

Investigation of Dy(Mn_{1-x}Fe_x)O₃ Multiferroic Perovskites

Fou-Kuo Chiang (蔣復國), Fei-Ting Huang (黃妃婷), and Ming-Wen Chu (朱明文)

Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan

Multiferroics are materials exhibiting magnetic and electric orders in the same phase. Such materials recently draw significant attention due to the possible manipulation of magnetic (electric) orders by electric (magnetic) fields, namely a *magnetoelectric effect*. Integrating the materials into modern memory storage media would enable a magnetic (electric) control of the electric (magnetic) properties, adding an extra degree of freedom in the performance and design of the devices. Nevertheless, few materials were reported to possess the coexistence of magnetic and electric orders and only some of them exhibit an intimate magnetoelectric coupling between both orders. Among all the reported multiferroics, DyMnO₃ perovskite (see Figure 1) could be considered as the most intriguing material due to its giant magnetoelectric effect.

DyMnO₃ with a centrosymmetric space group (orthorhombic, *Pbnm*) at RT exhibits three phase transition temperatures at ~42K, ~20K, and ~7K for the sinusoidal antiferromagnetic Mn³⁺ (a Jahn-Teller ion, $t_{2g}^3 e_g^1$), incommensurate-to-commensurate (lock-in), and antiferromagnetic Dy³⁺ orderings, respectively. The sinusoidal ordering along *b*-axis with a wave vector $\mathbf{q}_{spin} = (0, k_{spin}, 1)$, Fig. 1b, results from a *spin frustration* relevant to the combined effects of a GdFeO₃-type lattice distortion and a staggered orbital ordering for the Mn³⁺ moments. Previous study has indicated that this Mn³⁺ ordering is accompanied with a magnetoelastically induced lattice modulation along *c*-axis, showing a wavenumber $\mathbf{q}_{lattice} = (0, k_{lattice}, 1)$ with $k_{lattice} \approx 2k_{spin}$ (Fig. 1c). At $T < T_{lock-in}$, the commensurate phase shows the nearly constant $k_{lattice}$ value of ~0.78 with the onset of a long-range ferroelectric ordering along *c*-axis.

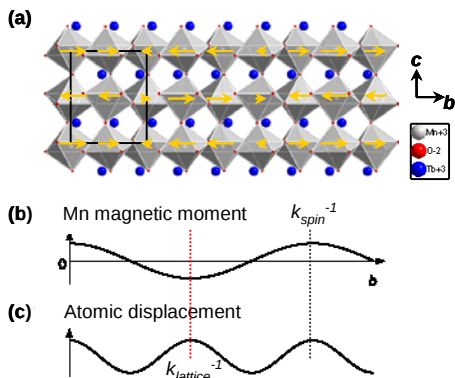


Figure 1. (a) The room-temperature crystal structure of orthorhombic DyMnO₃. The black rectangle indicates the unit cell and the yellow arrows denote the magnetic ordering of Mn³⁺ moments below $T_N \approx \sim 42K$. (b) The sinusoidal description of the antiferromagnetic ordering of Mn³⁺ spins indicated in (a). (c) The accompanied atomic displacements along *c*-axis.

T. Kimura *et al.*, *Nature* **426**, 55 (2003).

From the above, it is exciting to learn that the

centrosymmetry of the material can be fluctuated by the magnetic ordering of Mn³⁺, thus leading to the ferroelectricity, and the Jahn-Teller distortion of Mn³⁺ should play a role in such a conjugated phase transition. In this work, we intend to investigate the role of Jahn-Teller distortion (also the related orbital ordering) in details by substituting Fe³⁺ (Jahn-Teller distortion free, $t_{2g}^3 e_g^2$) for Mn³⁺ in the parent phase, DyMnO₃. The phase-pure powder samples of the Dy(Mn_{1-x}Fe_x)O₃ solid solution, $x = 0, 0.25, 0.5, 0.75$, and 1, were prepared by soft-chemistry method, and the powder X-ray diffraction data were collected using synchrotron radiation at NSRRC BL01C2 SWLS.

Figure 2 shows the variation of lattice parameters of Dy(Mn_{1-x}Fe_x)O₃ as a function of Fe³⁺ concentration. Intriguingly, the *a*-axis remains little affected by the Fe³⁺ substitution, while *b*- and *c*-axes are sensitive to that. This latter feature further shows certain correlation with the fact that the spin (magnetic) and the coupled lattice modulations in DyMnO₃ are along *b*- and *c*-axes, respectively. Moreover, *b*- and *c*-axes (see Fig. 2) do not exhibit a monotonic decrease and increase, respectively, with x going from null to unity. Instead, two abrupt “jumps” were observed at $x = 0.25$ and 0.75 . This characteristic in the lattice degree of freedom suggests that the substitution of Fe³⁺ has impacted the orbital ordering of Mn³⁺ in the parent phase DyMnO₃. The associated B-O-B bond angle in the materials should be accordingly modified, further influencing the magnetic exchange characteristics and the resultant magnetic, electric properties. Further determination of the bond lengths and bond angles in Dy(Mn_{1-x}Fe_x)O₃ is currently under way, and X-ray diffraction experiments at low temperatures have been scheduled to beam time 2006-01.

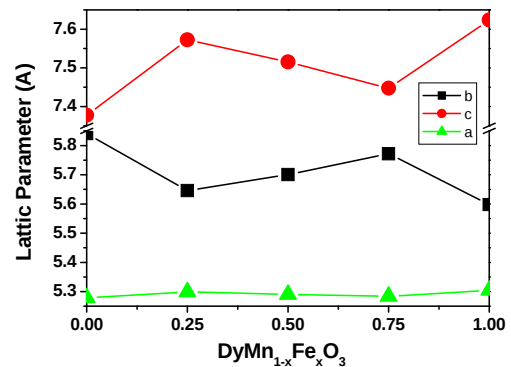


Figure 2. Lattice parameters of the Dy(Mn_{1-x}Fe_x)O₃ solid solution measured at room temperature.