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Valence states of copper in copper ferrite spinels $Cu_xFe_{3-x}O_4$ $(0 < x \leq 1)$ fine powders: Evidence of copper insertion

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Abstract

The oxidation in cation deficient spinels of copper iron spinels $Cu_xFe_{3-x}O_4$ $(0 < x \leq 1)$ synthesized by soft chemistry with a grain size < 50 nm has been investigated by thermal measurements (DTG and DSC). For stoichiometric synthesized spinels when the copper content determines the number of oxidizable cations $1-x$ per mole of ferrite, three oxidation phenomena corresponding to Cu^+ at B-sites (130°C), Fe^{2+} at B-sites (180°C) and Cu^+ at A-sites (240°C) have been found in close relation with the cation-oxygen distance of each oxidizable cation. For nonstoichiometric synthesized spinels $Cu_xFe_{3-x}O_{4+\delta}$ with $\delta < 0$ when the oxidation reveals a mass gain larger than that calculated with $1-x$, the presence of additional interstitial Cu^+ ions has been envisaged. The oxidation temperature of these interstitial ions (> 300°C) is higher than that for Cu^+ ions at A-sites suggesting that interstitial copper ions also essentially reside in A-sites. © 1997 Elsevier Science B.V.

Keywords: Copper ferrite; Copper insertion; Defect structure; Fine powder; Oxidation

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1. Introduction

The oxidation studies by derivative thermogravimetry (DTG) of transition-group metal ions in the spinel type structure $M_xFe_{3-x}O_4$ (M = metallic cation) have been the subject of intense investigations attempting to obtain information on cation distribution among the octahedral, B, and tetrahedral, A, sites available in the close-packed oxygen framework [1]. But, to obtain high accurracy either on the cation distribution or valence state of transition metal ions, it is most desirable to have these materials in fine powders consisting of particles uniform in size and shape that allow, in addition to iron, the oxidation of the transition ions (M = Mn, Mo, V), while keeping the spinel structure [2]. Cation deficient ferrites having specific characteristics and properties (i.e. magnetic recording) could thus be obtained [3] where DTG reveals a single peak for each type of oxidized cation. In fact, such reactions at low temperatures involve a change of the cation to anion ratio in the spinel phase leading to the composition $Fe_{3-x}M_xO_{4+\delta}$ where δ denotes deviation from stoichiometry. At low oxidation temperature (< 500°C) and for oxygen partial

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pressures in non-equilibrium conditions usually used ($PO_2 > 10^{-2}$ Pa) only the cation deficient region of positive δ has been found [4]. On the other hand, at high temperatures in the range of 900–1400°C, the dependence of the degree of oxidation at equilibrium with PO_2 has been widely studied for some spinels such as magnetite [5], Mn–Co [6] or Mn–Zn ferrites [7] where nonstoichiometric regions of both positive (cation vacancies region) and negative (cation interstitials or oxygen vacancies regions) δ have been considered. This has also been shown by Atkinson at 500°C in the case of magnetite [8] by using CO/CO_2 mixtures in a closed system.

However, there have also been many studies of low temperature lithium insertion/extraction in spinel type compounds [9,10] with little or no structural consequences (i.e. topotactically). The results suggest that the lithium ions enter the interstitial 16c sites as Li^+ and donate an electron to the host matrix; for example, reducing Fe^{3+} to Fe^{2+} or Mn^{3+} to Mn^{2+} ions. An initial study by Colombo et al. [11] has also shown by means of thermogravimetric and X-ray diffraction analyses that a spinel phase $Fe_3O_{4+\delta}$, with $\delta < 0$ more reduced than magnetite, can be obtained and should be regarded as a solid solution of FeO in Fe_3O_4, the additional interstitial Fe^{2+} ions being situated on octahedral sites 16c. Similarly, for the system $Cu_xFe_{3-x}O_4$ investigated in the range $0.5 < x < 1$, which can be expected to contain the mixed valences $Cu^{2+/+}$, it has been shown that the accommodation of Cu^+ ions in interstitial positions may be possible [12,13]. These data provide further information on the processes that occur during oxidation of $Cu_xFe_{3-x}O_4$ fine powders for $x > 0.35$ in which it has been found that the number of oxidized cations per mole of ferrite is greater than that corresponding to $1-x$, consequent to copper insertion.

In this paper, we report further investigations of DTG and differential scanning calorimetry data (DSC) of oxidation of spinel oxide particles, $Cu_xFe_{3-x}O_4$ with $0 < x \leq 1$ that were obtained at low temperature in $N_2/H_2/H_2O$ gas mixtures using the soft chemistry route. In order to fully understand the mechanism of copper insertion we also studied copper insertion in the $CuFe_2O_4$ spinel in which a non-oxidizable cation is present at the stoichiometry.

2. Experimental procedure

$Cu_xFe_{3-x}O_4$ particles with an acicular shape (acicular ratio around 4) were prepared by a soft chemistry method via decomposition of mixed oxalic precursors, $Cu_{x/3}Fe_{(3-x)/3}C_2O_4$, $2H_2O$ as reported in Ref. [14]. These oxalic precursors were then decomposed under air or N_2 flow at various annealing temperatures, depending on x, where after these treatments, either two phases are present (α-Fe_2O_3 and CuO) for $x < 0.23$ or a nonstoichiometric spinel phase for $0.23 < x < 0.50$. In a second stage, the stoichiometric single-spinel phases were obtained by further treatments between 130 and 290°C using $N_2/H_2/H_2O$ mixtures. In this preparation method, the appropriate conditions of temperature and oxygen partial pressure were determined by successive trials of different mixtures. The spinel formation was checked by X-ray diffraction until the lattice cell parameter was found to be the stoichiometric one ($\delta = 0$). However, it should be noted that in obtaining the lattice parameter in this way it is hard to avoid the formation of nonstoichiometric materials with $\delta > 0$. For this compositional range the variation of the lattice constant with x is given in Fig. 1 (curve a). The average crystallite size measured from the X-ray lines broadening was close to 30 nm.

$CuFe_2O_4$ was directly obtained by decomposition of oxalic precursors, $Cu_{1/3}Fe_{2/3}C_2O_4$, $2H_2O$ under air flow, treated at 710°C for 4 h and quenched (Q samples) or slowly cooled (SC samples). The resulting product is a single tetragonal phase with a c/a ratio = 1.040 for Q samples and 1.060 for SC samples. The average crystallite size was close to 45 nm.

The oxidation reactions were performed in a Setaram MTB 10-8 microbalance (symmetrical setup, resolution and noise level 0.1 μg) with the temperature increasing at a linear rate (2°C min^{-1}). The estimated error in the determination of the δ value was about 0.001. The material weighed 10 mg and the powder was spread out so that it would oxidize in the same way as independent particles. The DSC experiments were carried out under air or a nitrogen flow with a Setaram DSC 111G with about 65 mg of powder.

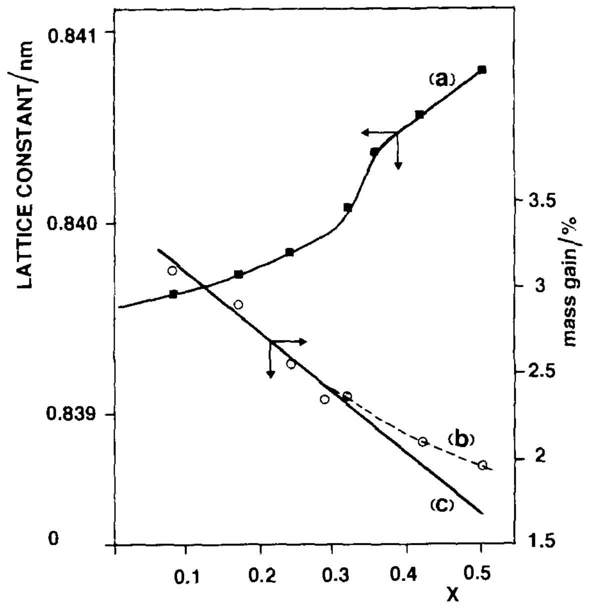

Fig. 1. Variation of lattice constant (a) and mass gain (b) and (c) vs. x for $Cu_xFe_{3-x}O_4$ spinels; (b) and (c) curves refer to experimental and theoretical mass gain, respectively.

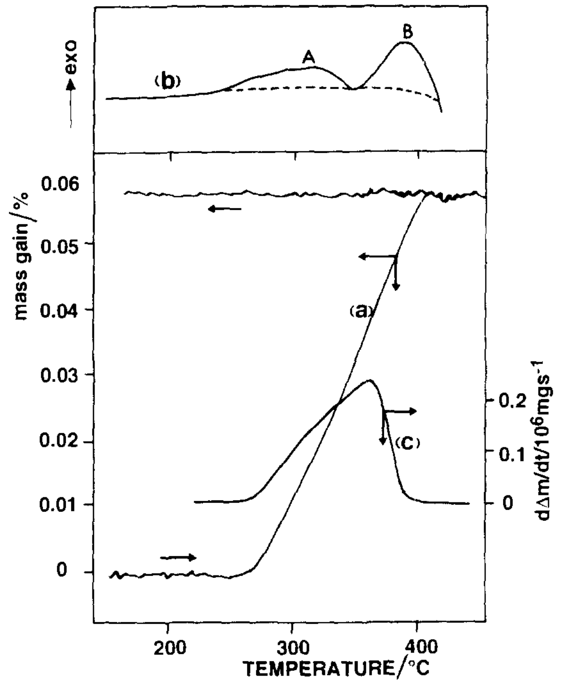

Fig. 2. (a) TG, (b) DSC and (c) DTG curves in O_2 for $CuFe_2O_4$ spinel obtained by annealing in air at 710°C and quenched.

3. Results

Fig. 1 shows the experimental mass gain associated with the oxidation of the stoichiometric ferrites $Cu_xFe_{3-x}O_4$. For $x > 0.35$, the oxidation reveals a mass gain larger (curve b) than that calculated with $1-x$ per mole of ferrite (curve c). For $CuFe_2O_4$ treated at 710°C and quenched in air, a mass gain was also observed (Fig. 2, curve a) in spite of the expected stoichiometry when Cu^{2+} and Fe^{3+} ions would be the only species present. One sample slowly cooled in air from the same temperature did not show such a mass gain. The DSC measurement performed in air on the quenched sample (Fig. 2, curve b) exibits two peaks appearing in the temperature range 250–350°C (A peak) and 350–420°C (B peak), the B peak does not occur in an inert atmosphere. The B peak seems thus to be related to the DTG peak (Fig. 2, curve c) which indicates the oxidation state of the ferrite. The A peak which is independent of the atmosphere of treatment has been ascribed to Cu^{2+} migration from tetrahedral to octahedral sites [15].

A more representative behavior of the oxidation process for samples with $x = 0.32$ and $x = 0.50$ is revealed by the DTG and DSC curves (Figs. 3 and 4). For $x = 0.32$ (Fig. 3) a previous study [16] has indicated that three oxidations (marked by arrows) in the temperature interval $100 < T < 300$°C should be implicated with this resolution temperature. An extension of the study for the compositional range $0.35 < x < 1$ has resulted for $T > 300$°C of the presence of a shoulder at around 320°C (Fig. 4), we suspect that this shoulder is due to additional oxidation occurring in comparison to samples with $x < 0.35$. Examination by X-ray diffraction of the phases with $x < 1$ obtained after oxidation below 400°C in a separate furnace shows that in all cases the spinel phase is maintained. The lattice parameter which is maximum at the stoichiometric composition decreases with the increasing vacancy content and increasing average oxidadion state of iron and copper cations (Fig. 5, curve a). It is also seen in Fig. 5 (curve b) that the lattice parameter decreases as a function of oxygen pressure.

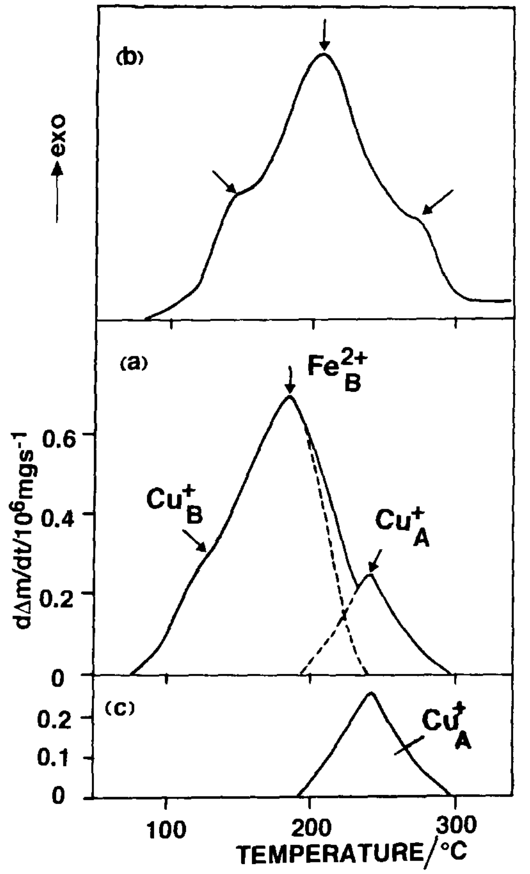

Fig. 3. Thermal behavior curves for $Cu_{0.32}Fe_{2.68}O_4$ spinel. (a) DTG, (b) DSC and (c) DTG curves showing the disappearance of the first (Cu^+_B) and second (Fe^{2+}_B) oxidation after selective oxidation at 140°C for 24 h at $PO_2 = 4 \times 10^3$ Pa.

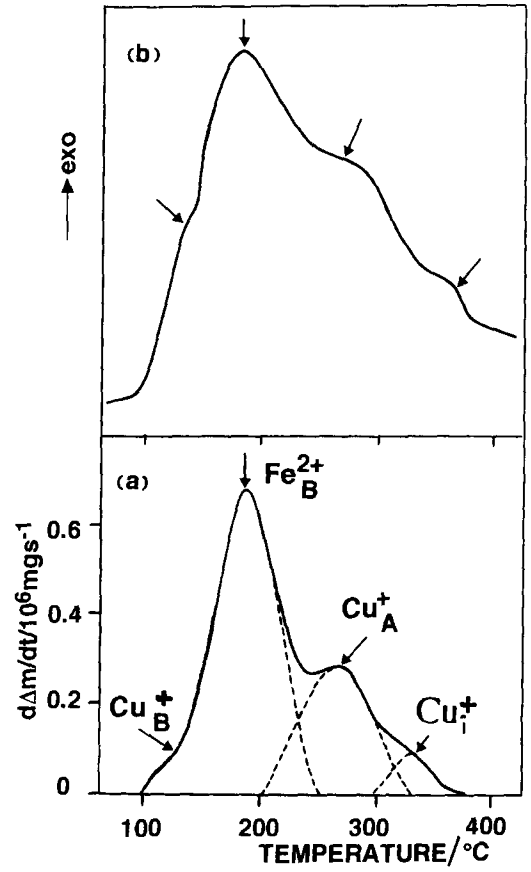

Fig. 4. Thermal behavior curves for $Cu_{0.50}Fe_{2.50}O_4$ spinel. (a) DTG and (b) DSC.

4. Discussion and conclusion

It has already been established that the three oxidations revealed by DTG and DSC for $x < 0.35$ result in some oxidizable cations leading to the formation of nonstoichiometric spinels where the point defects to be considered are only cation vacancies rather than interstitial oxygen ions [16]. It was demonstrated that Cu^+_B, Fe^{2+}_B and Cu^+_A oxidize into Cu^{2+} and Fe^{3+} ions, each oxidation temperature being closely related to the cation-oxygen distance of each oxidizable cation [17] as exemplified on Fig. 6. In fact, because the cation-oxygen bondings are more covalent on tetrahedral sites, the Cu^+ cations are more difficult to oxidize in this coordination than the Cu^+ and Fe^{2+}cations located on octahedral coordination. In the first approach, a general chemical formula can be proposed:

$$(Cu^+_{\alpha x}\,Fe^{3+}_{1-\alpha x})_A(Cu^{2+}_{(1-\alpha-\beta)x}\,Cu^+_{\beta x}\cdot Fe^{3+}_{1+(2\alpha+\beta)x}\,Fe^{2+}_{1-(1+\alpha+\beta)x})_B\,O_4^{2-} \qquad (1)$$

Insofar as it has been assumed that the area of a given DTG peak is proportional to the amount of the related ions, the measurement of the area of each peak, in principle, allows the same at low PO_2, the calculation of the quantity of each oxidizable cation in the stoichiometric ferrite. However, this method previously used to make a quantitative determination of cation distribution, is more suitable for cases where the oxidation temperatures for each oxidizable cation differ appreciably, was subsequently obtained for

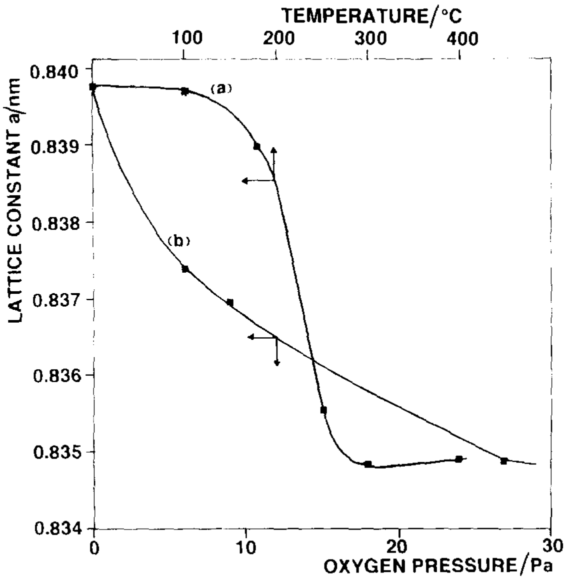

Fig. 5. Variation of lattice constant for $Cu_{0.32}Fe_{2.68}O_4$. (a) with oxidation temperature ($PO_2 = 4 \times 10^3$ Pa), (b) with oxygen pressure ($T = 230$°C).

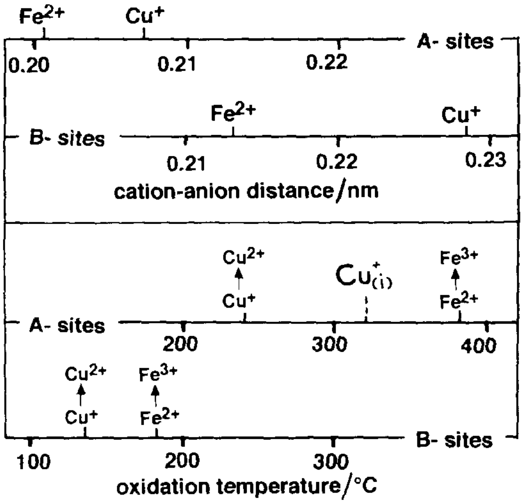

Fig. 6. Cation-oxygen distances and oxidation temperatures for copper and iron ions in dependence on their charge and location in the spinel lattice.

$Mo_xFe_{3-x}O_4$ or $V_xFe_{3-x}O_4$ ferrites [18,19]. In the present instance the oxidation temperature ranges from 130°C for Cu_B^+ to 270°C for Cu_A^+, but as Fe_B^{2+} ions oxidize at an intermediate temperature, the overlappings of each peak, in particular, those of Cu_B^+ and Fe_B^{2+} are important. The DTG selective oxidation method in isothermal conditions only allows separation of the Cu_A^+ oxidation peak (Fig. 3, curve c) and thus calculation from the peak area the α coefficient of Eq. (1). Therefore, since the oxidation temperatures of Cu^+ and Fe^{2+} ions on B-sites are too close to be distinguished by selective oxidation, it was considered of interest, with regard to the Fe-Cu-O phase diagram [20], to use TG analysis in varying the oxygen partial pressure since it has been found that Cu^+ ions do not oxidize at low oxygen pressure [16] whereas Fe^{2+} does. This feature is probably related to an oxidation mechanism that has strongly slowed down because of the decrease of the oxygen transport in the gas phase, directly dependent of PO_2.

A quantitative interpretation of these data leads to the evaluation of the amount of $Cu_B^+ + Cu_A^+$ ions initially present in the spinel lattice and thus to calculate the β coefficient of Eq. (1). The evolution of α and β coefficients versus copper content, together with the site occupancy fraction for Cu_B^+, Fe_B^{2+} and Cu_A^+ are shown in Fig. 7. The distribution parameters α and β indicate that from $x = 0.24$ Cu^+ ion on B-sites slighlty decreases with increasing x whereas Cu^+ ion on A-site continuously increases which confirms the assumption that Cu_A^+ ion has a definite tetrahedral site preference [21] so that for $x > 0.50$ the majority of Cu^+ ions would be present on A-sites.

As is shown in Fig. 4(a) the fourth peak at about 330°C can be evidenced for $x = 0.50$ from DTG and DSC curves. This peak which also occurs for quenched $CuFe_2O_4$ spinel (Fig. 2, curve c), leads reasonably to the consideration that $CuFe_2O_4$ has been reduced under air at high temperature, the loss of oxygen being accommodated as Cu^+ ions in interstitial positions rather that Fe^{2+} ions since it is more difficult to reduce iron than copper [16]. On the basis of the X-ray diagram and after an annealing at 400°C under inert atmosphere aiming at establishing the possibility of the presence of metallic copper in the over-reduced spinel, no lines characteristic of metallic copper can be detected from this pattern. Therefore, let us consider first what evidence there is for the possibility of interstitial ions associated with the spinel structure which is compatible with a small population of interstitial ions. The system $Cu_xFe_{3-x}O_4$ in the

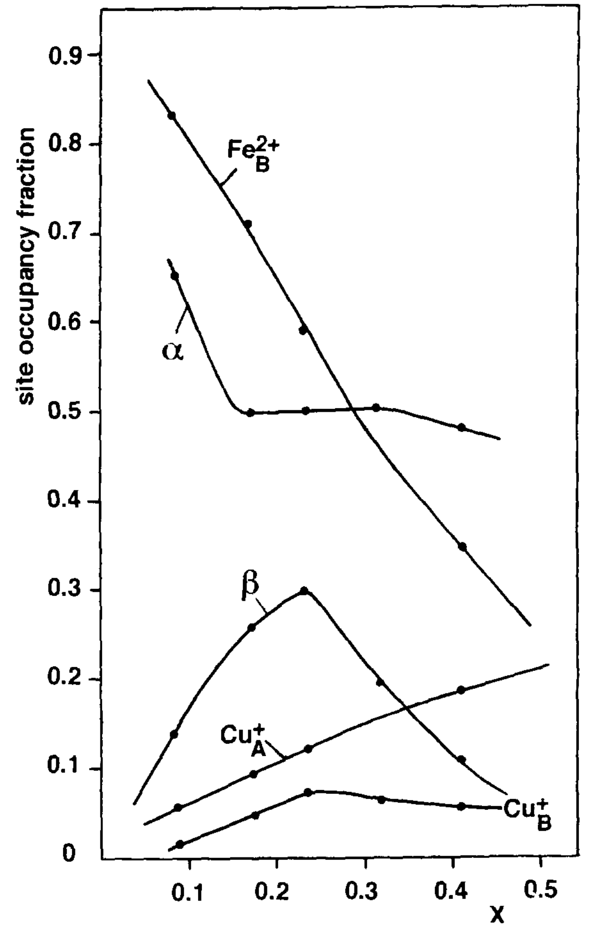

Fig. 7. Evolution of α and β coefficients (Eq. (1)) and site occupancy fraction for Cu^+ and Fe^{2+} at B-sites and Cu^+ at A-sites.

range $0.40 < x < 1$ which has been shown to contain, for stoichiometric phases, mixed valences $Cu^{2+/+}$ because of the reaction $Fe^{2+} + Cu^{2+} \rightarrow Fe^{3+} + Cu^+$ could also be slightly reduced during the experimental preparation procedure under a $N_2/H_2/H_2O$ gas mixture although provisions are made for control of the oxygen partial pressure and to maintain the powder in the spinel phase field at the stoichiometric composition. The existence of such over-reduced spinels can, among other considerations, explain the sharp increase of lattice parameter found for $x > 0.35$ (Fig. 1, curve b). Colombo et al. [16] were able to demonstrate convincingly that an increase of lattice parameter holds for over-reduced Fe_3O_4 spinel. Therefore, oxygen vacancies are excluded as main defects, because oxygen vacancies are considered to cause the lattice parameter to be low [1].

With this background, it is instructive to consider how the oxidation of Cu^+ and Fe^{2+} ions on B-sites, Cu^+ ions on A-sites and Cu^+ interstitial ions proceeds.

For a stoichiometric spinel of formula:

$$(M_m^{m+}, N_n^{n+}, \ldots)_A (P_p^{p+}, Q_q^{q+} \ldots)_B \, O_4^{2-} \tag{2}$$

$$\text{with}(m{+})m' + (n{+})n' + (p{+})p' + (q{+})q' + \ldots = 8$$

$$\text{and } m' + n' + \ldots = 1 \quad \text{and} \quad p' + q' + \ldots = 2$$

the generation of cation deficient spinels by oxidation proceeds via the incorporation of excess oxygen onto regular anionic sublattice sites. Since the number of cation ions remains fixed, the addition of oxygen ($\delta > 0$) generates cation vacancies that distribute themselves by diffusion [4]. For example, if we consider that the totality of M^{m+} oxidizes to $M^{(m+1)+}$ cations, the process may be schematically represented by the reaction:

$$m'M^{m+} + m'/4O_2 \rightarrow m'M^{(m+1)+} + m'/2O^{2-} + m'/8V_A + m'/4V_B \tag{3}$$

where V represents the vacancies in the Kröger and Vink notation [22].

From considerations involving mass and charge balance and from a writting formalism recently defined [23], one may represent the unit cell for four oxygen atom as:

$$(M_{\xi m'}^{m+}, N_{\xi n'}^{n+} \ {}_{\xi m'/8} \cdots)_A \, (P_{\xi p'}^{p+}, Q_{\xi q'}^{q+} \ {}_{\xi m'/4} \cdots)_B \, O_4^{2-} \tag{4}$$

with $\xi = 4/4 + m'/2$ and □ the vacancies.

For $x = 0.32$, the three oxidations proceed via the general reactions (5), (7) and (9) leading to the cation distributions (6), (8) and (10) where a distinction is made between cations and vacancies on A- and B-sites consistent with experimental observations [16], the vacancies are exclusively located on B-sites. Changes at each oxidation peak are explained by the following reactions:oxidation of Cu^+ ions on B-sites

$$Cu_B^+ + \tfrac{1}{8}Fe_B^{3+} + \tfrac{1}{4}O_2 \Rightarrow Cu_B^{2+} + \tfrac{1}{8}Fe_A^{3+} + \tfrac{3}{8}V_B + \tfrac{1}{2}O^{2-} \tag{5}$$

$$(\mathrm{Cu}^{+}_{0.159}\,\mathrm{Fe}^{3+}_{0.841})_A\,(\mathrm{Cu}^{2+}_{0.159}\,\mathrm{Fe}^{2+}_{0.452}\,\mathrm{Fe}^{3+}_{1.365\ 0.024})_B \cdot \mathrm{O}_4^{2-} \quad (6)$$

oxidation of Fe^{2+} ions on B-sites:

$$\mathrm{Fe}^{2+}_{\mathrm{B}} + \tfrac{1}{4}\mathrm{O}_2 \Rightarrow \tfrac{7}{8}\mathrm{Fe}^{3+}_{\mathrm{B}} + \tfrac{1}{8}\mathrm{Fe}^{3+}_{\mathrm{A}} + \tfrac{3}{8}V_B + \tfrac{1}{2}\mathrm{O}^{2-} \quad (7)$$

$$(\mathrm{Cu}^{+}_{0.15}\,\mathrm{Fe}^{3+}_{0.85})_A\,(\mathrm{Cu}^{2+}_{0.15}\,\mathrm{Fe}^{3+}_{1.665\ 0.185})_B\,\mathrm{O}_4^{2-} \quad (8)$$

oxidation of Cu^{+} ions on A-sites:

$$\mathrm{Cu}^{+}_{\mathrm{A}} + \tfrac{9}{8}\mathrm{Fe}^{3+}_{\mathrm{B}} + \tfrac{1}{4}\mathrm{O}_2 \Rightarrow \mathrm{Cu}^{2+}_{\mathrm{B}} + \tfrac{9}{8}\mathrm{Fe}^{3+}_{\mathrm{A}} + \tfrac{3}{8}V_B + \tfrac{1}{2}\mathrm{O}^{2-} \quad (9)$$

$$(\mathrm{Fe}^{3+})_A\,(\mathrm{Cu}^{2+}_{0.294}\,\mathrm{Fe}^{3+}_{1.468\ 0.0238})_B\,\mathrm{O}_4^{2-} \quad (10)$$

The formula of cation deficient spinels resulting from these three oxidations at maximum nonstoichiometry can be represented by:

$$(\mathrm{Fe}^{3+})_A\,(\mathrm{Cu}^{2+}_{8x/9-x}\,\mathrm{Fe}^{3+}_{15-7x/9-x\ 3(1-x)/9-x})_B\,\mathrm{O}_4^{2-} \quad (11)$$

The reduction reaction ($\delta < 0$) involves, from a stoichiometric spinel, the formation of cations in interstitial positions which may be represented as:

$$M^{m+} + \tfrac{3}{8}N^{n+} + \tfrac{1}{2}O^{2-} \rightarrow M^{(m-1)+} + \tfrac{3}{8}N^{n+}_{(i)} + \tfrac{1}{4}O_2 \quad (12)$$

with (i) denoting the interstitial sites.

The unit cell can be written:

$$(N^{n+}_{\xi/8}\,P^{p+}_{\xi/4})_i\,(M^{(m-1)}_{\xi m'},\,N^{n+}_{\xi(n'-1/8)})_A \cdot (P^{p+}_{\xi(p'-1/4)}\,Q^{q+}_{\xi q'}\ldots)_B\,O_4^{2-} \quad (13)$$

with $\xi = 4/4 - m'/2$.

In the case of the reduction reaction for quenched $\mathrm{CuFe_2O_4}$, the mechanism involves the formation of Cu^{+} interstitial, following oxygen loss, which may be written as:

$$\mathrm{Cu}^{2+} + \tfrac{1}{2}\mathrm{O}^{2-} \rightarrow \tfrac{5}{8}\mathrm{Cu}^{+} + \tfrac{3}{8}Cu^{+}_{(i)} + \tfrac{1}{4}\mathrm{O}_2 \quad (14)$$

with a corresponding cation distribution:

$$(\mathrm{Cu}^{+}_{3\delta/4-\delta})_i\,[\mathrm{Cu}^{+}_{5\delta/4-\delta}\,\mathrm{Cu}^{2+}_{4(1-2\delta)/4-\delta}\,\mathrm{Fe}^{3+}_{8/4-\delta}]\,\mathrm{O}_4^{2-} \quad (15)$$

If we consider that the Cu^{+} ion has a strong tetrahedral site preference, but the Cu^{2+} ion does not, the cation distribution between A and B-sites is given as:

$$(\mathrm{Cu}^{+}_{3\delta/4-\delta})_i\,[\mathrm{Cu}^{+}_{5\delta/4-\delta}\,\mathrm{Cu}^{2+}_{4b-8\delta b/4-\delta} \cdot \mathrm{Fe}^{3+}_{4-6\delta-4b+8\delta b/4-\delta})_A\,(\mathrm{Cu}^{2+}_{4-8\delta-4b+8\delta b/4-\delta} \cdot Fe^{3+}_{4+6\delta+4b-8\delta b/4-\delta})_B\,\mathrm{O}_4^{2-} \quad (16)$$

where b represents the Cu^{2+} ions content on the A-sites. In view of the strong octahedral sites preference of Cu^{2+} ions, b is assumed to be low, the same for Q samples which present a lower c/a ratio than that SC samples.

From the obtained mass gain value (0.063%), the number of interstitial Cu^{+} cation to be oxidized was found to be 0.007 which corresponds to $\delta = 0.01$. Regarding the experimentally observed oxidation temperature of the non-stoichiometric $\mathrm{CuFe_2O_4}$ spinel (> 300°C) we should point out that only copper ions are concerned with the reduction reaction. Given formula (15), Gleitzer et al. [13] have postulated for reduced $\mathrm{CuFe_2O_4}$ that the Cu^{+} ions could occupy interstitial sites as well as A-sites. Therefore, these authors assume that charge neutrality and electrostatic forces would stabilize about an A-site vacancy with a large Cu^{+}- ion cluster, Cu_8^{+}. In this case, half the Cu^{+} ions of the cluster $(\mathrm{Cu}_4^{+})_i$ occupy the four 16c octahedral sites neighboring the A-site vacancy, and half occupy the A sites $(\mathrm{Cu}_4^{+})_A$ that share octahedral-site faces with the Cu^{+} -occupied 16c sites. However, till now such clusters have not been observed.

If now we focus the discussion on the copper ferrites with $x > 0.35$, the reduction reaction which occurs during the treatment under $\mathrm{N_2/H_2/H_2O}$ involves additional reduced ions in the stoichiometric material via the following reactions:

$$2\mathrm{Fe}^{3+} + \tfrac{3}{4}N^{n+} + \mathrm{O}^{2-} \rightarrow 2\mathrm{Fe}^{2+} + \tfrac{3}{4}N^{n+}_{(i)} + \tfrac{1}{2}\mathrm{O}^{2-} \quad (17)$$

$$\mathrm{Fe}^{3+} + \mathrm{Cu}^{2+} + \tfrac{3}{4}N^{n+} + \mathrm{O}^{2-} \rightarrow \mathrm{Fe}^{2+} + \mathrm{Cu}^{+} + \tfrac{3}{4}N^{n+}_{(i)} + \tfrac{1}{2}\mathrm{O}^{2-} \quad (18)$$

$$2\mathrm{Cu}^{2+} + \tfrac{3}{4}N^{n+} + \mathrm{O}^{2-} \rightarrow 2\mathrm{Cu}^{+} + \tfrac{3}{4}N^{n+}_{(i)} + \tfrac{1}{2}\mathrm{O}^{2-} \quad (19)$$

These reduction reactions have been postulated because after reaction, on the one hand the oxidation peak of copper ions located on A-sites is spread over a large range of temperatures and on the other hand

Fe^{2+} peak area is greater than that expected if only the mole fraction of Fe^{2+} ions is deduced from formula (1). This suggests a possible contribution in the oxidation process of the reaction (18). However, if we consider that the Fe^{2+} ions provided by the reduction of iron from the ferric to the ferrous state cannot be located in interstitial sites (16c, 8a or 48f) but only in the 16d sites, the reduction reaction (18) becomes:

$$\mathrm{Fe}^{3+} + \mathrm{Cu}^{2+} + \mathrm{O}^{2-} \rightarrow \mathrm{Fe}^{2+} + \tfrac{5}{4}\mathrm{Cu}^{+} + \tfrac{3}{4}\mathrm{Cu}^{+}_{(i)} \cdot + \tfrac{1}{2}\mathrm{O}_2 \qquad (20)$$

Given reaction (20), reduction should create Cu^+ interstitial ions and we may expect Cu^+ ions to be similar to Li^+ ions in their ability to occupy the interstitial 16c sites.

Concerning the oxidation temperature of $Cu^+_{(i)}$ ions, it is observed that this temperature decreases with decreasing copper content; that is, when the number of Fe^{2+} ions increases. Thus it is thought that since the Fe^{2+} ions oxidize before the $Cu^+_{(i)}$ ions, a fraction of these ions, proportional to the number of cation vacancies generated from the oxidation of Fe^{2+} ions, has the possibility of migrating to the cation vacant site. This observation suggests that a part of additional Cu^+ ions can oxidize at a temperature similar to that of Cu^+_A ions (about 270°C), those remaining in the interstitial sites being oxidized at higher temperature (> 300°C). It must be mentioned, however, that thermogravimetry cannot meaningfully specify the location of $Cu^+_{(i)}$ ions in the different empty tetrahedral (8a, 48f) and octahedral (16c) sites.

In the present instance, if we disregard the iron and copper ion distribution between A and B-sites, a general chemical formula for reduced copper ferrospinels can be derived as follows:

$$(\mathrm{Cu}^{+}_{3\delta/4-\delta})_i\,[\mathrm{Cu}^{+}_{\delta+y/4-\delta}\,\mathrm{Cu}^{2+}_{4(x-\delta)-y/4-\delta} \cdot \mathrm{Fe}^{2+}_{4(\delta-x+1)-y/4-\delta}\,\mathrm{Fe}_{4(2-\delta)+y/4-\delta}]\,\mathrm{O}^{2-}_4 \qquad (21)$$

with $y = 4x(\alpha + \beta)$

The results indicate that for $x = 0.50$, the deviation from stoichiometry, δ, is 0.040 and $\alpha + \beta = 0.48$. Using the relation (21) and considering that Cu^{2+} cations occupy only B-sites, a cation distribution can be proposed:

$$(\mathrm{Cu}^{+}_{0.03})_i\,(\mathrm{Cu}^{+}_{0.210}\,\mathrm{Fe}^{3+}_{0.790})_A\,(\mathrm{Cu}^{+}_{0.042} \cdot \mathrm{Cu}^{2+}_{0.222}\,Fe^{2+}_{0.303}\,Fe^{3+}_{1.432})_B\,\mathrm{O}^{2-}_4 \qquad (22)$$

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