ESRF	**Experiment title: Variation of the cationic distribution during oxidation of magnetic ferrites having the spine1 structure : use of the difference between the anomalous scattering at Fe^{2+} and Fe^{3+} edges.**	**Experiment number:** CH273
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Report: The optimization magnetic properties of ferrites required the knowledge of cation distribution between octahedral and tetrahedral sites of spine1 structure. This distribution has been solved using anomalous powder diffraction by in-situ experiments in a rather simple case in which only the Fe cations distribution is concerned.. The aim of this report is to describe preliminary results obtained in the case of $Fe_{3-x}Ti_xO_4$ which is quite simple as there is only one cation with various valence (Fe^{2+} and Fe^{3+}), the other being fixed Ti^{4+} and only located in the octahedral sites. The structural refinements were achieved using the Rietveld method taking into account the anomalous effect in order to distinguish the different oxidation states of the iron cations. The chemical shift of the adsorption edge between oxidation states is very low, typically a few eV and if the EXAFS oscillations strongly depend on the neighbouring of the selected atom the edge position is quite stable for various oxidation states. This shift can then be used to characterize the occupancy of sites by the various states of an element. The effective values of the anomalous dispersion term strongly depend on the effective resolution of the experimental setting. We have recorded on the diffractometer the absorption edges of Fe simple oxides Fe0 and Fe_2O_3; these oxides well reproduce the oxidation states but induce some small deviation at high energy as the EXAFS oscillations are not the identical that in our sample. The shift between Fe^{2+} and Fe^{3+} appears to be only 6 eV.

Anomalous experiments have been carried out on the D2AM-CRG beamline at ESRF using the XRK900 reaction chamber (RT up to 900°C) and strictly controlling gas flows from N_2+0_2, N_2 or H_2. For each state 3 data sets have been collected on the 7-circles diffractometer equiped with a Si(111) analysor. For each state the data sets have been processed by the rietveld method using XNDl 10 program [2] which allows to refine simultaneously all sets. In the last experiments all performed at room temperature, where a nanometric Ti ferrite with a grain size of 40nm has been studied, some asymmetry around the low angles has be observed in the case of the stoichiometric compound. Since such an asymmetry disappears when the Fe cations are oxidized, it can not be related to an instrumental aberration, but to a gradient of the Fe^{2+}/Fe^{3+} ratio from the surface to the bulk in each particle.. Results are presented in table 1. To ensure they are consistent, we are tested other cation distribution, there is always one data set which looks worst and the overall goodness of fit increases. Previous results obtained with Ti ferrite varying the Fe^{2+}/Fe^{3+} ratio show that the anomalous powder diffraction allows the cation ordering to be obtained with good accuracy in such compounds [2,3,4]. Indeed, the values obtained from Rietveid refinement using this technique are in good agreement with additional thermogravimetric experiments, allowing the Fe^{2+}/Fe^{3+} ratio to be measured (Table 1). This comparison enables the method to be validated for the in situ characterization of the cation distribution of Ti ferrite with different Fe^{2+}/Fe^{3+} ratio obtained from different oxidoreduction annealings.

	Reduced state	oxided state	totally oxided state
$Fe^{3+}_{Tetrahedral}$	0.97±0.02	0.99±0.01	0.95±0.01
$\square_{Tetrahedral}$	0.03±0.02	0.01±0.01	0.05±0.01
$Fe^{2+}_{Octahedral}$	1.08±0.07	0.40±0.05	0
$Fe^{3+}_{Octahedral}$	0.65±0.07	1.19±0.05	B1 : 1.31±0.01 B2 : 0.12±0.01
$Ti^{4+}_{Octahedral}$	0.25	0.23	B1 : 0.18±0.01 B2 : 0.04±0.01
$\square_{Octahedral}$	0.02±0.07	0.18±0.05	B1 : 0.01±0.01 B2: 0.34±0.01
O^{2-}	4	4	4
λ1(7.105Kev) Gof	1.64	1.80	1.75
λ2(7.12Kev) Gof	1.18	1.84	8.23
λ3 (7.135Kev) Gof	1.10	1.05	6.53
Rwp	12%	11%	7%
XRD Fe^{2+} / Fe^{3+}	0.66	0.185	1
DTG Fe^{2+} / Fe^{3+}	0.61	0.20	1

Table 1 : Refinement results which are obtained during this experiment