Domain Formation and Ground State of Spin and Charge Order for RFe2O4 (R=Yb and Lu)

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The compound family RFe2O4 (R=Dy - Lu, and Y) has attracted much attention due to the possible multiferroic behavior arising from charge ordering. The crystals of these materials belong to the rhombohedral system. The Fe ions are arranged to form the hexagonal double layers and stack in the sequence of (AB), (CA), (BC),... along the rhombohedral unique axis. The average valence of the Fe ions is expected to be Fe+2.5 in these materials and hence a mixed valence state of Fe2+ and Fe3+ ions occupying the equivalent Fe sites on the hexagonal plane with equal probability is expected. Especially LuFe2O4 attracted a lot of attention, because experimental evidence was reported for a ferroelectricity arising from electron correlations in this frustrated triangular mixed valence oxide[1]. It also shows very complex charge and magnetic correlations with finite correlation lengths in zero and applied magnetic field[2]. Despite the intensive investigations on charge and magnetic ordering using both synchrotron x-ray and neutrons, the understanding of the physics in LuFe2O4 is far from complete.

Recently, we succeeded in making a fine stoichiometric crystal of YbFe2O4 and LuFe2O4 with the Floating Zone melting method in which the amount of the iron vacancies was controlled[3]. We found that a single crystal having less iron vacancy has longer spin coherence length and do not show the low temperature spin transition, as called TLT transition. This fact indicates that the unsettled discussion about the spin and charge structure on this material may arise from such iron stoichiometry effect of the crystal. We call such a sample having less iron vacancy as the stoichiometric sample.

We made three dimensional reciprocal space observation for YbFe2O4 using the wide-angle neutron diffraction instrument WOMBAT equipped with two dimensional neutron detector installed at OPAL neutron facility in ANSTO, Sydney, Australia. Also the magnetic component of the signal was examined with 3He spin polarizer and analyzer. Through the experiment, we found typical patterns of charge order signal and its modulations. In figure 1, we show three kind of super lattice points and its modulation in reciprocal space. These signals are found on (1/3 1/3 L) where L is integer and half integer, and (0 0 1.5+3n) where n is integer.

We applied the monoclinic charge order super lattice cell and its possible domain formation to interpret the modulated structure of the super lattices. Then all super lattice signals distributed in reciprocal space are successfully explained. This is the first result in explaining the extinction rule of super lattices of RFe2O4.

It was found that the super lattice signals of (1/3 1/3 L) develops below 390K, which indicates the three dimensional charge ordering transition (3DCO) at this temperature, that is slightly higher than the previous report of T3DCO of non-stoichiometric material.

Below 300K, a characteristic magnetic diffuse scattering appears along (1/3 1/3 L), indicating a short range spin correlation long c-axis, as shown in figure 2. Also the signal of (0 0 m) where m is half integer develops below 300K. Non-magnetic origin of (0 0 m) was confirmed with polarizer analysis. This is an indication of some kind of coupling between lattice modulation and short range spin correlation below 300K. So we expect a possible magneto-

lattice coupled phenomenon in this temperature range.

We also made the two-dimensional reciprocal space observation of the stoichiometric LuFe2O4. The experiment was performed using wide-angle neutron diffraction instrument WAND equipped with one dimensional neutron detector installed at HFIR neutron facility in Oakridge National Laboratory, Tennessee, USA.

The (h h l) plane mapping at 125K for the stoichiometric LuFe2O4 crystal of less iron vacancy is shown in figure 3. Although the diffuse magnetic scattering along (1/3 1/3 L) line in this temperature range has been previously reported in iron deficient non-stoichiometric LuFe2O4, our data shows only the super lattice spots on (1/3 1/3 L) without the diffuse component along L. With the observation of the temperature variation of macroscopic magnetization of this sample, we concluded the vanishing of low temperature spin transition TLT in stoichiometric LuFe2O4. The 3D charge ordering temperature was confirmed at 360K, which is also slightly higher than previous report of non-stoichiometric LuFe2O4.

As the WAND data do not have the three dimensional information in reciprocal space, we have not yet obtained the detailed structure of super lattice and its modulation in LuFe2O4. But the observed anisotropic structures of the super lattice spots may be accounted for by the 2-D projection of the diffraction patterns similar to fig. 1.

The essential conclusions were obtained as follows, 1) the stoichiometric RFe2O4 do not show the low temperature spin transition TLT. Previous report of TLT might arise from a vacancy and its pinned effect for the short range spin ordered region. 2) The three dimensional charge ordering transition of stoichiometric RFe2O4 is slightly higher than 360K. 3) Below 300K, we can expect an unknown lattice and spin coupled phenomenon.

References

[1] N. Ikeda, et al., Nature 436 (2005) 1136.
[2] J. de Groot, et al.,?Phys. Rev. Lett., 108?(2012) 037206.
[3] K. Fujiwara, et al., Trans. Mat. Res. Soc. Japan 41[1] (2016) 139-142.

captions

Figure 1 Three kind of super lattice points and its modulation of stoichiometric YbFe2O4 found 3D reciprocal space. Spots are projected on three planes. I-type and X-type modulations are found on (1/3 1/3 L) position, where L is integer or half integer. -type one is found on (0 0 1.5+3n) position, where n is integer.

Figure 2 Magnetic diffuse scattering along (1/3 1/3 L) of stoichiometric YbFe2O4 appears below 300K.

Figure 3 The (h h l) plane mapping at 125K of stoichiometric LuFe2O4 crystal. No diffuse scattering was found along (1/3 1/3 L) line, indicating no conflicting interaction between ferro- and anti-ferro ordering of spins.

Fig. 1

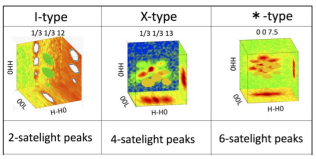

Fig. 2

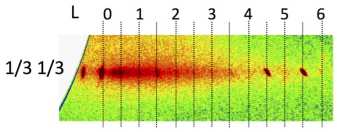

Fig. 3

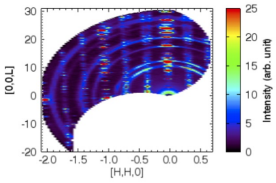

Fig. 1. Captions are given in text.