Comment on “Ferroelectrically Induced Weak Ferromagnetism by Design”

The question of how ferroelectric polarization is coupled to magnetism in magnetoelectric multiferroics is of considerable current interest. A recent Letter \[1\] analyzes the important “ABO\(_3\)” class of perovskite multiferroics. A symmetry argument is presented that materials with antiferromagnetism on the B site lack linear magnetoelectric coupling \(E_{PLM} = \mathbf{P} \cdot (\mathbf{L} \times \mathbf{M})\) in the free energy, unlike A-site antiferromagnets \[1, 2\]. Here \(\mathbf{P}\) is polarization and \(\mathbf{L}\) and \(\mathbf{M}\) are antiferromagnetic and ferromagnetic moments.

This Comment presents a distinct analysis of \(E_{PLM}\) in ABO\(_3\) multiferroics. We show that the argument of Ref. \[1\] does forbid \(E_{PLM}\) if the final low-symmetry phase contains only one distortion that, like \(\mathbf{P}\), breaks all inversion symmetries. In reality there are multiple distortions in this symmetry class, and cross-terms generate \(E_{PLM}\) even in B-site materials, although the mechanism is different than in A-site materials. Additional differences can emerge between A-site and B-site materials under dynamical assumptions beyond the static free energy.

For concreteness we use BiFeO\(_3\), whose electronic structure has been extensively studied \[3, 4\]. Below 1100K it shows ferroelectric order with space group R\(_{3c}\) and a 10-atom unit cell. In Ref. \[1\] the free energy is expanded from a model R\(_{3c}\) phase with inversion center on Fe. For now, assume that the polarization \(\mathbf{P}\) arises from relative motion of the ionic sublattices \[3\] along the threefold axis \(\hat{z}\). There is a 13.8° rotation \(\alpha\) of the O octahedra around Fe atoms (\(\alpha\hat{z}\) is \(\mathbf{D}\) in Ref. \[1\]), which is even under Fe-site inversion \(I_B\) and odd under Bi-site inversion \(I_A\). However, distortions beyond \(\mathbf{P}\) and \(\alpha\) must be present, either by counting R3c degrees of freedom or because the 1.4° counter-rotation of upper and lower triangles within an octahedron \[5, 6\] cannot be obtained by combining \(\mathbf{P}\) and \(\alpha\).

Coordinates for an oxygen distortion \(\beta\) (Fig. 1) that causes this counter-rotation and is orthogonal to \(\mathbf{P}\) are provided in EPAPS. The \(\beta\) distortion, like \(\mathbf{P}\), is odd under \(I_A\) and \(I_B\). For A-site magnetism, we have inversion eigenvalues \(I_A\mathbf{L} = +\mathbf{L}\), and \(I_B\mathbf{L} = -\mathbf{L}\). For B-site magnetism, \(I_A\mathbf{L} = -\mathbf{L}\) and \(I_B\mathbf{L} = +\mathbf{L}\). Allowed \(\mathbf{L} \times \mathbf{M}\) terms are, with constants \(\lambda_1, \lambda_2,\)

\[
F_A = \lambda_1 \alpha \mathbf{P} \cdot (\mathbf{L} \times \mathbf{M}) + \lambda_2 \alpha \beta \hat{z} \cdot (\mathbf{L} \times \mathbf{M}),
\]

\[
F_B = \lambda_1 \alpha \beta \mathbf{P} \cdot (\mathbf{L} \times \mathbf{M}) + \lambda_2 \alpha \hat{z} \cdot (\mathbf{L} \times \mathbf{M}).
(1)
\]

More generally, \(\mathbf{P}\) is some \(I_A = I_B = -1\) distortion, and \(E_{PLM}\) results from cross-terms.
FIG. 1: Distortions $\alpha$ and $\beta$ that reduce the ideal perovskite symmetry to R3c (along threefold axis). The distortion $\beta$ combines with $\alpha$ at order $\alpha\beta$ to give both the observed counter-rotation and a linear magnetoelectric coupling.

between $\mathbf{P}$ and other such distortions, here $\beta$. Magnetoelectric coupling should be sought in B-site structures with large $\beta$-type distortions as well as in A-site structures with large $\alpha$.

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[6] The $c$ and $d$ $O-O$ bond lengths in [5] indicate this counter-rotation of $1.4^\circ$. 
EXPLICIT CONSTRUCTION OF $\alpha$ AND $\beta$ DISTORTIONS (APPENDIX TO COMMENT ON “FERROELECTRICALLY INDUCED WEAK FERROMAGNETISM BY DESIGN”)

It is convenient to use the following notation: Vectors written without parenthesis denote components along the primitive vectors: $x, y, z \equiv xa + yb + zc$. A convenient set of primitive vectors for the 10-atom R3c unit cell is $a = (0, 1, 1)$, $b = (1, 0, 1)$, and $c = (1, 1, 0)$. Here vectors with parenthesis are in a cartesian basis, and for convenience we choose the origin to be on top of a B atom. Note that if $l, m, n$ is a set of integers, our notation implies that $x + l, y + m, z + n$ is equivalent to $x, y, z$ apart from a Bravais vector translation.

For a general ABO$_3$ perovskite with R3c symmetry, both A and B atoms are located at Wyckoff 2a positions: The A atoms are located at $x', x', x'$ and $x' + 1/2, x' + 1/2, x' + 1/2$, while the B atoms are located at $x'', x'', x''$ and $x'' + 1/2, x'' + 1/2, x'' + 1/2$.

The six oxygens must be located at Wyckoff 6b positions:

\[
\begin{align*}
x, y, z & \quad z, x, y & \quad y, z, x \\
y + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2} & \quad x + \frac{1}{2}, z + \frac{1}{2}, y + \frac{1}{2} & \quad z + \frac{1}{2}, y + \frac{1}{2}, x + \frac{1}{2}
\end{align*}
\]

We may parametrize a set of paraelectric R3c structures (under the definition of polarization assumed for this example in the text, in which the polarization is well described as translation of the anion and cation lattices; if the definition of $P$ changes, then that of $\beta$ changes, but by counting such a $\beta$ always exists) with two degrees of freedom $\alpha, \beta$ according to:

\[
\begin{align*}
x' &= \frac{1}{4} & x'' &= 0 \\
x &= -\frac{1}{4} + \alpha + \beta & y &= \frac{3}{4} - \alpha + \beta & z &= \frac{1}{4} - 2\beta
\end{align*}
\]

This leads to the following atomic positions:

\[
\begin{align*}
R_A &= \frac{1}{4}, \frac{1}{4}, \frac{1}{4} & \frac{3}{4}, \frac{3}{4}, \frac{3}{4} \\
R_B &= 0, 0, 0 & \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\
R_O &= -\frac{1}{4} + \alpha + \beta, \frac{3}{4} - \alpha + \beta, \frac{1}{4} - 2\beta & \text{and cyclic permutations} \\
& \frac{5}{4} - \alpha + \beta, \frac{1}{4} + \alpha + \beta, \frac{3}{4} - 2\beta & \text{and cyclic permutations.}
\end{align*}
\]
Note that any equivalent lattice site could equally well be chosen for the oxygen locations, e.g., the choice above $-\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$ is equivalent to $-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}$, or $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$, and so on.

The $\alpha$ and $\beta$ distortions defined in this way are non-polar, i.e., orthogonal to $P$. To see this, consider the electric dipole moment produced by the oxygens,

$$P_O = Q_O \sum_O \mathbf{R}_O = \sum_{l,m,n} [3 + 2(l + m + n)] \times 1, 1, 1. \quad (2)$$

This is seen to be independent of $\alpha, \beta$ and is equal to zero when summed over a symmetric set of lattice vectors (the electric dipole moment of the A and B atoms is also zero after a suitable summation). Direct computation shows that there is a counter-rotation by an angle proportional to $\alpha \beta$, as shown in Fig. 1 of the Comment.

The transformation properties under inversion on top of an A atom, $I_A$, and inversion on top of a B atom, $I_B$, are straightforward to compute from the atomic positions above. For $I_B$, just apply inversion directly to the $\mathbf{R}_O$ coordinates, while for $I_A$ we must first subtract $1/4, 1/4, 1/4$, invert, and then add $1/4, 1/4, 1/4$. The final result is simple to state: When $I_A$ is applied, the original structure is recovered if we apply the transformations $\alpha \rightarrow -\alpha$ and $\beta \rightarrow -\beta$. Under $I_B$, the original lattice will be recovered only if we apply $\alpha \rightarrow +\alpha$, and $\beta \rightarrow -\beta$. In summary,

$$I_A(\alpha, \beta) = (-\alpha, -\beta)$$

$$I_B(\alpha, \beta) = (\alpha, -\beta). \quad (3)$$