Chapter 5

Role of Te in the low dimensional multiferroic material FeTe_2O_5Br*

Multiferroic materials with simultaneous presence of ferroelectricity and magnetism, are in focus of attention in the recent times.\(^{(1,2)}\) Based on the microscopic origin of ferroelectricity (FE) multiferroic materials can be classified into two different classes namely type-I and type-II multiferroic materials. In type-I multiferroics, ferroelectricity and magnetism stem from independent origin and the coupling between magnetism and ferroelectricity is usually weak. In these materials, ferroelectricity typically appear at higher temperatures than magnetism, and the magnitude of spontaneous electric polarization (P) is often large (~ 10-100 \(\mu\)C/cm\(^2\)). One possible mechanism for ferroelectricity in type-I multiferroic material is lone-pair driven. It is well known that cations containing highly polarizable \(5s\) or \(6s\) lone pairs of valence electrons have a strong tendency to break the local inversion symmetry of the crystal. This lone-pair driven mechanism was identified as the source of the ferroelectric instability in BiFeO\(_3\).\(^{(3)}\) In contrast, in type II multiferroics where ferroelectricity may arise due to a particular kind of magnetic ordering that breaks the inversion symmetry, are more interesting from application point of view due to the strong coupling between magnetism and FE.\(^{(4,5)}\) However, the magnitude of electric polarization in these materials are usually very small (~ \(10^{-2}\) \(\mu\)C/cm\(^2\)). For type II multiferroics, non symmetric lattice distortion and ferroelectric order may be induced through exchange striction,\(^{(6,7)}\) spin current mechanism\(^{(8)}\) or inverse Dzyaloshinskii-Moriya (DM) interactions.\(^{(9)}\) In particular, the exchange striction is considered to induce ferroelectricity in some collinear antiferromagnets such as HoMnO\(_3\),\(^{(6)}\) Ca\(_3\)CoMnO\(_6\).\(^{(7,10,11)}\) While strong

*The contents of this chapter have been submitted for publication.
coupling between the magnetic and ferroelectric order parameters makes them attractive but
their real applications have been restricted by the small magnitude of the polarization values.
A possible way to overcome this difficulty could be to combine the best features of type-I and
type-II multiferroics. In this context, the transition metal (TM) selenium (Se) and tellurium
(Te) oxihalides have attracted attention both experimentally and theoretically because of their
exotic magnetic properties driven by the geometric frustration in low dimensions. In addi-
tion, the presence of stereochemically active lone pair in p element cations Te4+, Se4+ may
result in asymmetric coordination around the lone pair cation and is expected to enhance the
possibility of the realization of non centrosymmetric structure necessary for the system to be
ferroelectric. Therefore such systems offer an interesting possibility of combining the features
of type-I (presence of lone pair) and improper ferroelectricity (novel magnetic order in low
dimensions). Interestingly some of these systems exhibit multiferroic behavior. An example
of such a system is FeTe2O5Br. It adopts a layered structure, where individual layers consist of
geometrically frustrated iron tetramer units [Fe4O16] linked by the [Te4O10Br2]6− groups."12)
The structure remains centrosymmetric even in the presence of Te-5s2 lone pairs. The high
temperature fit to the susceptibility data shows negative Curie-Weiss temperature (θ\textsubscript{cw} = -98
K), indicating strong antiferromagnetic interactions between the Fe\textsuperscript{3+}(d\textsuperscript{5}) ions."12) The system
develops long range magnetic order at a considerable low temperature \(T_{N1} = 11\text{ K}\), followed
by a second magnetic transition at \(T_{N2} = 10.5\text{ K}\)."13) The first transition at \(T_{N1}\) is a paramag-
tetic to a high-temperature incommensurate magnetic state (HT-IC) with a constant wave vec-
tor \(q_{IC1} = (0.5, 0.466, 0.0)\) and is immediately followed by another transition at \(T_{N2} = 10.5
\text{ K}\) into the low-temperature incommensurate (LT-IC) multiferroic state. The amplitude modu-
lated magnetic order in the LT-IC phase is described with the wave vector \(q = (0.5, 0.463, 0.0)\)
and concomitantly with the magnetic order a ferroelectric polarization \((P = 8 \mu\text{C/m}^2)\) is in-
duced perpendicular to \(q\) and the direction of the Fe\textsuperscript{3+} moments."14) A recent study"15) on the
magnetic ordering in the HT-IC phase of FeTe2O5Br showed that while the inversion symme-
try is already broken in HT-IC phase, the ferroelectricity is only realized in the LT-IC phase.
The difference in the orientation of the magnetic moments and phase shift of the amplitude

5. Role of Te in the low dimensional multiferroic material FeTe\textsubscript{2}O\textsubscript{5}Br
modulated waves between the two magnetic structures is suggested to be responsible for the realization of ferroelectricity in the LT-IC phase. In addition, there is evidence of minute displacements of the Te\(^{4+}\) ions in the LT-IC phase and these subtle displacements may be important for the electric polarization in this phase.\(^{(15)}\) In the view of the above it is suggested that polarization is possibly driven by exchange striction on the interchain bond containing the highly polarizable Te lone pair electrons. In search for a suitable spin Hamiltonian the magnetic susceptibility was analyzed by various groups. An early report suggested that the magnetic susceptibility can be explained by considering the dominant interactions within the Fe tetramers.\(^{(12)}\) A recent study however shows that the system should be described as a system of alternating antiferromagnetic \(S = \frac{5}{2}\) chains with strong Fe-O-Te-O-Fe bridges weakly coupled by two-dimensional frustrated interactions.\(^{(16)}\)

The preceding discussion suggests that it will be important to clarify the role of Te ions in the multiferroic property of FeTe\(_2\)O\(_5\)Br. In particular, it will be interesting to understand the interplay of magnetic interaction and the activity of the Te\(^{4+}\) lone pairs and eventually their combined role in the ferroelectric polarization. In this chapter we have examined this issue in details using \textit{ab initio} electronic structure calculations. The remainder of the chapter is organized as follows. In section 5.1 we have described the crystal structure and the computational details. Section 5.2 is devoted to the detailed discussion of our results on electronic structure calculations. Finally summary and conclusions are given in section 5.3.

5.1 Crystal Structure and Computational Details

FeTe\(_2\)O\(_5\)Br crystallizes in the monoclinic space group \(P21/c\). The crystallographic unit cell has inversion centre. The lattice parameters for FeTe\(_2\)O\(_5\)Br are \(a = 13.396\ \text{Å}, b = 6.597\ \text{Å}, c = 14.289\ \text{Å}\) and \(\beta = 108.12^\circ\).\(^{(12)}\) The unit cell (depicted in Fig. A.2) contains 72 atoms. There are two crystallographically inequivalent Fe\(^{3+}\) ions in the structure which are in distorted [FeO\(_6\)] octahedral environment. Four such octahedra share their edges with each other and form a [Fe\(_4\)O\(_{16}\)] iron tetramer cluster (see inset of Fig. A.2). These iron clusters are linked
by \([\text{Te}_4\text{O}_{10}\text{Br}_2]^{6-}\) units forming a layered structure in the \(bc\) plane. The layers are weakly connected via Van der Waals forces as they stack along the monoclinic \(a\) axis.

The first principles density functional theory (DFT) calculations have been performed using the plane wave based projector augmented wave (PAW)\(^{(17)}\) method as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^{(18)}\) We have used local density approximation (LDA) to the exchange correlation functional. The localized Fe-\(d\) states were treated in the framework of LSDA+U method,\(^{(19)}\) where calculations were done for several values of \(U\) in the range 1 – 6 eV and \(J = 1\) eV. The calculations for the unit cell were performed with a \((4 \times 8 \times 4)\) \(\Gamma\) centered \(k\) point mesh and 550 eV as plane wave cut off energy. In order to simulate the magnetic structure we have neglected the amplitude modulation and have approximated the incommensurate wave vector \(q \sim (0.5, 0.463, 0)\) by a commensurate one \((0.5, 0.5, 0)\) and have generated a supercell \((2 \times 2 \times 1)\) of the original unit cell containing 288 atoms. For the calculations with the supercell, a plane-wave cutoff energy of 500 eV was used along with a \((1 \times 2 \times 2)\) \(\Gamma\) centered \(k\) point mesh. All structural relaxations were carried out till
5. Role of Te in the low dimensional multiferroic material FeTe$_2$O$_5$Br

5.2 Results and Discussions

5.2.1 Non-spin polarized calculation

To begin with we have investigated the electronic structure of FeTe$_2$O$_5$Br without magnetic order. The non-spin polarized total and partial density of states are shown in Fig. 5.2. The density of states (DOS) is consistent with the Fe$^{3+}$Te$^{2+}$O$_2^-$Br$^{1-}$ nominal ionic formula for the system. Fig. 5.2, reveals that O-$p$ and Br-$p$ states are completely occupied while the Fermi
level ($E_F$) is dominated by the Fe-$d$ states. The occupied Te-$5s$ states lie far below the $E_F$.

The empty Te-$5p$ states lie above the Fermi level spreading on an energy range 2 to 6 eV with respect to the Fermi level. There is significant admixture of Te-$5s$ and Te-$5p$ states with the O-$p$ states, suggesting a hybridization between Te and O. Further, both Te and O states also hybridize with Fe-$d$ states crossing the Fermi level (see Fig. 5.2 (inset)).

The presence of Te in 4+ oxidation state suggests the possibility of Te lone pair formed from $5s^2$ electrons. In order to visualize the lone pairs arising from $5s^2$ electrons of Te$^{4+}$ ions, we have calculated the electron localization function (ELF)\(^{(22)}\) that permits mapping in real space of the core, bonding and nonbonding regions in a crystal.\(^{(23)}\) The ELF is defined as follows:

$$
\text{ELF} = \left[ 1 + \left( \frac{D}{D_h} \right)^2 \right]^{-1} \quad (5.1)
$$

where

$$
D = \frac{1}{2} \sum_i |\nabla \phi_i|^2 - \frac{1}{8} \frac{1}{\rho} \text{and}
$$

$$
D_h = \frac{3}{10} (3\pi^2)^{5/3} \rho^{5/3}.
$$

$\rho$ is the electron density and $\phi_i$ are the Kohn Sham wave functions. The electron localization function (ELF) is defined in such a way that its value lies between 0 and 1. The values are close to 1 when in the vicinity of one electron, no other electron with the same spin may be found, for instance this occur in bonding pairs or lone pairs.\(^{(26)}\) From the plot of the electron localization function, displayed in Fig. 5.3, we find that the electron density around Te is asymmetric and form a usual lobe shape arising from the $5s$ lone pair of Te. It has been pointed out by Watson and Parker\(^{(25)}\) that the hybridization with anion $p$ orbitals (oxygen $2p$) plays an important role in the formation of asymmetric lobe shaped isosurface of electron localization function for sterically active lone pairs. We gather from the DOS shown in Fig. 5.2 that the occupied Te $s$ and O $p$ orbitals hybridized to form a pair of occupied bonding and antibonding states. This Te-$5s$ - O-$2p$ mixed state further hybridizes with empty Te-$5p$ states. As a consequence both the Te $5s$ and $5p$ states are involved in the formation of the asymmetric electron distribution.
Figure 5.3: Electron localization function within a unit cell. The isosurfaces are visualized for a value of 0.9.

where empty Te 5p orbitals are able to interact due to the presence of Te-s - O-p occupied antibonding states. This emphasizes the importance of the O-p states in the formation of lone pairs.

In order to quantify the hybridization, we have calculated the hybridization index defined as follows:

$$H_{I-l,J-l} = \sum_k \left( \sum_i h^{(I)}_{l,i,k} \right) \times \text{weight}(k),$$

where $h^{(I)}_{l,i,k}$ are the coefficients in the spherical harmonic decomposition of the local (partial) charge, associated with $i^{th}$ Kohn Sham orbital, around $I^{th}$ atom. $l, m$ indicates the orbital and the magnetic quantum numbers respectively, $I$ and $J$ are atom indices: $I \in \{\text{Te atoms}\}$ and $J \in \{\text{O atoms}\}$, $i$ and $k$ stand for band index and $k$-points respectively. Weight $(k)$ is the weight on each $k$-point in the irreducible Brillouin zone necessary for the integration. Our calculations find that the hybridization index between Te-p and O-p is 6.13 and between Te-s and O-p.
5. Role of Te in the low dimensional multiferroic material FeTe$_2$O$_3$Br

is 3.80 for the experimental structure without any magnetism indicating sizable hybridization between Te and O. It is interesting to note that these lone pairs do not promote structural distortion and the structure remains centrosymmetric, as the pair of lobes are arranged in an opposite manner such that any resulting polarization of the structure cancels out.

5.2.2 Spin polarized calculation

We next consider magnetism and its impact on the crystal structure and ferroelectric polarization. In order to simulate the low temperature magnetic order found in the LT-IC phase we have made a $(2\times2\times1)$ supercell which contains 288 atoms. As mentioned before, in our calculation we have neglected the amplitude modulation. We consider various antiferromagnetic (AFM) configurations (see Fig. 5.4), depending on the arrangement of Fe spins within each tetramer as well as between the neighboring tetramers. In AFM1 configuration, not only Fe1 spins are aligned antiparallel to Fe2 within each tetramer (see inset of Fig. 5.4(a)) but also each tetramers are antiferromagnetically coupled along $a$ and $b$ direction leading to $q = (0.5, 0.5, 0)$. The AFM2 configuration differs from the AFM1 configuration only by the arrangement of spins within each tetramer (see inset of Fig. 5.4(b)) where a pair of Fe1 spins in a tetramer are antiparallel and the same is true for a pair of Fe2 spins. Finally in AFM3 configuration, the arrangement of Fe1 and Fe2 spins in each tetramer is identical to AFM1 but the tetramers are coupled ferromagnetically along $a$, $b$ and $c$ directions leading to $q = (0, 0, 0)$.

The results of our calculations are displayed in Table 5.1. The results reveal that among the magnetic configurations considered here, AFM1 has the lowest energy. All magnetic states are found to be insulating and the magnetic moment at the Fe site is $m_{Fe} \sim 4.2\mu_B$. The rest of the moments are at oxygen ($m_{O} \sim .13\mu_B$) and bromine ($m_{Br} \sim .09\mu_B$) sites, arising due to Fe-O and Fe-Br hybridization effect.

The total density of states as well as its projection onto different atomic orbitals for AFM1 phase are shown Fig. 5.5(a-d). Focussing on Fig. 5.5(b), we find that Fe-$d$ states in the majority spin channel are completely occupied while the minority states are completely empty, which
Table 5.1: The relative energies, magnetic moments, band gap for different magnetic configurations are listed here.

<table>
<thead>
<tr>
<th>Magnetic Config.</th>
<th>$U - J = 3 \text{ eV}$</th>
<th></th>
<th></th>
<th></th>
<th>$U - J = 5 \text{ eV}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E$ (meV)</td>
<td>$\text{Band gap}$ (eV)</td>
<td>$m_{\text{Fe}1}$ ($\mu_B$)</td>
<td>$m_{\text{Fe}2}$ ($\mu_B$)</td>
<td>$\Delta E$ (meV)</td>
<td>$\text{Band gap}$ (eV)</td>
<td>$m_{\text{Fe}1}$ ($\mu_B$)</td>
<td>$m_{\text{Fe}2}$ ($\mu_B$)</td>
</tr>
<tr>
<td>FM</td>
<td>49.7</td>
<td>1.3</td>
<td>4.1</td>
<td>4.1</td>
<td>34.1</td>
<td>1.5</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>AFM1</td>
<td>0.0</td>
<td>1.2</td>
<td>4.1</td>
<td>4.1</td>
<td>0.0</td>
<td>1.6</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>AFM2</td>
<td>15.7</td>
<td>1.4</td>
<td>4.1</td>
<td>4.1</td>
<td>10.1</td>
<td>1.6</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>AFM3</td>
<td>9.0</td>
<td>1.5</td>
<td>4.1</td>
<td>4.1</td>
<td>5.8</td>
<td>1.7</td>
<td>4.2</td>
<td>4.2</td>
</tr>
</tbody>
</table>

is consistent with the Fe$^{3+}$ valence state of Fe with a $3d^6$ configuration. Such a half filled configuration promotes the AFM order.

Next, we have identified the dominant exchange paths and the relevant spin Hamiltonian using the $N^\text{th}$ order muffin-tin orbital (NMTO) downfolding method. In order to derive a low energy effective model Hamiltonian, we have retained the isolated Fe band complex near the Fermi level for a non spin polarized calculation and downfolded the rest with the choice of two energy points $E_0$ and $E_1$. The downfolded bands in comparison to the all orbital LDA band structure is shown in Fig. 5.6 and we note that the agreement is very good. The various hopping integrals obtained from NMTO downfolding method can be utilized to identify the dominant exchange paths. For strongly correlated systems, the antiferromagnetic contribution to the exchange integral can be computed using $J_{\text{AFM}} = 4 \frac{t^2}{U_{\text{eff}}}$, where $U_{\text{eff}}$ is the effective onsite Coulomb interaction and $t_{ij}$ corresponds to the hopping via superexchange paths. The ratio of the various exchange interactions are displayed in Table 5.2 and the various exchange paths are indicated in Fig. 5.7. In last two columns we have also reproduced the ratio of exchange interactions obtained in Ref. 16 using the total energy method. In Ref. 16, it is reported that the alternating spin chain model is more appropriate instead of a tetramer model suggested for this system as the inter tetramer super super exchange ($J_4$) mediated by Fe-O-Te-O-Fe bridges is appreciable. The values of exchange interactions obtained from the NMTO downfolding method are very similar to Ref. 16, where in addition to the intra cluster exchange interactions $J_1$, $J_2$, $J_3$, the inter cluster exchange interaction $J_4$ is substantial supporting the
Figure 5.4: Various antiferromagnetic configurations (a) AFM1, (b) AFM2, and (c) AFM3.
5. Role of Te in the low dimensional multiferroic material FeTe$_2$O$_5$Br

Figure 5.5: The density of states for FeTe$_2$O$_5$Br in AFM1 configuration with experimental structure. (a) Total DOS (States/eV Cell). Orbital projected DOS (States/eV atom) for (b) Fe-$d$, (c) Te-$s$ and Te-$p$, (d) O-$p$ and Br-$p$ states.

Figure 5.6: Downfolded band structure (red dotted line) compared with full orbital LDA band structure (black solid line) of FeTe$_2$O$_5$Br
We have next investigated the impact of magnetism on crystal structure viz. exchange striction. We have carried out the structure optimization with nonmagnetic, ferromagnetic and AFM1 magnetic configurations. In this optimization, the cell parameters were fixed to the experimental values, but the positions of the atoms were allowed to relax. The change in bond lengths with respect to the unrelaxed (experimental) structure corresponding to various exchange paths are displayed in Table 6.7 for AFM1, FM and non-spin polarized cases. The bond lengths hardly change due to the ionic relaxations for nonmagnetic and ferromagnetic cases indicating negligible exchange striction. The maximum change in ionic positions occur in the relaxed structure with AFM1 magnetic ordering. The maximum displacement corresponds to the exchange path $J_3$ involving oxygens and $J_5$ involving the Te ions. Our calculations provide a direct evidence that the exchange paths $J_3$ and $J_5$ are responsible for the spin-phonon coupling in this compound. The importance of the exchange path $J_5$ was also anticipated in Ref. 16.

The impact of structural distortion on the lone pairs was visualized by plotting electron...
5. Role of Te in the low dimensional multiferroic material FeTe$O_2$Br

Table 5.2: Exchange interactions along different exchange paths obtained from NMTO down-folding method and energy method (Ref. 16) have been tabulated here.

<table>
<thead>
<tr>
<th>Exchange Distance (Å)</th>
<th>Exchange paths, bond lengths and angles</th>
<th>$J_1/J_2$ from NMTO ($U - J = 3$ eV)</th>
<th>$J_1/J_2$ in Ref. 16 ($U - J = 3$ eV)</th>
<th>$J_1/J_2$ in Ref. 16 ($U - J = 4$ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1$</td>
<td>Fe1-O1-Fe2 101.8°, Fe1-O2-Fe2 99.5°</td>
<td>0.89</td>
<td>0.46</td>
<td>0.35</td>
</tr>
<tr>
<td>$J_2$</td>
<td>Fe1-O7-Fe2 110.2°, Fe1-O2-Fe2 95.79°</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$J_3$</td>
<td>Fe1-O2-Fe1 101.7°</td>
<td>0.44</td>
<td>0.33</td>
<td>0.34</td>
</tr>
<tr>
<td>$J_4$</td>
<td>Fe1-O-Te1-O-Fe2, Fe1-O-Te4-O-Fe2</td>
<td>0.26</td>
<td>0.62</td>
<td>0.59</td>
</tr>
<tr>
<td>$J_5$</td>
<td>Fe2-O-Te3-O-Fe2</td>
<td>0.05</td>
<td>0.04</td>
<td>0.0</td>
</tr>
<tr>
<td>$J_6$</td>
<td>Fe1-O-Te1-O-Fe1</td>
<td>0.15</td>
<td>0.27</td>
<td>0.26</td>
</tr>
<tr>
<td>$J_7$</td>
<td>O-O ~ 2.81</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Localization function for the relaxed structure in the AFM1 phase, but only a little difference of the lobe shapes was observed in comparison to the experimental structure for AFM1 phase. We computed the hybridization index for the relaxed structure in the AFM1 phase. The H-indices for the relaxed structure are 17.305 and 11.015 between Te-p and O-p, and Te-s and O-p respectively as opposed to 17.00 and 10.99 in the AFM1 phase for the experimental structure. This indicates that the Te-O hybridization increases as a result of the structural distortion, pointing to the importance of Te lone pairs. Finally to access the asymmetry between two neighboring lobe shaped charge distribution of the lone pairs we have calculated the moment of the electron localization function ($\vec{M}^i_{ELF}$) for the $i^{th}$ Te atom as follows:

$$\vec{M}^i_{ELF} = \int_{|\vec{r}|=0}^{R} d^3r ELF(\vec{r})\vec{r},$$  \hspace{1cm} (5.3)\

where $\vec{r}$ is the position vector assuming the $i^{th}$ Te atom at the origin and $R$ is a suitably chosen radius of a sphere that covers the range of ELF around the $i^{th}$ Te atom. We find that the sum of $\vec{M}^i_{ELF}$'s vanish for a pair of suitably chosen Te atoms in the experimental structure, (e.g. the pairs marked (1,2), (3,4), (5,6) in Fig. 5.8) whereas it has a substantial value for the same
Figure 5.8: Calculated electron localization functions for the (a) experimentally reported structure and (b) relaxed structure. The electron localization function (ELF) isosurfaces are visualized for a value of 0.85. The red lobes are the lone pairs on the black Te ions.

pairs of atoms in the relaxed structure (Average ELF moment for a pair of Te atoms in relax magnetic structure is 7.2 Å). This observation suggests that unlike the experimental structure where the local dipole moments are pairwise cancelled leading to no net polarization, the Te-5s lone pairs play an important role in inducing polarization for the relaxed structure.

5.2.3 Polarization

We have calculated the ferroelectric polarization using the Berry Phase method(27) as implemented in Vienna ab initio simulation package (VASP). The polarization calculations are carried out with two idealized magnetic configurations AFM1 and AFM2 for several $U$ values. Our results are summarized in Table 5.4. The direction of polarization is same with different $U$ values, but the magnitude decreases with the increasing value of $U$. The calculated polar-
Table 5.3: The distances between the magnetic atoms in the experimental structure and the change in distance upon relaxation within different magnetic configurations have been listed here. \(+(—)\) sign indicate increment (decrement) of the distance.

<table>
<thead>
<tr>
<th>Exchange paths (\text{in Exp. Struc.})</th>
<th>Distance (Å)</th>
<th>Change in the distance upon relaxation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J_1) (Fe1-Fe2)</td>
<td>3.16</td>
<td>(-0.04) (-0.01) (-0.01)</td>
</tr>
<tr>
<td>(J_2) (Fe1-Fe2)</td>
<td>3.34</td>
<td>(-0.03) (0.00) (0.00)</td>
</tr>
<tr>
<td>(J_3) (Fe1-Fe1)</td>
<td>3.43</td>
<td>(-0.11) (-0.04) (-0.02)</td>
</tr>
<tr>
<td>(J_4) (Fe1-Fe2)</td>
<td>4.76</td>
<td>(0.02) (0.00) (0.00)</td>
</tr>
<tr>
<td>(J_5) (Fe2-Fe2)</td>
<td>4.77</td>
<td>(0.05) (0.02) (0.01)</td>
</tr>
<tr>
<td>(J_6) (Fe2-Fe2)</td>
<td>5.10</td>
<td>(0.00) (0.00) (0.00)</td>
</tr>
</tbody>
</table>

The polarization for FeTe\(_2\)O\(_5\)Br is large compared to the experimental value. Such an overestimation is also reported for other systems, and may be attributed to the idealized magnetic structure considered in our calculation. In view of the fact that upon ionic relaxation the bond lengths corresponding to the exchange path \(J_3\) and \(J_5\) change substantially, we have investigated the impact of the change in bond length on the exchange interaction and hence on the values of the polarization. The exchange interaction \(J_3\) involve Fe-O-Fe, super exchange pathway and therefore obey the Anderson-Goodenough-Kanamori rules. When the Fe-Fe distance in the \(J_3\) exchange path is reduced, not only the \(J_3\) increases but also the value of the polarization increases, indicating the importance of this super exchange path on polarization. High resolution synchrotron X-ray diffraction however did not detect significant structural changes for this bond. Next we have investigated the \(J_5\) exchange path involving the Te ions. In Ref.

Table 5.4: Calculated electric polarization with AFM1 and AFM2 magnetic configurations with different value of Coulomb interaction parameter \(U\) for the relaxed structure are listed here.

<table>
<thead>
<tr>
<th>(U - J) values (eV)</th>
<th>Polarization ((\mu C/m^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AFM1</td>
</tr>
<tr>
<td>1</td>
<td>217.7</td>
</tr>
<tr>
<td>2</td>
<td>208.0</td>
</tr>
<tr>
<td>3</td>
<td>198.0</td>
</tr>
<tr>
<td>4</td>
<td>187.8</td>
</tr>
<tr>
<td>5</td>
<td>177.7</td>
</tr>
</tbody>
</table>
16, it is reported that the only sizable change at the ME transition corresponds to the shortening of Fe2-Te3 distance in the \( J_5 \) exchange pathway. In order to see how the displacement of Te3 ions affect the exchange interaction \( J_5 \) and in turn its effect the electric polarization, we have changed the distance between Fe2-Te3 \( (d_1) \) (also the distance \( d_2 \) between Fe2-Te3) (see inset of Fig. 5.9) and computed the exchange interaction \( J_5 \) and the ferroelectric polarization. In Fig. 5.9, we have plotted the polarization as a function of the change in exchange interaction \( \Delta J_5 \) (between the distorted and the experimental structure). \( \Delta J_5 \) may be considered as a measure of spin phonon interaction mediated by the Te ions. Polarization increases as \( \Delta J_5 \) is increased and this polarization originates from the spin phonon coupling corresponding to the \( J_5 \) exchange pathway. Our calculations reveal that the polarizable lone pairs enhance the spin phonon coupling upon exchange striction in the AFM1 phase which in turn lead to ferroelectric polarization. In order to check the role of Te ions in the polarization we have carried out constrained ionic relaxation calculation in which positions of Te ions were kept fixed and other ionic positions were allowed to relax for the AFM1 configuration with \( U = 4 \) eV. The value of polarization is calculated to be 102 \( \mu C/m^2 \), substantially reduced from the polarization (187.8 \( \mu C/m^2 \)) calculated for the relaxed structure where Te ions are also moved from their

Figure 5.9: Variation of polarization with \( \Delta J_5 \). Inset shows the \( J_5 \) exchange path involving Te3 ions.
centrosymmetric positions. This result suggests that exchange striction within the Fe tetramers as well as between them mediated by Te ions, are responsible for the magnetoelectric (ME) effect in FeTe$_2$O$_3$Br.

5.3 Conclusions

We have investigated the electronic properties of a multiferroic compound FeTe$_2$O$_3$Br by using density functional theory to elucidate the role of Te ions on the ferroelectric polarization of this system. We find in the absence of magnetism the system remains centrosymmetric due to the specific orientation of the lone pairs that does not promote structural distortion. The results from our calculations reveal that exchange striction within the Fe tetramers as well as between them is responsible for the magnetoelectric (ME) effect in FeTe$_2$O$_3$Br. We find that the electric polarization is very sensitive to the $J_5$ exchange path involving the polarizable Te$^{4+}$ lone pairs. While the lone pairs do not play any role in the absence of magnetism but the lone pairs enhance the spin phonon coupling upon exchange striction which in turn lead to ferroelectric polarization.

Bibliography

5. Role of Te in the low dimensional multiferroic material FeTe\textsubscript{2}O\textsubscript{3}Br


5. Role of Te in the low dimensional multiferroic material FeTeO$_2$Br


