

# Spin glass in [111] Fe-Mn ordered Bi<sub>2</sub>FeMnO<sub>6</sub>

Yue-Wen Fang<sup>1†</sup>, Lin Sun<sup>1</sup>, Rong Huang<sup>1</sup>, Qing He<sup>2</sup>, Junhao Chu<sup>1</sup>, Ying-Hao Chu<sup>3</sup>, Chun-Gang Duan<sup>1\*</sup>

<sup>1</sup>Key Laboratory of Polar Materials and Devices, Ministry of Education, Department of Electronic Engineering, East China Normal University, Shanghai 200241, China

<sup>2</sup>Department of Physics, Durham University, Durham DH1 3LE, UK

<sup>3</sup>Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, 30010, Taiwan, ROC

Y.-W.F. and L.S. contributed equally to this work.

E-mail: [†fyuewen@gmail.com](mailto:fyuewen@gmail.com) or [\\*wxbdcg@gmail.com](mailto:wxbdcg@gmail.com)

Multiferroics with robust ferroelectricity and magnetism at room temperature (RM) are still rare today owing to the incompatible ferroelectric and ferromagnetic orders. Bi<sub>2</sub>FeMnO<sub>6</sub> were suggested to be good candidate of RM multiferroics. However, previous first-principles calculations (L. Bi et al) predicted that the formation entropy of ordered Bi<sub>2</sub>FeMnO<sub>6</sub> is very large and the fabrication of thin films of them are quite challenging. Since then, no ordered Bi<sub>2</sub>FeMnO<sub>6</sub> were observed in experiment.

In present study (arXiv:1512.06360), Bi<sub>2</sub>FeMnO<sub>6</sub> thin films were prepared by pulsed laser deposition (PLD) methods. Their structure unexpectedly shows [111] Fe-Mn ordering (see Fig. 1), which is supported by the asymmetric X-ray diffraction (XRD), synchrotron reciprocal space mapping (RSM) and high resolution transmission electron microscopy results.

RM ferroelectricity is observed by Piezoelectric Force Microscopy measurements in these Bi<sub>2</sub>FeMnO<sub>6</sub> samples, however, the surprising finding revealed by superconducting quantum interference device is that Bi<sub>2</sub>FeMnO<sub>6</sub> with Fe-Mn ordering just exhibits  $\sim 0.02 \mu_B/\text{Fe-Mn pair}$  at RT. A exotic aging phenomenon is observed, which is one of the characteristics of spin glass. X-ray magnetic circular dichroism further shows that there is no magnetism at the Fe or Mn (111) planes.

The unexpected results for the magnetism motivated us to reconsider the exchange interactions within this highly ordered crystal. By performing orbital model analysis according to the Goodenough-Kanamori-Anderson empirical rules, we predict that ferroelectric displacements could have effects on the energy levels of  $d_{x^2-y^2}$  and  $d_z^2$  because of the slight difference between *a* (3.905 Å) and *c* (4.015 Å). In order to support this, total energy for several different magnetic structures were determined by first-principles calculations. By solving the Heisenberg equation, we find that spin frustration can be induced in certain phase with specific ferroelectric displacements. Different ferroelectric displacements largely modifies the values and even the signs of exchange interactions of nearest neighboring Fe-Mn and next nearest neighboring Fe-Fe and Mn-Mn. First-principles calculations propose a spin frustration model, where next nearest neighboring Fe-Fe or Mn-Mn exchange interactions are bigger than the nearest Fe-Mn superexchange, to explain the experimentally observed spin glass and very weak magnetism at RT.

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### References

- [1] L. Sun, et al., arXiv:1512.06360 (2015).
- [2] L. Bi, et al., Phys Rev B 78, 104106 (2008).
- [3] L. Pálková, P. Chandra, and K. M. Rabe, Phys Rev B 82, 075432 (2010).
- [4] L. Pálková, P. Chandra, and K. M. Rabe, Phys Rev Lett 104, 037202 (2010).

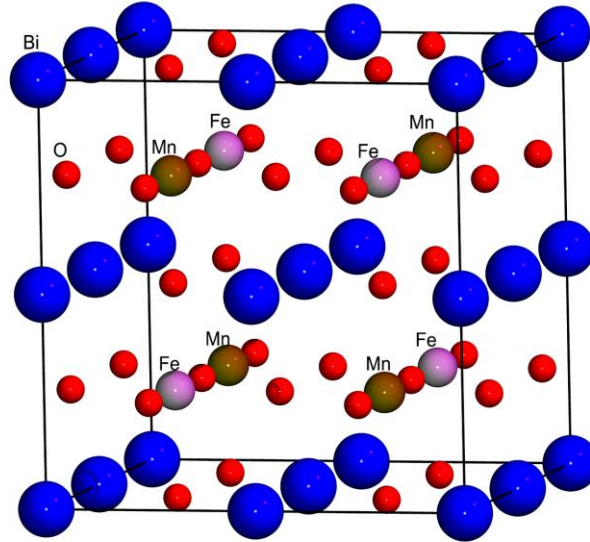


FIG. 1. [111] Fe-Mn ordered  $\text{Bi}_2\text{FeMnO}_6$ .