First-principles study of the lattice and electronic structures of TbMn$_2$O$_5$

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The structural, electronic and lattice dielectric properties of multiferroic TbMn$_2$O$_5$ are investigated using density functional theory within the generalized gradient approximation (GGA). We use collinear spin approximations and ignore the spin-orbit coupling. The calculated structural parameters are in excellent agreement with the experiments. We confirm that the ground state structure of TbMn$_2$O$_5$ is of space group $P6_2$2, allowing polarizations along the $b$-axis. The spontaneous electric polarization is calculated to be $1187 \text{nC cm}^{-2}$. The calculated zone-center optical phonon frequencies and the oscillator strengths of IR phonons agree very well with the experimental values. We then derive an effective Hamiltonian to explain the magnetically-induced ferroelectricity in this compound. Our results strongly suggest that the ferroelectricity in TbMn$_2$O$_5$ is driven by the magnetic ordering that breaks the the inversion symmetry, without invoking the spin-orbit coupling.

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I. INTRODUCTION

Recently, a large class of manganese oxides (RMn$_2$O$_5$ and RMn$_2$O$_{3,4,5}$ with R=Y, Tb, Dy, etc.) has been discovered to be multiferroic, with strong magnetoelectric (ME) coupling. The ME coupling leads to various novel physical effects, such as the “colossal magnetodielectric” (CMD) effects and magneto-spin-flop effects. For example, in TbMn$_2$O$_5$ the ME coupling is so strong, that the electric polarization can be reversed by applying a magnetic field. The remarkable ME effects revealed in these materials have attracted great attention because of the fascinating physics and their potential applications in novel multifunctional ME devices.

The crystal structure of TbMn$_2$O$_5$ is orthorhombic, with four chemical formula units per primitive cell (32 atoms in total), containing Mn$_{12}^{3+}$O$_6$ octahedra and Mn$_{16}^{3+}$O$_5$ pyramids, as shown in Fig. 1. TbMn$_2$O$_5$ shows several magnetic phase transitions accompanied with the appearance of electric polarizations and dielectric anomalies, when cooling down from the room temperature. Starting from an incommensurate antiferromagnetic (ICM) ordering at $T_N = 43K$ with a propagation vector $k$ ($0.50, 0, 0.30$), the structure locks into commensurate antiferromagnetic (CM) state at $T_{CM} = 33K$ with $k=$$(0.5, 0, 0.25)$, during which spontaneous polarization arises at $T_{FE} = 38K$. When the temperature lowers to $T_{ICM} = 24 K$, magnetic order becomes ICM again, with a sudden decrease of polarization and a jump of the $k$ vector to $(0.48, 0, 0.32)$. The spontaneous polarization increase again, when continuing to cool to about $10K$. During the magnetic phase transitions, a peak at $T_{FE}$ and a step at $T_{ICM}$ of the dielectric constant was observed indicating strong ME coupling in this compound. It was demonstrated the electric polarization can be reversed by applying magnetic field.

Experimental data show that the structure of TbMn$_2$O$_5$ has space group $Pbam$ which includes spatial inversion ($R^{-1}$) symmetry. It is therefore puzzling that the material can develop spontaneous electric polarizations. It has been suspected that the actual symmetry group of TbMn$_2$O$_5$ is $P6_2$2, allowing polarization along the $b$ axis. Indeed, there are several experiments supporting this hypothesis. For example, some Raman modes were found to be IR active in TbMn$_2$O$_5$ and the anomalies of atomic displacement parameters (ADP) have been observed Nevertheless, no direct evidence of the lower symmetry has yet been found.

Theoretically, the microscopic origin of the strong ME coupling and the electric polarization is still under intensive debates. The ME coupling could originate either from the symmetric superexchange interactions, or from the antisymmetric exchange interactions. The antisymmetric exchange comes from the spin-orbit coupling, and the noncollinearity of the spin structure is an essential ingredient for this mechanism. However it was shown in Ref. that the largest electric polarization in TbMn$_2$O$_5$ is associated with the CM state that is almost collinear. In our recent work we determined the ground-state structure of TbMn$_2$O$_5$ using the first-principles methods. The results show that the ground-state structure is indeed of polar space group $P6_2$2 and the electric polarization equals $1187 \text{nC cm}^{-2}$. In the calculations, we use collinear spin approximation and ignore the spin-orbit interaction, suggesting that ME coupling in TbMn$_2$O$_5$ is due to the symmetric superexchange interactions.

The aim of the present work to examine rigorously the ground state structural, electronic and lattice dielectric properties of TbMn$_2$O$_5$ using first-principles calculations to provide solid ground for further investigations. The rest of paper is organized as follows. After a brief discussion of the first-principles methods and the approxi-
TABLE I: The calculated lattice constants compared with experimental data. FM and L are the structures of spin configurations a and g in Fig. 2 respectively.

| lattice const. (Å) | FM | L | Exp. |
|------------------|----|---|------|
| a                | 7.3170 | 7.3014 | 7.3251 |
| b                | 8.5269 | 8.5393 | 8.5168 |
| c                | 5.6611 | 5.6056 | 5.6750 |

mations used in the calculations in Sec. III we provide a detailed analysis of the ground-state structural and electronic properties in Sec. III IV. In Sec. V we calculate all zone center optical phonon frequencies and the oscillator strengths of IR modes. The results are in excellent agreement with the known experimental IR and Raman spectra. In Sec. VI we calculate electric polarization in TbMn$_2$O$_5$. We then derive an effective Hamiltonian to explain the microscopic mechanisms of the ferroelectricity and the giant magnetoelectric coupling. We conclude in Sec. VII.

II. METHODOLOGY

Our calculations are based on the standard density-functional (DFT) theory with spin-polarized generalized gradient approximation (GGA). We adopt Perdew-Burke-Ernzerhof functional $^{27}$ implemented in the Vienna $ab$ initio Simulations Package (VASP).$^{18,19}$ A plane-wave basis and projector augmented-wave (PAW) pseudopotentials$^{20}$ are used, with Mn 3$p^3d^4s$, and Tb 5$p^5d^6s$ electrons treated self-consistently. A 500 eV plane-wave cutoff results in good convergence of the total energies. We relax the structure until the changes in the calculated total energies are less than 10$^{-5}$ eV, and the remaining forces are less than 1 meV/Å. Experimentally, TbMn$_2$O$_5$ is found to be incommensurate anti-ferromagnetic (AFM) below 24 K, with the propagation vector $k \approx (0.48, 0, 0.32)$. To accommodate the magnetic structure, one needs a huge supercell, which is computationally prohibitive. Instead, we use a 2$x$1$x$1 supercell, equivalent to approximating the propagation vector $k = (0.5, 0, 0)$. The validity of this approximation has been justified in our previous work.$^{24}$ For the supercell we used, a 1$x$2$x$4 Monkhorst-Pack k-points mesh converges very well the results.

It was demonstrated in Ref. 4 that the largest electric polarization is associated with a commensurate magnetic (CM) state that is almost collinear.$^{15}$ Therefore, in the calculations, we use the collinear spin approximation and ignore the spin-orbit coupling. Our results agree very well with the known experiments, indicating that these approximations capture the essential physics in TbMn$_2$O$_5$.

FIG. 1: (Color online) Structure of TbMn$_2$O$_5$ unit cell, showing Mn$^{4+}$O$_6$ Octahedra and Mn$^{3+}$O$_5$ pyramids.

III. GROUND-STATE STRUCTURE

We start the structural relaxation from the experimental structural parameters.$^{13}$ To determine the ground state structure, we tried various spin configurations (SCs). Eight selected SCs, four ferromagnetic/ferrimagnetic (FM) and four antiferromagnetic (AFM), are shown in Fig. 2. Here, we consider only the spins of Mn$^{3+}$ and Mn$^{4+}$ ions. The total energy of each SC is calculated with full relaxations of the (electronic and lattice) structures. The stablest SC, i.e., the SC of lowest total energy, labeled as g in Fig. 2 is AFM and is identical to the spin structure proposed in Ref. 4. SC g has an energetically degenerate SC$^{18}$ labeled as $g'$ in Fig. 3. In both SCs g and $g'$, Mn$^{4+}$ form an AFM square lattice in the $ab$ plane, whereas Mn$^{3+}$ couples to Mn$^{4+}$ either antiferromagnetically via $J_4$ along a axis or with alternating sign via $J_3$ along the $b$ axis. Mn$^{3+}$ ions in two connected pyramids also couple antiferromagnetically through $J_5$. Here, we adopt the notations $J_3$, $J_4$ and $J_5$ from Ref. 4, and define the $J_3$ to be the Mn$^{4+}$-Mn$^{3+}$ superexchange interaction through pyramidal base corners, and $J_4$ the superexchange interaction through the pyramidal apex, as indicated in Fig. 3. We label the two different Mn$^{4+}$ chains along the a axis I, II, respectively, also following Ref. 4. The magnetic structure of $g'$ can be obtained from g by shifting chain II to the right (or to the left) by one unit cell along the a axis.$^{2}$ The exchange integrals $J_3$, $J_1$, $J_5$, were fitted via a Heisenberg model assuming nearest neighbor (NN) coupling. We find that all the exchange energies are of AFM type, i.e., negative and $|J_4|, |J_5| \gg |J_3|$. Therefore, the spins must couple via $J_4$ and $J_5$ anti-ferromagnetically in the stable magnetic structures. More details about the spin structure is given in Appendix A.
IV. ELECTRONIC STRUCTURE

Figure 4 depicts the calculated total densities of states (DOS) of structure $L$. The DOS of spin-up and spin-down electrons are identical as expected for an AFM state. From the results, the band gap is estimated to be $\sim 0.4$ eV, confirming the experimental fact that TbMn$_2$O$_5$ is an insulator. However, it is well known that GGA greatly underestimates the band gap, especially for the $3d$ compounds, therefore the real band gap might be much larger. We further calculated the site-projected partial DOS (PDOS) for Tb, Mn $d$ electrons and O $p$ electrons in the energy range of -2.5 to 2.5 eV around the Fermi level, shown in Fig.5. In structure $L$, the Tb, Mn$^{3+}$, O$_2$, O$_3$ and O$_4$ each has two non-equivalent sites, and the PDOS are shown separately. The PDOS for other electrons are quite small in the selected energy range and therefore are not shown. We see the DOS near the Fermi level is mainly from Mn 3d and O 2p orbitals.

The local magnetic moments are estimated for Mn$^{3+}$ to be $\sim 2.37$ $\mu_B$, and for Mn$^{4+}$ to be $\sim 1.64$ $\mu_B$, in a good agreement with the refined magnetic moments. The ionic radii of 0.60 Å and 0.66 Å are used for Mn$^{4+}$ and Mn$^{3+}$ respectively taken from the periodic table. The local magnetic moments of Mn$^{3+}$, and Mn$^{4+}$ at different WPs are slightly different. O ions also have small induced magnetic moments, due to their hybridization with Mn ions. The calculated local moments of Tb are extremely small, whereas 1.6 $\mu_B$ is assumed in order to obtain a perfect fit of the neutron diffraction data in Ref.4. The difference might come from that the $f$ electrons are not included as valence electrons in the Tb pseudopotential.
FIG. 3: (Color online) Spin configurations with different combinations of chains I and II. $g$ and $g'$ are the ground state spin configurations for structure $L$ and $R$ respectively, whereas $dw$ and $dw'$ are the domain walls between structure $L$ and $R$.

TABLE II: Comparison of the calculated and measured atom positions of TbMn$_2$O$_5$. $L$ and $H$ are the ground state structure and the high-symmetry structure respectively. $|\delta a|$, $|\delta b|$, and $|\delta c|$ denote the atomic displacements from $H$ to $L$. The experimental values are taken from Ref. 13.

| atom   | $a$ (Pb$_2$$_m$) | $b$ (Pb$_2$$_m$) | $c$ (Pb$_2$$_m$) | $a$ (Pb$_m$) | $b$ (Pb$_m$) | $c$ (Pb$_m$) | $|\delta a|$ | $|\delta b|$ | $|\delta c|$ | Exp. (Pb$_m$) |
|--------|------------------|------------------|------------------|--------------|--------------|--------------|------------|------------|------------|----------------|
| Tb$^{3+}$ | 0.1410 | 0.1733 | 0.1407 | 0.1732 | 0 | 3.0 | 1.5 | 0 | 0.1399 | 0.1726 | 0 |
| Tb$^{3+}$ | 0.6404 | 0.3270 | 0 | 3.0 | 1.5 | 0 |
| Mn$^{4+}$ | 0.0001 | 0.5003 | 0.2558 | 0 | 0.5 | 0.2558 | 0.8 | 2.9 | 0 | 0 | 0.5 | 0.2618 |
| Mn$^{3+}$ | 0.4012 | 0.3558 | 0.5 | 0.4014 | 0.3551 | 0.5 | 2.2 | 6.6 | 0 | 0.4120 | 0.3510 | 0.5 |
| Mn$_2$ | 0.9016 | 0.1456 | 0.5 | 2.2 | 6.6 | 0 |
| O1 | 0.0008 | 0.0002 | 0.2709 | 0 | 0 | 0.2709 | 8.2 | 2.3 | 0 | 0 | 0 | 0.2710 |
| O2 | 0.1646 | 0.4480 | 0 | 0.1647 | 0.4481 | 0 | 1.2 | 1.2 | 0 | 0.1617 | 0.4463 | 0 |
| O2 | 0.6648 | 0.0517 | 0 | 1.2 | 1.2 | 0 |
| O3 | 0.1560 | 0.4329 | 0.5 | 0.1565 | 0.4337 | 0.5 | 5.3 | 7.8 | 0 | 0.1528 | 0.4324 | 0.5 |
| O3 | 0.6571 | 0.0655 | 0.5 | 5.3 | 7.8 | 0 |
| O4 | 0.3977 | 0.2077 | 0.2438 | 0.3968 | 0.2079 | 0.2430 | 8.8 | 2.2 | 8.5 | 0.3973 | 0.2062 | 0.2483 |
| O4 | 0.8959 | 0.2919 | 0.7579 | 8.8 | 2.2 | 8.5 |

TABLE III: The Wyckoff positions (WPs) for each inequivalent atom in TbMn$_2$O$_5$ under the space group Pb$_m$ and its subgroup Pb$_2$$_m$.

| Atoms | WP(Pb$_m$) | WP(Pb$_2$$_m$) |
|-------|------------|---------------|
| Tb$^{3+}$ | 4g | 2a, 2a |
| Mn$^{4+}$ | 4f | 4c |
| Mn$^{3+}$ | 4h | 2b, 2b |
| O1 | 4e | 4c |
| O2 | 4g | 2a, 2a |
| O3 | 4h | 2b, 2b |
| O4 | 8i | 4c, 4c |

We also calculated the DOS and PDOS of structure $H$ and find no obvious differences from structure $L$, suggesting that the effects of the lattice structure distortion and
TABLE IV: The relationships of irreducible representations relatively small in the selected energy range, and therefore and spin down respectively. The PDOS of other states are
The upper panel and lower panel show the PDOS for spin up between space group $L$ the symmetry lowering in structure are small.

V. LATTICE DYNAMIC PROPERTIES

The symmetry lowering and ferroelectricity in the traditional ferroelectrics, such as $\text{BaTiO}_3$, $\text{PbTiO}_3$, etc. are driven by the condensation of zone center soft phonons. In $\text{TbMn}_2\text{O}_5$, the low symmetry ($P\text{bam}$) structure was not observed directly in the experiments. However, a strong evidence that suggests the symmetry lowering is that one of the Raman-active phonons become also IR-active at low temperature, which is forbidden by the higher $P\text{bam}$ symmetry. To elucidate the origin of the symmetry lowering, we calculate the frequencies of all zone center phonons, using frozen phonon method, to exam if any soft modes exist in $\text{TbMn}_2\text{O}_5$ and the symmetry properties of all phonons. Furthermore, the validity of our theories can be examined by comparing the calculated phonons with experiments.

A. symmetry analysis

We first carry out symmetry analyses and decompose the symmetry-adapted modes into irreducible representations. The Hamiltonian remains invariant under a lattice translation of the 32-atom primitive cell combined with spin reversal. Therefore the force-constant matrix has the translational symmetry of the 32-atom primitive cell. We then perform the symmetry analyses on the 32-atom primitive cell (instead of the 64-atom AFM cell used in the calculations), using the SMODES symmetry-analysis software package.

For the high symmetry structure ($P\text{bam}$), all the 96 modes, including 3 acoustic modes, are decomposed into 8 irreducible representations (irreps):

$$\Gamma(P\text{bam}) = 9B_{1u} \oplus 15B_{2u} \oplus 15B_{3u} \oplus 13A_g \oplus 13B_{1g} \oplus 11B_{2g} \oplus 11B_{3g} \oplus 9A_u .$$

Among them $B_{3u}$, $B_{2u}$ and $B_{1u}$ modes are IR active, polarized along the $a$, $b$ and $c$ axis, respectively, whereas $B_{1g}$, $B_{2g}$, $B_{1g}$ and $A_g$ modes are Raman active and $A_u$ modes are silent. All these irreps are one dimensional, i.e., no degenerate phonons. The three acoustic modes are each in one of the three IR-active representations. As we see, the Raman- and IR-active modes do not couple under the $P\text{bam}$ symmetry.

For the crystal structure processes a $P\text{bam}$, the 96 phonons can be decomposed into 4 irreps:

$$\Gamma(P\text{bam}) = 28A_1 \oplus 20B_1 \oplus 28B_2 \oplus 20A_2 .$$

We found all modes are Raman active, among them $A_1$, $B_1$ and $B_2$ are also IR active, which are polarized along the $b$, $c$, and $a$ axis respectively. The relationships between the irreps of $P\text{bam}$ symmetry and its subgroup $P\text{bam}$ symmetry are given in Table IV together with the symmetry character for each irrep. The $A_1$ modes are coupled from the $A_g$ and $B_{2u}$ modes and the $A_2$ modes are composed of the $B_{2g}$ and $A_u$ modes. The $B_1$ modes are the coupled $B_{1g}$ and $B_{1u}$ modes whereas the $B_2$ modes are the coupled $B_{1g}$ and $B_{3u}$ modes.

FIG. 5: Site-projected partial density of states (PDOS) of Mn and Tb $d$ electrons, and O $p$ electrons for $\text{TbMn}_2\text{O}_5$. The upper panel and lower panel show the PDOS for spin up and spin down respectively. The PDOS of other states are relatively small in the selected energy range, and therefore not shown. The dashed lines represent the Fermi level.
TABLE V: Calculated phonon frequencies $\omega$, effective charges $Z_\lambda^*$ and oscillator strength $S_\lambda$ of $A_1$ modes, classified according to their major symmetry characters and compared with the experimental data. The IR-active phonons are extracted from Ref. [10] at 7K and Raman-active phonons are extracted from Ref. [24].

| $\omega$  | $B_{2u}$ (IR, $b$-polarized) | $S_\lambda^*$ | Raman% | $A_\theta$ (Raman) | $Z_\lambda^*$ | $S_\lambda$ | IR% |
|----------|-------------------------------|---------------|--------|-------------------|---------------|------------|-----|
| GGA Exp. | GGA Exp.                     | GGA Exp.      | GGA Exp.| GGA Exp.| GGA Exp.| GGA Exp.| GGA |
| 100.7    | 97.2                         | 0.09          | 0.17   | 0.11              | 0.42          | 0.08       | 110.1|
| 158.0    | 168.9                        | 0.28          | 0.31   | 0.44              | 0.46          | 0.12       | 136.9|
| 162.8    | 171.9                        | 0.31          | 0.25   | 0.49              | 0.30          | 0.04       | 221.6|
| 224.8    | 222.2                        | 0.30          | 0.20   | 0.24              | 0.11          | 1.85       | 231.1|
| 267.3    | 258.8                        | 0.25          | 0.28   | 0.12              | 0.17          | 0.36       | 312.5|
| 316.7    | 333.4                        | 0.78          | 0.37   | 0.82              | 0.17          | 1.02       | 340.2|
| 351.3    | 386                          | 0.28          | 0.15   | 0.09              | 0.02          | 2.94       | 405.6|
| 412.5    | 422.3                        | 0.39          | 0.60   | 0.13              | 0.28          | 0.23       | 445.1|
| 439.5    | 453.2                        | 2.58          | 2.25   | 4.81              | 3.43          | 2.65       | 489.2|
| 471.0    | 481.8                        | 1.40          | 2.18   | 1.23              | 2.86          | 5.89       | 529.2|
| 533.5    | 538.2                        | 0.52          | 0.72   | 0.27              | 0.25          | 5.95       | 612.0|
| 549.3    | 567.3                        | 0.50          | 1.09   | 0.12              | 0.52          | 1.33       | 613.5|
| 625.0    | 636.6                        | 1.01          | 0.88   | 0.36              | 0.27          | 11.20      | 673.6|
| 667.2    | 688.3                        | 0.17          | 0.10   | 0.01              | 0.0003        | 8.83       |

*IR-active and 703 cm$^{-1}$ measured by Aguilar [10].

TABLE VI: Calculated phonon frequencies $\omega$, effective charges $Z_\lambda^*$ and oscillator strength $S_\lambda$ of $B_2$ modes, classified according to their major symmetry characters and compared with the experimental data. The IR-active phonons are extracted from Ref. [10] at 7K and Raman-active phonons extracted from Ref. [24].

| $\omega$  | $B_{3u}$ (IR, $a$-polarized) | $S_\lambda^*$ | Raman% | $B_{1g}$ (Raman) | $Z_\lambda^*$ | $S_\lambda$ | IR% |
|----------|-------------------------------|---------------|--------|-----------------|---------------|------------|-----|
| GGA Exp. | GGA Exp.                     | GGA Exp.      | GGA Exp.| GGA Exp.| GGA Exp.| GGA Exp.| GGA |
| 111.8    | 111.9                        | 0.02          | 0.23   | 0.004           | 0.59          | 0.02      | 148.2|
| 152.2    | 157.5                        | 0.17          | 0.37   | 0.18            | 0.81          | 0.50      | 172.9|
| 159.8    | 164.2                        | 0.76          | 0.57   | 3.11            | 1.68          | 0.12      | 222.1|
| 217.4    | 218.5                        | 0.05          | 0.32   | 0.01            | 0.30          | 10.99     | 243.0|
| 264.5    | 254.8                        | 0.30          | 0.94   | 0.18            | 1.88          | 0.62      | 300.7|
| 317.0    | 333.1                        | 0.03          | 0.27   | 0.002           | 0.09          | 0.15      | 373.0|
| 353.1    | 364.9                        | 1.04          | 1.39   | 1.21            | 2.02          | 1.25      | 410.4|
| 379.1    | 397.6                        | 0.56          | 0.66   | 0.30            | 0.38          | 8.44      | 470.0|
| 465.2    | 494.8                        | 0.24          | 0.89   | 0.03            | 0.45          | 37.76     | 545.8|
| 474.4    | 494.8                        | 0.24          | 0.89   | 0.03            | 0.45          | 37.76     | 545.8|
| 500.2    | 518.3                        | 0.21          | 0.03   | 1.20            | 518.3         | 0.115     | 587.1|
| 595.4    | 613.5                        | 0.90          | 1.38   | 0.32            | 0.71          | 1.28      | 643.8|
| 617.1    | 627.5                        | 1.23          | 0.81   | 0.55            | 0.23          | 4.57      | 678.7|
| 672.7    | 704.2                        | 0.33          | 0.42   | 0.03            | 0.05          | 12.12     |

B. Zone Center Optical Phonons

The zone-center phonon frequencies are calculated via a frozen phonon technique. For each irrep $\Gamma$ in Eq. (1), we construct an $N_\Gamma \times N_\Gamma$ dynamical matrix from a series of frozen-phonon calculations in which the structure is distorted according to each of the $N_\Gamma$ symmetry modes in this irrep. For example, $N_\Gamma=28$ for the $A_1$ modes in Eq. (2). All calculations were performed in the 64-atom AFM cell respect to the correct AFM reference ground state. After calculating the residual Hellmann-Feynman forces we displace the ions according to the symmetry coordinate for each mode by 0.1% of lattice constant and calculate the forces $F_\alpha^\beta_{ij}$ on ion $i$ in Cartesian direction $\alpha$ due to displacements $u_j^\beta$ of ion $j$ in direction $\beta$. The force constant matrix

$$\Phi_{ij}^{\alpha\beta} = \frac{\partial F_{ij}^{\alpha}}{\partial u_j^\beta},$$

is then obtained by finite differences to the residual forces in the equilibrium structure to eliminate the numerical errors due to the residual forces. The normal modes $u_\lambda$ and their frequencies $\omega_\lambda$ are then obtained through solu-
tation of the eigenvalue equation

$$\Phi \cdot u_\lambda = \omega_\lambda^2 M \cdot u_\lambda.$$  \hspace{1cm} (4)

Here $M^{\alpha \beta}_{ij} = (m_i/m_0) \delta_{ij} \delta_{\alpha \beta}$ is the dimensionless diagonal mass matrix, where $m_i$ is the mass of atom $i$ and $m_0$ is a reference mass chosen here to be 1 amu, and the eigenvectors are normalized according to $u_\mu \cdot M \cdot u_\nu = \delta_{\mu \nu}$.

The phonon frequencies calculated from high structure $H$ are extremely close to those calculated from low-symmetry structure $L$. No soft mode is found in both high and low symmetry structures, excluding the possibility of ferroelectricity driven by the soft modes. We therefore show only the phonon frequencies for the ground state structure $L$ only. The calculated $A_1$, $B_2$, $B_1$ phonon frequencies are given in Table VII and Table VIII respectively, whereas the $A_2$ phonons are given in Table VI. To make a good contact with experiments, we divide the phonons of each irrep into two presentations according to their major symmetry characters (see Table VI). We found that for most of the modes the coupling between the major and minor characters (IR and Raman or Raman and silent) are extremely small, and such classification is unambiguous. All calculated phonon frequencies are in excellent agreement with the experiments especially for the low-frequency phonons. The errors are less than 5%.

In order to check the influences on phonons from different magnetic orderings and magnetic-ordering-induced lattice modulations, we also calculated the phonon frequencies for the FM structure, we find the differences are also small.

In the following sections, we compare the calculated IR and Raman spectra with the experiments in details.

1. IR spectra and dielectric properties

Aguilar et al. measured the frequencies of IR-active phonon polarized along the $b$ and $a$ axes. These phonon modes are compared with the calculated modes in Table VI and Table VII respectively.

For the IR phonons, we can further calculate their contribution to the dielectric constant. The dielectric function tensor in the frequency range near the phonon frequencies could be written as sum

$$\epsilon_{\alpha \beta}(\omega) = (\epsilon_{\infty})_{\alpha \beta} + (\epsilon_{ph})_{\alpha \beta}(\omega)$$  \hspace{1cm} (5)

of electronic contribution and lattice contribution, where $\alpha$, $\beta = a, b, c$ are the axis indices. For TbMn$_2$O$_5$, $(\epsilon_{\infty})_{aa}$ and $(\epsilon_{\infty})_{bb}$ were measured to be 5.31 and 6.82 respectively. In TbMn$_2$O$_5$, the phonons are polarized along the $a, b, c$ axis, and $\epsilon_{\alpha \beta}(\omega)$ is diagonal. We could therefore ignore the subscripts $\alpha, \beta$, but only give the polarization direction. The dielectric contribution from the $\alpha$-polarized IR-active phonons is then

$$\epsilon_{ph}^{(\alpha)}(\omega) = \Omega_{\alpha}^0 \sum_\lambda \frac{Z_{\lambda}^2}{\omega_\lambda^2 - \omega^2},$$  \hspace{1cm} (6)

where $\omega_\lambda$ and $Z_{\lambda}^2$ are the mode frequencies and mode dynamical charges respectively, and $\Omega_{\alpha}^0 = 4\pi e^2/m_0 V$ is a characteristic frequency having the interpretation of a plasma frequency of a gas of objects of mass $m_0=1$ amu, charge $e$, and density $V^{-1}$ ($V$ is the 32-atom primitive cell volume). The sum is restricted to the $\alpha$-polarized phonons. The mode dynamical charges are defined as

$$Z_{\lambda}^\alpha = V \frac{\partial P_{\alpha}}{\partial u_{\lambda}}$$  \hspace{1cm} (7)

in which $P_{\alpha}$ is the polarization in the $\alpha$ direction due to a small frozen-ion amplitude of the $\lambda$-th phonon modes. In practice we compute the mode dynamical charges by finite differences method following Ref. 22. Once we have the mode effective charges, we calculate the oscillator strengths of each IR-active modes $S_{\lambda} = \Omega_{\alpha}^0 Z_{\lambda}^2/\omega_\lambda^2$, and the total lattice contribution to the static ($\omega \to 0$) dielectric constant $\epsilon_{ph}(0) = \Omega_{\alpha}^0 \sum_{\lambda} Z_{\lambda}^2/\omega_\lambda^2 = \sum_{\lambda} S_{\lambda}$.

The results of the Born effective charges and oscillator strengths for the IR-active modes are also listed in Table VI and Table VII for the $A_1$ ($b$-polarized), $B_2$ ($a$-polarized) and $B_1$ ($c$-polarized) phonons respectively.

Let us first look at the $A_1$ ($b$-polarized) modes presented in Table VI. There are 28 $A_1$ modes in total, and 14 (plus one acoustic mode) of them are mainly $B_{2u}$ IR modes. The calculated phonon frequencies and oscillator strengths are in very good agreement with experiments. The calculated total oscillator strength is about 9.24 compared with the measures value 9.12. The rest 13 modes are mainly $A_g$ Raman modes. Under the low Pb$_2$In$_m$ symmetry, these modes also acquire some small oscillator strengths. More importantly, the 693 cm$^{-1}$ $A_g$ Raman mode (703 cm$^{-1}$ measured from IR spectra), that was found also IR active with oscillator strength $S_1=0.001$ in the experiment is well reproduced in the calculations, with oscillator strength $S_1=0.004$, therefore, confirming that the ground state structure is indeed of Pb$_2$I$_m$ symmetry. The oscillator strengths of other $A_g$ modes might be covered by the adjacent $B_{2g}$ modes, and therefore are not observed experimentally. To see more clearly between the coupling of the IR and Raman modes, we also list the percentage of the characters in the Table. We see the coupling between IR and Raman modes is fairly small.

The results of 28 $B_2$ phonons are given in Table VII classified into two presentation according to their major symmetry characters, including 14 IR ($B_{1u}$) modes, 13 ($B_{1g}$) Raman modes and one acoustic mode. Two of the $B_{1u}$ modes were missing in the experiments, possibly due to their small oscillator strengths. Here we tentatively assign them as the 465.2 and 509.2 cm$^{-1}$ modes. Again the phonon frequencies agree very well with the experiments. However, the IR oscillator strengths are in less agreement with the experimental values. Some modes have large discrepancy in the oscillator strengths compared to the experiments, e.g., the 264 cm$^{-1}$ mode. Nevertheless, the calculated total oscillator strength for $a$-polarized phonons is about 6.87, in a reasonable agree-
ment with the experiments value about 9.19. Similar to the $A_g$ modes, the $B_{1g}$ Raman modes also have small IR oscillator strengths due to the $Pb2_1m$ symmetry. For most modes, the coupling between the IR and Raman characters are small, except two modes: the 474 cm$^{-1}$ mode in the $B_{3u}$ presentation and the 470 cm$^{-1}$ mode in the $B_{1g}$ presentation. This is probably because they are accidentally degenerate in phonon frequencies, leading to large character mixing.

The phonon frequencies and oscillator strengths of the $c$-axis polarized $B_1$ phonons are given in Table VII including 8 (plus one acoustic mode) $B_{1u}$ IR modes and 11 $B_{3g}$ Raman modes. Interestingly, there are some modes that have very large IR and Raman modes mixing in this presentation. For example, the 426 cm$^{-1}$ Raman modes have about 49% IR character and very large oscillator strength of $S_\lambda=3.89$. However, this large Raman-IR mixing might come from that this modes accidentally degenerate with the 407 and 433 cm$^{-1}$ IR modes in the numerical calculations, and might not be the case in the real system. Unfortunately, we can not find suitable experimental IR spectra to compare with for the $B_1$ modes. We hope future experiment can clarify this problem.

2. Raman spectra

The temperature-dependent Raman spectra of HoMn$_2$O$_5$ and TbMn$_2$O$_5$ were measured by Mihailova et al. We compare the calculated and measured Raman spectra of TbMn$_2$O$_5$ in Table VII for the $B_{1g}$, $A_g$, $B_{3g}$ and $B_{2g}$ modes respectively. The $A_u$ silent modes are also given in Table VII for they also Raman-active in structure $L$. Some Raman modes were missing in the experiments probably because the missing modes are of very low intensity or out of the spectral range ($\omega < 100$ cm$^{-1}$) of the experimental setup. Once again, the calculated phonon frequencies are in very good agreement with the experimental values.

Table VIII: Calculated phonon frequencies $\omega$ of $A_2$ modes, classified according to their major symmetry characters and compared with the experimental data. The Raman-active phonons are extracted from Ref. 24.

| $A_2$ (Silent) | $B_{2g}$ (Raman) |
|---------------|------------------|
| $\omega$ | $\omega$ | Raman% | $\omega$ | $\omega$ | Raman% |
| GGA | GGA | Exp. | GGA | GGA | Exp. |
| 110.2 | 0.04 | 95.9 | 99.9 |
| 131.4 | 0.09 | 210.6 | 214 | 99.4 |
| 226.6 | 6.18 | 231.1 | 232 | 99.9 |
| 293.9 | 40.7 | 274.2 | 99.4 |
| 399.4 | 12.6 | 288.9 | 301 | 60.3 |
| 425.0 | 3.00 | 337.5 | 99.3 |
| 497.7 | 5.05 | 441.1 | 89.1 |
| 529.4 | 1.96 | 448.7 | 455 | 96.9 |
| 611.5 | 5.65 | 469.6 | 470 | 92.9 |
| 553.9 | 577 | 0.012 | 2.07 |

So far, no IR-active modes has been observed in the Raman spectra of TbMn$_2$O$_5$. However, there is an evidence that one of the IR modes become also Raman-active in HoMn$_2$O$_5$. Three low frequency $A_g$ Raman modes were observed at 10 K in HoMn$_2$O$_5$ and they are the 217 cm$^{-1}$, 219 cm$^{-1}$ and 226 cm$^{-1}$ modes, whereas the 219 cm$^{-1}$ mode disappears at room temperature. Since the phonons of frequencies at this range are mainly due to the vibrations of Mn and O, and less related to the $R$ atoms, one could therefore expect there are also three Raman modes in this frequencies range for TbMn$_2$O$_5$. However, only two $A_g$ modes (215 cm$^{-1}$ and 221 cm$^{-1}$ modes) were observed (nevertheless at $T=300$ K) in this frequency range in TbMn$_2$O$_5$, consistent with our first-principles calculations for the $A_g$ modes. We therefore propose that the 219 cm$^{-1}$ mode in HoMn$_2$O$_5$ is actually an IR-active phonon that become also Raman-active at low temperature.
VI. DISCUSSIONS ON THE MICROSCOPIC ORIGIN OF THE ELECTRIC POLARIZATIONS AND GIANT MAGNETOELECTRIC COUPLING

We have now firmly established that the ground state structure of TbMn$_2$O$_5$ (L or R) is indeed of symmetry $Pb2_1m$, allowing spontaneous polarization along the $b$ axis. We have calculated$^{18}$ the spontaneous polarization of structure $L$ ($R$) via Berry phase technique.$^{20}$ The intrinsic polarization in this material is calculated to be $1187\ nC\cdot cm^{-2}$. This value is an order of magnitude smaller than that of the traditional ferroelectrics (e.g., for BaTiO$_3$ $\sim 25\mu C\cdot cm^{-2}$), yet it is about 30 times larger than the currently measured value$^2$ ($\sim 40\ nC\cdot cm^{-2}$) for this compound. The reasons for the discrepancy between the calculations and experiments might because of the approximations used in calculations. For example, we approximate the magnetic propagation vector $k_z=0.32$ by zero. We also ignore the spin-orbit coupling and assuming collinear spins. Without these approximations, the polarization might be reduced. On the other hand, the experiments$^2$ measured polycrystalline samples, in which the grains polarize along different directions cancel each other, therefore might significantly underestimate the intrinsic polarization. We believe a high quality single crystal sample should greatly enhance the measured electric polarization.

To further elucidate the origin of the polarization, we calculate the spontaneous polarization for the high symmetry structure $H$ and get $P=228\ nC\cdot cm^{-2}$. It might be surprising to see a crystal that possesses inversion symmetry would develop spontaneous polarization at the first sight. However, to discuss the symmetry of a crystal with a magnetic ordering, the pure point groups may not be enough. One has to resort to the magnetic groups to take account of the spin components. Based on the symmetry considerations, there are three possibilities (but not exclusive) to develop spontaneous polarization:

(i) The crystal structure itself does not have inversion symmetry. This is the most familiar case to us, as it is seen in the traditional ferroelectrics.

(ii) The crystal structure itself has the $R^{-1}$ symmetry, but the magnetic structure does not have the $R^{-1}$ symmetry and the combination of the $R^{-1}$ and time-reversal ($T^{-1}$) symmetry, $(RT)^{-1}$. If the magnetic structure of a system does not have the $R^{-1}$ symmetry, but still has the $(RT)^{-1}$ symmetry, each spin channel may have finite electric polarization. However, the polarizations from spin up and spin down channels cancel each other, leading to zero total electric polarization.

(iii) Even both the crystal and magnetic structure have the inversion symmetry, but they do not have the common inversion center, as proposed by Betouras et al.$^{20}$

In the later two cases, the “electronic” inversion symmetry is broken because of the magnetic ordering. The electronic symmetry breaking will further couple to the lattice and lead to lattice distortion. It was shown$^{18}$ that in TbMn$_2$O$_5$, the SC $g$ does not have the $R^{-1}$ and the $(RT)^{-1}$ symmetry (case ii), because the special spin configurations of the Mn$^{3+}$-Mn$^{4+}$-Mn$^{3+}$ chains along the $b$ axis. Therefore, when holding atoms fixed at the centrosymmetric structure, turning on the magnetic order does two things: it generates a purely electronic polarization of 228 $nC\cdot cm^{-2}$, and it also applies forces to the atoms. These forces give rise to atomic displacements that yield an additional 959 $nC\cdot cm^{-2}$.

The above discussion is based solely on the symmetry argument. We now discuss the microscopic mechanism of coupling between the magnetic order and lattice. The microscopic origin of the ME coupling may come from:

(i) Symmetric superexchange interactions of the scalar field type: $S_n \cdot S_{n+1}$.

(ii) Antisymmetric superexchange interactions of the vector field type: $S_n \times S_{n+1}$. The antisymmetric superexchange interaction (also known as Dzyaloshinskii-Moriya interaction) originate from the spin-orbit interaction. For the antisymmetric superexchange mechanism, noncollinearity is essential for the ME coupling. Experimentally, it was shown that in TbMn$_2$O$_5$ the largest electric polarization is associated with a commensurate magnetic phase that is almost collinear,$^{4,15}$ therefore, in this phase, the spin-orbit contribution to the ME coupling is small. An alternative mechanism must be considered to account for the ME aspects. In the present calculations, we ignore the spin-orbit coupling and assume collinear spin ($S_i \parallel S_j$), therefore the symmetry breaking and ME coupling is merely due to the symmetric superexchange $S_n \cdot S_{n+1}$.

We now derive an effective model to describe the microscopic mechanism of the ME coupling in TbMn$_2$O$_5$, based on a Heisenberg model assuming NN interactions. The total energy of the system around the high-symmetry structure $H$ can be written as,

$$E(\{u_\lambda\}) = E_0 + \frac{1}{2} \sum_\lambda m_\lambda \omega_\lambda^2 u_\lambda^2 - \sum_{i,j} J_{ij}(\{u_\lambda\}) S_i \cdot S_j,$$

where $u_\lambda$ is the $\lambda$-th zone-center phonon, and $S_i$ is the magnetic moment of the $i$-th atom. Here, we consider only the magnetic moments of the Mn$^{3+}$ and Mn$^{4+}$ ions. $E_0$ is the total energy of structure $H$ without spin-spin interactions. Since the magnetic-ordering-induced lattice distortion from structure $H$ is small, we could expand the exchange interaction $J_{ij}(\{u_\lambda\})$ up to the second order of $u_\lambda$, i.e.,
\[ E(\{u_\lambda\}) = (E_0 - \sum_{ij} J_{ij}(0) S_i \cdot S_j) - \sum_\lambda \sum_{ij} \frac{\partial J_{ij}}{\partial u_\lambda} u_\lambda S_i \cdot S_j + \left( \frac{1}{2} \sum_\lambda m_\lambda \omega_\lambda^2 u_\lambda^2 - \sum_\lambda \sum_\rho \frac{\partial^2 J_{ij}}{\partial u_\lambda \partial u_\rho} u_\lambda u_\rho S_i \cdot S_j \right) . \] (9)

The above three terms play different roles in the multiferroics.

(i) The zeroth order term in \( u_\lambda \),
\[ E_0 - \sum_{ij} J_{ij}(0) S_i \cdot S_j , \] (10)
determines the ground state spin configurations which is further discussed in Appendix A.

(ii) The second term in Eq. (13) that is linear in \( u_\lambda \),
\[ - \sum_{ij} \sum_\lambda \frac{\partial J_{ij}}{\partial u_\lambda} u_\lambda S_i \cdot S_j , \] (11)
provides the driven forces for the lattice distortion from high symmetry structure \( H \). The force on the \( \lambda \)-th phonon modes is
\[ F_\lambda = - \frac{\partial E}{\partial u_\lambda} |_{u_\lambda = 0} = \sum_{ij} \frac{\partial J_{ij}}{\partial u_\lambda} S_i \cdot S_j , \] (12)
which is nonzero, provided \( \{S_i\} \) does not have the \( RT^{-1} \) symmetry.

In Ref. [16], we illustrated the lattice distortion from the high symmetry structure using a spin chain model. For SC 4, inside the Mn\textsuperscript{3+}-Mn\textsuperscript{4+}-Mn\textsuperscript{3+} segments along the \( b \)-axis, Mn\textsuperscript{4+} always have the same spin with the upper Mn\textsuperscript{3+} but opposite spin with the lower Mn\textsuperscript{3+}, whereas for g', the opposite is true. Mn\textsuperscript{4+} could therefore move closer to the Mn\textsuperscript{3+} with same spin to lower the exchange energy. According to Eq. (12), we have \( F_\lambda(g) = - F_\lambda(g') \). The high symmetry structure \( H \) then spontaneous relax to structure \( L \) or \( R \) according to its SC. The lattice distortion from high symmetry structure can be estimated as,
\[ \delta u \sim \frac{\partial J}{\partial u} / \bar{\omega}^2 , \] (13)
where \( \bar{\omega} \) is the weight averaged phonon frequency. We could therefore expect that a material with larger \( \partial J/\partial u \) and softer phonon frequencies would have larger ME effects, provided the symmetry requirements are satisfied.

(iii) The quadratic term in \( u_\lambda \),
\[ \frac{1}{2} \sum_\lambda m_\lambda \omega_\lambda^2 u_\lambda^2 - \sum_{ij} \sum_\lambda \frac{\partial^2 J_{ij}}{\partial u_\lambda \partial u_\rho} u_\lambda u_\rho S_i \cdot S_j \] (14)
describes the coupling between phonons and magnons, which renormalizes the phonon frequencies. For example, in ZnCr\textsubscript{2}O\textsubscript{4} there is a large splitting between IR active phonons along the \( x \) and \( z \) axis was observed due to the phonon-magnon coupling. The phonon-magnon coupling might be responsible to the “step” in dielectric constant at 24K in TbMn\textsubscript{2}O\textsubscript{5}. Detailed investigation of the phonon-magnon coupling in TbMn\textsubscript{2}O\textsubscript{5} is out of the scope of the present work, and we leave it for future investigations.

VII. SUMMARY

We have investigated the ground state structural and electronic properties of multiferroic TbMn\textsubscript{2}O\textsubscript{5} using density functional theory within GGA approximations to elucidate the microscopic origin of the ferroelectricity and giant magnetoelectric coupling. We use the collinear spin approximation and ignore spin-orbit coupling. The calculated lattice and electronic structures agree well with the known experiments. We confirm that the ground state structure of TbMn\textsubscript{2}O\textsubscript{5} is of space group \( Pb2_1m \), allowing polarizations. The spontaneous electric polarization is calculated to be 1187 nC\textpercm\textsuperscript{2} along the \( b \) axis. The calculated zone-center optical phonons frequencies and the oscillator strengths of IR phonons agree very well with the experimental values. Unlike the traditional ferroelectrics, no soft phonons is found in TbMn\textsubscript{2}O\textsubscript{5}. We derive an effective Hamiltonian to explain the magneto-electrically-induced ferroelectricity, in which the spin-lattice coupling is of symmetric superexchange interaction type. Our results strongly suggest that the ferroelectricity in TbMn\textsubscript{2}O\textsubscript{5} is driven by the magnetic ordering that breaks the the inversion symmetry without invoking the spin-orbit coupling.

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APPENDIX A: GROUND STATE SPIN CONFIGURATIONS

In this appendix, we discuss in more details about the magnetic structures of TbMn\textsubscript{2}O\textsubscript{5} and the (super)exchange interactions \( J_{ij} \). To determine the \( J_{ij} \) we calculate the total energies of eight SCs shown in Fig.
These results are in reasonable agreement with the first-principles calculations, suggesting that the Heisenberg model is valid even in the FM phase when applied to TbMn$_2$O$_5$. From Table IX we find all the three exchange integrals are negative, i.e., of AFM type, and $|J_4| < |J_3|, |J_5|$. Therefore the ground state SC are mainly determined by $J_4$ and $J_5$. It is easy to see that SC $g$ (and $g'$) indeed has the lowest energy in this model. In both SCs $g$ and $g'$, Mn$^{4+}$ form an AFM square lattice in the $ab$ plane, whereas Mn$^{3+}$ couples to Mn$^{4+}$ either antiferromagnetically via $J_4$ along the $a$ axis or with alternating sign via $J_3$ along the $b$ axis. The zigzag chains along the $b$ axis can be simplified as Mn$^{3+}$-Mn$^{4+}$-Mn$^{3+}$ segments linked via $J_5$ superexchange interactions. Inside the segments Mn$^{3+}$ and Mn$^{4+}$ interact through superexchange $J_3$, whereas the chains couple to each other through $J_4$. The AFM chains along the $a$ axis are of two types, labeled as I and II respectively in Fig. 3. Adjacent chains I and II along the $b$ axis couple to each other via $J_3$, in which half of them are frustrated.

The SCs $g$ and $g'$ have several energetically degenerate SCs as shown in Fig. 8. There are two relative positions between chain I and II, $l$ and $r$. "left" ("right") means that the Mn$^{4+}$ ions in chain I have the same spins to the Mn$^{4+}$ ions on their left (right) side in chain II in each unit cell. Figure 3 shows 4 different combinations of chains I and II. Figure 8(a) and (b) are the ground SC $g$ and $g'$ respectively, whereas Fig 8(c) and (d) are in fact two domain wall structures $dw$ and $dw'$. The two domain walls are energetically degenerate to $g$ and $g'$ in the NN Heisenberg model, because the $J_3$ exchange interactions between chain I and II cancel out no matter what their relative positions are. However, after turning on the spin-lattice coupling, the crystal structure $H$ will relax to $L$ or $R$, and the energy degeneracy between the domain wall structures ($dw$ and $dw'$) to SCs $g$ and $g'$ will be lifted.

| SC status | Energy | $\Delta E$ |
|-----------|--------|-----------|
| $a$ FM    | $E_0 + 16E_3 + 16E_4 + 4E_5$ | -197.84 |
| $b$ FM    | $E_0 - 16E_3 - 16E_4 + 4E_5$ | -158.22 |
| $c$ FM    | $E_0 - 16E_3 - 16E_4 + 4E_5$ | -1004.93 |
| $d$ FM    | $E_0 - 8E_3 - 8E_4$ | -910.32 |
| $e$ AFM   | $E_0 + 8E_3 + 8E_4$ | -596.59 |
| $f$ AFM   | $E_0 - 8E_3 - 8E_4$ | -1263.61 |
| $g$ AFM   | $E_0 - 16E_4 - 4E_5$ | -1624.95 |
| $h$ AFM   | $E_0 + 16E_4 - 4E_5$ | -1047.72 |

$J_3 = -0.45$, $J_4 = -4.92$, $J_5 = -1.85$

**Table IX**: The DFT-GGA calculated total energies of spin configurations (shown in Fig. 2) under the high symmetry structure $H$, where $E_3 = -2J_3 S_3 \cdot S_4$, $E_4 = -2J_4 S_4 \cdot S_5$, $E_5 = -2J_5 S_5 \cdot S_6$. The exchange integrals $J_3$, $J_4$, and $J_5$ are fitted using the total energies of four AFM structures. $\Delta E$ are the energy differences between the fitted energies from the Heisenberg model and the calculated ones. Unit of energy is meV, and the unit of exchange integrals are in meV/$\mu_B$. 

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