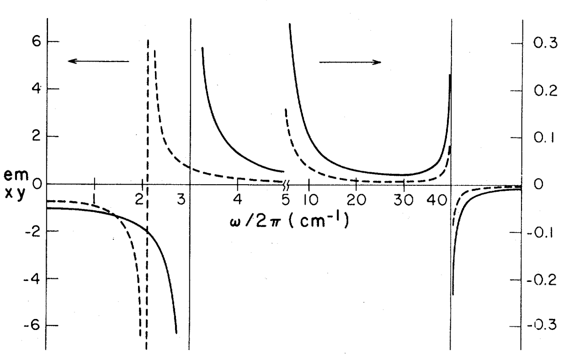

FIG. 3. Frequency dependence of the magnetoelectric susceptibility. The function plotted is $\mu\omega_{\mathrm{TO}}^2\omega_{\mathrm{AF}}^2\chi_{xy}^{em}/\beta_1 a L_0^3$, where all multiplying factors have their zero-temperature values. This function is normalized to unity at $\omega=0$ and $T=0$. — $T=0$. — — — $T=0.71T_N$. Note the changes in horizontal and vertical scales at $\omega/2\pi=5\ \mathrm{cm}^{-1}$.

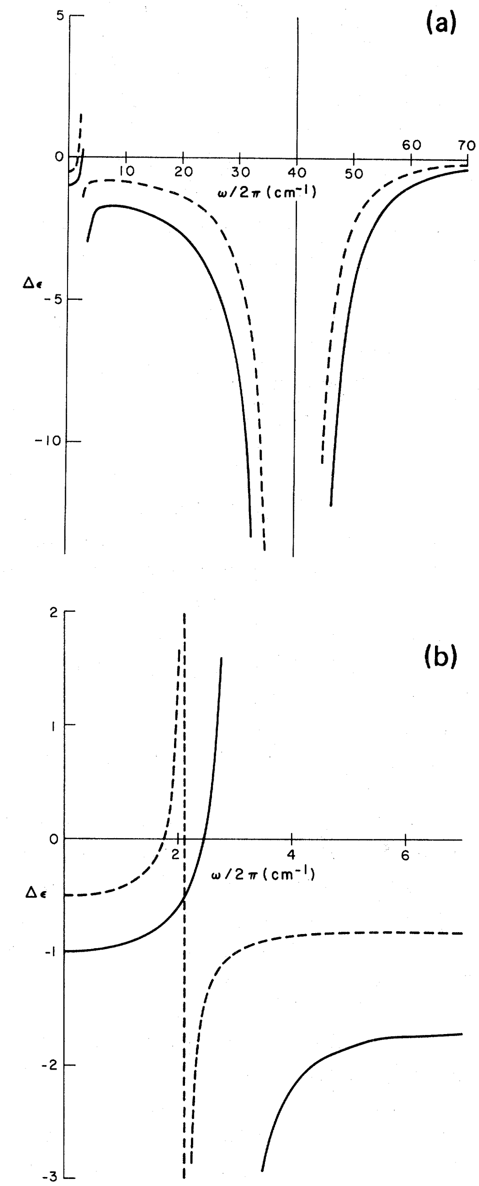

FIG. 4. Frequency dependence of the dielectric anomaly when $\beta_0\beta_2=-3\beta_1^2$. The function plotted is $\Delta\epsilon/\Delta\epsilon(\omega=0,T=0)$ normalized to unity at $\omega=0$ and $T=0$. — $T=0$. — — — $T=0.71T_N$. (a) Full frequency range. (b) Frequency range round ω_{AF}.

which shows the vicinity of $\omega=\omega_{AF}$ in more detail. That figure emphasizes, as is already clear from Eq. (60), that near ω_{AF} the β_1^2 term must dominate, with a positive value for $\Delta\epsilon$ on the low-frequency side of ω_{AF}. Like Fig. 3, Fig. 4 shows the general weakening with increasing temperature of effects due to the magnetoelectric coupling.

V. DISCUSSION

The postulated form (4) of the free-energy density leads to predictions for equilibrium values and static susceptibilities which were worked out in Ref. 21. By adding the equations of motion (15) and (16) we have extended the scope to find dynamic properties. The equations of motion are postulated and not derived, but since they give the usual results for an antiferromagnet and a dielectric when the coupling terms in (4) are dropped there is no reason to doubt their validity.

Our main results are the mode frequencies of Sec. III, particularly Eqs. (44) and (45), and the frequency-dependent susceptibilities, Eqs. (50)–(52) in Sec. IV. The coupling parameters β_0, β_1, and β_2 in Eq. (4) have quite distinct roles in these expressions. As indicated in Fig. 2, β_0 is primarily involved in the spin canting and consequent lifting of the degeneracy of the antiferromagnetic resonance modes, while the frequency shifts (44) and (45) due to the magnetoelectric coupling depend solely on β_1. The parameter β_2 plays a crucial part in expression (60) for the dielectric anomaly $\Delta\epsilon$, since it allows $\Delta\epsilon$ to be negative, but it is not otherwise important.

The present results may be compared with those found in the theory of improper ferroelectrics.[34] In that case, the polarization P may be coupled to the two-dimensional primary-order parameter by means of a term linear in P, analogous to our β_1 term, or by means of a term quadratic in P, analogous to β_2. The linear term leads to a step discontinuity in ϵ at the critical temperature, with $\epsilon(T<T_c)>\epsilon(T>T_c)$. The quadratic term, however, produces a term in ϵ which is continuous at T_c but with a discontinuity in $d\epsilon/dT$.[35] Here, by contrast, both the β_1 and the β_2 coupling terms produce discontinuities in $d\epsilon/dT$ but not in ϵ, although as we have shown the frequency dependences of the two contributions are quite different. This disparity between the present theory and the theory of improper ferroelectrics stems from the different mathematical structures of the free-energy expressions. In improper ferroelectrics, a two-dimensional primary order parameter is coupled to the secondary order parameter P. Here, however, the primary order parameter L_z is one-dimensional, and is coupled to two secondary order parameters M_x and P. In particular, the coupling terms $\beta_1 pM_xL_z$ and $\beta_2 p^2M_xL_z$ involve all three order parameters.

It was pointed out previously[21] that the free energy of Eq. (4) implies the existence of various nonlinear susceptibilities. As in Ref. 21, however, we have worked out the linear response functions without attempting to derive expressions for nonlinear effects. A systematic account would be quite difficult, and in any case would have to build on a proper understanding of the linear susceptibilities.

An earlier attempt[23] to give an account of frequency-dependent phenomena in $BaMnF_4$ was based on the model Hamiltonian (1). As implied in Sec. I, the present work is an advance on that in several ways. It is less schematic because the terms in Eq. (4) are invariants of the point group of the high-temperature phase, and it gives predictions for temperature dependences. Nevertheless, our results are broadly consistent with those of Ref. 23. The presence of the coupling terms leads to an increase in the phonon frequency ω_{TO} and a decrease in the magnon frequency ω_{AF}, although now we find $\delta(\omega_{TO}^2)=-\delta(\omega_{AF}^2)$ rather than the previous $|\delta(\omega_{TO})|=|\delta(\omega_{AF})|$. It may be pointed out that the more complete Hamiltonian

$$H=\omega_{AF}a^{\dagger}a+\omega_{TO}b^{\dagger}b+c_0(a^{\dagger}+a)(b^{\dagger}+b) \tag{62}$$

also leads to $\delta(\omega_{TO}^2)=-\delta(\omega_{AF}^2)$, in agreement with the present theory. With coupling included, the susceptibilities χ_{xx}^{mm}, χ_{xy}^{em}, and χ_{yy}^{ee} of Eqs. (50)–(52) have poles at ω_{TO} and ω_{AF}, and the relative strengths are in line with those found from Eq. (1).

It was mentioned before[21] that the experimental data on static properties of $BaMnF_4$ at low temperatures are not adequate for a critical test of the theoretical predictions. This has been emphasized recently[36] in a detailed comparison of the theory with available experimental results. The same comment applies with more force to the present dynamical results; there are no experiments with which the theory can be directly compared. Al'Shin *et al.*[20] observed strong frequency dependence of the magnetoelectric response in the kHz region, but as is seen from Fig. 3, for example, we are concerned with frequencies of the order of tens of GHz. We believe that the qualitative origin of the frequency-dependent effects reported by

Al'Shin *et al.* in the 1-kHz regime is domain wall oscillation, as suggested by them. Since the free energy employed in the present work ignores all domain effects, it does not yield predictions in the kHz regime with which comparisons can be made. However, we note that Al'Shin *et al.* recognized explicitly that their data were incompatible with what was then believed[37] to be the ferroelectric structure. The free energy employed in the present work, which incorporates both the correct antiferroelectric ordering and the spin orientations determined subsequent to the studies by Al'Shin *et al.* may serve as a starting point for the analysis of the latter.

Because of the limited extent of the comparison with experiment, the present theory must be regarded as tentative in some ways. It was mentioned in Sec. II that some terms which are allowed by symmetry have been omitted from Eq. (4) on physical grounds, and there is always the possibility that some of these might have to be reinstated.

The calculations presented here may be compared with the work of Bar'yakhtar and Chupis,[38] which as far as we know was the first paper to deal with the frequency dependence of the susceptibilities of magnetoelectric materials. They start with a Hamiltonian density which is a model for a system which is ferromagnetic and ferroelectric. As in Eq. (4), their density is a power series in $\vec{P}$ and $\vec{M}$, although the details are different and in particular they include terms in the spatial gradients with a view to discussing the spectrum away from $k=0$. Rather than use classical equations of motion, as we have done, they quantize the field operators, then introduce magnon operators via the Holstein-Primakoff transformation. Retaining only bilinear terms, they find a Hamiltonian which is a generalization of Eq. (1) and which like (1) can be diagonalized by a Bogoliubov transformation. They find typical mode mixing effects in the excitation spectrum. Their susceptibilities, like ours, have poles at the frequency of each normal mode.

Our calculations may also be compared with the recent work of Maugin.[39] Like Bar'yakhtar and Chupis, he considers a ferroelectric ferromagnet with a Lagrangian which is a power series in $\vec{P}$ and $\vec{M}$. Like us, however, he uses phenomenological equations of motion. Maugin does not give explicit expressions for susceptibilities, although they are derivable by his method; instead, he directly introduces coupling to the electromagnetic field equations in order to discuss polariton propagation. We have not dealt with polaritons, although it would be possible and interesting to derive their properties from our expressions for the susceptibilities together with the standard account[40] for electromagnetic wave propagation in magnetoelectric materials.

Finally, it is worth remarking that the present method is of fairly wide applicability. Although the use of equations of motion similar to (15) and (16) to obtain dynamical information from a Landau free-energy expression has been known for many years, it seems that the method is not much applied in practice. For example, in improper ferroelectrics such as boracites[34,41] there is an anomaly in the static dielectric constant due to coupling between the ferroelectric moment P and the primary order parameter. A term involving P^2, such as the β_2 term in Eq. (4), is introduced into the free energy in order that the theory should have enough flexibility to account for the range of observed anomalies. It should be possible and of value to use equations of motion to obtain detailed dynamical predictions from the free-energy expressions.

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