

Optical coupling to spin waves in the cycloidal multiferroic BiFeO₃

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The magnon and optical phonon spectrum of an incommensurate multiferroic such as BiFeO₃ is considered in the framework of a phenomenological Landau theory. The resulting spin wave spectrum is quite distinct from commensurate substances due to soft mode anisotropy and magnon zone folding. The former allows electrical control of spin wave propagation via reorientation of the spontaneous ferroelectric moment. The latter gives rise to multiple magnetodielectric resonances due to the coupling of optical phonons at zero wave vector to magnons at integer multiples of the cycloid wave vector. These results show that the optical response of a multiferroic reveals much more about its magnetic excitations than previously anticipated on the basis of simpler models.

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The coupling between different types of correlated electron order in “multiferroic” materials possessing simultaneous magnetism and ferroelectricity gives rise to several interesting phenomena.^{1–4} This coupling leads to rather complex broken-symmetry phases⁵ and excitation spectra. Recent examples are the magnetically induced ferroelectricity in TbMnO₃ (Ref. 2) and the switching of the magnetic state by an electrical probe observed in BiFeO₃.⁶ Crystals of these two materials show incommensurate magnetic order: in TbMnO₃, the incommensurate order established at 41 K is believed to generate the spontaneous polarization observed at 28 K, while in BiFeO₃, the cycloidal antiferromagnetic order is established at 650 K, well below the ferroelectric transition at 1120 K. The cycloid disappears in a strong (18 T) magnetic field⁷ or in thin films.⁸

This Brief Report studies the excitations and electromagnetic response in a cycloidal multiferroic such as bulk BiFeO₃. The combination of incommensurate order and magnetoelectric coupling is found to give a strong coupling between a long-wavelength electric field and spin waves at multiples of the cycloid wave vector. This leads to a series of resonances in the dielectric constant at integer and irrational multiples of a fundamental frequency determined by the magnon energy at the cycloid wave vector. The lowest-lying resonances created by this effect should be visible in standard transmission and reflectivity measurements at room temperature in the far infrared frequency range (below the lowest optical phonon at 2 THz). Recent Raman and optical reflectivity spectroscopy studies of bulk BiFeO₃ (Ref. 9) focused on the optical phonon resonances, without any interpretation of the far IR region. The optical phonon spectra seem to be well understood from first principles calculations.¹¹ Nevertheless, the latter completely ignores the underlying cycloidal magnetic structure and its magnetoelectric character. Our work reveals a rich subphonon dielectric response not yet explored by optical experiments or first principle calculations. Aside from allowing a direct observation of the basic physics of multiferroic coupling in BiFeO₃ and related materials, this effect could be used in devices based on electronic excitation of spin waves¹⁰ or in the development of fast magnetic probes for magnetic domain switching.

It has been known for many years that magnetoelectric coupling in uniformly ordered materials mixes spin waves (magnons) and polarization waves (optical phonons).^{12,13} This gives rise to low-frequency magneto-optical resonances in the dielectric susceptibility, the so-called electromagnon excitations, which may be visible in infrared experiments.^{3,4} However, the resonance frequencies are primarily determined by the zero-wave-vector magnon frequencies. The mixing with finite-wave-vector magnons found here results specifically from the *incommensurate* magnetic order; while such incommensurate order complicates the calculation of excitation spectra because a finite-wave-vector analysis is now necessary, incommensurate order is a common feature of many of the most studied multiferroic materials. Although recent theoretical work has clarified the relationship between ferroelectricity and spiral ferromagnetic order,^{14,15} the characteristic features of electromagnon excitations in incommensurate magnets seem not to have been studied before.

This Brief Report assumes that the ground state consists of a uniform polarization and an incommensurate magnetic structure, as in many important multiferroic materials; an interesting effect when the polarization and magnetization are both periodic and commensurate with each other has recently been discussed.¹⁶

Our calculation is based on a dynamical Ginzburg-Landau treatment of the coupled ferromagnetic, antiferromagnetic, and polarization orders in a cycloidal ground state and an applied ac electrical field, as shown in Fig. 1. It is assumed that the system is far below its critical temperature so that thermal fluctuations can be ignored in the dynamics. The long-period incommensurate cycloid is produced in our model by a Lifshitz term in the effective Ginzburg-Landau free energy; the existence of such a term was previously argued^{7,17–19} as the unique symmetry-allowed explanation for the observed order. The model free energy is

$$F = \frac{GL^4}{4} + \frac{AL^2}{2} + \frac{c\sum_i(\nabla L_i)^2}{2} - \alpha\mathbf{P} \cdot [\mathbf{L}(\nabla \cdot \mathbf{L}) + \mathbf{L} \times (\nabla \times \mathbf{L})] - \mathbf{P} \cdot \mathbf{E} + \frac{rM^2}{2} + \frac{aP_z^2}{2} + \frac{uP_z^4}{4} + \frac{a_\perp(P_x^2 + P_y^2)}{2}. \quad (1)$$

Here, $L = |\mathbf{M}_1 - \mathbf{M}_2|$ is a Néel vector describing the staggered

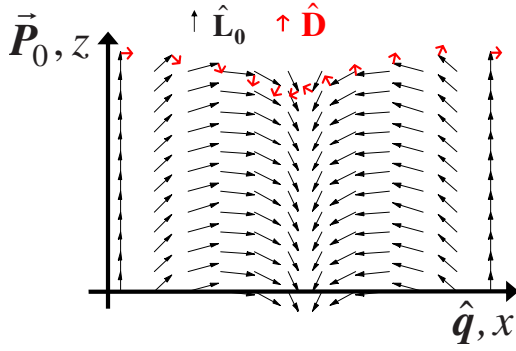


FIG. 1. (Color online) Antiferromagnetic lattice with harmonic cycloid order. The cycloid plane is pinned by the polarization \mathbf{P}_0 , with arbitrary propagation direction $\hat{\mathbf{q}}$ in the plane perpendicular to \mathbf{P}_0 . We also depict the tangent vector $\hat{\mathbf{D}}$ related to phase fluctuations of the cycloid.

sublattice magnetization, $M = |\mathbf{M}_1 + \mathbf{M}_2|$ is the total magnetization of the material, and P_z is the magnitude of the ferroelectric polarization along $\hat{\mathbf{z}}$ [the cubic (111) and equivalent directions in BiFeO_3]. Many possible terms have been omitted from the free energy as absent or unimportant in BiFeO_3 . Note that in the absence of the Lifshitz term, the antiferromagnetic (AFM) and ferroelectric orders are decoupled, and the ground state is a commensurate, isotropic Heisenberg antiferromagnet with $|\mathbf{L}_0|^2 = \frac{A}{G}$ and an easy-axis ferroelectric with uniform polarization given by $\mathbf{P}_0 = P_0 \hat{\mathbf{z}}$, $P_0^2 = -a/u$. Clearly, $A < 0$ and $r > 0$ for an antiferromagnetic ground state, while $a < 0$ and $a_\perp > 0$ for a ferroelectric ground state.

The Lifshitz term induces an incommensurate cycloidal order in which the antiferromagnetic moment rotates in an arbitrary plane including $\hat{\mathbf{z}}$. It also increases the magnitude of L_0 and P_0 . Our reference ground state is a cycloid with

$$\mathbf{L}_0(x) = L_0[\cos(qx)\hat{\mathbf{z}} + \sin(qx)\hat{\mathbf{x}}]. \quad (2)$$

Here, the cycloid direction has been chosen along $\hat{\mathbf{x}}$. The pitch is $q = \alpha P_0/c$ and the magnitudes of antiferromagnetic and polar order are $L_0^2 = (-A + \alpha^2 P_0^2/c)/G$ and $P_0^2 = (-a + \alpha^2 L_0^2/c)/u$. A check on the above indicates that there are two zero-energy symmetry actions for fixed \mathbf{P} : changing the cycloid phase and rotating the cycloid direction in the xy plane. The displacement for the phase change from the transformation $qx \rightarrow qx + \phi/L_0$ is

$$\delta \mathbf{L} = \phi[\cos(qx)\hat{\mathbf{x}} - \sin(qx)\hat{\mathbf{z}}]. \quad (3)$$

We can use the shorthand $\hat{\mathbf{D}}(x)$ for this spin vector direction transverse to the local ground-state spin direction and write $\delta \mathbf{L} = \phi \hat{\mathbf{D}}(x)$ for the phase change. The displacement for the cycloid direction change due to an infinitesimal rotation $q\hat{\mathbf{x}} \rightarrow q(\hat{\mathbf{x}} + \eta \hat{\mathbf{y}})$ is $\delta \mathbf{L} = \eta L_0 q y \hat{\mathbf{D}}(x) + \eta L_0 \sin(qx) \hat{\mathbf{y}}$. This cycloid direction symmetry is similar to the one found in smectic liquid crystals in that it requires large displacements relative to the original state at some point in the crystal.

The linearized equations of motion for the ferroelectric and antiferromagnetic order parameters are

$$\frac{\partial^2 \mathbf{L}}{\partial t^2} = -r(\gamma L_0)^2 \left[\frac{\delta F}{\delta \mathbf{L}} - \left(\hat{\mathbf{L}}_0 \cdot \frac{\delta F}{\delta \mathbf{L}} \right) \hat{\mathbf{L}}_0 \right], \quad (4a)$$

$$\frac{\partial^2 \mathbf{P}}{\partial t^2} = -f \frac{\delta F}{\delta \mathbf{P}}. \quad (4b)$$

Here, γ is a gyromagnetic ratio with dimensions of $(\text{sG})^{-1}$, while f has dimensions of s^{-2} and plays a similar role in the ferroelectric equation of motion. In the above polarization equation, we have ignored damping and the possible Poisson-bracket term between \mathbf{P} and \mathbf{M} .²⁰ The coupled spin and polarization equations are solved in terms of the parametrization,

$$\delta \mathbf{L} = \phi(\mathbf{r}) e^{-i\omega t} \hat{\mathbf{D}}(x) + \psi(\mathbf{r}) e^{-i\omega t} \hat{\mathbf{y}}, \quad (5a)$$

$$\delta \mathbf{P} = \delta \mathbf{p}(\mathbf{r}) e^{-i\omega t}. \quad (5b)$$

The field $\phi(\mathbf{r})$ denotes phase fluctuations of the cycloid ground state, while $\psi(\mathbf{r})$ refers to spin fluctuations out of the cycloid (xz) plane. The field $\delta \mathbf{p}(\mathbf{r}) = \mathbf{P} - \mathbf{P}_0$ denotes optical phonon fluctuations related to longitudinal and transverse vibrations of the ferroelectric moment \mathbf{P} .²³

Calculating $\delta F/\delta \mathbf{L}$ to linear order in the displacements, and inserting into Eq. (4a), leads to

$$[\omega'^2 + c\nabla^2] \phi = 2cq \sin(qx) (\partial_y \psi) - \alpha L_0 (\nabla \times \delta \mathbf{p}) \cdot \hat{\mathbf{y}}, \quad (6a)$$

$$[\omega'^2 - cq^2 + c\nabla^2] \psi = -2cq \sin(qx) (\partial_y \phi) - \alpha L_0 [2q \cos(qx) \times (\delta \mathbf{p}_y) - (\nabla \times \delta \mathbf{p}) \cdot \hat{\mathbf{D}}], \quad (6b)$$

with $\omega' = \omega/(\gamma L_0 \sqrt{r})$ defining the frequency in units of $\sim 10^{12}$ rad/s. The equation of motion for the polarization becomes

$$\xi \omega'^2 (\delta \mathbf{p}) = \frac{\delta F}{\delta \mathbf{P}} = a_\parallel (\delta \mathbf{p}_z) + a_\perp (\delta \mathbf{p}_\perp) - \alpha L_0 [q \cos(qx) (\psi) \hat{\mathbf{y}} + (\nabla \phi) \times \hat{\mathbf{y}} - (\nabla \psi) \times \hat{\mathbf{D}}] - \mathbf{E}, \quad (6c)$$

where we define $\xi = r(\gamma L_0)^2/f$ (~ 10 in BiFeO_3), $a_\parallel = -2a + 3\alpha^2 L_0^2/c$, and the ac electric field is $\mathbf{E} e^{-i\omega t}$.

Some intuition for Eqs. (6a)–(6c) may be gained by considering their invariance under rotations of the cycloid in the xy plane. Consider the $\omega=0$ symmetry operation $\phi \rightarrow \eta q y$, $\psi \rightarrow \eta \sin(qx)$, with $\delta \mathbf{p}$ left unchanged. This creates no terms in both sides of Eq. (6a). In Eq. (6b), the left hand side becomes $-2cq^2 \eta \sin(qx)$, which cancels the term generated in the right hand side due to the y dependence in ϕ . For the square brackets in Eq. (6c), the first term adds $q \cos(qx) \times [\eta \sin(qx)] \hat{\mathbf{y}}$, with the third term $-\nabla[\eta \sin(qx)] \times \hat{\mathbf{D}}$ giving the desired cancellation.

In the commensurate limit $\alpha, q \rightarrow 0$ and we recover two transverse AFM fluctuation modes with $\omega'^2 = ck^2$. There are two dispersionless polarization wave modes transverse to \mathbf{P}_0 with frequency $\omega'^2 = a_\perp/\xi$ and one longitudinal mode with frequency $\omega'^2 = a_\parallel/\xi$. The combination orthogonal to $\phi \hat{\mathbf{D}}$, and $\psi \hat{\mathbf{y}}$, $S = \hat{\mathbf{L}}_0 \cdot \delta \mathbf{L}$, is constant in time in the equation of

motion above but decays dissipatively if non-Poisson bracket terms are kept. It is not expected to modify the above propagating modes. For $k \rightarrow 0$ in the ϕ mode, we obtain a symmetry (the phase shift) which should be nondissipative. For $k \rightarrow 0$ in the ψ mode, there should be some finite dissipation.

We solve the system Eqs. (6a)–(6c) using the ansatz,

$$[\phi(\mathbf{r}), \psi(\mathbf{r}), \delta\mathbf{p}(\mathbf{r})] = \sum_n [\phi_n, \psi_n, (\mathbf{p})_n] e^{inqx} e^{ik\cdot\mathbf{r}}, \quad (7)$$

with n an integer running from $-\infty$ to ∞ and the restriction $|k_x| < q/2$. The complex numbers ϕ_n , ψ_n , and $(p_i)_n$ are independent of \mathbf{r} but have a \mathbf{k} dependence. Substitution of this ansatz into Eqs. (6a)–(6c) yields a linear system of equations whose characteristic polynomial determines the resonance frequencies.

Consider the unmixed spin waves in the limit $(\mathbf{p})_n \rightarrow 0$. Substitution of the ansatz into Eqs. (6a) and (6b) gives

$$[\omega'^2 - c\tilde{k}^2]\phi_n - ck_y(\psi_{n-1} - \psi_{n+1}) = 0, \quad (8a)$$

$$[\omega'^2 - c(\tilde{k}^2 + q^2)]\psi_n + ck_y(\phi_{n-1} - \phi_{n+1}) = 0, \quad (8b)$$

with $\tilde{k}^2 = (k_x + nq)^2 + k_y^2 + k_z^2$. We see that modes propagating along the cycloid plane (with $k_y = 0$) are simple plane waves with cyclon (ϕ) and out of plane (ψ) dispersions given by $\omega'^2 = c\tilde{k}^2$ and $\omega'^2 = c(\tilde{k}^2 + q^2)$, respectively. As expected from symmetry, the cyclon mode remains soft, but the out of plane mode ψ acquires a gap due to the pinning of the cycloid plane by the ferroelectric moment. Note that the ψ_0 gap equals the cyclon energy at $n = \pm 1$. At $\mathbf{k} = 0$, the AFM resonance modes are simply $\omega'_n = \sqrt{cq}|n|$ and $\omega'_n = \sqrt{cq}\sqrt{n^2 + 1}$ for the cyclon and out of plane excitations, respectively. For BiFeO₃, $cq^2 \sim 1$,^{18,19} and the modes are equally spaced by approximately 10^{12} rad/s intervals (0.16 THz or 10 K).

If the propagation vector has a small projection along the k_y direction, the dispersion curves in the cycloid plane will repel each other whenever they intersect. This leads to a series of small gaps (anticrossings) in the propagation frequency as a function of the reduced k_x , similar to the effect discussed by Bar'yakhtar and Stefanovskii in an helical ferromagnet.²¹ Apart from these small gaps, the high-frequency dispersion curves are nearly unaffected by the incommensurate order. A very different situation is found for the low-frequency modes along the nontrivial y direction. Consider, for example, the lowest-frequency mode ϕ_0 . Solving Eqs. (8a) and (8b) within $\mathcal{O}(k^6)$ leads to

$$\omega'^2 \approx c \left[k_x^2 + k_z^2 + \frac{3k_y^4}{8q^2} - \frac{k_x^2 k_y^2}{q^2} \right]. \quad (9)$$

This soft mode dispersion is strongly anisotropic and may be useful for electrical control of the spin wave group velocity via switching of the \mathbf{P}_0 direction. A similar effect is found for phase fluctuations in smectic liquid crystals and in an helical ferromagnet such as MnSi.²² The anisotropy is related to the \mathbf{q} rotation symmetry discussed above, which forbids a k_y^2 term in the dispersion.

A full numerical solution for propagation along y is shown in Fig. 2. Note that in addition to the soft mode an-

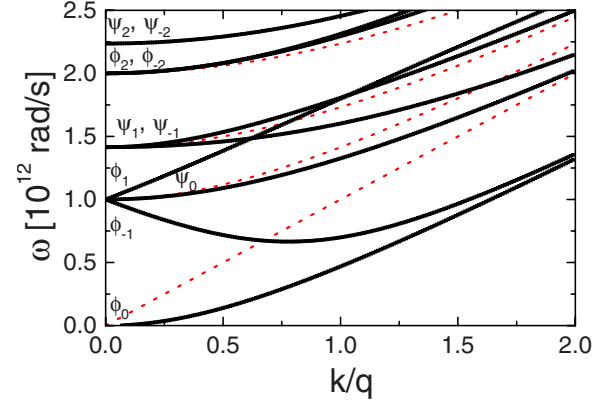


FIG. 2. (Color online) Spin wave spectra for a cycloidal multiferroic including one optical phonon mode (not shown). The solid lines are for propagation along the nontrivial direction perpendicular to the cycloid plane (y in Fig. 1). The dashed lines are the spectra for propagation along z , including zone folding. The magnon modes at nq are labeled by ϕ_n (cyclon) and ψ_n (out of plane).

isotropy effect, $k_y \neq 0$ admixes the modes at nq and $-nq$, splitting their dispersions. Moreover, the second lowest-frequency mode (connected to $\phi_{\pm 1}$) acquires a negative group velocity.

The full solution of Eqs. (6a)–(6c) with $(\delta\mathbf{p}) \neq 0$ shows avoided crossings between the optical phonon dispersion and magnon branches at finite k . At these anticrossings, the spin wave excitations are highly mixed with the polarization wave. However, an optical experiment only probes modes at $\mathbf{k} \approx 0$ due to the large value of the velocity of light when compared to the magnon velocity ($\sim 10^6$ cm/s). One can ask whether any $n > 0$ mode responds to optical excitation with wavelength much larger than $2\pi/q \approx 600$ Å. The answer is affirmative as now shown by calculation of the ac electric susceptibility.

An ac electric excitation $\mathbf{E}e^{-i\omega t}$ may excite spin waves due to the appearance of magnetoelectric fields such as $2q \cos(qx)(\delta p_y)$ on the right hand side of Eq. (6b). This couples ψ to an optical phonon at $k=0$. Solving the system of equations shows that the ac electrical susceptibility tensor $(p_i)_0 = \chi_{ij} E_j$ is diagonal for our model, with $\chi_{xx} = -1/(\xi\omega'^2 - a_{\perp})$ and $\chi_{zz} = -1/(\xi\omega'^2 - a_{\parallel})$. Therefore, the optical response with light polarized within the cycloid plane contains no magnetic anomaly but only simple poles at the bare optical phonon frequencies. However, if the light is polarized along the direction perpendicular to the cycloid plane, the situation is quite different,

$$\chi_{yy}(\omega) = \frac{-(\omega'^2 - 2cq^2)}{(\omega'^2 - \Omega_{\text{PH}}'^2)(\omega'^2 - \Omega_{\text{AFM}}'^2)}. \quad (10)$$

This ac susceptibility has two poles at the following shifted phonon and AFM ($\psi_{\pm 1}$ mode) frequencies: $\Omega_{\text{PH}}'^2 = a_{\perp}/\xi + 2cq^2$ and $\Omega_{\text{AFM}}'^2 = 2cq^2 - 2(\alpha q L_0)^2/a_{\perp}$.

Hence, we conclude that the simplest model for BiFeO₃ already contains a low-frequency magneto-optical resonance. Note the prominent importance of magnon zone folding: Even though the ac electric field is a zero-wave-vector exci-

tation, it couples to a magnon at wave vector $\pm q$. This is a special feature of electromagnetic excitations in an incommensurate multiferroic material.

The magnon excitations of a cycloid with wave vector q may violate momentum conservation by a multiple of q (a reciprocal lattice vector for the cycloid). In the case of a multiferroic material with incommensurate magnetic order, this allows the possibility of observing additional magnetodielectric resonances due to the coupling of a zero-wave-vector phonon to magnon modes at other multiples of q . To see this effect, consider a contribution to the free energy in the form of an easy-plane anisotropy $\frac{\lambda}{2}(\mathbf{P}\cdot\mathbf{L})^2$, which is known to add anharmonicity to the cycloid order.¹⁷ To first order in λ , this term adds a third harmonic to Eq. (2). This gives an additional magnetoelectric contribution to the right side of the equation determining the cyclon field ϕ [Eq. (6a)]: $\lambda P_0 L_0 / 2 [\cos(2qx)(\delta p_x) - \sin(2qx)(\delta p_z)]$. As a result, the ac electric susceptibilities χ_{xx} , χ_{zz} develop poles at the magnon modes $\phi_{\pm 2}$. Similarly, the out of plane field ψ is excited by a term of the form $\cos(3qx)(\delta p_y)$, showing that χ_{yy} has an additional electromagnon pole at the mode $\psi_{\pm 3}$. Considering additional powers of λ (higher harmonics of the cycloid) shows that higher-frequency resonances at nq are present, with strength falling off as higher powers of λ .

In conclusion, we determined the electromagnon spectra

for a class of cycloidal multiferroics including bulk BiFeO₃. A simple Landau-Ginzburg model shows that a low-frequency optical probe will couple to magnons at multiples of the cycloid wave vector, leading to a series of magnetodielectric resonances at integer n and irrational $\sqrt{1+n^2}$ multiples of a fundamental cyclon frequency (ϕ_n and ψ_n magnons, respectively). Interestingly, only one mode ($\psi_{\pm 1}$) becomes electric dipole active due to the strong linear magnetoelectric effect driving the harmonic cycloid order. The remaining modes acquire a small electric dipole character due to weaker quadratic magnetoelectric effects and anharmonicity in the cycloid order. As a result, optical experiments such as transmittivity, reflectivity, and Raman spectroscopy will reveal much more about the magnetic order of multiferroics than previously expected on the basis of homogeneous models. For example, the direction dependence and intensity of higher resonances is directly related to anharmonicity in the magnetic order. Other incommensurate multiferroics may show similar phenomena even if the details of the multiferroic coupling are different.

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²³While there are many optical phonons in a ferroelectric, this field \mathbf{P} should be thought of as describing the particular polar phonon that goes soft at the ferroelectric transition.