

Study of the magnetoelectricity of the Fe-based oxides

Yu-Hui Liang,^{1,*} Naoshi Ikeda and Chao-Hung Du^{1,†}

¹*Department of Physics, Tamkang University, New Taipei City 251301, Taiwan*

²*Department of Physics, Okayama University, Okayama, 700-8530, Japan*

I. Scientific Background

In recent years, multiferroic materials with both ferroelectricity and magnetism arouse the intense interest of scientists due to the strong magneto-electric coupling effect which means that an external magnetic field can cause the material to be polarized (polarization), or to be magnetized (magnetization) by applying an external electric field. However, such materials are uncommon because of the different symmetries of magnetism and electricity, and the mechanisms and conditions that give rise to the order parameters are often mutually exclusive¹⁻³. Cheong et al. classified the multiferroics according to the different inversion symmetry breaking mechanism into two groups³, i.e., proper and improper multiferroics. In proper materials, the main cause of electric polarization is the collective shift of cations and anions. Or the shift away from the centrosymmetric position of lone pair electrons on 6s orbital. There are long-range ordered magnetic moments in these materials, however the coupling between ferroelectricity and magnetism is very weak. On the other hand, the polarization results from the complex lattice distortions or ordered arrangements of other properties is called “improper”. Among them, materials that are electrically polarized due to the long-range ordered magnetic moments have great potential in the application including data storage, sensor and controller. However, the very low transition temperature is a drawback for many reported improper multiferroic materials, which limits the possible applications⁴⁻⁹. It has been known that there are only two well-known systems which electric polarization is induced by magnetic ordering and with an effective transition temperature around 200 K. One is CuO¹⁰⁻¹², which the temperature of the ferroelectricity and ICM magnetic structure phases coexist is the range from 213 to 230 K. The other is the layered perovskites RBaCuFeO₅ with a transition temperature up to ~ 200K¹³⁻¹⁸. But from the literature, the results of YBCFO measurements using neutron powder do not match well. In order to establish the correct magnetic structure and then find the mechanism of the magnetoelectric coupling effect, an accurate low-temperature spiral magnetic structure is needed.

II. Completed Sections

Using high-resolution neutron scattering (NS) on a single crystal, we have explored the detail magnetic structures. In Fig. 1(a), it is shown the temperature-dependent diffraction peaks along [0 0 1] direction across the magnetic peak $\mathbf{q}_{CM} = (0.5$

0.5 0.5) by using elastic neutron scattering. At 250 K, only the CM peak was measured. Cooled down to 200 K, two broad ICM peaks next to the CM peak are observed. Upon cooling. These two peaks split into four peaks as temperature close to 190 K. This shows that below T_{N2} , there are two magnetic structures with different periods. The peaks nearest CM peak were the modulation peaks of incommensurate phase 1 (ICM1). And next-nearest peaks were incommensurate phase 2 (ICM2). The q -vector of ICM1 and ICM2 are $\mathbf{q}_{\text{ICM1}} = (0.5 \ 0.5 \ 0.5 \pm \delta_{\text{ICM1}})$ and $\mathbf{q}_{\text{ICM2}} = (0.5 \ 0.5 \ 0.5 \pm \delta_{\text{ICM2}})$. When the temperature reaches 150 K, the CM phase disappears. At 10K, the lowest temperature measured, there are only two strong phases, ICM1 and ICM2. The detailed fitting results are shown in Fig. 1 (b). δ_{ICM1} and δ_{ICM2} increase upon cooling. The difference between δ_{ICM1} and δ_{ICM2} is reduced at low temperatures, there are still two different values at the lowest temperature we measured. The different values of δ reveal the periods of different spiral magnetic structures with an incommensurate q -vector along the c -axis and the rotation angle of the respective magnetic moments below T_{N2} . We can determine more precisely the rotation angle of the magnetic moment between the neighboring unit cells by δ . Below T_{N2} , the relative angles of magnetic moments of ICM1 and ICM2 increase as a function of temperature, and again no CM phase. In addition, the angles of ICM1 ($\sim 32^\circ$ at 10 K) and ICM2 ($\sim 36^\circ$ at 10 K) are still different, although the difference in rotation angles of them becomes smaller at a lower temperature. Furthermore, the more detailed information can be obtained from the analysis of the reflection intensity versus temperature. The diffraction intensities of ICM1 and ICM2 increase as temperature decreased because of the reduction of thermal fluctuation at low temperature. According to Hund's rules, the magnetic moment of Fe^{3+} is larger than that of Cu^{2+} . Therefore, we can preliminarily speculate that the contribution of ICM1 mainly comes from Fe^{3+} , while the contribution of ICM2 comes from Cu^{2+} .

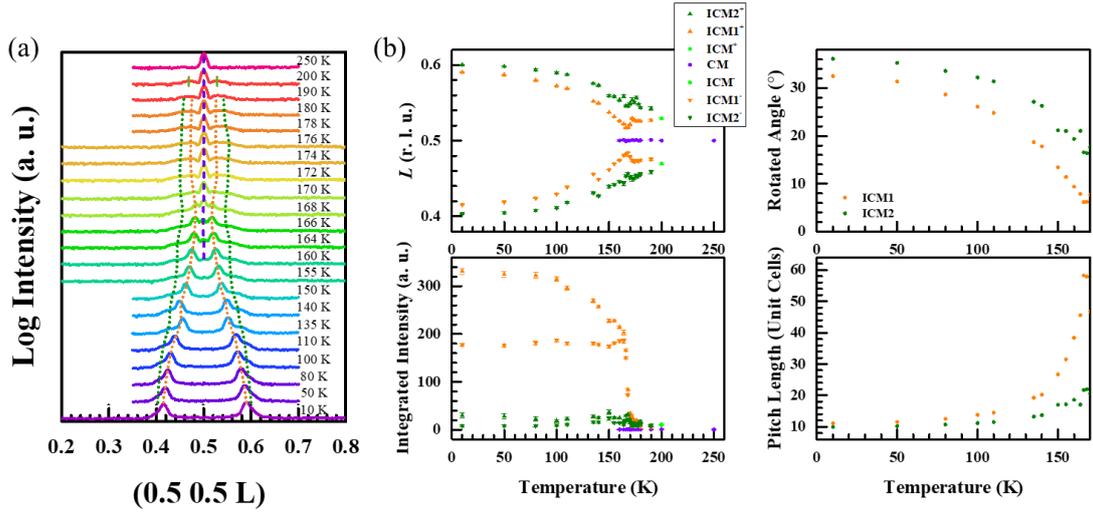


Fig. 1 (a) Temperature-dependent diffraction peaks along (0.5 0.5 L). (b) The fitting results of NS data. Below T_{N2} , rotation angle and pitch length of ICM1 and ICM2 as function of temperature.

The magnetic structure of YBCFO is so complicated, and it is hard to distinguish the contributions of iron and copper to the magnetic ordering using neutron scattering. However, this problem can be overcome by using resonant elastic X-ray scattering. Resonant x-ray scattering possesses the capability of local element-selectivity and enhancement of reflection intensity, so it is a powerful probe for studying the electronic structure. Figure 2 shows a comparison of the magnetic reflections as measured by neutron (blue lines) and x-ray (red lines) scattering. In Fig. 2 (a), for X-ray results which are represented in the red line, there are the diffraction patterns across the magnetic peak $\mathbf{q}_{CM} = (1.5 \ 1.5 \ 0.5)$ along $[0 \ 0 \ 1]$ direction and fixed the incident X-ray energy at pre-edge 7.1155 keV. And compared with the neutron scattering result which is plotted in blue lines together at different temperatures. At 200K and 180K, there is a strong signal at $L = 0.5$, which is CM phase, and without incommensurate phase signal, although ICM1 and ICM2 are obvious in the neutron results. It is probably because both the magnetic structures of ICM1 and ICM2 are still in less orderly states as the temperature above T_{N2} . The reason is that the intensities of diffraction peaks of incommensurate phases are very weak for X-rays even though neutrons are sensitive to magnetic structures, it needs to take much longer counting time to improve the signal-to-noise ratio. As the temperature cooled down to 150 K, it shows the disappearance of the CM phase for the X-ray, consistent with neutron results. And there are two diffraction peaks that coincide with the q -vector of ICM1 which are $L = 0.5 \pm \delta_{ICM1}$ for neutron. However, there are no signals at $L = 0.5 \pm \delta_{ICM2}$ for ICM2. It strongly suggests that the main contribution of ICM1 comes from Fe^{3+} . Upon cooling to 130 K, the behavior is similar to the 150K results. In order to further prove that the contribution of ICM1 is only from Fe^{3+} rather than from Cu^{2+} . It is an effective method that measures the X-ray absorption spectrum at Fe and Cu K -edge with the fixed geometry $\mathbf{q}_{ICM1} =$

(1.5, 1.5, 0.55) which corresponds to the propagation vector of ICM1 for X-ray, and the results are plotted in the red line. By moving the detector away from this q , we obtained the normal X-ray absorption spectra which are plotted in the blue line. Comparing the absorption spectrum together, as shown in Fig.2 (b), there is an obviously resonant behavior at the pre-edge of Fe but not less pronounced at the Cu K -edge for the ICM1 phase. This result demonstrates that the contribution of ICM1 is purely from Fe. About ICM2, according to the reference of X-ray absorption spectrum¹⁹, there is no clear pre-edge in the spectrum of Cu K -edge of YBCFO. It is difficult to study the contribution of the magnetic structure of copper by using the resonant X-ray scattering experiment. For YBCFO, only the transition-metal Fe^{3+} and Cu^{2+} are magnetic, thus it is indirectly speculated that the contribution of ICM2 comes from Cu. In addition, the magnetic moment below T_{N2} of Cu^{2+} is much smaller than Fe^{3+} from the fitting results of neutron scattering. The results of the magnetic structure of ICM2 which require much more counting time will be obtained through an X-ray experiment without the resonant effect.

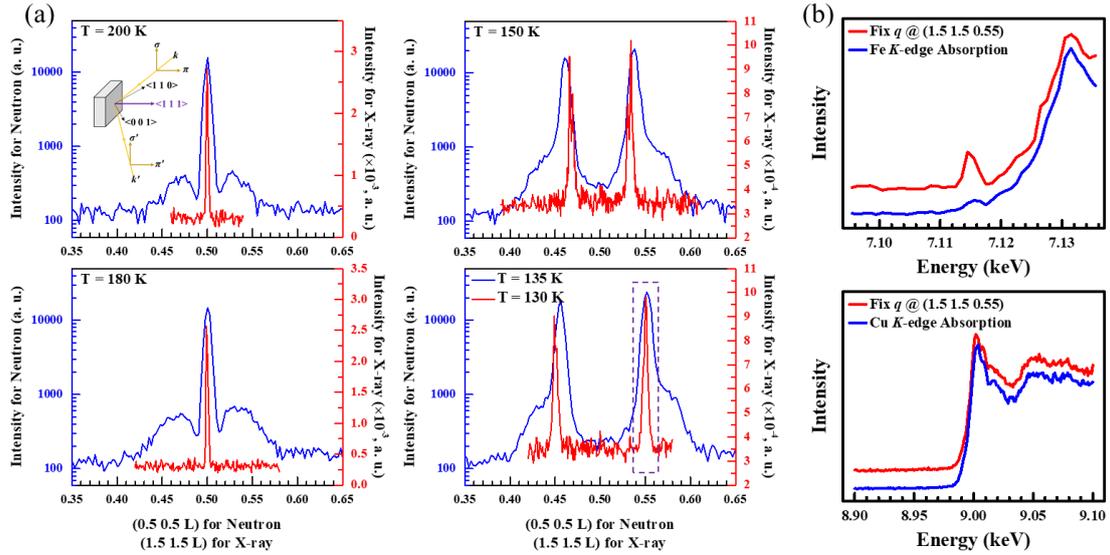


Fig. 2 (a) Comparison of the NS with RXS around Fe K -edge results. Temperature-dependent diffraction peaks along L -direction. (b) Fix- q at ICM1 and normal X-ray absorption spectra around Fe K -edge and Cu K -edge at 130 K.

In summary, we have established a new and complete magnetic structure. The magnetic structure below T_{N2} is called “double-flat-spiral magnetic structure”. The first magnetic structure was found in the ternary intermetallic silicides containing rare earth (RE) and transition metal $\text{RE}^{\text{RE}}\text{RhSi}^{20}$. Currently, this magnetic structure is mainly found in kagome-net magnet $\text{RE}^{\text{RE}}\text{Mn}_6\text{Sn}_6$ which the periods of Mn^{2+} and Mn^{3+} is different²¹. However, it is a new discovery and will create more application possibilities in YBCFO, as the double helix magnetic structure contributes from

different elements.

III. Obstacles and Future Work

A. Resonant elastic X-ray scattering experiment with magnetic field

According to the article published by J. Lyu et al.²², the temperature-dependent magnetization of YBCFO was measured at high magnetic fields. The warming and cooling paths are not the same below T_{N2} . We also measured the very complex diffraction patterns by neutron scattering experiment with applied magnetic field. The high quality of single crystals will support a more complete study of anisotropy. Next, resonant elastic X-ray scattering experiments with magnetic fields will be carried out to solve the behavior under the magnetic field and to establish the complete phase diagram. Further understanding of the physical mechanism of YBCFO is needed to find other similar systems for more real-life applications. The proposal for the photon factory has been approved and the experiment will be conducted in June this year.

B. Electric polarization measurement

Among the multiferroic materials, ferroelectricity is a very important feature. The electropolarization of powder YBCFO has been measured¹⁴, but the characteristic curve of electropolarization has not been measured in our single crystal. In addition, the phase transition temperature of YBCFO varies in different process conditions, so now we are currently preparing the single crystal. After discussion with Prof. Ikeda and Prof. Kano, we will try to measure the electric-field-dependent electric polarization curve during the summer exchange period in June this year. And also we will also try to use the low temperature control system. Prof. Du's lab is working on the physical properties of other novel powder materials, so such measurements will bring more information about the materials to further investigate the physical mechanisms and their applications. The experiment will use the double-wave method measurement, also called Positive-Up Negative-Down (PUND) method, such the method can reduce leakage current²³. The overall electric polarization of the sample has the contribution of ferroelectricity, paraelectricity, and leakage. Among the ferroelectricity that we want to measure most, the first two added (P and U) positive field measurements do not change the direction of polarization. So the contribution of ferroelectricity is discerned by this PUND method to measure the complete PE curve of ferroelectricity. We would like to thank Prof. Kano's student, Mr. Huang, for providing the detail of the experimental detail.

C. Second-Harmonic Generation (SHG)

Prof. Ikeda's main research area is RFe_2O_4 which is magnetoelectric coupling materials, and it is induced by charge ordering. In collaboration with Prof. Okimoto of

Tokyo Institute of Technology, Prof. Ikeda has successfully measured the charge-ordered structure and its ordered arrangement by SHG in YbFe_2O_4 ²⁴. In general, ferroelectric polarization inversion is observed using P-E curves (B part). Therefore, in this system, it was confirmed that there is spontaneous polarization. It has not yet been confirmed whether the polarization can be reversed by an external electric field. However, since the current flows easily in this system which means the material is not so insulating, the P-E curve cannot be obtained. A new method is needed to confirm whether the polarization can be reversed or not. Mr. Yu, a student of Prof. Okimoto at Tokyo Institute of Technology, has used the SHG method to measure PE curves, and the method can be applied to semiconductors or insulators which are more susceptible to electrical conductivity. In the case of my main project YBCFO, there is one more possibility, because I want to keep the single crystal sample, which cannot be processed in another way, such as grinding. SHG can also be used to measure the order and periodicity of samples, and we are actively discussing to establish cooperation in this area to solve more basic material problems.

References

1. N. A. Hill, *The Journal of Physical Chemistry B* **104** (29), 6694-6709 (2000).
2. W. Eerenstein, N. D. Mathur and J. F. Scott, *Nature* **442** (7104), 759-765 (2006).
3. S.-W. Cheong and M. Mostovoy, *Nature Materials* **6** (1), 13-20 (2007).
4. T. Goto, T. Kimura, G. Lawes, A. P. Ramirez and Y. Tokura, *Phys Rev Lett* **92** (25 Pt 1), 257201 (2004).
5. H. Katsura, N. Nagaosa and A. V. Balatsky, *Phys Rev Lett* **95** (5), 057205 (2005).
6. M. Mostovoy, *Phys Rev Lett* **96** (6), 067601 (2006).
7. I. A. Sergienko and E. Dagotto, *Physical Review B* **73** (9) (2006).
8. Y. Yamasaki, S. Miyasaka, Y. Kaneko, J. P. He, T. Arima and Y. Tokura, *Phys Rev Lett* **96** (20), 207204 (2006).
9. K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa and T. Arima, *Phys Rev Lett* **97** (9), 097203 (2006).
10. G. Giovannetti, S. Kumar, A. Stroppa, J. van den Brink, S. Picozzi and J. Lorenzana, *Phys Rev Lett* **106** (2), 026401 (2011).
11. D. Meng, X.-G. Zheng, X. Xu, J. Nakauchi, M. Fujihala, X. Liu, Q. Guo and M. Maki, in *Proceedings of the International Conference on Strongly Correlated Electron Systems (SCES2013)* (2014).
12. T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist and A. P. Ramirez, *Nat Mater* **7** (4), 291-294 (2008).
13. V. Caignaert, I. Mirebeau, F. Bourée, N. Nguyen, A. Ducouret, J. M. Greneche and B. Raveau, *Journal of Solid State Chemistry* **114** (1), 24-35 (1995).

14. B. Kundys, A. Maignan and C. Simon, *Applied Physics Letters* **94** (7) (2009).
15. M. Morin, A. Scaramucci, M. Bartkowiak, E. Pomjakushina, G. Deng, D. Sheptyakov, L. Keller, J. Rodriguez-Carvajal, N. A. Spaldin, M. Kenzelmann, K. Conder and M. Medarde, *Physical Review B* **91** (6) (2015).
16. M. Morin, E. Canevet, A. Raynaud, M. Bartkowiak, D. Sheptyakov, V. Ban, M. Kenzelmann, E. Pomjakushina, K. Conder and M. Medarde, *Nat Commun* **7**, 13758 (2016).
17. C. M. L. Er-Rakho, Ph. Lacorre, B. Raveau, *Journal of Solid State Chemistry* **73** (2), 531-535 (1988).
18. Y. Kawamura, T. Kai, E. Satomi, Y. Yasui, Y. Kobayashi, M. Sato and K. Kakurai, *Journal of the Physical Society of Japan* **79** (7) (2010).
19. M. K. Srivastava, X. S. Qiu, Y. Y. Chin, S. H. Hsieh, Y. C. Shao, Y. H. Liang, C. H. Lai, C. H. Du, H. T. Wang, J. W. Chiou, Y. C. Lai, H. M. Tsai, C. W. Pao, H. J. Lin, J. F. Lee, K. Asokan and W. F. Pong, *Sci Rep* **9** (1), 18586 (2019).
20. W. Bażela, J. Leciejewicz and A. Szytuła, *Journal of Magnetism and Magnetic Materials* **50** (1), 19-26 (1985).
21. E. V. Rosenfeld and N. V. Mushnikov, *Physica B: Condensed Matter* **403** (10-11), 1898-1906 (2008).
22. J. Lyu, M. Morin, T. Shang, M. T. Fernández-Díaz and M. Medarde, *Physical Review Research* **4** (2) (2022).
23. H. Naganuma, Y. Inoue and S. Okamura, *Applied Physics Express* **1** (2008).
24. K. Fujiwara, Y. Fukada, Y. Okuda, R. Seimiya, N. Ikeda, K. Yokoyama, H. Yu, S. Koshihara and Y. Okimoto, *Sci Rep* **11** (1), 4277 (2021).