Electronic, magnetic and ferroelectric properties of rhombohedral AgFeO$_2$: an \textit{ab initio} study

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Using first principle calculations under the framework of density functional theory we have investigated the electronic structure, magnetism and ferroelectric polarization in the triangular lattice antiferromagnet AgFeO$_2$, and its comparison to the isostructural system CuFeO$_2$. Our calculations reveal that spin orbit interaction plays an important role in determining the magnetic property of AgFeO$_2$ and is possibly responsible for its different magnetic ground state in comparison to CuFeO$_2$. Calculations of ferroelectric polarization of AgFeO$_2$ suggest that the spontaneous polarization arises from noncollinear spin arrangement via spin-orbit coupling. Our calculations also indicate that in addition to electronic contribution, the lattice mediated contribution to the polarization are also important for AgFeO$_2$.

In recent times two dimensional triangular lattice antiferromagnets have attracted much attention both theoretically as well as experimentally because of the fascinating magnetic properties displayed by them due to geometric frustration.\textsuperscript{1-3} In addition, some of these compounds exhibit ferroelectricity. ABO$_2$-type compounds with delafossite structure provide a good example of triangular lattice antiferromagnets (TLA) and present an opportunity to study the influence of geometric spin frustration in magnetic properties.\textsuperscript{4,5} In ABO$_2$ compounds, the A-site cation has completely filled d orbitals, (Cu$^{3+}-3d^{10}$ and Ag$^{1+}-4d^{10}$), while the B-site cation has partially filled d orbitals (Cr$^{3+}-3d^3$ and Fe$^{3+}-3d^5$). Examples of ABO$_2$ systems include CuFeO$_2$, AgCrO$_2$, CuCrO$_2$, AgFeO$_2$ etc.\textsuperscript{6-8} The magnetic ground state of the delafossite CuFeO$_2$ has $\uparrow\uparrow\downarrow\downarrow$ collinear spin structure with their spins parallel to the c axis.\textsuperscript{9} It shows multistep metamagnetic phase transitions when a varied magnetic field is applied along the c axis. Between the applied field 7T and 13T, there exists a noncollinear phase with a modulation vector $(q,0,0)$ with $q = \frac{1}{3}$. At a magnetic field above 13T, CuFeO$_2$ adopts the five-sublattice magnetic structure ($\uparrow\uparrow\downarrow\downarrow\downarrow$) with collinear moments along the c axis.\textsuperscript{10,11} An in-plane electric polarization is observed only in the intermediate-field (between 7T and 13T) when the system adopts proper skew type of magnetic ordering. There are three possible mechanism for electric polarization in improper multiferroics: (i) magnetostriiction, (ii) spin current model\textsuperscript{12} or inverse Dzyaloshinskii-Moriya (DM) effect, and (iii) spin-orbit coupling dependent d-p hybridization. Due to strong coupling between magnetism and ferroelectricity, the improper multiferroics are very interesting to study.\textsuperscript{13-15} Arima\textsuperscript{16} showed that the electric polarization in CuFeO$_2$ can be explained by the third mechanism, when the proper skew type of magnetic ordering can induce ferroelectricity through the variation in the metal (Fe-3d)-ligand (O-p) hybridization with spin-orbit coupling. Other delafossites CuCrO$_2$ and AgCrO$_2$ also exhibit ferroelectricity for a particular kind of magnetic ordering.\textsuperscript{11,17} AgCrO$_2$ exhibits ferroelectric polarization below the temperature 21 K, in which each triangular layers of Cr$^{3+}$ ions form parallel chains with helical spiral spin order.\textsuperscript{5,18} The ferroelectric polarization is also observed for CuCrO$_2$ with a noncollinear 120$^\circ$ spin structure $(q \sim (\frac{1}{3}, \frac{1}{3}, 0))$, below 23.6 K.

The triangular lattice antiferromagnet rhombohedral (3R) AgFeO$_2$ has recently been under focus after the synthesis of the high quality samples under high pressure by Tsujimoto et al.\textsuperscript{19} Silver ferrite crystallizes in hexagonal structure also.\textsuperscript{20} 3R-AgFeO$_2$ shows interesting magnetic, thermodynamic and ferroelectric properties.\textsuperscript{7,19,21} 3R-AgFeO$_2$ exhibits negative Curie-Weiss temperature $(\theta_{CW} = -140 \text{ K})$ indicating antiferromagnetic interactions between Fe$^{3+}$ $(3d^6)$ ions. The system has two magneto-structural phase transitions at $T_{N1} = 15 \text{ K}$ and $T_{N2} = 9 \text{ K}$. The magnetic structure (ICM1 phase) for 9 K $\leq T \leq 15$ K is a spin-density wave with incommensurate propagation vector $k = (1, q, \frac{1}{3})$ with $q = 0.384$. At temperature below 9 K, the magnetic structure (ICM2 phase) of 3R-AgFeO$_2$ turns into an elliptical cycloid with the incommensurate propagation vector $k = (-1, q, \frac{1}{3})$ with $q = 0.2026$.\textsuperscript{19} The magnetic ground state of AgFeO$_2$ is drastically different from the commensurate magnetic ground state of CuFeO$_2$, that indicates that the A-site cation plays a crucial role in magnetism. In ICM2 phase of 3R-AgFeO$_2$, the system shows ferroelectric polarization $(\sim 300 \mu\text{C/m}^2)$ for the powder sample. It is suggested that polarization is possibly driven by the spin current mechanism.\textsuperscript{12} In view of the above it is important to investigate the origin of ferroelectricity in AgFeO$_2$. Since by replacing the nonmagnetic A-site (Cu with Ag) the magnetic properties are drastically changed, it is also interesting to compare the electronic and magnetic properties of these two systems.

In this paper, we have employed \textit{ab initio} density functional calculations to investigate the electronic, magnetic and ferroelectric properties of the two dimensional system AgFeO$_2$, where Fe$^{3+}$ ions $(3d^6, S = \frac{1}{2})$ form a triangular lattice and also compare our results with the isostructural analogue CuFeO$_2$. The remainder of this paper is organised as follows: in section I we have de-
scribed the crystal structure and computational details. Section II is devoted to the detailed discussion of our results on electronic structure calculations. Finally we conclude in section III.

I. CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

The crystal structure of 3R-AFeO$_2$, (A = Cu, Ag) shown in Fig. 1 belongs to the rhombohedral space group $R$

The density-functional-theory (DFT) calculations were carried out within two different methods: (a) the plane-wave-basis-based projector augmented wave (PAW) method as implemented in the Vienna $ab$ initio Simulation package (VASP), (b) the linear-muffin-tin-orbital (LMTO) basis within atomic sphere approximation (ASA) with Stuttgart TB-LMTO-ASA-47 code. The basis set for the self-consistent electronic structure calculations for AgFeO$_2$ in TB-LMTO ASA includes Ag ($s, p, d$), Fe ($s, p, d$), and O ($s, p$) and the rest are downfolded. The density of states calculated using the TB-LMTO ASA method is found to be in good agreement with the density of states calculated using plane wave basis. We have analyzed the chemical bonding by computing the crystal orbital Hamiltonian population (COHP) as implemented in the Stuttgart tight-binding linear muffin-tin orbital (TB-LMTO) code. The COHP provides the information regarding the specific pairs of atoms that participate in the bonding, and also the range of such interactions.

FIG. 1: (a) The unit Cell of AgFeO$_2$, (b) Hexagonal $ab$ plane, (c) Edge sharing FeO$_6$ octahedra.

II. RESULTS AND DISCUSSIONS

A. Electronic and magnetic properties

1. Spin unpolarized calculation

To get insight on the electronic structure of AgFeO$_2$ and CuFeO$_2$, we have started with spin-unpolarized calculations. The band structures calculated with the LMTO method for these systems are plotted along the various high symmetry points of the Brillouin zone of the rhombohedral lattice (see Fig. 2). The bands are plotted with respect to the Fermi energy ($E_F$) of the compounds. Since Fe is in Fe-3$d^7$ configuration and in an octahedral environment, the $t_{2g}$ states, that can accommodate 6 electrons, are partially occupied, while the $e_g$ bands are completely unoccupied. The Fe-$d$ bands are well separated from the filled Ag-$d$ and O-$p$ bands for AgFeO$_2$ and Cu-$d$ and O-$p$ bands for CuFeO$_2$.

The total density of states (DOS) as well as its projection onto various atomic orbitals (PDOS) are shown in Fig. 3. The DOS are projected onto Fe-$d$, Ag-$d$, and O-$p$ orbitals for AgFeO$_2$ and Fe-$d$, Cu-$d$, and O-$p$ orbitals for CuFeO$_2$. The spin unpolarized calculation give rise to a metallic solution with states dominated by Fe-$d$ character at the Fermi level ($E_F$) for both the systems. The Fe-$d$ density of states are spread over $-1$ eV below the Fermi level to 2.0 eV above the Fermi level for both the sys-

For plane wave based calculations, we have used a plane-wave energy cutoff of 500 eV and $\Gamma$ centered $k$-space sampling on (4 × 4 × 1) $k$-mesh. The localized Fe-$d$ states are treated in the framework of LSDA+U method. In order to find out the importance of spin-orbit coupling (SOC) we have also carried out the electronic structure calculation with SOC in the framework of the LSDA+U+SOC method. All structural relaxations are carried out until the Hellman-Feynman forces on each atom became less than 0.01 eV/Å. To estimate the ferroelectric polarization we have used Berry phase method as implemented in the Vienna $ab$ initio simulation package (VASP).

FIG. 2: LDA band structure of (a) AgFeO$_2$ and (b) CuFeO$_2$. The zero of the energy has been set up at the LDA Fermi energy.
FIG. 3: Total and partial density of states (i) for AgFeO$_2$ and (ii) for CuFeO$_2$.

FIG. 4: (i) COHPs and integrated COHPs (ICOHP) per bond (a) for Fe-O for AgFeO$_2$ and CuFeO$_2$, and (b) Ag-O and Cu-O for AgFeO$_2$ and CuFeO$_2$ respectively.

FIG. 5: Total and orbital decomposed density of states for AgFeO$_2$.

Cu-O covalency as revealed by the integrated COHP at the Fermi level where ICOHP value for Ag-O is $-6.44$ eV and for Cu-O, ICOHP value is $-2.95$ eV. Interestingly, the nearest-neighbor Fe-O covalency is larger for AgFeO$_2$ (ICOHP values are $-6.09$ and $-2.53$ eV for AgFeO$_2$ and CuFeO$_2$ respectively). This difference in hybridization with oxygen may be responsible for different magnetic ground state of AgFeO$_2$ and CuFeO$_2$.

2. Spin polarized calculations

In order to study the magnetic properties we have carried out spin-polarized calculations for AgFeO$_2$. The total and orbital decomposed density of states for ferromagnetic configurations are plotted in Fig. 5. As suggested in Ref. 28, we have used the onsite Coulomb interaction term $U = 3$ eV and the onsite exchange interaction $J = 1$ eV for Fe $d$ states in AgFeO$_2$. From Fig. 5(a), we find that the ferromagnetic state is insulating with $U = 3$ eV and $J = 1$ eV in LSDA+U calculation. The plot of the density of states (DOS) reveal the presence of five electrons in Fe-3$d$ spin up channel, which is consistent with the picture of high-spin Fe$^{3+}$ ions in AgFeO$_2$. The O-$p$ and Ag-$d$ states are completely occupied. In ferromagnetic configuration, the spin moment of Fe site is 4.23 $\mu_B$ with $U = 3$ eV and $J = 1$ eV, and the rest are partly accommodated in O ($m_O = 0.09 \mu_B$).

3. Symmetric exchange interactions

In order to determine the various exchange parameters ($J_i$), (indicated in Fig. 1(b)), we have first calculated the
actions are denoted by parentheses are the exchange interactions for CuFeO$_2$ from the Heisenberg spin Hamiltonian:

\[ H = \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j \]  

We have calculated the total energies of five ordered spin states (FM, AF1, AF2, AF3, AF4) shown in Fig. 6. The total spin exchange energies (per three formula units) of the five ordered spin states are expressed as:

\[
\begin{align*}
E(FM) &= \frac{25}{4}(-9J_1 - 9J_2 - 9J_3 - 9J_4) \\
E(AF1) &= \frac{25}{4}(3J_1 + 3J_2 - 9J_3 - J_4) \\
E(AF2) &= \frac{25}{4}(-J_1 + 3J_2 - J_3 - J_4) \\
E(AF3) &= \frac{25}{4}(3J_1 - J_2 - J_3 - J_4) \\
E(AF4) &= \frac{25}{4}(-9J_1 - 9J_2 - 9J_3 + 3J_4)
\end{align*}
\]

The relative energies for AgFeO$_2$, calculated from LSDA+U method are summarized in Table I. The nearest neighbor, next-nearest-neighbor and diagonal interactions are denoted by $J_1$, $J_2$ and $J_3$ respectively. $J_4$ denotes the coupling between nearest neighbors in adjacent layers. The exchange interactions are displayed in Table II. In last column of Table II, the values in the parentheses are the exchange interactions for CuFeO$_2$ obtained from Ref. 5. We find that all the exchange interactions ($J_1$, $J_2$, $J_3$, and $J_4$) are antiferromagnetic type. As a consequence both the intra-layer and the inter-layer exchange interactions are spin-frustrated in AgFeO$_2$ as well as in CuFeO$_2$. In AgFeO$_2$, the inter-layer exchange interaction $J_4$ is strongest in comparison to intra-layer exchange interactions $J_2$ and $J_3$, while $J_3$ is dominant in CuFeO$_2$. The exchange interactions are of super exchange type for both the systems. The intra-plane $J_1$ exchange interaction is mediated by Fe-O-Fe super-exchange path. Other intra-plane exchange interactions $J_2$ and $J_3$ are mediated through Fe-O, O-Fe super super exchange path. The inter plane exchange coupling $J_4$ is mediated via the Fe-O-A-O-Fe path. As we have shown by plotting COHP (see Fig. 4) that the hybridization of Ag with oxygen for AgFeO$_2$ is greater than the hybridization of Cu with oxygen for CuFeO$_2$, the inter layer coupling is much stronger for AgFeO$_2$. The antifer-

| Configuration | $\Delta E$ (for $U_{eff} = 2 \text{ eV}$) | $\Delta E$ (for $U_{eff} = 4 \text{ eV}$) |
|---------------|-------------------------------------|-------------------------------------|
| FM           | 0.0                                 | 0.0                                 |
| AF1          | -234.5                              | -99.54                              |
| AF2          | -212.33                             | -94.03                              |
| AF3          | -254.5                              | -111.57                             |
| AF4          | -66.0                               | -31.4                               |

TABLE II: Symmetric exchange interactions (in meV) for AgFeO$_2$ and CuFeO$_2$ are tabulated here. The exchange interactions for CuFeO$_2$ inside the parentheses, are adapted from Ref. 5.

| Exchange   | AgFeO$_2$ | CuFeO$_2$ |
|------------|-----------|-----------|
|            | $U_{eff} = 2 \text{ eV}$ | $U_{eff} = 4 \text{ eV}$ |
| $J_1$      | -1.92     | -0.83     |
| $J_2$      | -0.62     | -0.21     |
| $J_3$      | -0.81     | -0.35     |
| $J_4$      | -0.88     | -0.42     |

FIG. 6: The four ordered spin states (AF1, AF2, AF3, AF4) of AgFeO$_2$ constructed using a $(3 \times 2 \times 1)$ supercell. (a) AF1: spins are arranged ferromagnetically along $a$ and $c$ direction and antiferromagnetically along $b$ direction, (b) AF2: the spin arrangement is $\uparrow\downarrow\downarrow$ along $a$ direction and ferromagnetic along other two directions, (c) AF3: spins are antiferromagnetically arranged along $a$ and $b$ directions and ferromagnetically along $c$ direction, (d) AF4: spin arrangement is such that intra-layer couplings are ferromagnetic and inter-layer couplings are antiferromagnetic.
romagnetic nature of the exchange interactions in each FeO₂ layer results in spin frustration in the \((J₁, J₁, J₁)\) and \((J₂, J₂, J₂)\) triangles and in the \((J₁, J₂, J₂)\) line segments. Between adjacent FeO₂ layers, spin frustration occurs in the isosceles \((J₁, J₁, J₄)\) triangles. The silver ferrite appears to be a more frustrated system with higher values of exchange interaction parameters as compared to the copper ferrite. We have also calculated the Curie-Weiss temperature \(θ_{CW}\) for AgFeO₂. In the mean field limit, the Curie-Weiss temperature \(θ\) is related to the exchange interactions as follows:

\[
θ = \frac{S(S + 1)}{3k_B} \sum_i z_i J_i
\]

where, the summation runs over all nearest neighbors of a given spin site, \(z_i\) is the number of nearest neighbors connected by the spin exchange interaction \(J_i\), and \(S\) is the spin quantum number of each spin site (i.e., \(S = 5/2\) in the present case). The calculated Curie-Weiss temperature \(θ_{CW}\) for AgFeO₂ is −363 K and −252 K for \(U_{eff} = \pm 2\) and 4 eV respectively, while the experimental value is −140 K. Thus, according to the experimental Curie-Weiss temperature and the mean-field theory, the calculated \(J₁, J₂\) values are overestimated by a factor of \(f = 2.6\) and 1.9 for \(U_{eff} = \pm 2\) and 4 eV respectively. The \(θ_{CW}\) for CuFeO₂ is −299 K with overestimation factor \(f = 3.24\) as reported in Ref. 5.

From the magnitude of the symmetric exchange interactions for AgFeO₂ and CuFeO₂, we conclude that the difference in the magnetic ground state for AgFeO₂ and CuFeO₂ probably do not stem from the symmetric part of the spin Hamiltonian.

In the following, we have investigated the magnetic properties of AgFeO₂ and CuFeO₂ by calculating the total energy by choosing the spin quantization axes and the result of our calculation is displayed in Table III. An estimation of magnetocrystalline anisotropy is obtained from the energy difference between calculations with spin quantization chosen along the \(c\) direction (001) and perpendicular to the \(c\) direction, yield values 0.33 meV and 0.21 meV per Fe ion for AgFeO₂ and CuFeO₂ respectively within LSDA+U+SOC (for \(U_{eff} = 4\) eV) calculation.

The magnetocrystalline anisotropy energy is larger for AgFeO₂ than CuFeO₂ indicating important role of SOC for AgFeO₂.

### 5. Antisymmetric exchange interactions

Next, we have considered the antisymmetric part of the spin Hamiltonian \(H = \frac{1}{2} \sum_{\langle ij \rangle} \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j)\) and calculated the Dzyaloshinskii-Moriya interactions parameter \(\vec{D}\) from the total energy calculations with spin orbit coupling as discussed in Ref. 35. Here we have calculated the three components \(D_{12}^x, D_{12}^y, D_{12}^z\) of the DM vector (between nearest neighbor spin sites 1 and 2) for AgFeO₂ and CuFeO₂ by performing LSDA + U + SOC calculations. In order to calculate \(x\) component of \(\vec{D}_{12}\), we consider the following four spin configurations in which the spins 1 and 2 are oriented along the \(y\) and \(z\) axes, respectively: (i) \(S₁ = (0, S, 0), S₂ = (0, 0, S)\), (ii) \(S₁ = (0, −S, 0), S₂ = (0, 0, S)\), (iii) \(S₁ = (0, S, 0), S₂ = (0, 0, −S)\), (iv) \(S₁ = (0, −S, 0), S₂ = (0, 0, −S)\). In these four spin configurations, the spins of all the other spin sites are the same and are aligned along the \(x\) direction.

The spin interaction energy for the four spin configurations can be written as

\[
E_{\text{spin}} = E_{\text{other}} + D_{12}^x S₁^x S₂^z − S₁^y \sum_{i=3,4} D_{1i}^x S_i^x + S₂^z \sum_{i=3,4} D_{2i}^y S_i^y
\]

Similarly for \(y\) and \(z\) components of \(\vec{D}_{12}\). Our calculated values (in meV) of the components of \(\vec{D}_{12}\) for AgFeO₂ are \(D_{12}^x = 0.0104, D_{12}^y = −0.42, D_{12}^z = 0.005\) and the magnitude of DM vector is 0.4202 (\(\frac{|D_{12}|}{J₁} = 0.55\) ) for \(U_{eff} = 4\) eV. We have also computed \(\vec{D}_{12}\) for \(U_{eff} = 2\) eV and corresponding components of \(\vec{D}_{12}\) are \(D_{12}^x = 0.011, D_{12}^y = −0.87, D_{12}^z = 0.01\) and \(\frac{|D_{12}|}{J₁} = 0.5\). The large \(y\) component of \(\vec{D}_{12}\) term makes the two spins perpendicular to each other in the \(ac\)-plane.

We have also calculated the components of \(\vec{D}_{12}\) (between nearest neighbor spin sites 1 and 2) for CuFeO₂.

The components are \(D_{12}^x = 0.004, D_{12}^y = −0.16, D_{12}^z = 0.012\) and the magnitude of DM vector is 0.161 (\(\frac{|D_{12}|}{J₁} = 0.2\) for \(U_{eff} = 4\) eV. For \(U_{eff} = 2\) eV, the components are \(D_{12}^x = 0.004, D_{12}^y = −0.23, D_{12}^z = 0.012\) with \(\frac{|D_{12}|}{J₁} = 0.15\). The DM vector for nearest neighbor sites, is much smaller for CuFeO₂ compared with AgFeO₂. These calculations suggest that SOC has a profound impact on AgFeO₂ and plays a key role in determining its magnetic ground state.
6. Low temperature magnetic structure

In order to simulate the low temperature (below 9 K) magnetic order of AgFeO$_2$, we have made a (2×4×2) supercell which contains 192 atoms. We have considered two magnetic configurations AFM1 and AFM2 as shown in Fig. 7. In AFM1 configuration ($q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$) the spin arrangement along b direction is ↑↑↓↓ and they are antiferromagnetically aligned along a and c direction. For AFM2 configuration ($q = (\frac{1}{2}, \frac{1}{4}, \frac{1}{2})$), we have made the noncollinear spin arrangements along b directions. Spins are antiferromagnetically aligned along a and c directions. The three components of spin at Fe sites for a Fe-O layer is displayed in Table IV.

We have calculated the electronic structure for the FM, AFM1, and AFM2 using LSDA+U method. The results of our calculations are displayed in Table V and we find that the AFM1 magnetic configuration has the lowest in energy. The total and partial density of states in the AFM1 magnetic configuration for AgFeO$_2$ calculated using LSDA+U method, is shown in Fig. 8. The band gap in AFM1 state is calculated to be 0.54 eV and 1.03 eV for $U_{eff} = 2$ and 4 eV respectively. The majority Fe-d states are completely occupied while the minority states are empty, which is consistent with the Fe$^{3+}$ valence state of Fe with a 3d$^5$ configuration. Such a half-filled configuration promotes the antiferromagnetic order. The spin magnetic moment of Fe is 3.982 µ$_B$ and 4.18 µ$_B$ with $U_{eff} = 2$ and 4 eV respectively.

We have added the spin orbit coupling (SOC) in our calculation. The results of our calculation for AFM1 and AFM2 structures is displayed in Table V. Our calculations clearly reveal AFM2 is the ground state for AgFeO$_2$ upon inclusion of SOC, indicating important role of spin orbit interaction as anticipated earlier. The spin and orbital moments at Fe sites are 4.15 µ$_B$ and 0.027 µ$_B$ respectively.

### TABLE III: The energy differences between calculations with spin quantization chosen along different directions within LSDA+U+SOC calculations.

| Quantized axis | $\Delta E$ for AgFeO$_2$ ($U_{eff} = 2$ eV) | $\Delta E$ for CuFeO$_2$ ($U_{eff} = 4$ eV) |
|----------------|------------------------------------------|------------------------------------------|
| (001)          | 0.0                                      | 0.0                                      |
| (010)          | 0.83                                     | 0.33                                     |
| (100)          | 0.83                                     | 0.65                                     |

### TABLE IV: The three components of spin (in µ$_B$) for one Fe-O layer in AFM2 magnetic configuration for AgFeO$_2$ determined from LSDA+U calculations ($U_{eff} = 2$ eV).

| $m_x$   | $m_y$   | $m_z$   |
|---------|---------|---------|
| -0.822  | 2.690   | 3.0990  |
| 0.801   | -2.600  | -3.152  |
| 3.038   | 2.872   | 0.012   |
| 0.128   | 2.801   | -3.100  |
| -3.027  | 2.875   | -0.215  |
| -0.165  | -0.363  | 4.157   |
| -3.046  | -2.845  | -0.228  |
| 3.055   | -2.845  | 0.019   |

FIG. 7: (a) AFM1 collinear magnetic ordering (b) AFM2 noncollinear magnetic ordering.

FIG. 8: The plot of total and orbital projected density of states in AFM1 magnetic configuration for AgFeO$_2$ within LSDA+U calculation (for $U_{eff} = 2$ eV).
B. Ferroelectric properties

Finally, we have calculated the ferroelectric polarization with AFM1 and AFM2 magnetic configuration using Berry phase method$^{27}$ as implemented in the VASP.$^{24}$ We do not find the electric polarization for the centrosymmetric crystal structure with AFM1 and AFM2 magnetic structure within LSDA+U for $U_{\text{eff}} = 2$ eV. With the application of spin orbit coupling (SOC), there is no polarization for AFM1 structure, however AFM2 magnetic configuration attains a polarization value of 34 $\mu$C/m$^2$ respectively, which suggests that the non-collinear magnetic order induces polarization via spin orbit coupling. Therefore spin-current mechanism is one source of the electric polarization in this system. But our calculated magnitude of electric polarization is much smaller than the observed experimental value of polarization ($\sim 300$ $\mu$C/m$^2$ for powder sample). This result suggests that although there is electronic contribution to the polarization but the lattice mechanism also important for the ferroelectric polarization in AgFeO$_2$.

In order to obtain the lattice contribution to polarization, we have carried out relaxation calculations within the framework of LSDA+U and LSDA+U+SOC method. In this optimization, the cell parameters were fixed to the experimental values, but the positions of the atoms were allowed to relax. The maximum change in bond lengths occurs for the nearest neighbor. The bond lengths before and after relaxations are listed in Table VI. The ferroelectric polarization of 282 $\mu$C/m$^2$ is found for the relaxed AFM1 collinear structure without SOC. This result suggests that symmetric spin exchange induces the polarization in this material through the exchange-striction mechanism. Application of SOC, the polarization turn out to be 324 $\mu$C/m$^2$. The polarization is increased for relaxed AFM2 noncollinear structure, and the value of polarization is 407 $\mu$C/m$^2$ with $U_{\text{eff}} = 2$ eV in LSDA+U calculation without SOC. We find that the polarization in relaxed structure with AFM2 magnetic configuration with spin-orbit coupling is 485 $\mu$C/m$^2$. We have also calculated the electric polarization with a larger value of $U$. Our results are summarized in Table VII. Our results suggest that the exchange striction mechanism as well as spin current model$^{12}$ are responsible for electric polarization in this system.

III. CONCLUSION

In this paper, we have studied the electronic structure, magnetism, and ferroelectric properties of the triangular lattice antiferromagnet AgFeO$_2$ and compared our results with isostructural compound CuFeO$_2$. While Fe is in $d^6$ configuration in both the systems, the magnetic ground state of AgFeO$_2$ markedly different from CuFeO$_2$. In order to understand the origin of this difference, we calculated the symmetric exchange interactions offered by the Heisenberg model. Our calculations reveal that the symmetric exchange interactions are nearly identical for both the systems and therefore hardly play any role for the different magnetic ground state. Next, we incorporated spin-orbit coupling and our calculations regarding the orbital moment, magneto-crystalline anisotropy and DM parameters clearly indicate that SOC has a profound effect on AgFeO$_2$. It is interesting to note that SOC is operative in Fe $3d^6$ manifold possibly by induced mechanism due to either mixing of Fe-$d$ with oxygen $p$ states or mixing of $t_{2g}$ - $e_g$ orbitals in the distorted octahedra. We recover the experimental magnetic ground state of AgFeO$_2$ upon the inclusion of SOC. Calculations of ferroelectric polarization suggest that the spontaneous polarization arises from noncollinear spin arrangement via spin-orbit coupling. Our calculations also indicate that in addition to electronic contributions, lattice me-
uated contribution to the polarization is also important for AgFeO$_2$.

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