Oxygen excess, order/disorder and structural mechanisms in the multiferroïc $LuFe_2O_{4\pm\delta}$

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The RFe_2O_4 (R= Y, and rare earths from Dy to Lu) compounds crystallize in a structure built up on the alternation of one $[LuO_2]_\infty$ layer and one $[Fe_2O_4]_\infty$ bilayer (fig.1a), where Fe^{2+} and Fe^{3+} cations are ordered. Multiferroic materials, where ferroelectricity, antiferromagnetism and ferroelasticity are associated, have been extensively studied because of considerable potential applications. The Fe^{2+}/Fe^{3+} charge ordering adopts different structural modulations, strongly dependent on the synthesis process and temperature. The role of the oxygen deficiency has been mainly investigated in these ferrites, showing a direct influence on the CO. Recently [1], we showed that a new type of ordering takes place in $LuFe_2O_4$, involving an incommensurate modulation, which is till observed at 700K, whereas the temperature of destruction of the CO is close to 330K. The structural, nanostructural and magnetic structures have been determined, as well as the magneto-transport properties, the Mossbauer spectroscopy and thermal analyses [2].

A monoclinic distortion of the structure, with regard to the R-3m one, commonly used, is observed and the structure refined in the monoclinic *C*2/*m* space group (a_M = 5.9563(1) Å, b_M = 3.4372(1) Å, c_M = 8.6431(1) Å, b = 103.243(1) °). A new type of incommensurate order has been observed which is characterized by a vector $\vec{q}_1 = \alpha_1 \vec{a}^*_M + \gamma_1 \vec{c}^*_M$, with $\alpha_1 \cong 0.54\pm0.03$ and $\gamma_1 \cong 0.14\pm0.02$, in addition with the three other modulations previously reported, distinctive of the charge ordering. The $[010]_M$ ED pattern, Fig. 1b, is indexed by using *hklm* indices (those with $m \neq 0$ are the satellites). In situ heating ED observations from 300 to 773K confirm that the satellites associated with the vector $\vec{q}_1$ evolve and vanish completely only at a temperature significantly higher than the charge order temperature and restored by cooling down to RT. In the course of this evolution, both α_1 and γ_1 evolve but one direction remains unchanged: the satellites are aligned along the $20\bar{3}^*$ direction.

The enlarged scanning electron microcopy images evidence the formation of steps, of the order of the hundred nanometers, associated to the growth mechanism (Fig 2a). The TEM images show that the actual height of the steps is a few nanometers.

The behavior of the oxygen dependent modulation I is highly different from that associated to the CO, in the image contrast and intensity as in the way it evolves with the synthesis process. It is established in the form of large modulated areas, occurring in a non-ordered C2/m matrix whereas the CO domains are pancake-like shaped, a few ten nanometers wide, as previously observed [3-4].

The incommensurate modulation has a displacive character with primary a transverse displacive modulation wave for the Lu cations, as revealed by the HAADF-STEM images (Fig.2b) and synchrotron data refinements. The HREM images evidence the local stabilization of a commensurate super-cell, corresponding to an approximant $a_{app} \cong 2a_M \cong 12$Å, $c_{app} = 1/3c_R \sin^{-1}129 \cong 10$ Å and $\beta_{app} \cong 129$.

Different origins of twinning mechanisms have been observed; the domains exhibit an average width of the order of a few tens nanometers but do not modify the integrity of the $LuFe_2O_4$ unit.

Possible shifting of one $[LuO]_\infty$ layer with regard to the adjacent $[Fe_2O_4]_\infty$ bi-layer have been observed, which suggests that such a mechanism can be easily engaged under specific conditions.

Analyses of vacuum-annealed samples converge towards the hypothesis of new ordering mechanisms, associated with a tiny oxygen deviation from the O_4 stoichiometry .

References

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Modulation	$\vec{S}=h\vec{a}^*+k\vec{b}^*+l\vec{c}^*+m\vec{q}$	Components values	origin
I	$\vec{q}_1 = \alpha_1 \vec{a}^* + \gamma_1 \vec{c}^*$.	Commensurate: α_1 = 4/7 and γ_1 = 1/7 and α_1 = 7/13 and γ_1 = 0.128 to incommensurate (0.52 0 0.124)	Oxygen excess
II	$\vec{q}_2 = \beta_2 \vec{b}^*_M + \gamma_2 \vec{c}^*_M$,	Commensurate : β_2 = 2/3 and γ_2 = 1/6 to incommensurate β_2 = 2/3-ε and γ_2 = 1/6	CO
III	$\vec{q}_3 = \beta_3 \vec{b}^*_M + \gamma_3 \vec{c}^*_M$	Commensurate :β_3 = 2/3 and γ_3 = 1/2	CO
IV	$\vec{q}_T = \beta_3 \vec{b}^*_M + \gamma_3 \vec{c}^*_M$	Commensurate :β_T = 2/3 and γ_3 = 1	CO

Table 1: *characteristic of commensurate and incommensurate modulations observed.*

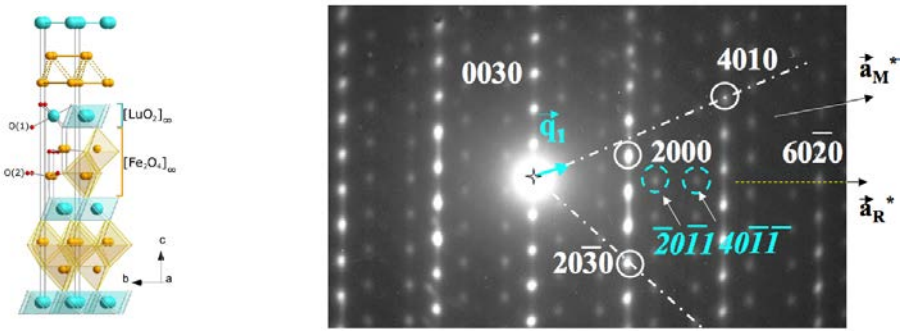

Figure 1. *a) $LuFe_2O_4$ layered structure and b) $[010]_M$ ED pattern, illustrating the modulation ($\vec{q}_1 = \alpha_1 \vec{a}^* + \gamma_1 \vec{c}^*$) induced by the introduction of oxygen excess in the matrix (satellites are indexed in blue)*

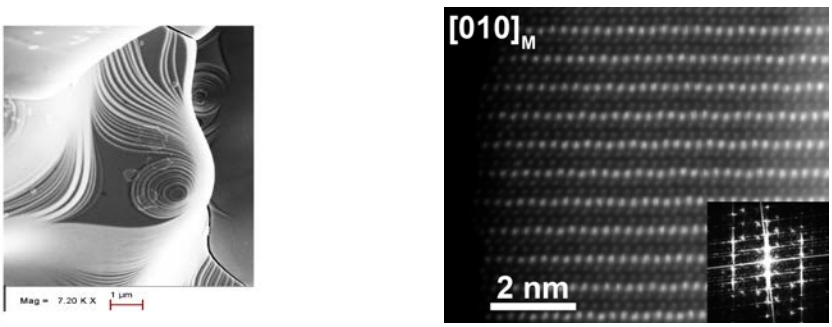

Figure 2. a) *SEM image showing the formation of steps, associated to the growth mechanism and b) $[100]_M$ HAADF image associated to the $\vec{q}_1$ modulation.*