The Microscopic Model of BiFeO$_3$

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Many years and great effort have been spent constructing the microscopic model for the room temperature multiferroic BiFeO$_3$. However, earlier models implicitly assumed that the cycloidal wavevector $\mathbf{q}$ was confined to one of the three-fold symmetric axis in the hexagonal plane normal to the electric polarization. Because recent measurements indicate that $\mathbf{q}$ can be rotated by a magnetic field, it is essential to properly treat the anisotropy that confines $\mathbf{q}$ at low fields. We show that the anisotropy energy $-K_3S^3\sin^3\theta \cos 6\phi$ confines the wavevectors $\mathbf{q}$ to the three-fold axis $\phi = 0$ and $\pm 2\pi/3$ within the hexagonal plane with $\theta = \pi/2$.

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Multiferroics have attracted a great deal of attention due to their possible technological applications. In multiferroic materials, the magnetization can be controlled by an electric field and the electric polarization can be controlled by a magnetic field. The ability to reverse the voltage with a magnetic field offers the possibility of magnetic storage without Joule heating loss due to electrical currents [2]. To take advantage of this capability, however, we must first learn how to manipulate magnetic domains with a magnetic field.

In type I multiferroics, magnetic order develops at a lower temperature than the ferroelectric polarization. In type II multiferroics but type I multiferroics have much higher transition temperatures. To date, the highest magnetic transition temperature has been found in the type I multiferroic BiFeO$_3$ with $T_N \approx 640K$ [4].

The long-wavelength spin cycloid of BiFeO$_3$ [4] has wavevector $\mathbf{Q} + \mathbf{q}$ where $\mathbf{Q} = (\pi/a)(1,1,1)$ is the antiferromagnetic reciprocal lattice vector in terms of the lattice constant $a \approx 3.96 \text{ Å}$ of the pseudo-cubic unit cell. If $\mathbf{q} = 0$, then the spin state of BiFeO$_3$ would be a G-type antiferromagnet. The wavelength of the spin cycloid $\lambda = 2\pi/q$ is about 62 nm and its spins lie primarily in the plane defined by the electric polarization $\mathbf{P}$ and the wavevector $\mathbf{q}$. There are three possible magnetic domains with $\mathbf{q}$ lying along one of the three-fold symmetric axes normal to $\mathbf{P}$, which itself lies along one of the cubic diagonals. With $\mathbf{P} \parallel \mathbf{z'} = [1,1,1]$ ($\{a,b,c\}$ is a unit vector normalized to 1), the wavevectors $\mathbf{q}$ can lie along the [$1,1,0$], [1,0,−1], or [0,−1,1] directions in zero field. The hexagonal plane normal to [1,1,1] is sketched in Fig.1, with points given by $\mathbf{R} = a(n_1\mathbf{x} + n_2\mathbf{y} + n_3\mathbf{z})$ in terms of the integers $n_i$. All points in this hexagonal satisfy $\mathbf{z'} \cdot \mathbf{R} = 0$ or $n_1 + n_2 + n_3 = 0$.

Previous microscopic models for BiFeO$_3$ such as used in Ref. [4] implicitly assumed that the domain wavevector $\mathbf{q}$ remains fixed along one of the three-fold axis in a magnetic field. Because the magnetic susceptibility perpendicular to $\mathbf{q}$ is much larger than the susceptibility parallel to $\mathbf{q}$, a magnetic field $\mathbf{B}$ favors domains with $\mathbf{q} \perp \mathbf{B}$. Recent evidence [5] reveals that a magnetic field rotates the wavevectors $\mathbf{q}$ within the hexagonal plane away from the three-fold axis towards an orientation perpendicular to $\mathbf{B}$.

Our recently revised Hamiltonian is valid for any $\mathbf{q}$ and given by

$$
\mathcal{H} = -J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + D_1 \sum_{\langle i,j \rangle} (\mathbf{z'} \times \mathbf{e}_{i,j}/a) \cdot (\mathbf{S}_i \times \mathbf{S}_j) + D_2 \sum_{\langle i,j \rangle} (-1)^{h_i} \mathbf{z'} \cdot (\mathbf{S}_i \times \mathbf{S}_j) - K_1 \sum_i (\mathbf{z'} \cdot \mathbf{S}_i)^2 - 2\mu_B B \sum_i \mathbf{m} \cdot \mathbf{S}_i, $$ (1)

where $\mathbf{e}_{i,j} = ax, ay$, or $az$ connects the $S = 5/2$ spin $\mathbf{S}_i$ on site $\mathbf{R}_i$ with nearest-neighbor spins $\mathbf{S}_j$ on site $\mathbf{R}_j$.
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While susceptibility measurements [15] indicate that \( \tau \sim 0.3^\circ \), neutron-scattering measurements [17] indicate that \( \tau \sim 1^\circ \) is about three times larger.

Although they ignore higher harmonics \((2m + 1)\mathbf{q} \cdot \mathbf{R}_i (m > 1)\) produced by the easy-axis anisotropy and the second DM interaction, these simplified expressions are useful for taking averages over the lattice. The error introduced by neglecting higher harmonics is of order \( C_3 / C_1 \approx 5 \times 10^{-3} \) where \( C_{2m+1} \) are the coefficients for the \(2m+1\) harmonic [18]. Only odd harmonics contribute in zero field and those harmonics fall off rapidly with \(2m+1\).

To avoid confusion with the \(\{x', y', z'\}\) reference frame of the cycloid, we define \(X = [1, 0, -1]\) and \(Y = [-1, 2, -1]\) as fixed axis in the hexagonal plane normal to \(Z = X \times Y = [1, 1, 1]\). Of course, \(Z = z'\) lies along \(P\). The different reference frames for BiFeO\(_3\) are summarized in Table I.

To lift the rotational invariance of the microscopic model constructed above, we consider all possible anisotropy terms consistent with the \(R3c\) rhombohedral symmetry of BiFeO\(_3\) [23]. Up to order \(S^6\), those terms are

\[
\mathcal{H}_{K_1} = -K_1 \sum_i S_i z_i^2, \tag{5}
\]

\[
\mathcal{H}_{K_2} = -\frac{1}{2} K_2 \sum_i S_i z_i \left( (S_{iX} + iS_{iY})^3 + (S_{iX} - iS_{iY})^3 \right), \tag{6}
\]

\[
\mathcal{H}_{K_3} = -\frac{1}{2} K_3 \sum_i \left( (S_{iX} + iS_{iY})^6 + (S_{iX} - iS_{iY})^6 \right), \tag{7}
\]

\[
\mathcal{H}_{K_4} = - K_4 \sum_i S_i z_i^4. \tag{8}
\]

\[
\mathcal{H}_{K_5} = - K_5 \sum_i S_i z_i^6. \tag{9}
\]

In terms of the spin-orbit coupling constant \(l |J_1| \) where \(l \ll 1\), the DM interactions \(D_1\) and \(D_2\) are of order \(l |J_1|\) and the anisotropy constants \(K_m\) and \(K_m^\prime\) are of order \(l^{m+1} |J_1|\) [22].

The anisotropy terms have classical energies \(E_K = \langle \mathcal{H}_K \rangle\):

\[
E_{K_1} = -S^2K_1 \sum_i \cos^2 \theta_i, \tag{10}
\]

\[
E_{K_2} = -S^4K_2 \sum_i \cos \theta_i \sin^3 \theta_i \cos 3\phi_i, \tag{11}
\]

\[
E_{K_3} = -S^6K_3 \sum_i \sin^6 \theta_i \cos 6\phi_i, \tag{12}
\]

\[
E_{K_4} = -S^4K_4 \sum_i \cos^4 \theta_i, \tag{13}
\]

\[
E_{K_5} = -S^6K_5 \sum_i \cos^6 \theta_i. \tag{14}
\]

where the angles \(\theta_i\) and \(\phi_i\) of the spin

\[
(S_i) = S \left\{ \cos \phi_i \sin \theta_i \mathbf{X} + \sin \phi_i \sin \theta_i \mathbf{Y} + \cos \theta_i \mathbf{Z} \right\} \tag{15}
\]

are defined in the fixed reference frame defined above. Other anisotropy energies such as \(S^2K_1' \sum_i \sin^2 \theta_i \cos 2\phi_i\) and \(S^4K_2' \sum_i \sin^4 \theta_i \cos 4\phi_i\) vanish for the \(R3c\) crystal structure of BiFeO\(_3\) [24].

Like \(E_{K_1}, E_{K_2}\) and \(E_{K_3}\), strengthen or weaken the easy-axis anisotropy along \(Z\). Because these three energies
have qualitatively the same effects and are very hard to disentangle, we neglect $K_2$ and $K_3$.

Using the expressions for the cycloid in Eqs. (2-4), we find that $E_{K_2} = 0$. Consequently, $K_2$ will distort the cycloid to produce an energy reduction of order $(K_2)^2/\langle J_l \rangle \sim \ell^6 \langle J_1 \rangle$. So $E_{K_2} \sim \ell^6 \langle J_1 \rangle$ can be neglected compared to $E_{K_3} \sim \ell^4 \langle J_1 \rangle$. A firm estimate for $K_3$ will have to wait until we report results for the metastability of cycloidal domains in a magnetic field. But assuming that $\ell \approx 0.1$, $S^4K_3 \sim \ell^2 S^4 K_1$ or $K_3 \approx 6 \times 10^{-6}$ meV as in Table II.

It may be necessary to slightly modify the estimates in Table II for $K_1$ and $D_2$ to compensate for the effect of $K_1$. While $D_2$ favors the spins to lie perpendicular to $Z$, $K_1 > 0$ favors the spins to lie along $Z$. Based on fits to the spectroscopic modes [18], the net anisotropy favors the spins along $Z$. Regardless of its sign, the new anisotropy $K_3$ favors the spins to lie in the $X - Y$ plane rather than along $Z$. The energy difference between a spin lying along $Z$ and along a three-fold axis like $X$ is $-S^6 K_3$. So to offset the effect of $K_3$, $K_1$ must be increased by $S^4 K_3$. For $K_1 \approx 0.004$ meV and $K_3 \approx 6 \times 10^{-6}$ meV, $\Delta K_1 \approx 2.3 \times 10^{-4}$ meV constitutes an increase of about 6%.

How does this estimate for $K_3$ in BiFeO$_3$ compare with that in other materials? The three-fold anisotropy constant $K_3$ can be estimated from the angular dependence of the basal-plane magnetization or the torque. For Co$_2$Y ($Y = $ Ba$_2$Fe$_{12}$O$_{22}$ and Co$_2$Z ($Z = $ Ba$_3$Fe$_{24}$O$_{41}$), $K_3 \approx S^6 K_3/V_c \approx 600$ erg/cm$^3$ and $1500$ erg/cm$^3$, respectively [24] ($V_c$ is the unit cell volume with one magnetic ion). Torque measurements were used to estimate [27] that $K_3 \approx 1.2 \times 10^5$ erg/cm$^3$ for pure Co. Anisotropy energies are much larger for rare earths than for transition-metal oxides [28]. While $K_3 \approx 6300$ erg/cm$^3$ for Gd, it is about 1000 times higher for the heavier rare earths Tb, Dy, Ho, Er, and Tm. An anisotropy of $K_3 = 6 \times 10^{-6}$ meV for BiFeO$_3$ corresponds to $K_3 = 4 \times 10^4$ erg/cm$^3$, larger than for Gd but smaller than for pure Co or the heavy rare earths.

To conclude, we have added an additional anisotropy energy to the “canonical” model for BiFeO$_3$ in order to lift its rotational invariance in the hexagonal plane normal to the polarization. While the anisotropy constant is quite small, it is comparable to that measured in other materials. Future work will demonstrate that this three-fold anisotropy has a profound effect on the rotation of domains in a magnetic field.

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