

DISCOVERY OF THE FERROELECTRICITY ORIGINATED FROM ELECTRON-ELECTRON INTERACTION

Ferroelectric material is ubiquitous. You can find it in any electrical devices such as handy phones, music players, computers, cars, microwave ovens and even in the magnetic hard disks. This is because a ferroelectric can store electric charges and has an enormously large dielectric permittivity. Thus, it can shrink down the size of an electric condenser in any electrical devices.

It is known that the ferroelectricity (that is, the name for the character of ferroelectric material) occurs from the coherent arrangement of electric dipoles in the material. The electric dipole had been believed to arise from the spontaneous displacement of an anion and a cation forming a polar symmetry. Such a situation is schematically modeled in Fig. 1, which provides a typical explanation of Perovskite ferroelectrics where the center of a negative charge (anion, oxygen ion) and the center of a positive charge (cation, B-site ion) do not coincide. The occurrence of the off-centering of the anion and cation is explained by the slowing down and freezing processes of an optical phonon.

Such motion of an anion and a cation is called "displacement." The concept of the displacement of ions had been a central paradigm on the origin of ferroelectricity in the last half century. An example is seen in the recent research achievement in SPring-8,

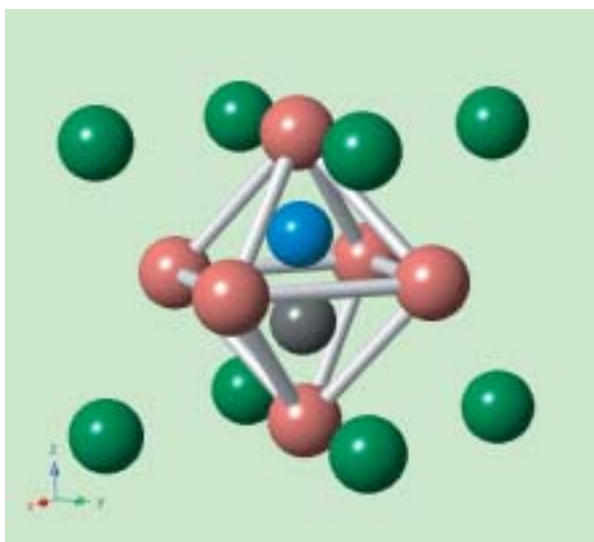


Fig. 1. Schematic drawing for origin of displacement-type ferroelectrics; for perovskite. The center of an anion (oxygen; red) and the position of a B site cation do not coincide. The B site cation has two stable positions drawn in blue and gray.

where the covalent bonding between the anion and cation has the central role in the formation of such displaced ions [1].

On one hand, we found a new ferroelectric mechanism in triangular mixed valence material RFe_2O_4 behaving as a ferroelectric [2]. A possible new ferroelectricity had suggested in the formation of the charge superstructure in this material. With the appearance of the electric polarization the superstructure appears as an order parameter. If this superstructure is confirmed to be the charge superstructure it would be a new ferroelectricity.

In order to clarify the origin of the superstructure, we performed a resonant X-ray scattering (RXS) experiment, which is the most sensitive technique for detecting the charge superstructure. The experiment on single-crystal LuFe_2O_4 was performed with a four-circle diffractometer at beamlines **BL02B1** and **BL22XU**. A crystal sample grown by the floating zone melting method was cut to orient the c -axis normal to the sample surface. The intensity of a superlattice spot ($n/3$ $n/3$ $m+0.5$) where n and m are integers was recorded as a function of the X-ray energy near the K -absorption edge of iron. The sample was cooled in a refrigerator down to 18 K, which is far below the ferroelectric transition temperature.

A typical result of the RXS experiment is shown in Fig. 2. In the spectrum, a maximum and a minimum at around 7.113 keV and 7.120 keV, respectively, and a background independent of X-ray energy were found. The maxima at 7.113 keV and 7.120 keV arise from the in-phase component of the anomalous atomic scattering factor of Fe^{2+} and Fe^{3+} , respectively. The corresponding K -absorption edges for both ions were confirmed by the X-ray absorption near-edge structure measurements for LuCoFeO_4 and LuFeGaO_4 , which are isostructural to RFe_2O_4 but contain only Fe^{3+} and Fe^{2+} , respectively.

This result clearly indicates that the structure factor of this superlattice point is contributed by the positive atomic scattering factor of Fe^{3+} and the negative factor of Fe^{2+} . Therefore, we can conclude that the structure factor at this Bragg point arises from the 'difference' in atomic scattering factor for Fe^{2+} and Fe^{3+} . This is the evidence for the formation of the long-range ordering of Fe^{2+} and Fe^{3+} with the 3×3 structure as shown in Fig. 3.

Materials Science: Structure

This structure is consistent with the proposed charge-ordering model for Fe^{2+} and Fe^{3+} in RFe_2O_4 [3,4], which had been derived from the consideration on the competitive Coulomb interaction between electrons on a triangular lattice. Interestingly, the charge structure allows the presence of a local electrical polarization, since the centers of Fe^{2+} (excess electron) and Fe^{3+} (electron deficiency) do not coincide in the cell of the superstructure. This indicates the ferroelectricity originating from the electron density modulation without a dipole of a cation and anion pair.

Therefore, we concluded that RFe_2O_4 is a novel ferroelectric material, reflecting the correlated nature of the electrons. This conclusion is consistent with the previously reported dielectric properties of this material. For example a large dielectric dispersion found in this material was explained with the electron fluctuation proceeding the ferroelectric domain boundary motion [5,6].

This ferroelectricity by the electron correlation offers great potential when designing future ferroelectric devices to be coupled or controlled with the degrees of freedom of the electron: charge, spin and orbital. Such properties may lead to a new multiferroic material. Also, the low activation energy of electron motion of this material, which suggests less coupling between polarization switching and the lattice

distortion, may enable the development of a fatigue-free solid charge capacitor. These possibilities of new ferroelectric materials will be examined in future studies.

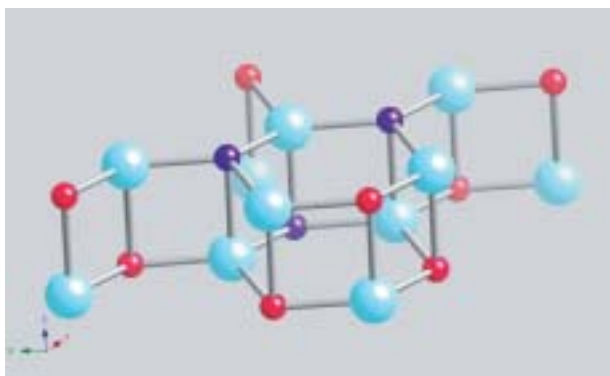


Fig. 3. Charge-ordering model of iron double layer in charge superstructure for RFe_2O_4 . Fe^{2+} (negative charge) and Fe^{3+} (positive charge) are represented with red and light blue balls. The negative ions (oxygen atoms, light blue balls) do not have the role in the formation of the polarization in this model.

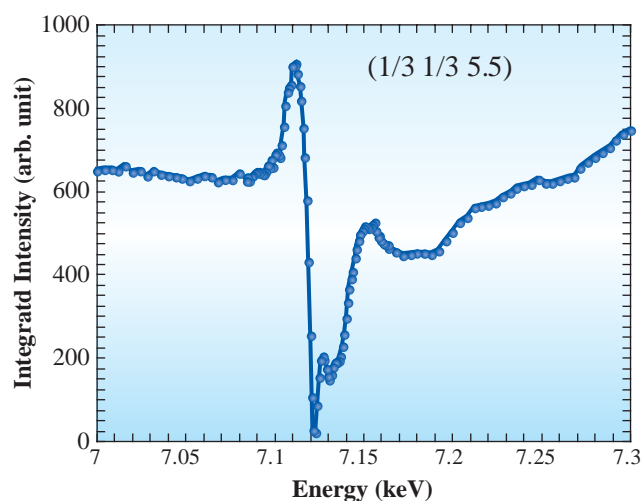


Fig. 2. X-ray energy dependence of superlattice reflection (1/3, 1/3, 5.5) for LuFe_2O_4 . The peak and minimum arise from the in-phase component of the anomalous atomic scattering factor for Fe^{2+} and Fe^{3+} , respectively.

Naoshi Ikeda[†]

SPring-8 / JASRI

E-mail: ikedan@science.okayama-u.ac.jp

[†]Present address: Department of Physics,
Okayama University

References

- [1] Y. Kuroiwa *et al.*: Phys. Rev. Lett. **87** (2001) 217601.
- [2] N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe and H. Kitô: Nature **436** (2005) 1136.
- [3] Y. Yamada *et al.*: J. Phys. Soc. Jpn. **66**(1997) 3733.
- [4] K. Siratori *et al.*: Proc. 6th Int. Conf. on Ferrites Tokyo and Kyoto, The Japan Society of Powder and Powder Metallurgy (1992) p.703 .
- [5] N. Ikeda *et al.*: J. Phys. Soc. Jpn. **63** (1994) 4556.
- [6] N. Ikeda: J. Phys. Soc. Jpn. **69** (2000) 1526.