The Spin State and Spectroscopic Modes of Multiferroic BiFeO₃

Randy S. Fishman,¹ Jason T. Haraldsen,²,³ Nobuo Furukawa,⁴ and Shin Miyahara⁵

¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
²Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
³Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
⁴Department of Physics and Mathematics, Aoyama Gakuin University, Sagamihara, Kanagawa 229-8558, Japan and
⁵Asia Pacific Center for Theoretical Physics, Pohang University of Science and Technology, Pohang, Gyeongbuk, 790-784, Korea

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Spectroscopic modes provide the most sensitive probe of the very weak interactions responsible for the properties of the long-wavelength cycloid in the multiferroic phase of BiFeO₃ below \( T_N \approx 640 \text{ K} \). Three of the four modes measured by THz and Raman spectroscopies were recently identified using a simple microscopic model. While a Dzyaloshinskii-Moriya (DM) interaction \( D \) along \([-1,2,-1]\) induces the cycloid with wavevector \((2\pi/a)(0.5 + \delta, 0.5, 0.5 - \delta) (\delta \approx 0.0045)\), easy-axis anisotropy \( K \) along the \([1,1,1]\) direction of the electric polarization \( P \) induces higher harmonics of the cycloid, which split the \( \Psi_1 \) modes at 2.49 and 2.67 meV and activate the \( \Phi_2 \) mode at 3.38 meV. However, that model could not explain the observed low-frequency mode at about 2.17 meV. We now demonstrate that an additional DM interaction \( D' \) along \([1,1,1]\) not only produces the observed weak ferromagnetic moment of the high-field phase above 18 T but also activates the spectroscopic and inelastic neutron-scattering measurements.

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I. INTRODUCTION

As the only known room-temperature multiferroic, BiFeO₃ continues to attract a great deal of attention. Multiferroic materials offer the tantalizing prospect of controlling magnetic properties with electric fields or electric polarizations with magnetic fields. Although the ferroelectric transition temperature \( T_c \approx 1100 \text{ K} \) of BiFeO₃ is far higher than its Néel temperature \( T_N \approx 640 \text{ K} \), the electric polarization \( P \) is enhanced by its coupling to the long-wavelength cycloid below \( T_N \). As a result, the magnetic domain distribution below \( T_N \) can be manipulated by an electric field.

Before BiFeO₃ can be used in technological applications, however, it is essential to understand the microscopic mechanisms and interactions responsible for its magnetic behavior. At frequencies above a few meV up to about 70 meV, the spin-wave (SW) spectrum of BiFeO₃ has been used to determine the nearest-neighbor and next-nearest neighbor exchange interactions \( J_1 \approx -4.5 \text{ meV} \) and \( J_2 \approx -0.2 \text{ meV} \) between the \( S = 5/2 \text{ Fe}^{3+} \) spins on a pseudo-cubic lattice with lattice constant \( a \approx 3.96 \text{ Å} \). As shown in Fig.1(a), \( J_1 \) is the antiferromagnetic (AF) interaction between spins on neighboring \((1,1,1)\) planes separated by \( c = a/\sqrt{3} \) while \( J_2 \) is the AF interaction between neighboring spins on each hexagonal layer.

Below \( T_N \), a long-wavelength cycloid with wavevector \( Q = (2\pi/a)(0.5 + \delta, 0.5, 0.5 - \delta) (\delta \approx 0.0045)\) is produced by the Dzyaloshinskii-Moriya (DM) interaction \( D = D\hat{y}' \) along \( \hat{y}' = [-1,2,-1] \) (all unit vectors are assumed normalized to one). As shown in Fig.1(b), the spins of the cycloid lie predominantly in the \((-1,2,-1)\) plane normal to \( \hat{y}' \).

Whereas the high-frequency portion of the SW spectrum determines the Heisenberg exchange interactions, the low-frequency modes measured by THz and Raman spectroscopies can be used to determine the small microscopic interactions that control the cycloid. Four modes have been detected at frequencies of 2.17, 2.49, 2.67, and 3.35 meV. By comparison, a model with the single DM interaction \( D \) only produces a single spectroscopically-active mode labeled \( \Psi_1 \) at about 2.37 meV.

A more realistic model also contains the easy-axis
anisotropy $K$ along $\mathbf{z}' = [1, 1, 1]$, parallel to the electric polarization $\mathbf{P}$. When $K > 0$, $\Psi_1$ splits into two and $\Phi_2$ at 3.38 meV is activated. Although this model successfully described the upper three spectroscopic modes, with predicted frequencies very close to the measured frequencies, it failed to explain the low-frequency 2.17 mode. In addition, it provides conflicting estimates for $K$ based on spectroscopic and inelastic neutron-scattering measurements.

Several authors have examined the effects of another DM interaction $\mathbf{D}' = D' \mathbf{z}'$ between neighboring hexagonal layers. For a G-type AF, $D'$ produces a weak ferromagnetic moment along $\mathbf{y}'$ due to the canting of the uniform moments on each hexagonal plane. The moment $M_0 = 2\mu_0 S_0 \Psi_0 \approx 0.03\mu_0 \Psi_0$ was subsequently observed in the metamagnetic phase above 18 T. Below 18 T, $D'$ was predicted to induce an oscillatory component of the cycloid along $\mathbf{y}'$, which has recently been confirmed by neutron-scattering measurements.

Based on a model that includes both $D$ and $D'$ in addition to the easy-axis anisotropy $K$, we evaluate the spin state and spectroscopic modes of BiFeO$_3$. Even when $K = 0$, $D'$ induces higher harmonics of the cycloid that split $\Psi_1$ and activate $\Phi_2$. More remarkably, $D'$ activates $\Psi_0$ and $\Phi_1$ at the cycloidal wavevector.

We believe that these nearly-degenerate modes are responsible for the low-frequency 2.17 meV peak observed in spectroscopy measurements. Although a model with $K = 0$ can produce four spectroscopic modes, the $\Psi_1$ selection rules are reversed and their mode frequencies are too small. Therefore, both $D'$ and $K$ are required to explain the experimental measurements. With $D' \approx 0.054$ meV, corresponding to the observed value $S_0 = 0.015$, we estimate that $D \approx 0.11$ meV and $K \approx 0.0035$ meV, which also provide a good description of inelastic neutron-scattering measurements below 5 meV.

This paper is divided into seven sections. Section II constructs the spin state of BiFeO$_3$. Section III evaluates the spin dynamics of that state, Section IV evaluates the spectroscopic modes of that state, and Section V discusses the selection rules for those modes. Section VI discusses the inelastic neutron-scattering spectrum for the low-frequency modes. Section VII contains a brief conclusion. Results for the SW intensities are provided in Appendix A. The polarization and magnetic matrix elements are provided in Appendix B.

II. SPIN STATE

With $\mathbf{P} = P\mathbf{z}'$, the three magnetic domains have cycloidal wavevectors $\mathbf{Q} = (2\pi/a)[0.5 + \delta, 0.5, 0.5 - \delta]$ (domain 1), $(2\pi/a)[0.5, 0.5 + \delta, 0.5 - \delta]$ (domain 2), or $(2\pi/a)[0.5 + \delta, 0.5 - \delta, 0.5]$ (domain 3). By contrast, the G-type AF stabilized by a magnetic field, doping, or in thin films has wavevector $(2\pi/a)[0.5, 0.5, 0.5]$. In our discussion of the selection rules governing the spectroscopic modes in Section V, we will assume that all three domains are equally populated. Since the spin state and dynamics are the same for all three domains, we now concentrate on domain 1 with $x' = [1, 0, -1]$ and $y' = [-1, 2, -1]$, as shown in Fig.1(b).

The spin state and SW excitations of BiFeO$_3$ are evaluated from the Hamiltonian

$$H = -J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - K \sum_i S_{iz}^2$$

$$-D \sum_{\mathbf{R}_j = R_i + a(x-z)} \mathbf{y}' \cdot (\mathbf{S}_i \times \mathbf{S}_j)$$

(1)

$$-D' \sum_{\mathbf{R}_j = R_i + a(x-z)} (-1)^{R_{iz}/c} \mathbf{z}' \cdot (\mathbf{S}_i \times \mathbf{S}_j).$$

The first and second exchange terms contain sums $\langle i, j \rangle$ and $\langle i, j \rangle'$ over nearest and next-nearest neighbors on the pseudo-cubic lattice. The third term arises from the easy-axis anisotropy along $\mathbf{z}'$ and the fourth term from the DM interaction with $\mathbf{D} = D\mathbf{y'}$.

Compared to the model for BiFeO$_3$ introduced in Ref. and studied in our earlier work, $H$ adds the DM interaction $\mathbf{D}' = D'\mathbf{z}'$. This term alternates in sign with increasing $z'$: $(1)^{R_{iz}/c}$ changes sign from layer $n$ to layer $n+1$ so the DM interaction $(-1)^{R_{iz}/c}/D'$ between layers $n$ and $n+1$ has opposite sign to the DM interaction between layers $n+1$ and $n+2$. Hence, the DM interaction $\mathbf{D}'$ has the same wavevector $(2\pi/a)[0.5, 0.5, 0.5]$ as a G-type AF.

Because $\delta \approx 1/222$, a unit cell containing $M = 222$ sites within each of two neighboring $(1,1,1)$ planes is used to characterize the distorted cycloid. In zero magnetic field, the cycloid can be expanded in odd harmonics of the fundamental wavevector $\mathbf{Q}$ (even harmonics are also required in non-zero fields). If $S_{y'}(\mathbf{R})$ is proportional to $S_{z'}(\mathbf{R})$, then

$$S_{y'}(\mathbf{R}) = (-1)^{R_{iz}/c} \sqrt{(1 - \kappa^2) S^2 - S_{z'}(\mathbf{R})^2} \text{sgn}(\sin(2\pi\delta R_{z'}/a)),$$

(2)

$$S_{y'}(\mathbf{R}) = \kappa \sqrt{S^2 - S_{z'}(\mathbf{R})^2} \text{sgn}(\sin(2\pi\delta R_{z'}/a)),$$

(3)

$$S_{z'}(\mathbf{R}) = (-1)^{R_{iz}/c} S \sum_{m=0}^{\infty} C_{2m+1} \cos((2m+1)2\pi\delta R_{z'}/a).$$

(4)

Odd-order coefficients $C_{2m+1}$ in $S_{z'}(\mathbf{R})$ satisfy $\sum_{m=0}^{\infty} C_{2m+1} = 1$. Although $S_{y'}(\mathbf{R})$ (unlike $S_{z'}(\mathbf{R})$ and $S_{z'}(\mathbf{R})$) does not change sign from one layer to the next, the average value of $S_{y'}(\mathbf{R})$ vanishes and there is no net moment in any direction. The ratio $S_{y'}(\mathbf{R})/S_{z'}(\mathbf{R})$ has magnitude $\kappa/\sqrt{1 - \kappa^2}$, which is proportional to $D'/J_1 \ll 1$. Hence, the tilting angle $\tau$ indicated in Fig.1(b) satisfies the relation $\tan \tau = \kappa/\sqrt{1 - \kappa^2} \approx \kappa$.

Although the cycloid remains coplanar for each hexagonal layer, the cycloidal planes rotate by $2\tau$ from one layer to the next.

The parameters of the spin state are evaluated by minimizing the energy $E = \langle \mathcal{H} \rangle$ in a unit cell $x'y'z'$ of dimensions $15,000a \times a \times 2c$ containing two $(1,1,1)$ layers.
Open boundary conditions are employed along the $x'$ direction. With the exchange interactions $J_1 = -4.5$ meV and $J_2 = -0.2$ meV fixed at the values required to describe the SW spectrum\textsuperscript{5,9} at high frequencies, the four variational parameters are $\delta$, $\kappa$, $C_3$, and $C_5$. A solution with $\delta = 1/222$ is obtained by varying the DM interaction $D$ for fixed $K$. After minimizing the energy, we verify that the corresponding spin state provides at least a metastable minimum by checking that the classical forces on each spin vanish.

With a magnetic field oriented along $z'$, the metamagnetic state observed\textsuperscript{25} above 18 T can be written
\begin{align}
S_1 &= S(\cos \theta \cos \phi, \cos \theta \sin \phi, \sin \theta), \quad (5) \\
S_2 &= S(-\cos \theta \cos \phi, \cos \theta \sin \phi, \sin \theta), \quad (6)
\end{align}

for $R_{z'} = 2mc$ and $(2m + 1)c$, respectively. Extrapolating to zero field with $\theta = 0$, we obtain $\tan 2\phi = D'/J_1$. Hence, the weak ferromagnetic moment of the metamagnetic phase is
\begin{equation}
M_0 = 2\mu_B S_0 = 2\mu_B S \sin \phi \approx \frac{\mu_B S D'}{J_1}, \quad (7)
\end{equation}

independent of $D$, $K$, and $J_2$. Using $J_1 = -4.5$ meV and the experimental result\textsuperscript{6,25} $S_0 = 0.015$, we estimate that $|D'| = 0.054$ meV, which is slightly larger than the estimate $|D'| = 0.046$ meV provided in Ref.\textsuperscript{24}.

For the distorted cycloid given by Eqs.\textsuperscript{[24]}, it is straightforward to show that if $\delta \ll 1$, then $\kappa \approx D'/2J_1$. Therefore, the maximum cycloidal spin $|S_y'(R)|$ equals the weak ferromagnetic spin $S_0$ of the metamagnetic phase. For the tilting angle, we estimate $\tau \approx 0.34^\circ$, a bit smaller than the recent neutron-scattering\textsuperscript{25} estimate of $\sim 1^\circ$.

In Fig.2(a), we plot the DM interaction $D$ versus $S_0$ for several values of the anisotropy $K$ ranging from 0 to 0.0035 meV. For $K = 0$ and 0.0005 meV, $D$ increases slightly with $S_0$. But for $K \geq 0.001$ meV, $D$ decreases with $S_0$. Nevertheless, the variation of $D$ with $S_0$ is rather modest.

By contrast, the higher harmonics of the cycloid exhibit a much stronger variation with $S_0$. Fig.2(b) reveals that the ratio $C_3/C_1$ increases with $S_0$ for all $K$. Since $C_1 = 1 - \sum_{n=1}^{2n} C_{2n+1}$ and $|C_5| \ll |C_3|$, $C_1 \approx 1 - C_3$ and $C_3/C_1 \approx C_3/(1+C_3)$. For $K = 0$ and $S_0 > 0$, $C_3 > 0$ and
\begin{equation}
\langle S_{z'}^2 \rangle = \frac{1}{2} \sum_{n=0}^{\infty} \left( C_{2n+1} \right)^2 \approx \frac{1}{2} (1 - 2C_3) < \frac{1}{2}, \quad (8)
\end{equation}

Because the $D'$ interaction energy is optimized when the spins lie in the $x'y'$ plane, higher harmonics favor the $z'$ nodal regions of the cycloid. When $S_0$ is sufficiently small and $K > 0$, $C_3 < 0$ and $\langle S_{z'}^2 \rangle > 1/2$ so that higher harmonics favor the $z'$ antinodal regions of the cycloid. Experimentally, the ratio of the neutron-scattering intensity from the third to the first harmonics is given by $(C_3/C_1)^2$.

Notice that the third (and higher) harmonics can vanish for nonzero $S_0$ and $K$. When $S_0 = 0.015$, $C_3 < 0$ when $K$ is less than about 0.001 meV and $C_3 > 0$ when $K$ is greater than about 0.001 meV. For $K \approx 0.001$ meV, the higher harmonics of the cycloidal vanish and $\langle S_{z'}^2 \rangle = 1/2$.

III. SW EXCITATIONS

The SW frequencies are calculated using the equations-of-motion technique for non-collinear spins outlined in Ref.\textsuperscript{31}. A unit cell containing $M = 222$ sites on each of two hexagonal layers is constructed to evaluate the 2$M$ SW frequencies $\omega_n(q)$. SW intensities are obtained from the spin-spin correlation function defined by Eq.\textsuperscript{[A9]} in Appendix A. In the absence of damping, the inelastic scattering cross section $S(q, \omega)$ can be expanded as the sum over delta functions at each frequency:
\begin{equation}
S(q, \omega) = \sum_{n, \alpha} \left( 1 - (q_\alpha/q)^2 \right) \delta(\omega - \omega_n(q)) S^{(n)}_{\alpha\alpha}(q). \quad (9)
\end{equation}

The amplitudes $S^{(n)}_{\alpha\alpha}(q)$ are evaluated using Eq.\textsuperscript{[A11]}.
For fixed $S_0 = 0.015$, the SW frequencies are plotted in Fig.3 for $K = 0$, 0.001, and 0.002 meV. Although there are $2M$ modes for every wavevector $2\pi/a(0.5 + \eta, 0.5, 0.5 - \eta)$, plotted by the dashed lines, only a few of those modes have any significant intensity. Modes with intensity above an arbitrary cutoff are plotted in the dark lines.

When $K \approx 0.001$ meV in Fig.3(b), the higher harmonics of the cycloid vanish and the SW frequencies are similar to those for $S_0 = 0$ and $K = 0$ discussed in Ref.11. In the absence of harmonics, de Sousa and Moore\textsuperscript{12} labeled the SW frequencies $\omega_n(mQ)$ ($n = 1$ or 2) of a one-dimensional cycloid at multiples $m$ of the cycloidal wavevector $Q = 2\pi/\alpha a$ as $\Phi_m$ and $\Psi_m$. Using an extended zone scheme and assuming that $|m|\delta < 1$, $\omega_n(mQ)$ can be approximated by $\Phi_m = \Phi_1|m|$ and $\Psi_m = \Psi_11 + m^2$. These relations imply that $\Phi_1 = \Psi_0$, as seen in Fig.3(b), and that the $\Phi_{\pm m}$ and $\Psi_{\pm m}$ modes cross without repulsion at the zone center $q = 0$ and zone boundary $q = 0$.

Whether produced by the tilt $\tau$ or by the anisotropy $K$, higher odd harmonics of the cycloid introduce higher even harmonics in the Hamiltonian $H$. A $2mQ$ potential will split the $\Phi_{\pm m}$ and $\Psi_{\pm m}$ modes. As shown in Figs.3(a) and (c), the new $m = 1$ eigenmodes are labeled $\Phi_1(2)$ and $\Psi_1(2)$. Notice that $\Psi_0$ and $\Phi_1(1)$ are nearly degenerate for all $K$. Although too small to see in Fig.3, even $\Phi_{\pm 2}$ are split by anharmonicity.

**IV. SPECTROSCOPIC MODES**

Because the wavelength of far infrared light greatly exceeds atomic length scales, the SW modes measured by THz and Raman spectroscopies lie at the zone center $q = Q$ or $\eta = \delta$. A magnetic resonance (MR) mode has nonzero matrix element $\langle \delta | M_{n} | 0 \rangle$, where $|0\rangle$ is the ground state and $|\delta\rangle$ is an excited state with a single magnon of wavevector $Q$. An electromagnon (EM) mode has nonzero matrix element $\langle \delta | P_{\alpha}^{\text{ind}} | 0 \rangle$ so that the induced polarization directly couples the ground state to the excited state.

In order to evaluate the MR and EM matrix elements, we must first express the magnetic moment $M$ and induced polarization $P_{\alpha}^{\text{ind}}$ operators in terms of the spin operators $S_i$. The magnetic moment $M = 2\mu B\sum_{R_i} S_i$ contains a sum over the $2M$ unique sublattices. In BiFeO$_3$, the coupling between the cycloid and electric polarization is produced by the inverse DM mechanism\textsuperscript{34–35} with induced polarization

$$P_{\alpha}^{\text{ind}} = \lambda \sum_{R_i, R_j = R_i + e_{ij}} \left\{ e_{ij} \times (S_i \times S_j) \right\},$$

(10)

where the sum is restricted to the $2M$ sublattices using periodic boundary conditions. Within each $\{1,1,1\}$ plane, $e_{ij} = \sqrt{2}ax'$ connects spins at sites $R_i$ and $R_j$. So if $|0\rangle|S_i \times S_j |0\rangle$ points along $y'$, then $|0\rangle|P_{\alpha}^{\text{ind}} |0\rangle$ points along $z'$.

Expressions for the matrix elements $\langle \delta | M_{n} | 0 \rangle$ and $\langle \delta | P_{\alpha}^{\text{ind}} | 0 \rangle$ are provided in Appendix B. Although there is no simple relation between the MR matrix elements and the SW intensities, the MR and EM modes only appear at mode frequencies $\omega$ with $S_{\omega}^{(n)}(\delta) > 0$. Generally, $\Phi_n$ modes with $\langle \delta | M_{\nu} | 0 \rangle \neq 0$ also have nonzero SW intensities $S_{\omega}^{(n)}(\delta)$ and $S_{\omega'}^{(n)}(\delta)$. Hence, those modes...
excite spins within the $x'z'$ plane of the cycloid (neglecting its small tilt). On the other hand, $\Psi_{1\alpha}$ modes with $\langle \delta | M_{x'} | 0 \rangle \neq 0$ or $\langle \delta | M_z | 0 \rangle \neq 0$ also have $\langle \delta | [M_x^{(n)}] | \delta \rangle > 0$. Hence, those modes excite spins out of the $x'z'$ plane.

Zone-center modes with nonzero MR matrix elements are indicated by the filled circles in Fig.3. In addition to $H_0$, those modes excite spins out of the $x'z'$ plane.

FIG. 5: (Color online) (a) The frequencies of the predicted modes versus $S_0$ for $K = 0.0035$ meV. Horizontal dashed lines are the measured spectroscopic frequencies. \( \Phi_0 \) (solid) and $\Phi_{1\alpha}$ (dashed) versus $S_0$ for $K = 0.0035$ meV. Also plotted are the intensities $|\langle \delta | M_{x'} | 0 \rangle|/\mu_B$ for those modes $(\alpha' = y'$ for $\alpha = y$ and $\alpha' = x'$ or $\alpha' = z'$ for $\alpha = y'$) with $M = 222$. The normalized matrix element $|\langle \delta | M_{x'} | 0 \rangle|/\mu_B S_{\alpha'\alpha'}(\delta)^{1/2}$ is independent of $S_0$. The dash-dot curve plots the MR matrix element for $\Phi_{1\alpha}^{(1)}$ with $\alpha = y'$.

The measured SW intensities of the cycloid have the ratio $C_3/C_1 = -0.050$ or $(C_1/C_3)^2 = 400$. Elastic neutron-scattering and NMR measurements indicate that $(C_1/C_3)^2$ is 500 and 25, respectively. However, the NMR measurement may overestimate the third harmonic due to the high $^{57}$Fe isotope content of the sample. Our estimate for $(C_3/C_1)^2$ is in very good agreement with the elastic neutron-scattering result.
V. SELECTION RULES

We now consider the selection rules for the THz modes\textsuperscript{14,15} for a sample with the single polarization domain \( P = Pz' \), where \( z' = [1, 1, 1] \). As mentioned in Section II, the three possible magnetic domains have wavevectors \((2\pi/\alpha)(0.5 + \delta, 0.5, 0.5 - \delta), (2\pi/\alpha)(0.5, 0.5 + \delta, 0.5 - \delta), \) and \((2\pi/\alpha)(0.5 + \delta, 0.5 - \delta, 0.5) \). Since these domains have the same energy, we expect them to be equally populated. The mode spectrum was measured for crossed fields \( h_1 = [1, -1, 0] \) and \( h_2 = [1, 1, 0] \).

To predict the selection rules for BiFeO\(_3\), \( h_1 \) and \( h_2 \) are expressed in terms of the cycloidal unit vectors \( x' \), \( y' \), and \( z' \) as

\[
\begin{align*}
h_1 &= (x' - \sqrt{3}y')/2, \\
h_2 &= x'/2 + \sqrt{3}y'/3 + \sqrt{2}/3z', \tag{11}
\end{align*}
\]

in domain 1 with \( x' = [1, 0, -1] \) and \( y' = [-1, 2, -1] \);

\[
\begin{align*}
h_1 &= -(x' + \sqrt{3}y')/2, \\
h_2 &= x'/2 - \sqrt{3}y'/3 + \sqrt{2}/3z', \tag{12}
\end{align*}
\]

in domain 2 with \( x' = [0, 1, -1] \) and \( y' = [-2, 1, 1] \); and

\[
\begin{align*}
h_1 &= x', \\
h_2 &= (y' + \sqrt{2}z')/\sqrt{3}, \tag{13}
\end{align*}
\]

in domain 3 with \( x' = [1, -1, 0] \) and \( y' = [1, 1, -2] \). Although the following discussion assumes that all three domains are equally populated, our qualitative conclusions remain unchanged even if one or two domain populations dominate the sample.

While \( \Psi_1^{(1)} \) (\( \langle \delta|M_{x'}|0 \rangle \neq 0 \)) and \( \Phi_2^{(1)} \) (\( \langle \delta|M_{y'}|0 \rangle \neq 0 \)) should appear in both fields \( h_1 \) and \( h_2 \), \( \Psi_1^{(2)} \) (\( \langle \delta|M_{x'}|0 \rangle \neq 0 \)) should only appear in field \( h_2 \), which contains a \( z' \) component. This agrees with the selection rule observed by Talbayev et al.\textsuperscript{14}. But Nagel et al.\textsuperscript{17} recently found that \( \Psi_1^{(2)} \) survives in field \( h_2 \), although with drastically reduced intensity. Notice that the position of \( \Psi_1^{(1)} \) above \( \Psi_1^{(2)} \) requires that \( K > 0.001 \) meV. Therefore, both nonzero \( K \) and \( S_0 \) are required to explain the spectroscopic frequencies and selection rules.

Whereas Talbayev et al.\textsuperscript{14} found that the low-frequency mode appears only in field \( h_1 \), our model indicates that the nearly-degenerate \( \Psi_0^{(0)} \) (\( \langle \delta|M_{x'}|0 \rangle \neq 0 \)) and \( \Phi_1^{(1)} \) (\( \langle \delta|M_{y'}|0 \rangle \neq 0 \)) modes should appear in both fields \( h_1 \) and \( h_2 \). However, more precise THz measurements\textsuperscript{14,15} have recently detected the low-frequency mode in both fields \( h_1 \) and \( h_2 \). At 4 K, Nagel et al.\textsuperscript{17} even observed distinct low-frequency peaks at 2.03 and 2.26 meV. The observed three-fold splitting of the 2.03 meV peak in a magnetic field may help to distinguish \( \Psi_0^{(0)} \) and \( \Phi_1^{(1)} \).

To address the observability of the THz modes more carefully, we evaluate the spectroscopic intensities \( I(h_1) \) and \( I(h_2) \) for each mode. The spectroscopic intensity for any mode is given by\textsuperscript{39}

\[
I(h) = \sum_\alpha h_\alpha^2 |\langle \delta|M_\alpha|0 \rangle|^2. \tag{14}
\]

Averaging over the three domains, we find

\[
\begin{align*}
I(h_1) &= \frac{1}{2}\left\{ |\langle \delta|M_{x'}|0 \rangle|^2 + |\langle \delta|M_{y'}|0 \rangle|^2 \right\}, \\
I(h_2) &= \frac{1}{6}\left\{ |\langle \delta|M_{x'}|0 \rangle|^2 + |\langle \delta|M_{y'}|0 \rangle|^2 \right\} \\
&\quad + \frac{2}{3}|\langle \delta|M_{z'}|0 \rangle|^2, \tag{15}
\end{align*}
\]

For \( \langle \delta|M_{x'}|0 \rangle \neq 0 \), \( I(h_1)/I(h_2) = 3 \) for any mode (like \( \Phi_1^{(1)} \), \( \Psi_1^{(1)} \), \( \Psi_1^{(0)} \), and \( \Phi_1^{(1)} \)) with \( \alpha = x' \) or \( y' \) while \( I(h_1)/I(h_2) = 0 \) for any mode (like \( \Psi_1^{(2)} \)) with \( \alpha = z' \). The spectroscopic intensities for \( K = 0.0035 \) meV and \( S_0 = 0.015 \) are summarized in Table I. These numerical results indicate that \( \Psi_1^{(1)} \) and \( \Phi_1^{(2)} \) should be the strongest of the four modes, in agreement with the THz results\textsuperscript{14,15}. Surprisingly, Table I indicates that the intensity \( I(h_2) \) of \( \Phi_1^{(2)} \) is roughly 20 times smaller than that of \( \Psi_1^{(1)} \). By contrast, recent THz measurements\textsuperscript{15} indicate that \( \Phi_1^{(1)} \) is only about 3 times less intense than \( \Psi_1^{(1)} \) in field \( h_2 \). Those measurements do, however, agree with our prediction that \( \Psi_1^{(2)} \) is several times more intense than \( \Psi_1^{(1)} \) in \( h_2 \).

| Table I: Spectroscopic Frequencies, Matrix Elements, and Intensities |
|-----------------|-----------------|-----------------|-----------------|
| \( \Psi_0^{(0)}/\Phi_1^{(1)} \) | \( \Psi_1^{(2)} \) | \( \Psi_1^{(1)} \) | \( \Phi_1^{(1)} \) |
| measured \( \omega \) (meV) | 2.17 | 2.49 | 2.67 | 3.38 |
| predicted \( \omega \) (meV) | 2.03/2.05 | 2.53 | 2.75 | 3.40 |
| magnetic field index \( x' \) | \( y' \) | \( z' \) | \( x' \) | \( y' \) |
| \(|\langle \delta|M_{x'}|0 \rangle|/\mu_B\rangle \) | 5.20/1.86 | 3.96 | 4.59 | 1.01 |
| \(|\langle \delta|M_{y'}|0 \rangle|/\lambda\rangle \) | 0 | 0 | 12.2 | 0 |
| intensity index \( y' \) | \( y' \) | \( y' \) | \( x' \) | \( z' \) |
| \( S_{x'y'} \) | 4.94 \times 10^{-8} | 19.7 | 18.1 | 5.43 |
| \( I(h_1)/\mu_B^0 \) | 4.75 | 0 | 10.54 | 0.51 |
| \( I(h_2)/\mu_B^0 \) | 1.58 | 10.47 | 3.51 | 0.17 |

VI. INELASTIC NEUTRON-SCATTERING MEASUREMENTS

In earlier work\textsuperscript{16} with \( D' = 0 \), we obtained conflicting estimates for the easy-axis anisotropy \( K \) based on the spectroscopic and neutron-scattering spectra. Because the instrumental resolution is broader than \( 4\pi\delta/\alpha \)\textsuperscript{3}, inelastic neutron-scattering measurements at the AF Bragg point \((2\pi/\alpha)[0.5, 0.5, 0.5] \) average over a range of \( q \) that includes both cycloidal satellites at \((2\pi/\alpha)[0.5 \pm \delta, 0.5, 0.5 + \delta] \). For \( D' = 0 \), the spectroscopic mode frequencies indicated that \( K \approx 0.002 \) but the inelastic-scattering spectra indicated that \( K \approx 0.004 \).
We now re-examine the spectrum $\chi''(\omega)$ for $D' \neq 0$. The upper left-hand corner of Fig. 6 plots the measured spectrum\textsuperscript{9,19}. The resolution-averaged intensity spectrum is plotted versus $\omega$ in Figs. 6(b-d) for three values of $K$ and six values of $S_0$ from 0 to 0.015. The very low-frequency rise of $\chi''(\omega)$ due to $\Phi_0$ at $\eta = \delta$ has been removed from both the measured and predicted spectra.

Below 5 meV, the measured $\chi''(\omega)$ contains four peaks at 1.2, 2.4, 3.4, and 4.4 meV. The peaks at 1.2 and 2.4 meV are primarily caused by $\Phi_1^{(1,2)}$ and $\Psi_0$. As shown in Fig. 4 for $S_0 = 0.015$, the separation between $\Phi_1^{(2)}$ and $\Phi_1^{(1)}/\Psi_0$ increases as $K$ exceeds 0.001 meV. Correspondingly, the gap in the predicted spectrum centered at 2 meV widens with increasing $K$ beyond 0.001 meV.

As shown in Fig. 5(b), $\Phi_2^{(2)}$ is slightly enhanced by $S_0$. But the resolution-averaged spectrum $\chi''(\omega)$ also involves nearby modes and shifts to lower frequencies with increasing $S_0$. For $S_0 = 0.015$ and $K = 0.0035$ meV, the low-frequency peak lies at 1.2 meV. So based on this single peak, $K \approx 0.0035$ meV provides good agreement with both the spectroscopic and inelastic measurements. Although its intensity increases with $S_0$ and it is more pronounced than in our previous work\textsuperscript{12}, the predicted low-frequency peak at 1.2 meV is still considerably weaker than the measured peak.

For $K = 0.0035$ meV, the second peak lies at 2.5 meV when $S_0 = 0$ but shifts down to 2.3 meV when $S_0 = 0.015$. More problematically, the predicted spectrum contains three peaks between 2 and 4 meV (although the third peak is suppressed with $S_0$) whereas the measured spectrum contains only two. For $K = 0.0035$ meV and $S_0 = 0.015$, there are no predicted SW excitations between 4 and 5 meV at $\eta = 0$ or $\delta$. Consequently, the observed peak at 4.4 meV is missing from our spectrum, which falls off much more rapidly than the measured $\chi''(\omega)$ above 4 meV. Keep in mind, however, that the predicted shape of $\chi''(\omega)$ sensitively depends on the resolution function used to perform the averaging.

VII. CONCLUSION

A primary motivation of this work was to see how well a microscopic model can describe the properties of one of the simplest and most technologically important multiferroic materials. We have demonstrated that all four modes observed by THz and Raman spectroscopies in BiFeO$_3$ are predicted by a model that includes two DM interactions, one along $y'$ responsible for the cycloid periodicity and the other along $z'$ responsible for its tilt of the cycloid out of the $x'z'$ plane. Using reasonable values for the easy-axis anisotropy and the DM interactions, we obtain excellent agreement with the measured mode frequencies. The parameters $D = 0.11$ meV, $D' = 0.054$ meV, and $K = 0.0035$ meV provide very good descriptions of both the spectroscopic and inelastic neutron-scattering measurements, thereby resolving an earlier disagreement\textsuperscript{15}.

The spectroscopic modes evolve with the complexity of the cycloid. With a single DM interaction $D = D y'$, the cycloid is coplanar and purely harmonic. For nonzero frequencies, the only spectroscopically-active mode is $\Psi_1((\delta|M_{z'}|0) \neq 0, (\delta|M_{z'}|0) \neq 0)$, which coincides with the EM $(\delta|P^{\text{ind}}_{y'}|0) \neq 0)$. Easy-axis anisotropy $K$ along $z'$ distorts the coplanar cycloid and introduces higher even harmonics in the Hamiltonian $H$. The 2Q potential splits $\Psi_{\pm 1}$ into $\Psi_1^{(1)}(\delta|M_{z'}|0) \neq 0, (\delta|P^{\text{ind}}_{y'}|0) \neq 0$ and $\Psi_2^{(2)}((\delta|M_{z'}|0) \neq 0); the 4Q potential splits $\Psi_{\pm 2}$ into $\Psi_2^{(1)}$ and $\Psi_2^{(2)}$. Hybridized with $\Phi_0$ by the 2Q potential, $\Psi_2^{(2)}((\delta|M_{z'}|0) \neq 0)$ becomes spectroscopically active. Finally, the DM interaction $D' = D'z'$ tilts the non-coplanar cycloid out of the $x'z'$ plane. Then, $\Psi_0((\delta|M_{z'}|0) \neq 0)$ and $\Psi_1^{(1)}((\delta|M_{y'}|0) \neq 0)$ are dynamically and spectroscopically activated by their hybridization with $\Psi_1^{(1,2)}$ and $\Phi_0$, respectively. Thus, additional interactions modify the mode spectrum as more modes hybridize with $\Phi_0$ and $\Psi_1^{(1,2)}$.

Several experiments indicate that the low-temperature, low-field cycloid of BiFeO$_3$ undergoes a transition at about 140 K or 10 T. In THz measurements\textsuperscript{14}, the low-frequency $\Psi_0/\Phi_1^{(1)}$ mode disappears above 120 K and the high-frequency $\Phi_2^{(1)}$ mode disappears above 150 K. Nevertheless, the selection rules governing the $\Psi_1^{(1,2)}$ modes do not change\textsuperscript{14}. In Raman measurements, all modes persist for all temperatures but their frequencies\textsuperscript{16} and intensities\textsuperscript{17} display kinks at about 140 K. Optical\textsuperscript{18} and electron-spin resonance\textsuperscript{16} measurements show anomalies at about 10 T with indications that the cycloidal phase above 10 T is the same as the one above 140 K. Recently, Nagel et al.\textsuperscript{19}
found that the THz modes exhibit kinks at about 5.5 T. But the nature of these transitions and the difference between the two cycloidal phases remain unknown.

With magnetic field along $z'$, the Hamiltonian of Eq. [2] does not produce a transition between different cycloidal phases. Therefore, the proposed model may be incomplete. Since $D'$ is responsible for the low-frequency $\omega_0/\Phi_1^{(1)}$ mode, a sudden change in $D'$ at 140 K or 10 T would produce anomalies in its spectroscopic features. A jump in $D'$ at 140 K would also produce a jump in the weak ferromagnetic moment $M_0(T)$. We hope that future experimental and theoretical work will resolve this and other mysteries surrounding BiFeO$_3$.

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Appendix A: SW Intensities

This section describes how to evaluate the SW intensities and eigenvectors $X$, which are required in the next section to evaluate the spectroscopic matrix elements.

The local reference frame for each spin $S_i$ on site $i$ is defined in terms of the unitary matrix $U^\dagger$ by $\tilde{S}_i = U^\dagger S_i$. For spin

$$S = S(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta),$$

the matrices $U$ and $U^{-1}$ are given by

$$U = \begin{pmatrix} \cos \theta \cos \phi & \cos \theta \sin \phi & -\sin \theta \\ -\sin \phi & \cos \phi & 0 \\ \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta \end{pmatrix},$$

$$U^{-1} = \begin{pmatrix} \cos \theta \cos \phi & -\sin \phi & \sin \theta \cos \phi \\ \cos \theta \sin \phi & \cos \phi & \sin \theta \sin \phi \\ -\sin \theta & 0 & \cos \theta \end{pmatrix},$$

so that $S U^{-1} \cdot z = S$.

A Holstein-Primakoff transformation is used to express the local spin operators $\tilde{S}_i$ in terms of the bosons $a_i$ and $a_i^\dagger$ with $\tilde{S}_{iz} = S - a_i^\dagger a_i$, $\tilde{S}_{iz} = \sqrt{2S} a_i$, and $\tilde{S}_{iz} = \sqrt{2S} a_i^\dagger$. The Hamiltonian is then expanded in powers of $1/\sqrt{S}$ as

$$H = E_0 + H_1 + H_2 + \ldots$$

While $E_0$ is the classical energy and $H_1$ must vanish,

$$H_2 = \sum_q \mathbf{v}_q \cdot \mathbf{L}(q) \cdot \mathbf{v}_q,$$

where $\mathbf{v}_q = (\alpha^{(1)}_q, \ldots, \alpha^{(2M)}_q, a_{-q}^{(1)}\dagger, \ldots, a_{-q}^{(2M)}\dagger)$ is a 4$M$-dimensional vector and $\mathbf{L}(q)$ is a 4$M$-dimensional matrix. Boson operators $a_{\alpha}^{(r)}$ with $1 \leq \alpha \leq M = 222$ reside on layer 1 of the unit cell while those with $M + 1 \leq \alpha \leq 2M$ reside on layer 2. The sublattice index $r$ refers to sites on either layer with $\mathbf{R} \cdot \mathbf{x}' = |r|a/\sqrt{2}$ where $|r| \equiv \text{mod}(r, M)$.

Since $a_{\alpha}^{(r)}$ and $a_{\alpha}^{(r)}\dagger$ obey the commutation relations $[a_{\alpha}^{(r)}, a_{\alpha'}^{(r)}\dagger] = \delta_{\alpha,\alpha'} \delta_{\alpha,q}$ and $[a_{\alpha}^{(r)}, a_{\alpha}^{(s)}] = 0$, $\mathbf{v}_q$ and $\mathbf{v}_q \dagger$ satisfy the commutation relation $[\mathbf{v}_q, \mathbf{v}_q \dagger] = \mathbf{N}^\dagger \delta_{\alpha,q}$, where

$$\mathbf{N} = \begin{pmatrix} L & 0 \\ 0 & -L \end{pmatrix}$$

and $L$ is the 2$M$-dimensional unit matrix.

A diagonal form for $H_2$ is given by

$$H_2 = \sum_q \mathbf{w}_q \cdot \mathbf{L}(q) \cdot \mathbf{w}_q,$$

where $\mathbf{w}_q = (\alpha^{(1)}_q, \ldots, \alpha^{(2M)}_q, \alpha_{-q}^{(1)}\dagger, \ldots, \alpha_{-q}^{(2M)}\dagger)$ and the boson operators $a_{\alpha}^{(n)}$ and $a_{\alpha}^{(n)}\dagger$ also obey canonical commutation relations. The 4$M$-dimensional matrix $\mathbf{L}(q)$ is diagonal with real eigenvalues $\epsilon_n(q) = \omega_n(q)/2 > 0$ ($n = 1, \ldots, 2M$) and $\epsilon_n(q) = -\omega_n(q)/2 < 0$ ($n = 2M + 1, \ldots, 4M$). So for each $q$, there are 2$M$ positive and 2$M$ negative eigenvalues. The commutation relations yield

$$H_2 = \sum_{n,k} \omega_n(q) \left( \alpha_{\alpha}^{(n)\dagger} \alpha_{\alpha}^{(n)} + \frac{1}{2} \right),$$

which identifies $\omega_n(q)$ as the SW frequency for mode $n$ with wavevector $q$.

Vectors $\mathbf{w}_q$ and $\mathbf{v}_q$ are related by $\mathbf{w}_q = \mathbf{N} \cdot \mathbf{v}_q$ or $\mathbf{v}_q = \mathbf{N}^{-1} \cdot \mathbf{w}_q$, where the 4$M$-dimensional matrix $\mathbf{N}$ is normalized by $\mathbf{N} \cdot \mathbf{N}^\dagger = \mathbf{I}$. For fixed $q$,

$$\sum_j \left( \mathbf{L}(q) - \delta_j \epsilon_n(q) \right) \mathbf{X}_{nj}(q) = 0,$$

where $\mathbf{L}(q) = \mathbf{L}(q) \cdot \mathbf{N}$. The inverse $\mathbf{X}^{-1} = \mathbf{X} \cdot \mathbf{N}^\dagger \cdot \mathbf{N}$ is required to evaluate $\langle \delta | \mathbf{P}^\dagger | 0 \rangle$ and $\langle \delta | \mathbf{M} | 0 \rangle$.

The wavevector $\mathbf{Q}$ and harmonic coefficients of the cyclod are obtained by minimizing $E_0$ using the “trial” spin state provided by Eqs. [24]. If the spin angles on site $r$ of layer 1 are $\theta_r$ and $\phi_r$, then the angles on layers 1 and 2 are related by $\theta_{r+M} = \theta_r + \pi$ and $\phi_{r+M} = -\phi_r$. We assume that $\phi_r = \tau$ and $\phi_{r+M} = -\tau$ are independent of site position $r$ on layers 1 and 2.
The spin-spin correlation function is defined by
\[
S_{\alpha\beta}(\mathbf{q}, \omega) = \frac{1}{2\pi N} \int dt e^{-i\omega t} \sum_{i,j} e^{-i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \langle S_{\alpha i}(0) S_{\beta j}(t) \rangle
\]
where the final expression assumes that the SWs are undamped. The inelastic neutron-scattering cross section is given by
\[
\frac{\sigma}{\text{d}^3q} = \frac{1}{M} \left| \sum_{\alpha,\beta} \delta(\omega - \omega_n(\mathbf{q})) S_{\alpha\beta}^{(n)}(\mathbf{q}) \right|^2,
\]
where \(\omega_n(\mathbf{q})\) is the reduced electric polarization between the ground state \(\ket{\text{M}}\) and an excited state \(|\delta\rangle\) with a single magnon at the cycloidal wavevector \(\mathbf{Q}\).

After some work, we obtain the EM matrix element \(y'\) for SW mode \(n\):
\[
\langle \delta | P^{\text{ind}}_{y'} | 0 \rangle = \lambda S \sqrt{\frac{S}{2}} \sum_{r=1}^{M} \sin \theta_r e^{iq_0 a r} \left\{ \left[ \cos \theta_{r[+2]} \sin(\phi_r - \phi_{r[+2]}) + i \cos(\phi_r - \phi_{r[+2]}) \right] - \left[ e^{2iq_0 a} X_{r[+2]+M,n,2M}^{-1} - e^{-2iq_0 a} X_{r[+2]+M,n,2M}^{-1} \right] \right\}.
\]

For SW mode \(n\), the magnetic form factor for \(\text{Fe}^{3+}\) should also be included in \(S(\mathbf{q}, \omega)\).

**Appendix B: Spectroscopic matrix elements**

This section evaluates the matrix elements for the induced electric polarization \(P^{\text{ind}}\) and the magnetic moment \(M\) between the ground state \(|0\rangle\) and an excited state \(|\delta\rangle\) with a single magnon at the cycloidal wavevector \(\mathbf{Q}\).

Since \(P^{\text{ind}}_{y'} = 0\), only the \(y'\) and \(z'\) components are considered. Expanded about equilibrium, \(P^{\text{ind}}_{y'}\) becomes
\[
P^{\text{ind}}_{y'} = \lambda S \left\{ \sum_{r=1}^{M} \sin \theta_r \cos \phi_r \left[ -S_{r[+2],y'} + S_{r[-2],y'} + S_{r[+2]+M,y'} - S_{r[-2]+M,y'} \right] + \sum_{r=1}^{M} \sin \theta_r \sin \phi_r \left[ S_{r[+2],x'} - S_{r[-2],x'} + S_{r[+2]+M,x'} - S_{r[-2]+M,x'} \right] \right\}.
\]

Similarly, \(P^{\text{ind}}_{z'}\) can be expanded as
\[
P^{\text{ind}}_{z'} = \lambda S \left\{ \sum_{r=1}^{M} \cos \theta_r \left[ S_{r[+2],x'} - S_{r[-2],x'} - S_{r[+2]+M,x'} + S_{r[-2]+M,x'} \right] - \sum_{r=1}^{M} \sin \theta_r \cos \phi_r \left[ S_{r[+2],z'} - S_{r[-2],z'} - S_{r[+2]+M,z'} + S_{r[-2]+M,z'} \right] \right\}.
\]

The EM matrix element \(z'\) for SW mode \(n\) is
\[
\langle \delta | P^{\text{ind}}_{z'} | 0 \rangle = \lambda S \sqrt{\frac{S}{2}} \sum_{r=1}^{M} e^{iq_0 a r} \left\{ \left[ g_{r[+2]} + i \cos \theta_r \sin \phi_{r[+2]} \right] X_{r[+2],n,2M}^{-1} - X_{r[+2]+M,n,2M}^{-1} e^{2iq_0 a} \right\}.
\]
For $K = 0.0035$ meV and $S_0 = 0.015$, $\Phi_0$ has the small matrix element $|\delta P^\text{ind}_y(0)| \approx 0.19$, about 60 times smaller than $|\delta P^\text{ind}_y(0)| \approx 12.2$ for $\Psi_1^{(1)}$.

The MR matrix element for SW mode $n$ is much more simply given by

$$\langle \delta | M_n | 0 \rangle = \sqrt{2S\mu_B} \sum_{r=1}^{2M} e^{i\theta_0[r]} \text{sgn}(M - r + 1/2) W_{r,n}^{(\alpha)}(Q), \quad (B6)$$

which uses

$$e^{i\mathbf{Q}\cdot\mathbf{R}} = e^{i\theta_0[r]} \text{sgn}(M - r + 1/2). \quad (B7)$$

Notice that $W_{r,n}^{(\alpha)}(Q)$ also enters the SW intensity $S_{\text{SW}}^{(n)}(Q)$ of Eq.(A11). While the SW intensity $S_{\text{SW}}^{(n)}(Q)$ is proportional to the sum of $|W_{r,n}^{(\alpha)}(Q)|^2$ over $r$, the matrix element $|\delta | M_n | 0 \rangle$ is proportional to the Fourier transform of $W_{r,n}^{(\alpha)}(Q)$ over $r$.

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