Despite being known since 1934, ε-Fe_2O_3 has been much less studied than other iron (III) oxides such as the α and γ polymorphs. Its crystalline structure presents an orthorhombic cell in the *Pna2₁* space group which is isomorphous to $GaFeO_3$ and $AlFeO_3$ and presents four different Fe sites, three in octahedral and one in tetrahedral environments (E. Tronc, C. Chanéac and J. P. Jolivet, J. Solid State Chem. **139**, 93 (1998)). It has been recently shown that this material exhibits a huge room-temperature coercivity of about 20 kOe (J. Jin *et al.* Adv. Mater. **16**, 48 (2004)) and a magnetic transition at low temperature (M. Kurmoo *et al.*, Chem Mater. **17**, 1106 (2005) & M. Gich *et al.* J. Appl. Phys. **98**, 044307 (2005)). However this two works have interpreted it quite differently.On the one hand, according to Kurmoo *et al.*, all Fe^{3+} cations in ε-Fe_2O_3 carry the same magnetic moment and its room-temperature magnetic structure is that of a canted antiferromagnet which, on cooling to below 150 K would undergo a Morin-like transition resulting in a second canted antiferromagnetic phase with smaller canting angles. In contrast, we have proposed that at room-temperature, ε-Fe_2O_3 is a collinear ferrimagnet with the net magnetization arising from the lower magnetic moment of the Fe^{3+} in tetrahedral coordination and we have related the anomalies in the magnetic properties at low temperatures to the appearance of an incommensurate magnetic order, revealed by preliminary neutron diffraction experiments. The aim of the diffraction experiment was to elucidate the high temperature (HT) and low temperature (LT) structures of ε-Fe_2O_3 and to shed some light into the nature of this transition. The data collected in ID31 have been joint refined with neutron powder diffraction patterns measured at ILL (D20) and complemented with Mössbauer spectroscopy and magnetic and heat capacity measurements. The comparison of the experimental and calculated data obtained with the joint Rietveld refinement of the SXRD patterns at 200 K (HT structure) and 10 K (LT structure) are presented in Fig. 1.

It has been found that the HT magnetic structure of ε–Fe_2O_3 is that of a collinear ferrimagnetic material with the Fe^{3+} magnetic moment antiferromagnetically coupled along *a* (see Fig. 2). The Fe^{3+} magnetic moments in the green and cyan distorted octahedral positions mutually cancel and the net magnetisation of this phase results from the uncompensated magnetic moment of the atoms in tetrahedral (blue) and regular octahedral (yelow) positions. The LT magnetic structure is incommensurate (see the appearance of satellites at Q ~1 $Å^{-1}$) which presents a propagation vector $\boldsymbol{k}$=(0,

0.1047, 0) and the best fit has been obtained for a sine modulated structure with all the magnetic moments laying in the *xy* plane. The fitting was also attempted considering an helical structure but completely failed. However, the small crystalline size of the ε-Fe_2O_3 nanoparticles (below 20 nm), causes a strong peak overlapping thus reducing the number of effective reflections which make difficult to obtain reliable model for the LT structure since according to the symmetry analysis the 4 Fe^{3+} sites are split into two orbits and the magnetic phases have to be taken into account in a sine-modulated structure. one has to take into account. Moreover the Mössbauer spectra at 10 K show sextets with narrow linewidth. This is not what one would expect if the LT magnetic structure of ε-Fe_2O_3 is supposed to be sine-modulated with a periodicity of about 10 unit cells. In this case, since for the *Pna2₁* space group there is only one Wyckoff position of fourfold multiplicity, an average of 40 atoms for every Fe site with magnetic moments ranging from zero to a maximum value are involved in one period of the amplitude-modulated structure which would yield a broad hyperfine field distribution. Therefore, the only magnetic structure that can make compatible both the Mössbauer and the diffraction data is a square-wave modulated structure.

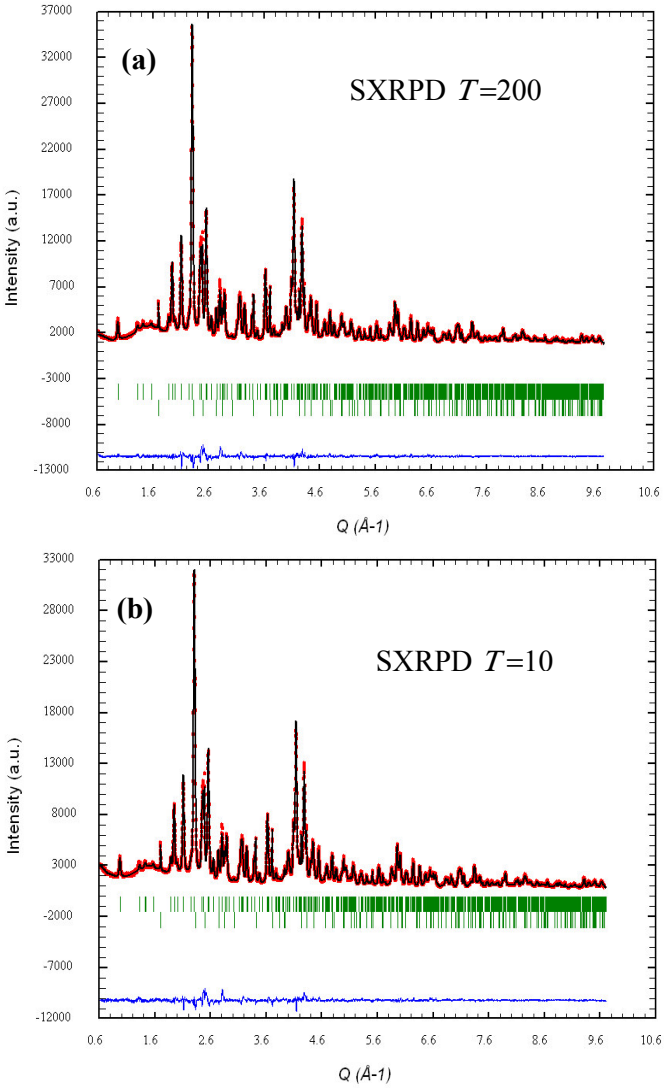

Figure 1:

(a) Refinement of SXRPD data at 200 K: R_B=2.26 %, R_{wp} = 3.59 %, R_{exp} = 1.94 %, χ^2=3.43

(b) Refinement of SXRPD data at 10 K: R_B=2.98 %, R_{wp} = 7.33 %, R_{exp} = 3.66 %, χ^2=4.015

Thus, in order to determine the magnetic structure it would be necessary to identify the higher order reflections and determine the new propagation vectors but this cannot be carried out due to the peak overlapping and the low intensity of the harmonic reflections. However, on the grounds of the above discussion one may consider the structure represented in Fig. 3 to be a very simplified model of the LT magnetic cell.

A full paper describing in more detail this results has been published in Chemistry of Materials **18** (2006) 3889-97

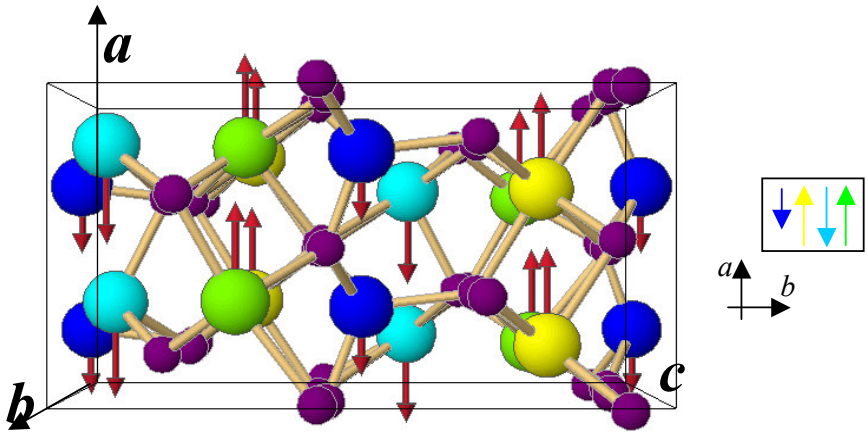

Figure 2: Magnetic structure of the HT phase of ε-Fe_2O_3. The couplings are between the spins of the different sites are schematically represented in the figure.

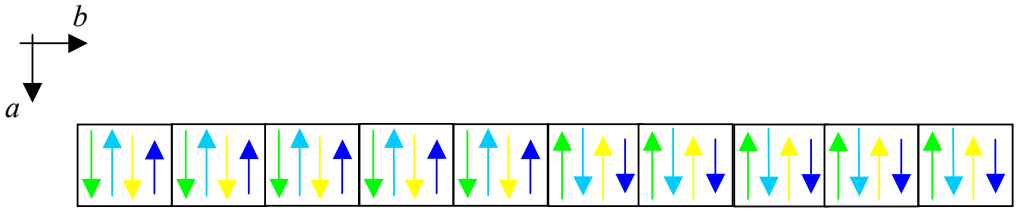

Figure 3: Schematic and simplified representation of the square-wave magnetic structure of the LT phase of ε-Fe_2O_3.