

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Thermal expansion and cation partitioning of MnFe₂O₄ (Jacobsite) from 1.6 to 1276 K studied by using neutron powder diffraction

This is a pre print version of the following article:

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/151683> since

Published version:

DOI:10.1016/j.ssc.2014.10.001

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



UNIVERSITÀ DEGLI STUDI DI TORINO

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in SOLID STATE COMMUNICATIONS, 201, 2015, 10.1016/j.ssc.2014.10.001.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), 10.1016/j.ssc.2014.10.001

The definitive version is available at:

<http://linkinghub.elsevier.com/retrieve/pii/S0038109814003949>

Thermal Expansion, and Cation Partitioning of MnFe_2O_4 (Jacobsite) from 1.6 to 1276 K Studied by Using Neutron Powder Diffraction

Davide Levy^{a*}, Linda Pastero^b, Andreas Hoser^c, Gabriele Viscovo^d

^a School of Physics and Astronomy, Tel-Aviv University, Ramat-Aviv 69978, Tel-Aviv, Israel

^b Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy

^c Helmholtz-Zentrum Berlin für Materialien und Energie, Sitz Berlin, AG Charlottenburg, 89 HRB 5583, D-14109 Berlin, Germany

^d Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 7, 10125 Torino, Italy

*Corresponding Author:

School of Physics and Astronomy, Tel Aviv University, 69978 Tel Aviv, Israel

E-mail: davide.levy69@gmail.com

Tel: +972(0)528698231

Abstract

MnFe_2O_4 is a low cost and stable magnetic spinel ferrite. In this phase, the influence of the inversion degree on the magnetic properties is still not well understood. To understand this relationship, Mn-ferrite was synthesized by a chemical co-precipitation method modified in our laboratory and studied by using the Neutron Powder Diffraction from 1.6 K to 1243 K. A full refinement of both crystal and magnetic structures was performed in order to correlate the high-temperature cation partitioning, the Curie transition and the structure changes of the Mn-ferrite. In this work three main temperature intervals are detected, characterized by different Mn-ferrite behaviors: the first one, ranging from 1.6 K to 573 K where MnFe_2O_4 is magnetic, the second

one, from 573 K to 623 K, where MnFe_2O_4 becomes paramagnetic without cation partitioning and the last one, from 673 K to 1243K, where cation partitioning occurs.

Highlights

- Mn-ferrite was synthesized by a modified chemical co-precipitation method.
- The material was studied by Neutron Powder Diffraction.
- Diffraction experiments were performed at variable temperature from 1.6 K to 573 K.
- Three temperature intervals and related magnetic behavior were identified.

Keywords A. Magnetic Materials; B. Chemical Synthesis; C. Neutron Scattering and Diffraction; D. Rietveld Analysis

1. Introduction

Spinel ferrites are important for their application as low cost stable magnetic phases in the electrical and electronic industry. Spinel ferrites are double oxides with a cubic cell spinel-like structure and general formula $\text{M}^{2+}\text{Fe}^{3+}_2\text{O}_4$, where M^{2+} is usually a transition cation or Mg^{2+} . The bivalent and trivalent cations occupy the two structural sites forming two different configurations: *direct spinel* and *inverse spinel*. Between these two ideal configurations, there is a continuous of intermediate configurations that are usually described by an order parameter called *inversion degree* x . The inversion degree parameter corresponds to the quantity of Fe^{3+} in the tetrahedral site [1] and it can vary between 0 and 1, direct and inverse spinel respectively. Zn- and Cd-ferrites are the only ones having a *normal* or *quasi-normal* configuration [1, 2]; the other ferrites have a partially inverted configuration. Magnetite, $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$, and magnesoferrite, MgFe_2O_4 , are ferrites with a completely *inverted* configuration [3, 4]. It has been demonstrated that at high temperature, there is a cation partitioning in these phases [2-6]. In general it has been established that both *normal* and *inverse* ferrites tend to the most disordered configuration at high temperature [7].

A previous work on the structure of the magnetite (Fe_3O_4) at high temperature, [3] studied by Neutron Powder Diffraction (NPD), demonstrated that the changes of the crystal structure at the Curie temperature is due to cation partitioning.

The same procedure is proposed in this work for the analysis of the MnFe_2O_4 spinel. This composition is one of the most interesting because of its problematic magnetic properties. The experimental magnetic moment at 4 K is reported to be about $4.6\mu_B$, smaller than that predicted by theory ($5.0\mu_B$ [8]). So far, only one study investigated the cation partitioning at high-temperature of a stoichiometric Mn-ferrite [9] on a quenched sample analyzed by neutron diffraction. The authors report that the cation partitioning starts at about 600 K with a freezing of the inversion degree parameter at about 873 K. Furthermore, they also collected three diffractograms *in situ* at high temperature and they demonstrated that the cation partitioning occurs up to 1050 K. Another study was performed on cation partitioning of MnFe_2O_4 [10], but the results reported are not comparable with the previous because the sample was a non-stoichiometric nano-crystalline powder.

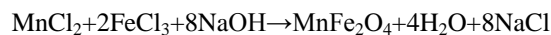
The aim of this work on Mn-ferrites is to study the effect of the temperature on cation partitioning and to find out if is possible to establish a correlation between the Curie transition and the crystal structure change of the Mn-ferrite by using NPD

2. Material and methods

2.1 Synthesis

The chemical co-precipitation method described by Zhang et al. [11] and Chen et al. [12] was chosen as starting point to synthesize the MnFe_2O_4 .

The synthesis of the Mn-ferrite was run in a well-defined temperature range (353K-363 K). The powder obtained was a pure nanosized spinel, according to the chemical reaction:



In each synthesis, the starting concentrations of the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solutions were chosen in order to obtain a MnFe_2O_4 solution $3 \cdot 10^{-2}$ M, corresponding to 3.46 g of product supposing a reaction's performance of 100%. The Mn^{2+} and Fe^{3+} chloride solutions, 0.03 M and 0.06 M respectively, were prepared from analytical grade Sigma-Aldrich reagents. This solution was stirred thoroughly keeping the temperature constant at 358 K inside the reaction vessel for the whole synthesis procedure to prevent jerk variations in the supersaturation. After few minutes, a solution 1.5 M of NaOH (final concentration after mixing 0.24 M) was dripped into

the chlorides solution as reaction agent. A dripping procedure was chosen in order to slow down the rise of the supersaturation value, avoiding a sudden nucleation of many small nuclei with high surface area and high reactivity.

The nanosized powders obtained by this chemical co-precipitation were sintered in furnace with an inert atmosphere at 1173 K and then slowly cooled to room temperature to obtain a pure micro-crystalline sample.

The quality of the samples obtained in this way was very reproducible, so several synthesis runs were done in order to collect about 10 g of Mn-ferrite (the minimum quantity of sample necessary for NPD experiments).

2.2 NPD Experimental

The sample was studied by NPD at variable temperature. The angle dispersive diffraction experiment was performed on the E6 powder diffractometer at the Helmholtz-Zentrum, Berlin (HZB, Germany) using the BERII neutron source. About 10 g of powdered sample were sealed in a quartz tube holder and studied *in situ* first by cooling from room temperature to 150 K, 50 K and 1.6 K using a standard helium cryostat and then by heating *in situ* by means of a furnace in high vacuum. After cryogenic measurements, the sample was heated from room temperature to 373 K and then by steps of 100 K up to $T = 573$ K, above this temperature by steps of 50 K up to 1223 K. The last experimental point was collected at 1243 K. The neutron wavelength used was $\lambda = 2.447$ Å. The data collection time for each temperature step was 3 hours. The collected patterns are reported in Figure 1.

The NPD patterns were refined by using the Rietveld method [13] by means of the GSAS/EXPGUI [14, 15] software. The starting structural parameters are: space group $Fd\bar{3}m$, the octahedral and tetrahedral sites in $(1/2, 1/2, 1/2)$ and $(1/8, 1/8, 1/8)$ respectively and the oxygen $(0.255, 0.255, 0.255)$ [16]. In order to describe the contribution of the magnetic diffraction to the intensity of the peaks, a magnetic phase was added to the model as reported in our work on magnetite [3].

To determine the grade of inversion of the manganese and iron cation, the occupancies at 573 K (where no magnetic phase is present as explained hereafter) were firstly refined and then used in the refinements of the diffractograms collected at lower temperature. In this way the correlation between magnetic contribution and cation partitioning is avoided, allowing to formulate the

hypothesis that below 573 K there is no cation partitioning. A constrain was added to the occupancy of the different atomic sites in order to maintain the full occupancy of the two site and the stoichiometric ratio Mn/Fe=1/2. In order to check the stoichiometry of the sample, the occupancy of the oxygen was refined at 573K. The refined value do not change appreciably from the unit value of full occupancy.

3. Results and Discussion

From an early analysis of the collected diffractograms (Figure 1), the magnetic peaks (220), (222), (331) and (422), decrease in intensity with the temperature and disappear at 573 K confirming the change in the magnetic properties of the phase that becomes paramagnetic between 473 K and 573 K. The refined pattern at 50 K is reported in Figure 2. Refined structural data are reported in Table 1 and their temperature dependent trend is shown in Figure 3.

From this figure, it is possible to highlight two different behaviors for each parameter:

- The cell edge dimension is constant below 50 K, then it increases with parabolic bias up to 573K. Above this temperature the trend is quasi-linear
- The oxygen coordinates do not change for temperatures lower than 400 K. Between 573 and 623 K they increase. For higher temperatures they linearly decrease.
- The occupancy of Mn in the octahedral sites (*inversion degree*) was not refined for temperatures below 573 K. For temperatures between 573 K and 623 K it is constant and for higher temperatures it increases linearly.

Based on an examination of the refined parameters, we can state that the cation partitioning begins between 573 K and 623 K.

Since the neutron powder data for a cubic phase are insensitive to the magnetic moment directions [17], the magnetic moments in the tetrahedral and octahedral sites of the structure were calculated by the module of the three components of the magnetic vector. The module magnetic moments in the octahedral and tetrahedral sites at 1.6 K are $3.95(4) \mu_B$ and $4.54(4) \mu_B$ respectively and the total magnetic moment is $3.35(8) \mu_B$ for each unit cell. This value is very close to $3.5 \mu_B$ extrapolated at 0 K found by means of a magnetic measurement [18], but smaller than the values reported by other neutron diffraction measurements (4.60-4.85) [1, 8]. For nanocrystalline $(Mn,Fe)(Mn,Fe)_2O_4$ spinel, the magnetic moment at room temperature is $1.8 \mu_B$

Commento [d11]: Commento 1
The Rietveld refinement of the neutron diffraction patterns has been carried out by giving constrain on occupancies (full) of Fe and Mn. Have the authors checked if the sample is non stoichiometric?
@linda va bene?

Commento [d12]: What is the direction of ordered magnetic moment?

Commento [d13]: Commento 3
The magnetic structure being ferrimagnetic, one of the site moments should, therefore, be with a negative sign.

Commento [d14]: Is total magnetic moment $3.35 \mu_B$ per formula unit?

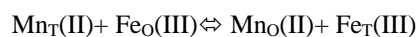
as reported by Zhang et al. [10] very close to the result of this work, $1.4(2) \mu_B$. The differences between these values are probably due to a different degree of inversion, crystal dimension and/or stoichiometry between the different samples. As seen above, the diffractogram at 573 K does not present any magnetic contribution to the peak intensities. To test the magnetic contribution, the magnetic moment was refined also at this temperature. The refined magnetic moment values at 573 K are comparable with the calculated error smaller than ($<2\sigma$), showing that the Curie transition already occurred (Table 1).

Commento [15]: Variations?

The coordinate of the oxygen begins to increase above 400K, when the magnetic moment approaches to zero, as can be highlighted in Figure 3. This effect can also be observed in the cation-oxygen bond length for tetrahedral site, as plotted in Figure 4. In this plot, the tetrahedral bond length increases between 400 and 623 K. In the same temperature range, the octahedral site does not substantially change dimension.

Above 623 K, when the cation partitioning begins, the cation-oxygen bond length changes dramatically with the octahedron expansion and the tetrahedron shrinkage. This effect is correlated to the dimension of the cations in the different coordination: the Mn^{2+} radius in coordination 4 is 0.63 \AA and in coordination 6 is 0.83 \AA , while the radius of Fe^{3+} in the two coordination numbers is 0.49 \AA and 0.645 \AA respectively [19]. So, when a Mn^{2+} cation moves from the tetrahedral site to the octahedral one, the former increases and the last decreases. Since the difference in the dimensions of cations is larger, the tetrahedron shrinkage due to cation partitioning prevails on the thermal expansion of this site. As shown in Figure 3, the cation partitioning starts at 623K and continue monotonically up to 1247 K. The $MnFe_2O_4$ phase at room temperature has a configuration 12.6% inverted, that at 1247 K becomes 40.6% inverted. Similar results are reported in the previous study on the behavior of the cation partitioning of $MnFe_2O_4$ [9] by using the Neutron Diffraction. As in the aforementioned article, here the cation partitioning begins at the same temperature, as highlighted in Figure 5. Moreover, the cation partitionings are quite similar up to 873 K. As stated by the authors three more measurements were collected at high temperature *in situ* and the results are reported as white circles in Figure 5. These values are in good agreement with the ones determined in this work.

From a thermodynamic point of view, the chemical formula describing the cation partitioning in $MnFe_2O_4$ is:



where the indexes T and O are referred to the cation in the tetrahedral and octahedral sites respectively. Using this formula the equilibrium constant K_{CD} is defined as [1]:

$$K_{CD} = \frac{\lambda^2}{(1-\lambda)(2-\lambda)} = \exp\left(-\frac{\Delta G^0}{RT}\right) = \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(-\frac{\Delta H^0}{RT}\right) \text{ eq.1}$$

where λ is inversion degree, T the temperature in Kelvin, R the perfect gas constant and ΔG , ΔS and ΔH are the Gibbs energy, entropy and enthalpy respectively.

Confirming the thermodynamic model, the behavior of the experimental $\ln K_{CD}$ vs $1/T$ is linear as seen in Figure 6. The refined value of entropy and enthalpy for temperatures between 623 K and 1246 K are $\Delta H^0=30.4(2)$ kJmol⁻¹ and $\Delta S^0=9.7(2)$ JK⁻¹mol⁻¹. This values are smaller than the entropy and enthalpy of ZnFe₂O₄, the other ferrite spinel with a direct configuration that have been studied at high temperature [2]. The calculated values from the order degree reported in the text are $\Delta H^0=66(2)$ kJmol⁻¹ and $\Delta S^0=24(2)$ JK⁻¹mol⁻¹.

5. Conclusions

In this work, a modified chemical co-precipitation method for Mn-ferrite synthesis was proposed. Following this procedure a well crystallized MgFe₂O₄ sample was obtained. The traditional chemical co-precipitation followed by the furnace recrystallization in nitrogen atmosphere was demonstrated to be effective for the production of large quantities of homogenous sample for its high reproducibility.

The NPD characterization of MnFe₂O₄ covers a wide temperature range from 1.6 K to 1243 K. Essentially, three main temperature intervals can be defined to describe the magnetic behavior of MnFe₂O₄:

- 1- From 1.6 K to 473 K, the phase is magnetic,
- 2- From 573 K to 623 K, the phase is paramagnetic without cation partitioning,
- 3- From 673 K to 1243 K, cation partitioning occurs.

The first interval is characterized by a progressive loss of magnetic ordering. The magnetism either does not influence the crystal structure, or the influence is so small that the resulting bond relaxation is hidden by the thermal expansion.

Commento [dl6]: Results & Discussion section: The numbering of the equation is not correct. It is numbered as eq 3. Where are the equations 1 and 2?

Commento [l7]: Siamo dei pirilli..

In the second interval, the structure changes are only due to the thermal expansion, as shown in Figure 4. The thermal expansion coefficient increases linearly following the same trend as in the previous interval.

In the third interval, above 623 K the structure is influenced by the cation partitioning. The huge difference between the dimensions of the cations in the two sites causes a sharp decrease of thermal expansion coefficient, mainly due to the increasing of iron quantity in tetrahedral site. The cation partitioning occurs at lower temperature with respect to other ferrites [2].

Acknowledgements

This research project has been supported by the European Commission under the 7th Framework Programme through the 'Research Infrastructure' action of the 'Capacities' Programme, *NMI3-II Grant number 283883*

We wish to thank Dr. Angelo Agostino for its willingness to help us to synthesize our samples

⊗willingness...

Commento [d18]: Acknowledgements:
The last sentence is incomplete.

Commento [d19R8]:

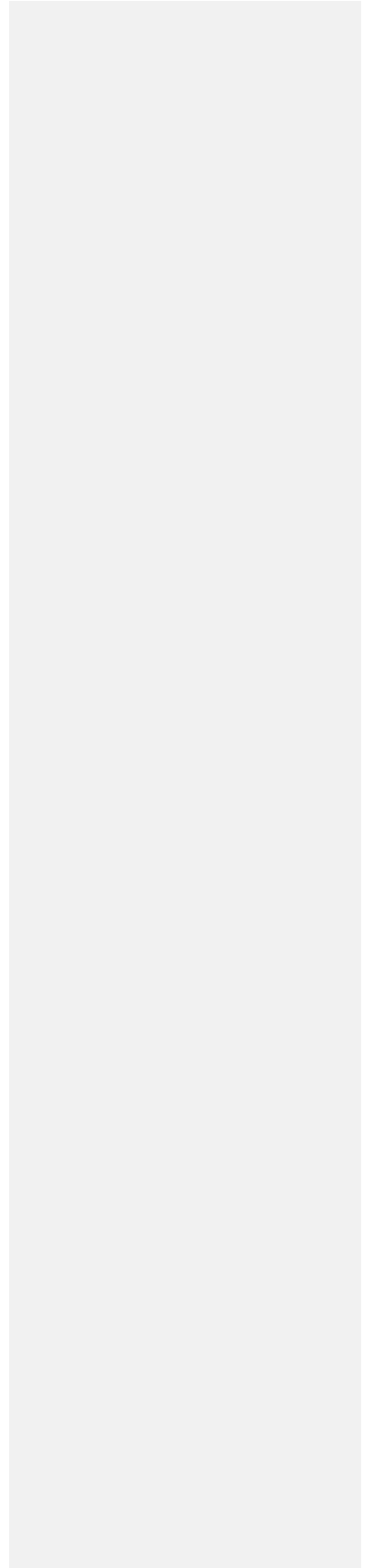
Commento [d110R8]:

Commento [111]: Mi sembra brutto finire la frase... in fondo perché ringraziare qualcuno che ci ha permesso di lavorare? Non dovrebbe essere normale? Roba da italiani... che dici, la lasciamo?

- [1] V.A.M. Brabers, in: K.H.J. Buschow, (Ed.), Handbook of Magnetic Materials, Elsevier, 1995, pp. 189-324.
- [2] A. Pavese, D. Levy, A. Hoser, *American Mineralogist* 85 (2000) 1497-1502.
- [3] D. Levy, R. Giustetto, A. Hoser, *Physics and Chemistry of Minerals* 39 (2012) 169-176.
- [4] D. Levy, V. Diella, M. Dapiaggi, A. Sani, M. Gemmi, A. Pavese, *Physics and Chemistry of Minerals* 31 (2004) 122-129.
- [5] A. Pavese, G. Artioli, U. Russo, A. Hoser, *Physics and Chemistry of Minerals* 26 (1999) 242-250.
- [6] N. Marinoni, D. Levy, M. Dapiaggi, A. Pavese, R. Smith, *Physics and Chemistry of Minerals* (2011) 11-19.
- [7] H.S.C. O'Neill, H. Annersten, D. Virgo, *American Mineralogist* 77 (1992) 725-740.
- [8] J.M. Hastings, L.M. Corliss, *Physical Review* 104 (1956) 4.

- [9] Z. Jiráček, S. Vratislav, *Czechoslovak Journal of Physics B* 24 (1974) 642-647.
- [10] Z.J. Zhang, Z.L. Wang, B.C. Chakoumakos, J.S. Yin, *Journal of the American Chemical Society* 120 (1998) 1800-1804.
- [11] B. Zhang, G. Tang, Z. Yan, Z. Wang, Q. Yang, J. Cui, *Journal of Wuhan University of Technology-Mater. Sci. Ed.* 22 (2007) 514-517.
- [12] J.P. Chen, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, E. Devlin, A. Kostikas, *Physical Review B* 54 (1996) 9288-9296.
- [13] H. Rietveld, *Journal of Applied Crystallography* 2 (1969) 65-71.
- [14] A.C. Larson, R.B. Von Dreele, *Los Alamos National Laboratory Report* 86-748 (2004).
- [15] B.H. Toby, *Journal of Applied Crystallography* 34 (2001) 210-221.
- [16] M.E. Fleet, *Acta Crystallographica B* 37 (1981) 917-920.
- [17] J.P. Wright, J.P. Attfield, P.G. Radaelli, *Physical Review B* 66 (2001) 214422.
- [18] K.H. Jani, M.C. Chhantbar, H.H. Joshi, *Journal of Magnetism and Magnetic Materials* 320 (2008) 2208-2214.
- [19] R. Shannon, *Acta Crystallographica Section A* 32 (1976) 751-767.

Tables



T(K)	<i>x</i>	I.D.	<i>a</i> (Å)	V(Å ³)	M _{oct.} (μ _B)	M _{tet.} (μ _B)	M _{total} (μ _B)
1.6	0.2602(1)	0.126	8.5060(3)	615.43(7)	3.95(4)	4.54(4)	3.35(8)
50	0.2595(1)	0.126	8.5052(3)	615.25(7)	4.07(9)	4.74(9)	3.4(2)
150	0.2597(1)	0.126	8.5076(3)	615.78(7)	3.65(8)	4.28(9)	3.0(2)
296	0.2596(2)	0.126	8.5152(9)	617.4(2)	2.8(1)	4.2(1)	1.4(2)
373	0.2598(1)	0.126	8.5228(6)	619.1(1)0	2.47(8)	3.8(9)	1.1(2)
473	0.2602(1)	0.126	8.5350(5)	621.7(1)	1.68(9)	3.07(9)	0.3(2)
573	0.2606(1)	0.126(2)	8.5498(7)	625.0(1)	0.2(3)*	0.6(3)*	-0.2(3)*
623	0.2611(1)	0.126(2)	8.5543(6)	626.0(1)			
673	0.2610(1)	0.148(2)	8.5583(7)	626.9(1)			
723	0.2607(1)	0.174(2)	8.5622(6)	627.7(1)			
773	0.2606(1)	0.200(2)	8.5658(6)	628.5(1)			
823	0.2602(1)	0.226(2)	8.5689(6)	629.2(1)			
873	0.2602(1)	0.249(1)	8.5723(7)	629.9(2)			
923	0.2599(1)	0.278(1)	8.5753(7)	630.6(2)			
973	0.2598(1)	0.301(1)	8.5786(7)	631.3(2)			
1023	0.2596(1)	0.323(1)	8.5821(7)	632.1(2)			
1073	0.2595(1)	0.344(1)	8.5860(8)	633.0(2)			
1123	0.2595(1)	0.359(1)	8.5907(8)	634.0(2)			
1173	0.2592(1)	0.379(1)	8.5938(8)	634.7(2)			
1223	0.2592(1)	0.398(1)	8.5971(8)	635.4(2)			
1243	0.2591(1)	0.406(1)	8.5992(8)	635.9(2)			

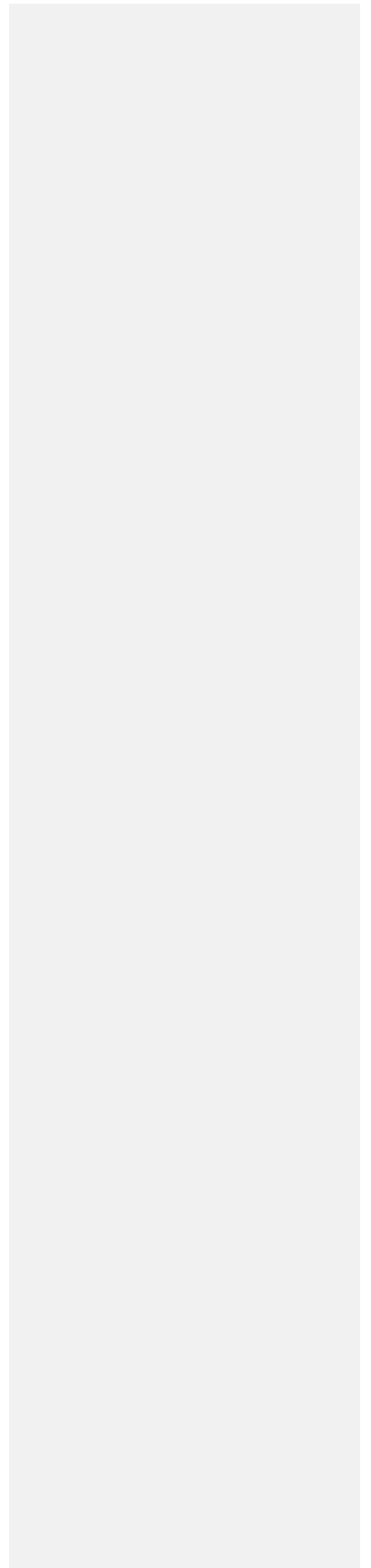
Commento [dl12]: The units of T, a, V and Mtotal (μB) are missing in Table 1.

Mtct in the Table should read as Mtet
What is X in Table?

Formattato: Evidenziato

Table 1- Refined structural data table: T temperature, *x* coordinate of the oxygen atom, I.D. inversion degree, *a* cell edge, V volume, M_{oct.} M_{tet.} M_{tot.} magnetic moment of octahedral and tetrahedral site and total of the cell (μ_B=9.27400949(80)×10⁻²⁵ J/T). *The values of magnetization at 573 K have been reported only to show that the refined value are smaller than 2σ.

Figures



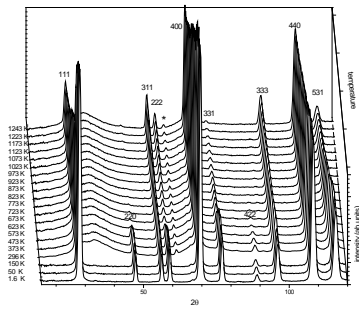


Figure 1- Neutron Powder Diffractograms collected at variable temperature. The temperature ranges between 1.6 K and 1243 K. The strong change of the intensity of the peaks 220, 222, 331 and 422 according to the increase of temperature is related to the change in the magnetic properties of the phase (from magnetic to paramagnetic)

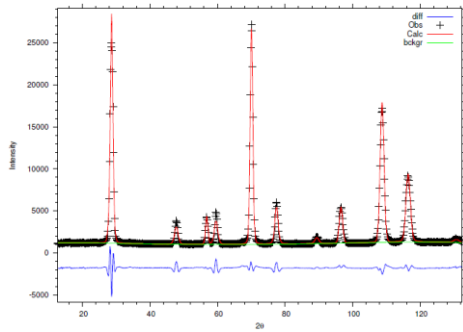


Figure 2- example of Rietveld refinement achieved at 50 K.

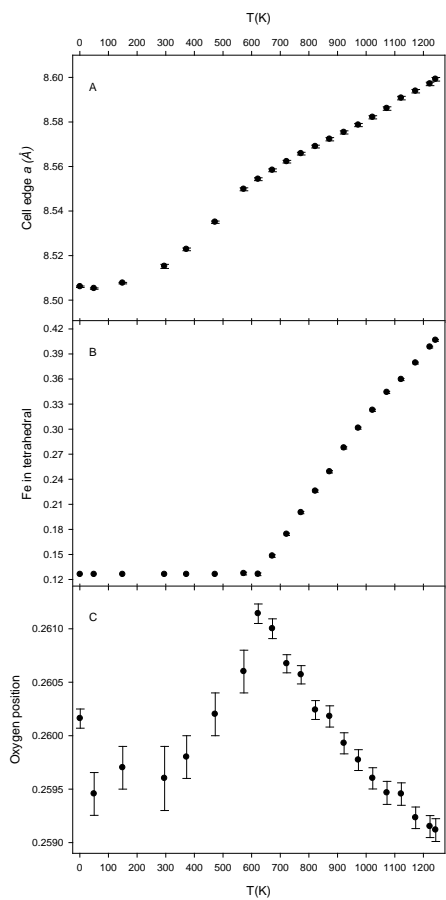


Figure 3- A) Cell edge vs. temperature; B) Fe^{3+} in tetrahedral site vs. temperature; C) unique coordinate of oxygen vs. temperature

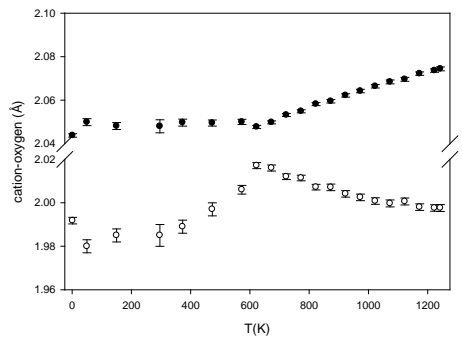


Figure 4 – Cation-oxygen bond-length: black circles octahedral site and white circles tetrahedral site

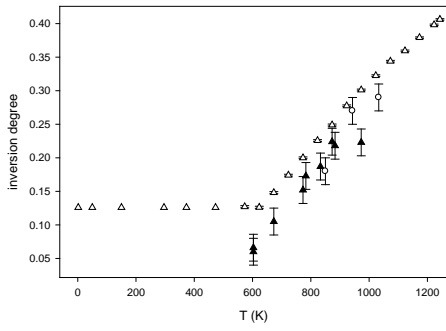


Figure 5- inversion degree found in this work (white triangles), in previous work (black triangles quenched data and white circles *in situ* data) [9]

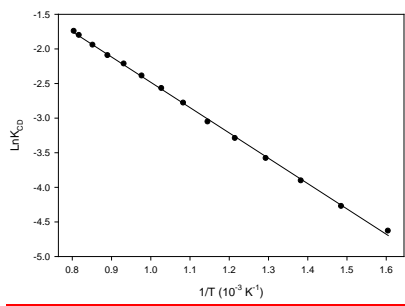


Figure 6 – logarithm of the K_{CD} vs. $1/T$ calculated as described in the text