Effective Modulation of the Magnetic Properties of $YBaCuFeO_5$

Very low concentrations of Cu/Fe self-doping can effectively change the magnetic properties of $YBaCuFeO_5$.

Multiferroic materials, in which ferroelectricity and magnetic ordering coexist, have been actively studied with interests in fundamental and applied sciences. Several decades of investigations reveal that the incommensurate orientation-modulated spin structures, such as spiral and cycloidal, are good candidates for hosting ferroelectricity. In such materials, termed type II ferroelectrics, the electrical polarization is coupled with the magnetic structures triggered by the Dzyaloshinskii–Moriya interaction or magnetic frustration. Nevertheless, the magnetic ordering temperature T_N and ferroelectric Curie temperature T_C are generally well below the ambient temperature and are unfavorable for daily-life applications. While pursuing multiferroic materials with high T_c, the oxygen-deficient double perovskite, $YBaCuFeO_5$ (YBCFO), arouses wide attention. YBCFO possesses the layered structure of $MM'O_9$ bipyramids (**Fig. 1(a)**), and Cu/Fe resides within the double pyramids. The Cu/Fe spins undergo antiferromagnetic transition to a commensurate, collinear antiferromagnetic order characterized by the propagation vector of k_{c1} = (1/2, 1/2, 1/2) at T_{N1}. Below the second magnetic phase-transition temperature T_{N2}, the spin structure transits into an incommensurate chiral structure, with propagation vector k_i = (1/2, 1/2, 1/2 ± δ).[1] The reported values of T_{N1} and T_{N2} are inconsistent in the literature, and the differences are as large as several tens of degrees. Such differences are unlikely due to the experimental errors but imply a tunable magnetic property of the compound. It is demonstrated that T_{N2} is successfully tuned by chemical substitution and a post-sintering cooling rate.[2,3] Chemical substitution can tune the lattice, change the interlayer distances, and subsequently alter the strength of interlayer interactions. Increasing the cooling rate or quenching the sample after the sintering has been proven to be an effective way of controlling the Cu/Fe distribution within the bipyramids. Theoretical studies show that disorder in the Cu/Fe distribution is crucial for the onset of commensurate to incommensurate magnetic transition (CM–ICM). At the same time, the CM phase persists down to low temperature without transiting into the ICM phase in the sample with highly ordered cation distribution.[4]

Magnetic transition temperatures are correlated with the degree of disorder. T_{N2} increases while T_{N1} is slightly suppressed when the Cu/Fe distribution is more disordered. Therefore, the ICM order temperature can be enhanced by tuning the Cu/Fe distribution. In the noncentrosymmetric *P*4*mm* structure, the bipyramids are occupied by one Fe and one Cu, with ordered arrangement. The in-plane nearest-neighbor interactions are strongly antiferromagnetic despite the Cu/Fe distribution; therefore, the spins order into the checkerboard arrangement in the ab-plane.

Meanwhile, the interplane interactions alternate the sign along the c-axis and are ferromagnetic within the bipyramids and antiferromagnetic between bipyramids, resulting in the [+--+] ground state characterized by the propagation vector of k_{c1} = (1/2, 1/2, 1/2). By increasing the post-annealing cooling speed or quenching, disorder is introduced. Fe–Fe and Cu–Cu pairs could occupy the bipyramid sites locally. Theoretical works suggest that the Fe–Fe pairs occupying the bipyramid impurities serve as "impurities", introducing antiferromagnetic interactions to the matrix of ferromagnetic coupling. When the concentration is sufficiently high and the temperature is sufficiently low, the incommensurate spiral structure sets in.

Chao-Hung Du (Tamkang University) proposed an alternative way to tune the magnetic properties of YBCFO by directly modifying the B site. By introducing additional Fe/Cu to the B sites, the local Fe/Cu arrangement could be changed to avoid the potential effects of the foreign

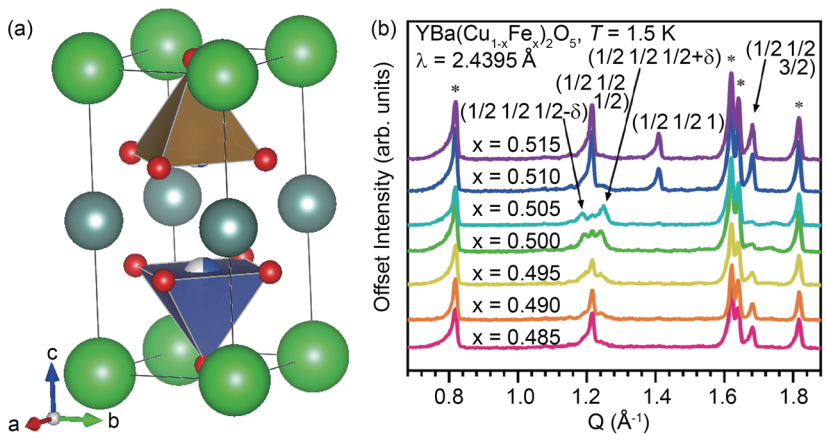

Fig. 1: (a) Crystal structure of YBCFO. (b) NPD patterns of selected $YBa(Cu_{1-x}Fe_x)_2O_5$ samples. The asterisks indicate the nuclear reflections, and the Miller indexes of magnetic peaks are labeled. [Reproduced from Ref. 6]

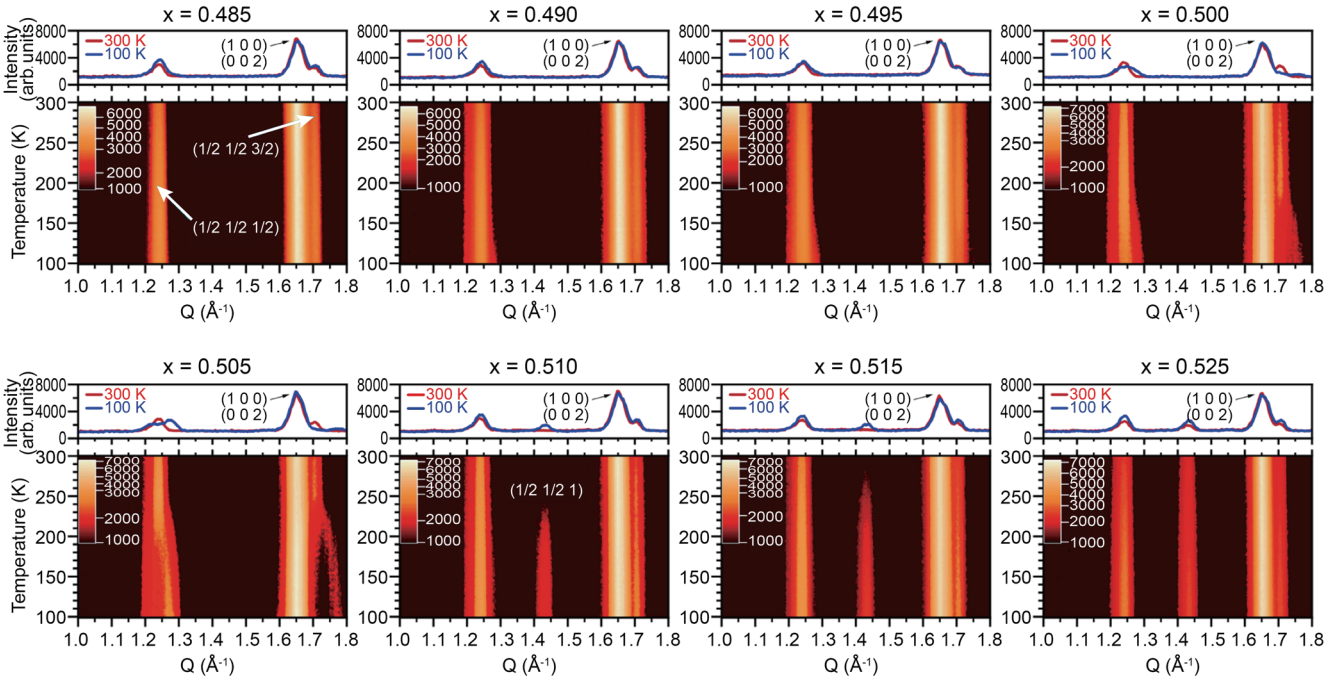

Fig. 2: Two-dimensional contours of eight $YBa(Cu_{1-x}Fe_x)_2O_5$ samples with distinct Cu/Fe ratios illustrate the temperature dependence of NPD patterns measured from 100 to 300 K. These figures focus on the low-Q region where the magnetic reflections appear NPD-pronounced. [Reproduced from Ref. 6]

element dopants. Polycrystalline $YBa(Cu_{1-x}Fe_x)_2O_5$ with x ranging between 0.485 and 0.525 were synthesized. **Figure 1(b)** shows the neutron powder diffraction (NPD) patterns collected at 1.5 K, employing the high-resolution neutron powder diffractometer, **ECHIDNA**. The patterns reveal various magnetic structures. The thermal evolution of magnetic structures was studied on the high-intensity neutron powder diffractometer, **WOMBAT**. **Figure 2** displays the temperature evolution of the magnetic structures of $YBa(Cu_{1-x}Fe_x)_2O_5$ and is summarized in the phase diagram shown in **Fig. 3**. The k_{c1} and k_{icm} magnetic phases coexisted at 1.5 K in the x = 0.500 sample. Noticeably, the incommensurate phase was most pronounced in the x = 0.505 sample, and the associated peaks were weaker because the iron content increased above 0.505. Compared to the parent YBCFO sample, T_{N2} was enhanced by 65 K by adding merely 1% iron. When the iron content was reduced from x = 0.505, the CM–ICM transition temperature, T_{N2}, gradually decreased, suggesting that the impurity bond density was gradually reduced. By contrast, the k_{icm} phase diminished much more quickly, and there were only extremely weak peaks of k_{icm} in the NPD of x = 0.510 and 0.515 samples. In samples with high iron content (x = 0.510 and 0.515), a new commensurate magnetic phase k_{c2} = (1/2, 1/2, 1) emerged. In the k_{c2} phase, the checkerboard arrangement was preserved in the ab-plane, and the sequence of spin arrangement along the c-axis was [+-+-], contrary to [+--+] in the k_{c1} phase. The additional iron content likely introduced excessive antiferromagnetically coupled Fe–Fe pairs to the bipyramid layers and destroyed the delicate balance for the emergence of the incommensurate spiral structure. The coexistence of k_{c1}, k_{c2}, and k_{icm} phases was observed in isostructural $NdBaCuFeO_5$ as magnetic texturing due to the partial ordering of Fe/Cu[5] and is similar to the behavior of highly ordered YBCFO.[4]

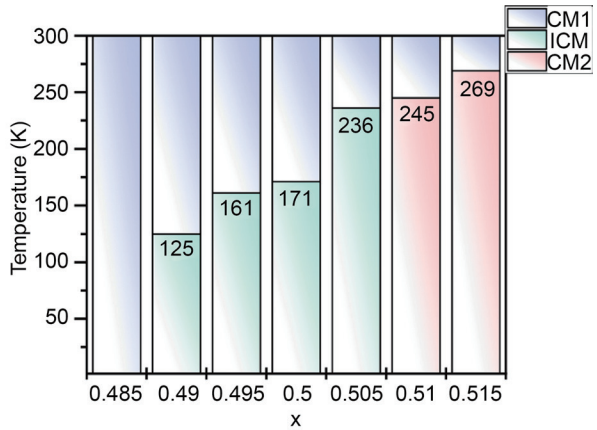

Fig. 3: Phase diagram of $YBa(Cu_{1-x}Fe_x)_2O_5$. [Reproduced from Ref. 6]

The magnetic properties of the oxygen-deficient double perovskite YBCFO can be tuned by A-site doping by adjusting the crystal structure to affect the magnetic coupling strength. By controlling the post-sintering cooling rate, the cation distribution on the B sites where the magnetic species Cu/Fe resides was determined. The current work proposed a more effective route that can simultaneously introduce the lattice effect and tune the Cu/Fe distribution. (Reported by Chin-Wei Wang)

*This report features the work of Chao-Hung Du and his collaborators published in Phys. Rev. Mater. **8**, 054404 (2024).*

ANSTO ECHIDNA – High Resolution Powder Diffractometer
ANSTO WOMBAT – High-Intensity Powder Diffractometer

- NPD
- Materials Science, Chemistry, Condensed-matter Physics

References

1. Y. C. Lai, C. H. Du, C. H. Lai, Y. H. Liang, C. W. Wang, K. C. Rule, H. C. Wu, H. D. Yang, W. T. Chen, G. J. Shu, F. C. Chou, J. Phys.: Condens. Matter **29**, 145801 (2017).
2. A. Romaguera, X. Zhang, O. Fabelo, F. Fauth, J. Blasco, J. L. García-Muñoz, Phys. Rev. Res. **4**, 043188 (2022).
3. T. Shang, E. Canévet, M. Morin, D. Sheptyakov, M. T. Fernández-Díaz, E. Pomjakushina, M. Medarde, Sci. Adv. **4**, eaau6386 (2018).
4. A. Romaguera, X. Zhang, R. Li, O. Fabelo, J. L. García-Muñoz, EPJ Web of Conferences **286**, 05005 (2023).
5. M. Pissas, J. M. M. M. **432**, 224 (2017).
6. C. H. Lai, C. W. Wang, H. C. Wu, Y. H. Kiang, A. J. Studer, W. T. Chen, C. H. Du, Phys. Rev. Mater. **8**, 054404 (2024).

Inelastic Neutron Scattering Reveals Strong Electron–Phonon Interactions Driving Ultrahigh *zT* Values

Through inelastic neutron scattering, strong electron–phonon interactions in Sb–Bi codoped GeTe crystals are revealed, unlock ultrahigh zT values. This breakthrough redefines thermoelectric innovation and accelerates the development of materials such as PbTe, SnTe, and SnSe.

Imagine a world where we can recover and utilize heat that would normally be lost. This includes the heat produced by automobile engines, the warmth radiating from industrial machines, and even the heat generated during physical exercise. The possibility of turning this heat into usable electricity could radically change how we consume energy. This is the promise of thermoelectric materials, which have the remarkable ability to convert thermal energy into electrical energy.[1] The range of potential applications is extensive—everything from making vehicles more fuel-efficient to developing more energy-efficient homes and appliances.

A significant advancement in the understanding and improvement of thermoelectric materials was achieved through the research conducted by Yang-Yuan Chen and his team at the Institute of Physics, Academia Sinica. By utilizing the powerful **SIKA** Cold Neutron Triple-axis Spectrometer at the Australian Nuclear Science and Technology Organisation (ANSTO),[2] Chen and his team discovered a novel mechanism in thermoelectric materials: the presence of ultrahigh *zT*, which serves as a figure of merit for thermoelectric performance driven by strong electron–phonon (EP) interactions and a low-dimensional Fermi surface. These discoveries offer new possibilities for enhancing thermoelectric performance, paving the way for applications that may revolutionize how we capture and use energy in our everyday lives.

Thermoelectric materials are designed to capture heat and convert it into electrical energy. However, they face a challenge: the heat usually travels through the material in a way that reduces its efficiency in generating electricity. The *zT* value is a key metric that indicates the efficiency of a thermoelectric material; the higher the *zT*, the better the material can convert heat into electrical power. By studying the intricate interactions between electrons (which carry electricity) and phonons (which transport heat), Chen's team identified a method to develop a material with an exceptionally high *zT*, enabling it to convert heat into electricity with remarkable efficiency.

The discovery is based on EP interactions, which occur at the atomic level, as shown in **Figs. 1(a) and 1(b)**. In many thermoelectric materials, heat dissipates too quickly because of weak coupling between electrons and phonons. However, in the materials studied by Chen's team, the strong EP interaction allows efficient electrical conduction while maintaining a temperature gradient that drives the thermoelectric process. Such as behavior leads to an ultrahigh *zT*, which is a game-changer in the thermoelectric field.