Supplementary Information: Magnetic, Electronic and Optical Properties of Double Perovskite Bi$_2$FeMnO$_6$

Towfiq Ahmed, Aiping Chen, Dzmitry A. Yarotski, Stuart A. Trugman, Quanxi Jia, and Jian-Xin Zhu

1 Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
2 Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Dated: August 28, 2016)
I. COMPUTATIONAL METHOD

To study the electronic, optical and magnetic properties of double perovskite Bi$_2$FeMnO$_6$, we applied density functional theory (DFT) as implemented in the full-potential LAPW code Wien2k.$^1$ The unstrained crystal structure of BFMO is shown in Fig. 1(a) in the main text. Lattice parameters considered for this calculation were taken from the experimental values.$^2$ The lattice parameters for the double perovskite BFMO unit cell are $a = b = 5.5579 \ \text{Å}$, $c = 8.06 \ \text{Å}$, and $\alpha = \beta = \gamma = 90^\circ$. Electronic relaxation was achieved self-consistently using a $10 \times 10 \times 10$ k-point mesh in the Brillouin zone. Spin polarized calculations were performed using an exchange-correlation functional within the generalized gradient approximation.$^3$ The spin-orbit coupling for the valence electrons, was taken into account within a second variational approach.$^4,5$ In our calculation, we used the muffin-tin radius of $2.5a_0$ for Bi, $1.99a_0$ for Fe and Mn, and $1.71a_0$ for O, and the cutoff $RK_{\text{max}} = 7.0$.

For the x-ray XMCD calculations,$^6$ the core-states were obtained fully relativistically by solving the Dirac equations.$^7$ For $L_2$ and $L_3$ edge XMCD calculations of Fe and Mn sublattices, the $P_{1/2}$ and $P_{3/2}$ core level energies and core-hole lifetime broadening were obtained from experimental values.$^8$ For Fe, $P_{1/2}$ and $P_{3/2}$ core level energies are -49.95470 eV and -50.873489 eV, while the core-hole broadening is 0.37 eV and 0.2 eV, respectively. For Mn, $P_{1/2}$ and $P_{3/2}$ core level energies are -45.04057 eV and -45.80827 eV, while the core-hole broadening is 0.34 and 0.34 eV, respectively.

To account for the onsite Coulomb interaction in Fe and Mn ions, we used the mean-filed approximation of GGA+$U$ method. To study the electronic structure of BFMO, we calculated the spin resolved band structure and DOS. The band structure is calculated along the high symmetry lines in BZ: $\Gamma \rightarrow N \rightarrow P \rightarrow G_1 \rightarrow G_2 \rightarrow S \rightarrow Z \rightarrow \Gamma \rightarrow G_3 \rightarrow S_2 \rightarrow \Gamma$ following the CDML$^9$ convention. The Brillouin zone and high symmetry lines are shown in Fig. 1(b) in the main text.

For the optical conductivity calculations, the momentum matrix elements were constructed and integrated over the brillouin zone following the prescription of Draxl et al.$^{10}$ The interband and intraband contributions to the imaginary part of the dielectric tensors ($\varepsilon_2$) for both spin up and down were then computed. The real part of $\varepsilon$ ($\varepsilon_1$) is then computed using Kramers-Kronig transformation. These quantities were then used to calculate the optical conductivity.$^{10}$ In this work, we calculated the $\sigma_{xx} = \sigma_{yy}$ and $\sigma_{zz}$ contribution of the optical conductivity ignoring all the off-diagonal terms.
II. EFFECTS OF THE ONSITE COULOMB $U$ ON MAGNETISM AND BAND GAP

Corresponding to Fig. 2(b-c) in the main text, we present in Tables S-I and S-II the net moment and gap in BFMO, as a two-dimensional parameter space formed by $(U_{Fe}, U_{Mn})$. These results provide a path forward on the optimization of magnetic moment through the strain in insulating BFMO crystals as well as how it can be affected by the electronic correlation of Fe and Mn ions.

**TABLE S-I: Total magnetic moment ($\mu_B$) in Bi$_2$FeMnO$_6$ for different values of Hubbard $U$ parameters.**

| $m = m_{Mn} + m_{Fe}$ | $U_{Fe} = 0$ eV | $U_{Fe} = 2$ eV | $U_{Fe} = 4$ eV | $U_{Fe} = 6$ eV |
|----------------------|----------------|----------------|----------------|----------------|
| $U_{Mn} = 0$ eV      | 1.140          | 1.159          | 1.163          | 1.167          |
| $U_{Mn} = 2$ eV      | 1.101          | 1.101          | 1.110          | 1.113          |
| $U_{Mn} = 4$ eV      | 1.046          | 1.056          | 1.050          | 1.053          |
| $U_{Mn} = 6$ eV      | 1.023          | 1.032          | 1.032          | 1.035          |

**TABLE S-II: Band gap $\Delta$ in Bi$_2$FeMnO$_6$ for different values of Hubbard $U$ parameters in Fe and Mn ions.**

| Gap=$\Delta$ (eV) | $U_{Fe} = 0$ eV | $U_{Fe} = 2$ eV | $U_{Fe} = 4$ eV | $U_{Fe} = 6$ eV |
|-------------------|----------------|----------------|----------------|----------------|
| $U_{Mn} = 0$ eV   | 0.00           | 0.00           | 0.00           | 0.00           |
| $U_{Mn} = 2$ eV   | 0.00           | 0.00           | 0.00           | 0.00           |
| $U_{Mn} = 4$ eV   | 0.01           | 0.03           | 0.09           | 0.25           |
| $U_{Mn} = 6$ eV   | 0.20           | 0.49           | 0.50           | 0.80           |

III. XMCD SUM RULES

The magnitude of spin and orbital moments can be obtained by the well known XMCD sum rules:$^{11-13}$ These sum rules are expressed as,

$$m_{spin}[\mu_B/\text{atom}] = -\frac{(6p - 4q)(10 - n_{3d})}{r}, \quad (S1)$$

and

$$m_{orb}[\mu_B/\text{atom}] = -\frac{4q(10 - n_{3d})}{3r}, \quad (S2)$$
FIG. S1: (Color online) The $L_2/L_3$ XMCD sum rule for Mn sublattice in BFMO.

where

$$p = \int_{L_3} \left[ \mu^+ (\omega) - \mu^- (\omega) \right] d\omega,$$

$$q = \int_{L_3+L_2} \left[ \mu^+ (\omega) - \mu^- (\omega) \right] d\omega,$$

$$r = \int_{L_3+L_2} \left[ \mu^+ (\omega) + \mu^- (\omega) \right] d\omega,$$

(S3)

and $n_{3d}$ is the number of $3d$ electrons in Fe and Mn ions. From the measured XMCD spectra, these quantities can be easily extracted. In Figs. S1 and S2, we present theoretical $L_2$ and $L_3$ XMCD spectra as well as the sum rule components of Fe and Mn ions.

These XMCD sum rules give rise to spin and orbital moment of Fe and Mn. In Table S-III, we list all of our calculated sum rule components $p$, $q$, $r$ as well as the orbital and spin magnetic moments along with other quantities.

* To whom correspondence should be addressed.

Electronic address: jxzhu@lanl.gov; URL: http://cint.lanl.gov

1 Blaha, P., Schwarz, K., Madsen, G. K. H., Kvasnicka, D. & Luitz, J. An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Schwarz K., Tech. Universität Wien, Austria,
FIG. S2: (Color online) The $L_2/L_3$ XMCD sum rule for spin and orbital magnetic moments in Fe sublattice of BFMO.

2 Choi, E.-M. et al. Strong room temperature magnetism in highly resistive strained thin films of BiFe$_{0.5}$Mn$_{0.5}$O$_3$. Appl. Phys. Lett. 98, 012509 (2011).

3 Perdew, J. P., Burke, S. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865 (1996).

4 Koelling, D. D. & Harmon, B. N. A technique for relativistic spin-polarised calculations. J. Phys. C: Solid State Phys. 10, 3107 (1977).

5 MacDonald, A. H., Picket, W. E. & Koelling, D. D. A linearised relativistic augmented-plane-wave method utilising approximate pure spin basis functions. J. Phys. C: Solid State Phys. 13, 2675 (1980).

6 Pardini, L., Bellini, V., Manghi, F. & Ambrosch-Draxl, C. First-principles calculation of x-ray dichroic spectra within the full-potential linearized augmented planewave method: An implementation into the Wien2k code. Comput. Phys. Commun. 183, 628–636 (2012).

7 Desclaux, J. A multiconfiguration relativistic DIRAC-FOCK program. Comput. Phys. Commun. 9, 31–45 (1975).

8 Fuggle, J. C. & Inglesfield, J. E. (Eds.) Unoccupied electronic states: Fundamentals for XANES, EELS, IPS and BIS (Top. Appl. Phys.) (Springer-Verlag, New York, 1992).
TABLE S-III: XMCD sum-rule for spin and orbital magnetic moments in Fe and Mn sublattice of Bi$_2$FeMnO$_6$ for $U_{Fe} = U_{Mn} = 6.0$ eV. Note that the values of spin magnetic moment listed here are only the contributions from the $d$-orbitals of Fe and Mn. For comparison, the magnetic moments from the DFT self-consistent (SCF) calculations are also listed.

| Element | Mn   | Fe   |
|---------|------|------|
| $Z$     | 25   | 26   |
| $p$     | $6.52 \times 10^{-4}$ | $-6.50 \times 10^{-4}$ |
| $q$     | $3.23 \times 10^{-5}$ | $-7.11 \times 10^{-5}$ |
| $r$     | $6.03 \times 10^{-3}$ | $4.12 \times 10^{-3}$ |
| $n_d$(up) | 0.42 | 4.74 |
| $n_d$(down) | 3.97 | 0.57 |
| XMCD spin magnetic moment $(\mu_B)$ | $-3.512$ | $+4.210$ |
| XMCD orbital magnetic moment $(\mu_B)$ | $-0.04$ | $+0.08$ |
| SCF spin magnetic moment $(\mu_B)$ | $-3.563$ | $+4.203$ |
| SCF orbital magnetic moment $(\mu_B)$ | 0.016 | 0.013 |

9 Aroyo, M. I., Kirov, A., Capillas, C., Perez-Mato, J. M. & Wondratschek, H. Bilbao Crystallographic Server. II. Representations of crystallographic point groups and space groups. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **62**, 115–128 (2006).

10 Ambrosch-Draxl, C. & Sofo, J. O. Linear optical properties of solids within the full-potential linearized augmented planewave method. *Comput. Phys. Commun.* **175**, 1–14 (2006).

11 Carra, P., Thole, B. T., Altarelli, M. & Wang, X. X-ray circular dichroism and local magnetic fields. *Phys. Rev. Lett.* **70**, 694–697 (1993).

12 Chen, C. T. *et al.* Experimental confirmation of the x-ray magnetic circular dichroism sum rules for iron and cobalt. *Phys. Rev. Lett.* **75**, 152–155 (1995).

13 Piamonteze, C., Miedema, P. & de Groot, F. M. F. The accuracy of the spin sum rule in xmc. *J. Phys.: Conf. Series* **190**, 012015 (2009).