Journal of Solid State Chemistry 247 (2017) 13–19

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Morin-like spin canting in the magnetic $CaFe_5O_7$ ferrite: A combined neutron and Mössbauer study

C. Delacotte[a], Y. Bréard[a], V. Caignaert[a], V. Hardy[a], J.M. Greneche[b], S. Hébert[a], E. Suard[c], D. Pelloquin[a,*]

[a] Laboratoire CRISMAT ENSICAEN UMR CNRS 6508, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex 04, France
[b] Institut des Molécules et Matériaux du Mans, IMMM UMR CNRS 6283, Avenue Olivier Messiaen, 72085 Le Mans, France
[c] Institut Laue-Langevin, 71 avenue des Martyrs, 38042 Grenoble Cedex 9, France

ARTICLE INFO

Keywords:
Magnetic structure
Neutron diffraction
Mössbauer spectroscopy

ABSTRACT

Magnetic structure of $CaFe_5O_7$ ferrite has been studied jointly from neutron powder diffraction data and spectroscopic Mössbauer measurements in the thermal range from 5 to 500 K. This coupled work highlights three distinct magnetic domains around two specific temperatures: T_M=125 K and T_N=360 K. The latter corroborates the structural monoclinic-orthorhombic transition previously reported by transmission electron microscopy techniques and X-ray thermodiffractometry. Complementary heat capacity measurements have confirmed this first order transition with a sharp peak at 360 K. Interestingly, this large study has revealed a second magnetic transition associated to a spin rotation at 125 K similar to this one reported by Morin in α-Fe_2O_3 hematite at T_M=260 K.

1. Introduction

Iron oxides and related iron rich materials focus large attentions due to numerous and complex structural properties reported. A large part of this richness results from some oxygen non stoichiometry effects or intergrowth mechanisms which can generate potentially several crystallographic iron sites in the structure. Such a structural multiplicity offers the possibility to have different valence states or electronic configurations for iron species inside the structure like exemplified by the $Fe_{1-x}O$ [1] oxides or the hexaferrite-type compounds [2] and more recently by $CaBaFe_4O_7$[3]. Assuming these mixed state valences, some strongly correlated electron systems are thus obtained which lead to fascinating magnetic – transport properties. The magnetite Fe_3O_4 spinel like structure is a well-known example of a mixed valent Fe^{II}/Fe^{III} ferrimagnetic oxide (T_N=860 K). Apart from its magnetic behavior, its fame is the occurrence of a reversible structural transition at around 120 K –so called Verwey transition- associated to an ordering of the ionic charge state [4,5]. Among the different iron based oxide systems, the Ca-Fe-O one and especially the intergrowth $(CaFe_2O_4)$ $(FeO)_n$ series has given rise to numerous studies [6–8]. This series is attractive since different Fe^{III}/Fe^{II} distributions can be expected according to the n member. Some recent works of n=3 member $CaFe_5O_7$ by transmission electron microscopy (TEM) and X-ray diffraction techniques depending on temperature have revealed some complex structural features [7] and a concomitant correlation with the possible charge ordering versus T. Thus beside a superstructure associated to a monoclinic symmetry at room temperature [7], the $CaFe_5O_7$ ferrite exhibits a reversible transition from monoclinic *P*2*₁*/*m* superstructure to orthorhombic *Cmcm* structure at 360 K. That structural transition is associated to a sharp peak in magnetic susceptibility and a clear regime change in resistivity curve [7]. To understand such an interplay between structure and physical properties and the phenomenon that induces this structural transition, a neutron diffraction study combined with some zero-field and in-field ^{57}Fe Mössbauer spectrometry measurements were carried out on $CaFe_5O_7$. This coupled study has given the opportunity to finely analyze the distribution of iron III/II species and follow its evolution and their associated electronic features. Experimental neutron diffraction data were collected at selected temperatures on a large thermal range typically from 5 to 500 K. On the same sample, transmission Mössbauer spectra were recorded at different temperatures and in presence of an external magnetic field at low temperature to better understand the magnetic structure. Owing to this combined approach, three distinct magnetic behaviors are highlighted and described in this paper.

2. Experimental

The $CaFe_5O_7$ sample was synthesized by a standard solid state reaction process using CaO, Fe_2O_3 and Fe as starting materials according to the method previously reported [7]. Purity of the sample

---

[*] Corresponding author.

http://dx.doi.org/10.1016/j.jssc.2016.12.021
Received 25 October 2016; Received in revised form 20 December 2016; Accepted 21 December 2016
Available online 22 December 2016
0022-4596/ © 2016 Elsevier Inc. All rights reserved.

was checked by analyzing powder X-ray diffraction (XRPD) pattern collected with an Xpert Pro Panalytical diffractometer working with the Co Kα radiation and equipped with an X′Celerator detector. Neutron Powder diffraction (NPD) data were collected on the D2B diffractometer at the ILL (Institut Laue Langevin) reactor using two wavelengths: λ=1.594 Å and 2.40 Å. Sample was put in cylindrical vanadium can. Low temperatures data were collected using He_{liq} Cryostat whereas a furnace has been installed for room and higher temperature data collections. All neutron diffraction data collections have been performed under dynamic vacuum. Atomic resolution STEM-HAADF study has been carried out on JEOL ARM200 FEG microscope equipped with aberration correctors.

^{57}Fe Mössbauer spectra were collected using a conventional constant acceleration transmission spectrometer with a ^{57}Co(Rh) source and a bath cryostat for low temperature and a home-made cryofurnace for high temperature. In addition, in-field Mössbauer spectra were collected at different temperatures using a cryomagnetic device generating an external magnetic field parallel to the γ-beam. The spectra were fitted by means of the MOSFIT program with either quadrupolar doublets in the paramagnetic range or magnetic sextets in the magnetically ordered state, both composed of Lorentzian lines. Their relative proportions of these Fe species are given from the corresponding absorption areas, assuming thus the same values of their recoilless Lamb-Mössbauer factors. An α-Fe foil was used as calibration sample while the values of isomer shift are quoted relative to that of α-Fe at 300 K. Susceptibility and magnetization were measured from a dc SQUID Quantum Design magnetometer. Zero field heat capacity measurements were carried out from 2 to 400 K using a semi-adiabatic relaxation technique coupled with a 2τ fitting procedure (PPMS, Quantum Design). Note that all characterizations (XRPD, NPD, ^{57}Fe Mössbauer spectrometry and physical analyses) have been performed on crystalline powders prepared from the same $CaFe_5O_7$ batch.

3. Results and discussions

As recently reported, the $CaFe_5O_7$ oxide which the monoclinic structural model is shown in Fig. 1, exhibits two transitions in the thermal magnetic susceptibility curve at T*=125 K and T_N=360 K [7] respectively. The present analysis of whole NPD patterns collected in the large thermal range from 5 K to 500 K is in agreement with these first results since three different data sets can be evidenced as illustrated in Fig. 2: $T > T_N$=360 K, $125 K < T < 360 K$ and $T <$ T*=125 K respectively. Based on that observation and combining Mössbauer spectrometry measurements in the same thermal range, both the magnetic behavior evolution and the iron species distribution have been tuned according to T* and T_N.

$T > T_N = 360$ K

Fig. S.I.1 shows the neutron-diffraction pattern of $CaFe_5O_7$ recorded at 500 K. According to our previous study [7], the nuclear cell can be described in an orthorhombic *Cmcm* setting at this temperature. In the present case, the observed neutron pattern is well fitted with these structural data, especially the oxygen content has been refined and corresponds perfectly to the one expected. No magnetic contribution is detected during these calculation series. The difference pattern attests of the goodness of the fit, which is confirmed by the conventional reliability factors. All these calculations are summarized in Table 1.

Above 360 K the Mössbauer spectra exhibit a paramagnetic structure as illustrated in Fig. S.I.2 confirming thus that the compound is in the paramagnetic state. However, as listed in Table 2, the values of isomer shift do not correspond strictly to those of Fe^{3+} and Fe^{2+}, but to the presence of Fe ions with delocalized electron. The hyperfine structure has to be decomposed into two quadrupolar components: it is important to emphasize that among both fitting A and B models describing correctly the hyperfine structure versus temperature, only the A model shows clearly a physically realistic meaning. The second solution involving two quadrupolar doublets with rather similar values of isomer shifts gives rise to a decomposition where the distribution Fe^{3+}/Fe^{2+} differ from expected $2Fe^{3+}:3Fe^{2+}$. Indeed, the values of isomer shift have to be assigned to intermediate valence states estimated at about $2.68(5)^+$ and $2.17(5)^+$ respectively; in addition, the monotonic increase of the paramagnetic splitting values with the decreasing temperature up to 360 K suggests also weak changes in the Fe probe atomic neighboring giving rise to a less symmetric environment below T_N=360 K concomitant with the neutron spectra evolution shown in Fig. 2.

$T_N = 360$ K $> T >$ T* $= 125$ K

Neutron diffraction data shown in Fig. S.I.3 confirms that below T_N the $CaFe_5O_7$ oxide undergoes to a structural transition from an orthorhombic symmetry (*Cmcm*) to a monoclinic one ($P2_1/m$) like revealed by combining electron microscopy and X-ray diffraction analyses [7]. Nevertheless the a_o doubling observed at RT on electron diffraction patterns and on single crystal X-ray diffraction data, induced by the shifting of Ca rows [6,7], is not detected. This is probably due to the weakness of the extra peaks compared to the background as it was already reported in $HoBaCo_2O_5$ for the charge ordered state [9]. Consequently, calculations have been done with the following cell a=3.05 Å, b=17.97 Å, c=5.25 Å and β=106.99° and the

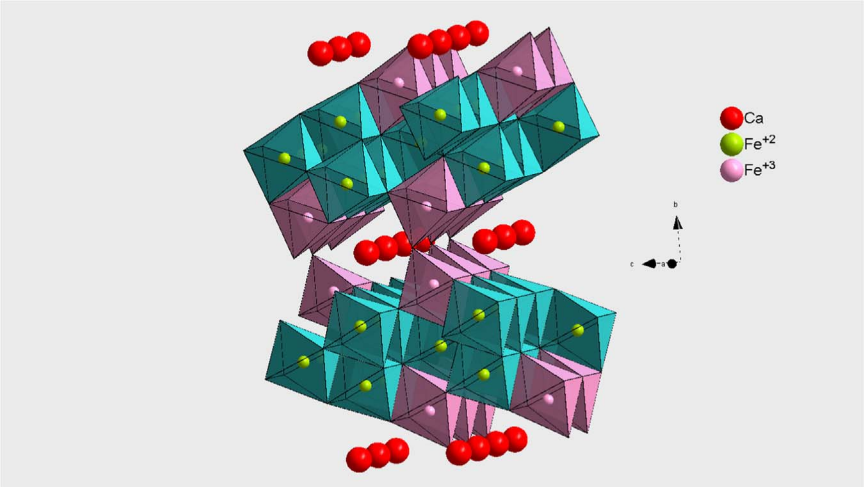

Fig. 1. Structural model of $CaFe_5O_7$ projected along [100] direction. Pink and blue octahedra are related to Fe(III) and Fe(II) species respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

Download English Version:

https://daneshyari.com/en/article/5153514

Download Persian Version:

https://daneshyari.com/article/5153514

Daneshyari.com