Experimental report

14/02/2020

Proposal:	**5-31-2615**	**Council:**	4/2018
Title:	Charge redistribution, orbital moment collapse and new high-temperature magnetic phase in magnetoelectric epsilon-(Fe,Cr)2O3 polymorph		
Research area:	Materials		

This proposal is a new proposal

Main proposer: **Jose Luis GARCIA MUNOZ**

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Samples: epsilon-Fe2O3
epsilon-Fe2-xCrxO3 (x=0.02, 0.06, 0.10, 0.20, 0.40)
(x[Cr]=0.02, 0.06, 0.10, 0.20, 0.40)

Instrument	Requested days	Allocated days	From	To
D20	3	3	05/07/2019	08/07/2019

Abstract:

Epsilon-Fe2O3 displays remarkable properties such as huge coercivity, magnetoelectric coupling, multiferroicity at room temperature in film form and rich magnetic and magnetostructural properties that are still poorly studied. It is one of the less studied ferrimagnetic iron oxides due to its difficult preparation. It presents a complex non-centrosymmetric Pna21 frustrated structure isomorphous to the multiferroic GaFeO3. We have recently identified up to five different magnetic transitions in our nanograin pure and doped with Cr samples (between 70 and 870K) and, associated to them, magnetoelectric, structural, magnetoelastic anomalies, abrupt orbital moment quenching, super-hard ferrimagnetism, charge-redistributions not yet well described, etc. This experiment aims to monitor and describe subtle structural changes and magnetic changes that activate/desactivate the spin-orbit coupling in selected sites of the structure at particular temperatures. The substitution by Cr produces appealing changes which strongly depend on the considered magnetic phase.

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Technical issues during the experiment.-

The experiment 5-31-2615 was scheduled for 5-8/July/2019. The plan included using the cryofurnace and the furnace to reach 550ºC. Mainly, two unexpected technical issues prevented completing the program of measurements. FIRST, after a long period without using that furnace on d20, the Local Contacts realized that there was a configuration (or software) problem concerning the DRIVER for the furnace that required external help. The driver problems affecting the communication between NOMAD and the furnace took a long time in hours to be solved. SECOND, another unexpected important technical issue during the experiment was a problem with the Beam Shutter Control System at D20. We had to interrupt the experiment between the 6th and 7th of July due to a technical failure of the Beam Shutter Control System allowing the access to d20 area. Again, specialized external help was required during the night. When closing the beam to access the instrument, a failure of the Beam Shutter Control kept the gate locked for hours after closing the beam, although the light signal was indicating that the beam was off. Further details about the need of the additional time to complete the experiment can be found below.

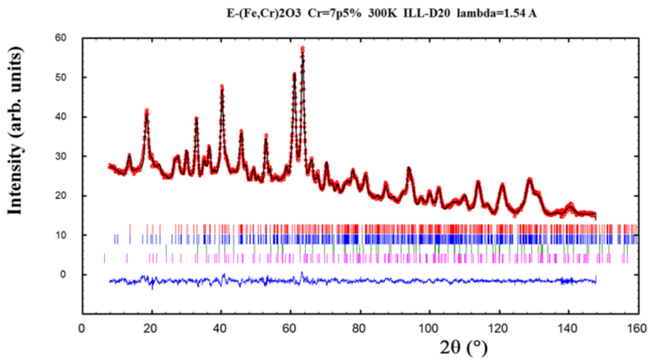

Fig. 1. *Structural and magnetic refinement at RT for the nanopowder of the epsilon polymorph with composition* ε-$(Fe_{1-x}Cr_x)_2O_3$ *x=7.5% . A residual impurity of the alpha-*Fe_2O_3 *phase (≈1.4%) is included. This refinement confirms a selective distribution of Cr ions among the four Fe sites in the* $Pna2_1$ *structure of the epsilon phase.*

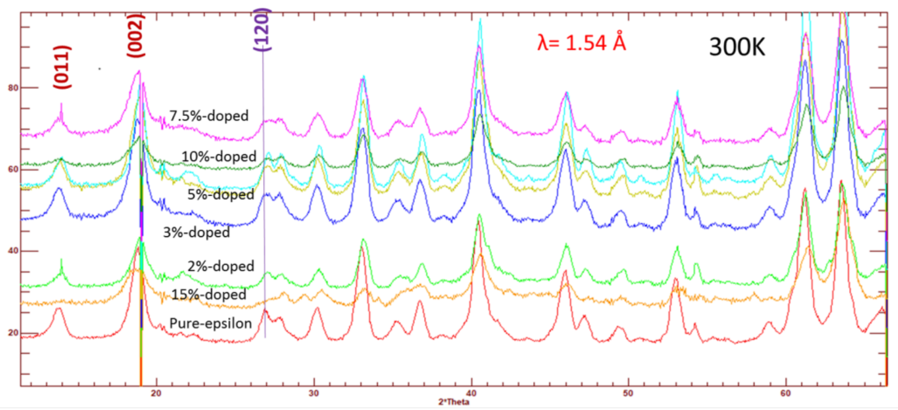

Fig. 2. *Comparison of neutron patterns collected at 300K for* $(Fe_{1-x}Cr_x)_2O_3$ samples with compositions x=0, 2%, 3%, 5%, 7.5%, 10% and 15%.

*As outlined in the proposal, NPD measurements were performed on the D20 diffractometer in the temperature range between 10K (using cryofurnace) and up to 923K (using furnace).

*From D20 data at RT we have confirmed that the *Pna2₁* structure of ε-Fe_2O_3 is very robust against the substitution of Fe by Cr. So, even the sample with highest doping [$(Fe_{1-x}Cr_x)_2O_3$ x= 25% Cr] has been satisfactorily refined at RT against the *$Pna2_1$* symmetry of the epsilon-phase.

* The main contraction in the unit cell dimensions (although small) is found along the *c*-axis, in contrast to the evolution of *a*, *b* parameters, for which changes increasing x[Cr] are tiny.

* Rietveld refinements of the neutron diffraction patterns for the compositions measured at RT have confirmed that the distribution of Cr3+ ions is very selective respect to the four possible TM sites. We have found that Cr preferably settles in one of the three octahedra, and two out of the four metal sites are occupied only by Fe atoms in all the compositions investigated. Detailed results will be published elsewhere. The distribution of Cr offers key information to investigate the Fe site responsible for the remarkable spin-lattice (spin-orbit) coupling at the origin of the giant responses and magnetic anisotropy of this system.

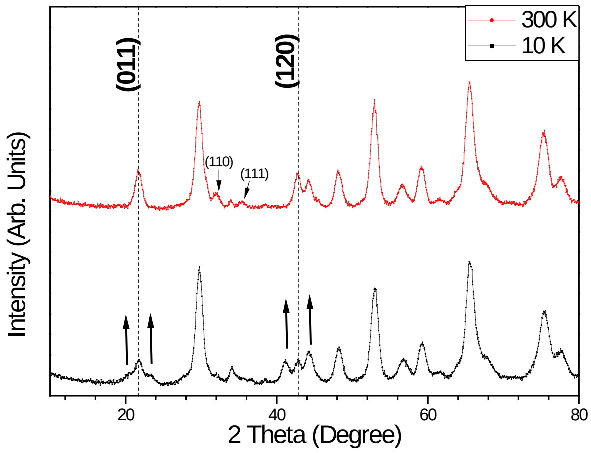

Fig. 3. Neutron powder diffraction patterns recorded at 10 and 300K for epsilon type NPs

* The cryofurnace and the furnace was used. The temperature evolution across the successive transitions between 10K-540K was fully/satisfactorily measured before installing the furnace only for the samples with 0, 2, 7.5 and 20% Cr doping. Two pairs of satellites appear at both sides of the (011) and (120) reflections of the ferrimagnetic phases, as indicated by upward arrows in Fig. 3. They correspond to the low temperature incommensurate magnetic transition. From the temperature dependent intensity profile (Fig. 4), the FM2 and ICM phases can be easily distinguished, and the incommensurability is determined. Intensive analysis of the low temperature neutron diffraction data is ongoing to fully resolve the nature of the ICM magnetic phase and the evolution with Cr.

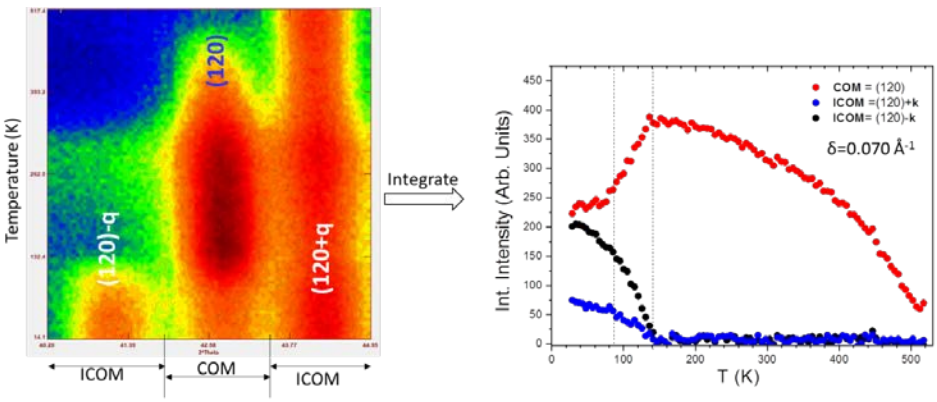

Fig. 4. Ferrimagnetic and incommensurate magnetic transitions in a low-doped ε-(Fe1-xCrx)2O3 sample (λ= 2.41 Å). (right) Evolution of magnetic integrated intensities.

* The large structural anomalies (associated to charge redistribution) reported at the ICM-FM2 transition for the pure compound (Tseng PRB 79, 094404 (2009)) have not been detected in our samples doped with Cr.

* The onset of the ICM magnetic phase seems unaffected by Cr-doping up to 7.5 at.%. In contrast to the incommensurability of the propagation vector that continuously decreases with increasing Cr content (Fig. 5).

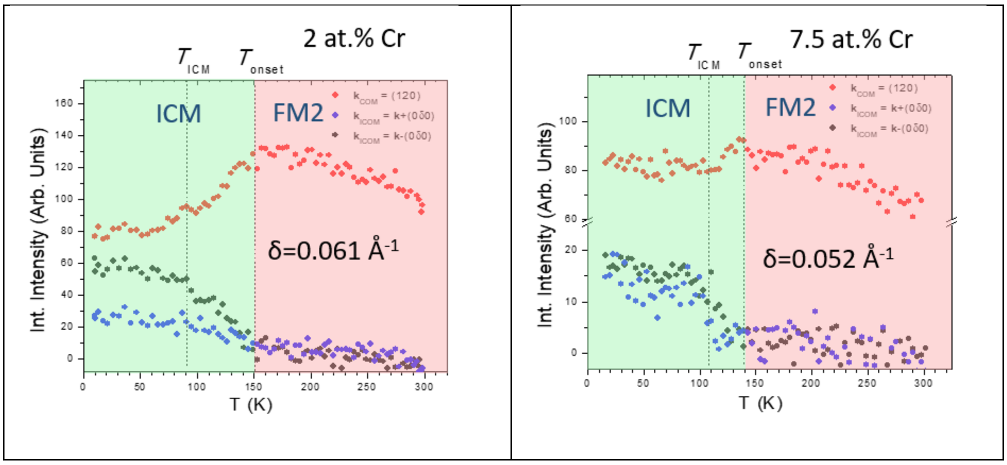

Fig. 5. Integrated intensity for (120) reflection and its satellites, showing the ICM and FM2 magnetic phases for 2 and 7.5 at.% doped samples.

* A structural transition from epsilon- to alpha-Fe2O3 phase at around 850K was observed favored by partial vacuum (~10^{-4} mbar) and high temperature conditions (Figure 5). The magnetoelastic effects and magnetic changes at the FM2/FM1 soft-hard magnetic transition were easily observed and it will be described from recorded data.

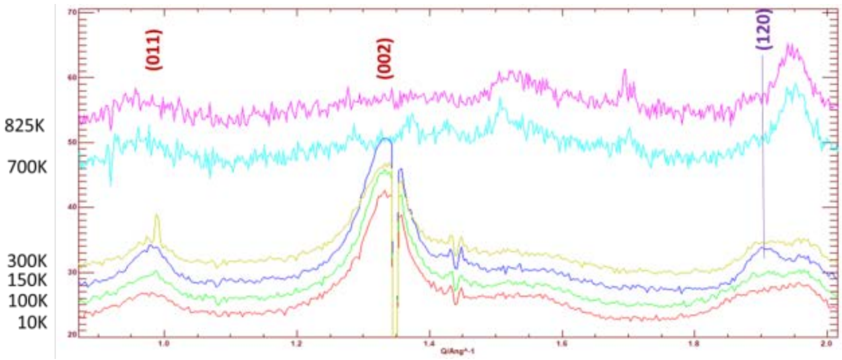

Fig. 6. Evolution at characteristic temperatures of some structural and magnetic peaks collected on epsilon-(Fe1-xCrx)2O3 x= 7.5% Cr-doped specimen.

*** Full structural and magnetic analysis of the neutron data collected in this experiment is in progress. A first publication is now in preparation but half of the planned compositions couldn't be studied at low temperatures due to the commented technical issues during the experiment. Additional time is required to complete the set of measurements and compositions, especially for high dopings.

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