

Mossbauer Studies on Lithiated Magnetites, $\text{Li}_x\text{Fe}_3\text{O}_4$

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Lithium was inserted into the structure of magnetite ($Fd\bar{3}m$) by ceramic methods. Analysis of these lithiated magnetites, $\text{Li}_x\text{Fe}_3\text{O}_4$, by Mossbauer and x-ray diffraction techniques at room temperature indicated, for non-annealed materials and concentrations up to a value around $x=0.13$, an increase of the bulk material lattice parameter. For higher concentrations, a new disordered paramagnetic phase, LiFe_3O_4 ($Fm\bar{3}m$), appears due to the reduction and displacement of Fe^{3+} in tetrahedral sites into empty neighbour $16c$ sites. For annealed samples the phase LiFe_3O_4 becomes ordered and appears for all Lithium concentrations, increasing linearly with x in such way that when $x=1$ it is the only phase present. In both processes the hyperfine parameters of magnetite are not significantly affected. The paramagnetic phase was analysed by Mossbauer spectroscopy in terms of three doublets. It was observed that the electron hopping is affected for $x \geq 0.27$.

I. Introduction

Studies on the mobility of alkaline ions, and the possible modifications produced in the host structure, for several transition-metal oxides and sulfides that allow the insertion and/or extraction of these ions reversibly at room temperature have been performed with the objective of finding low cost materials for possible application as battery electrodes. The incentive of finding such materials has led some workers to insert lithium in planar compounds such as TiS_2 [1,2] and CoO_2 [3], for example. In TiS_2 where the anions S^{2-} form an hcp structure with the TiS_2 planes bound together by van der Waals forces, the insertion of Li leads to a compound of stoichiometry Li_xTiS_2 ($0 < x < 1$). In these compounds Li^+ and $\text{Ti}^{4+}/\text{Ti}^{3+}$ occupy alternate planes of octahedral coordination, and the lattice parameter c increases continuously with the Li concentration, consequently increasing the mobility of the lithium ions. A similar process occurs in the planar compound Li_xCoO_2 ($0 < x < 1$) where the anions O^{2-} form a ccp structure. As in the case of TiS_2 , Li^+ and $\text{Co}^{4+}/\text{Co}^{3+}$ occupy alternate planes of octahedral sites, and for small concentrations of lithium vacancies in Li_xCoO_2 an increase of the lattice parameter

c is observed that has as a consequence a corresponding increase of the lithium mobility in the host structure. These studies show that Li^+ can move along a planar structure through the spaces formed by octahedral interstices that share the same edges^[3]; they also show the stability of these ions in sites of octahedral symmetry. These results have led to an interest in the study of the Li^+ mobility in a three dimensional structure like spinels because this structure presents channels in the three dimensions where the lithium can move. The compounds with the spinel structure have the general formula AB_2X_4 , where A and B are positive cations and X is a divalent anion. This structure is cubic closed packed with 96 interstices divided into 64 tetrahedral sites and 32 octahedral sites. Of the tetrahedral sites only 8 are occupied (8a) and of the octahedral sites, sixteen are occupied (16d) and each occupied tetrahedral site has four empty $16c$ octahedral sites as nearest neighbours. In studies of the insertion and/or extraction of lithium in the spinel structure at room temperature, particular attention has been paid to the following spinels: Fe_3O_4 [4], Mn_3O_4 [5], Co_3O_4 [6], LiMn_2O_4 [5,7,8,9], LiTi_2O_4 [10,11,12] and LiV_2O_4 [11]. Thackeray et al., in 1982 [4], employing chemical and

electrochemical methods, inserted lithium at room temperature into the structure of magnetite obtaining a compound with stoichiometry $\text{Li}_x\text{Fe}_3\text{O}_4$. Their analysis by x-ray diffraction showed that Li^+ ions, when inserted into the host structure, occupy empty octahedral sites (16c sites). They also proposed that above a given concentration ($x \approx 0.1$), the lithium ions induce and displace cooperatively the Fe^{3+} in tetrahedral sites (8a sites) to empty neighbour octahedral 16c sites, generating a partially ordered phase LiFe_3O_4 with NaCl structure (rocksalt). The important results along this process of lithiation is that the framework of the spinel structure, (Fe_2O_4), remains intact, and the iron ions displaced to interstitial sites block the lithium mobility in the magnetite.

To investigate in more detail and from a different point of view what happens when lithium is inserted into magnetite, we prepared a series of lithiated magnetites using ceramic methods in order to compare the results with those obtained with the methods above indicated. In this work it is intended essentially to identify and analyse, using Mossbauer spectroscopy and x-ray diffraction, the phases that are developed during the process and the influence of lithium in the mechanisms of electron hopping that occurs in the magnetite.

II. Experimental

In this work seven samples of lithiated magnetite, $\text{Li}_x\text{Fe}_3\text{O}_4$, were prepared (with $x = 0.05, 0.08, 0.10, 0.13, 0.27, 0.43$ and 0.60) by mixing stoichiometric P.A. grade quantities of lithium carbonate (Li_2CO_3) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). The materials, after being mixed and finely ground, were fired at 750°C in the presence of air during 8h to allow all Li to react, and then cooled at a rate of $4^\circ\text{C}/\text{min}$ in order to homogenize the solid solution and allow lithium to diffuse into the sample. The resulting material was a homogeneous mixture of lithium ferrite and hematite^[13]. Magnetite was produced by holding this mixture at 450°C in hydrogen atmosphere for a time of one hour per gram of sample and then cooling it at a rate of $0.5^\circ\text{C}/\text{min}$ ^[14]. The samples were then ground and the process repeated until

all traces of hematite and/or lithium ferrite had disappeared. The completeness of the reaction was monitored by x-ray diffraction. In a second pass, the samples were annealed in argon atmosphere at 780°C for one hour and then cooled at a rate of $2^\circ\text{C}/\text{min}$.

All samples were analyzed by x-rays at the end of both first and second steps; the results for the lattice parameters are shown in Fig. 1. There it can be seen that for the non-annealed materials up to $x \approx 0.13$ the introduction of lithium in the structure leads to an increase of the lattice parameter^[13]. For $x \geq 0.27$ the x-ray diffractograms show two miscible phases: the magnetite (M-phase) and a lithiated phase (L-phase) whose relative contribution increases with the concentration of lithium. For the annealed samples, the x-ray shows a split of $\text{Li}_x\text{Fe}_3\text{O}_4$ into two phases for all values of x , that is,

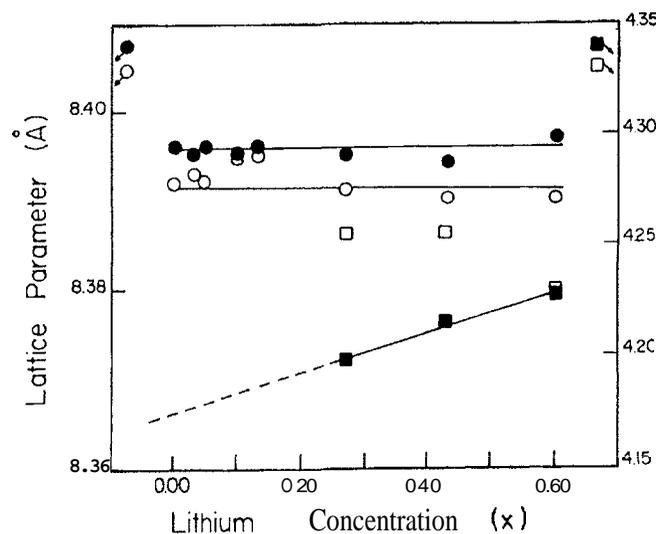
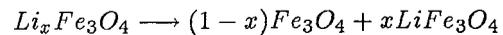


Figure 1: The behaviour of the lattice parameter as a function of the Li annealed (black symbols) and non-annealed (open symbols) samples. The circles represent the M-phase (left scale) and the squares the L-phase (right scale).

Fig.2 shows the relative contribution of magnetite (M-phase) as seen from x-ray diffraction as a function of concentration. There it can be observed that for the non-annealed samples x-ray do not detect the lithiated phase until $x=0.13$ while for annealed samples it is observed for all concentrations.

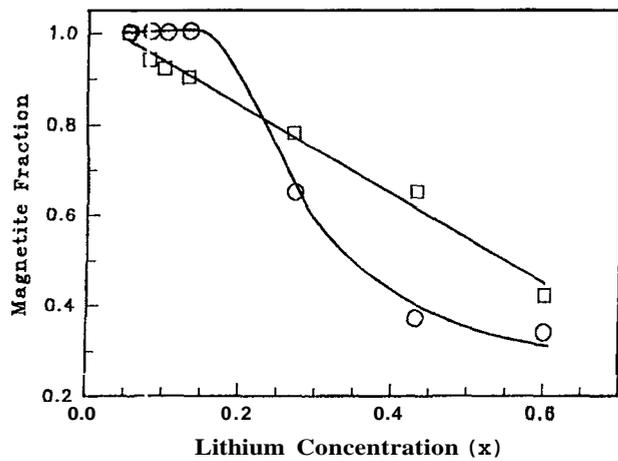


Figure 2: The relative contribution of the M-phase for non-annealed (o) and annealed (O) samples as a function of the concentration obtained by x-ray diffraction.

The Mossbauer experiments were done with a $^{57}\text{Co}/\text{Rh}$ source and a conventional constant-acceleration spectrometer (Wissel). The samples, both as-cast and annealed, were measured at room temperature. In Fig.3 the spectra of both series are shown. This figure also shows that the two phases are always present in the annealed materials. The measured values for the hyperfine parameters of the M-phase remain about the same for all concentrations studied. In order to allow a better comprehension of the L-phase (paramagnetic), the annealed samples were also measured with lower maximum velocity in such way that only the internal peaks of the magnetite as well as the paramagnetic phase appeared in the spectrum. These spectra for some of the annealed samples are shown in Fig.4.

All spectra were analyzed by least square methods with the following conditions: the normal spectra (high velocity) was fitted considering two sextets for the magnetite and two paramagnetic doublets; the low velocity spectra were fitted under the following assumptions: 1) the two largest doublets belong to the magnetite; 2) there are three paramagnetic sites in the lithiated phase. The last condition comes from the following assumptions: i) $\text{Fe}^{2.5+}$ is always present; ii) the electron hopping between B-sites may be partially interrupted, creating a pair of non-interacting $(\text{Fe}^{3+})^B$ and $(\text{Fe}^{2+})^B$; and iii) $(\text{Fe}^{2+})^{16c}$ and $(\text{Fe}^{2+})^{16d}$ have about the same

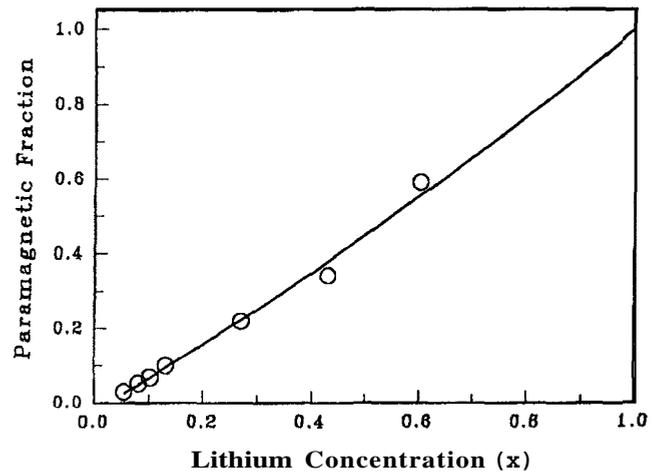


Figure 3: The Mossbauer spectra of the samples at room temperature.

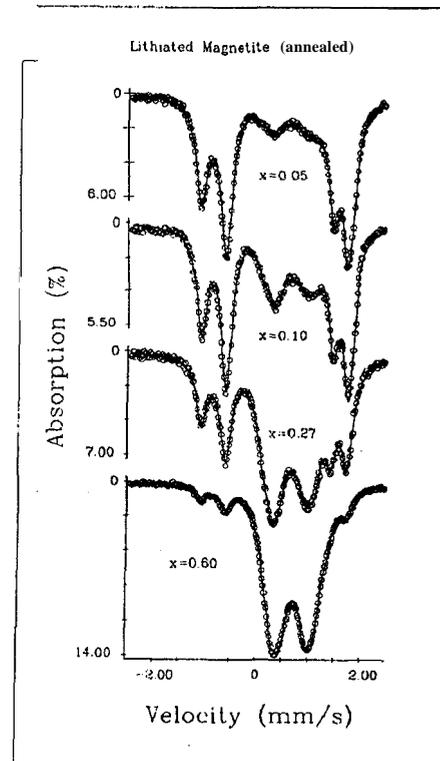


Figure 4: Low velocity spectra for some annealed samples.

values for quadrupole interaction and isomer-shifts.

III. Analysis and Discussion

a) Non-annealed Samples

The results of Mössbauer spectroscopy show that for low concentrations ($x < 0.10$) the insertion of Li^+ does not cause any perceptible changes in the Mössbauer spectrum of the magnetite. X-rays indicate for $x \leq 0.13$ an increase of the lattice parameter of the bulk material with x , suggesting the existence of a cation-deficient magnetite and leading to a lower lattice parameter than in the annealed sample, with Li^+ entering into interstitial positions. For concentrations above $x=0.10$ a paramagnetic phase begins to appear in the Mössbauer spectrum, indicating that the reduction of some Fe^{3+} ions may be occurring. In Fig. 1 it can be seen that for $x \geq 0.27$ the material is clearly split into two phases, the magnetite phase $\text{Fd}3\text{m}$ (M-phase) and a lithiated phase (L-phase) indexed according to the spacial group $\text{Fm}3\text{m}$ (rocksalt). This result is also confirmed by Mössbauer experiments where, for $x=0.27$, the two phases appear to contribute equally to the spectrum. A possible interpretation for the absence of L-phase in the x-ray diffractograms for low concentrations is the absence of long-range order. For these concentrations the insertion of Li^+ does not increase sufficiently the lattice energy to alter the structure of the magnetite and the only result is an increase of the lattice parameter and some internal charge compensation in the lattice. For concentrations above a given value, around $x=0.13$, the lattice energy is sufficiently high to reduce and displace iron ions in tetrahedral sites into octahedral neighbour sites leading to the corresponding splitting of the lithiated magnetite into two phases. This result is confirmed by both Mössbauer and x-rays. For all measured Mössbauer spectra, the hyperfine parameters of the magnetite remain practically constant. An extrapolation of our results for non-annealed compounds, Fig.2, seems to indicate that for $x=1$ the M-phase should be present. It is interesting to observe that in Mössbauer results for $x=2$, published in the literature^[15] for lithiated magnetite obtained by electro-chemical methods,

the M-phase is still present. This can be attributed to the structural disorder in the material. The results for non-annealed materials are essentially the same as those obtained from electro-chemical methods^[4], showing that the effect of the insertion of lithium in depends on the way it is inserted.

b) Annealed Samples

For the annealed samples it is clear from Fig.2 that the L-phase is always present. The process of annealing allows the material to reach an ordered state of lower energy with the corresponding formation of the paramagnetic lithiated phase (L-phase) identified in both Mössbauer and x-rays analysis, for all concentrations. Fig. 1 shows that, when compared with the as-cast materials, in this process there is an increase of the lattice parameter of the M-phase, while that of L-phase decreases. This can be attributed to the elimination of cation deficient sites in the magnetite and to the rearrangement of Li^+ in the cell due to the annealing process. It can also be seen in Fig. 1 that the lattice parameter of magnetite remains constant while the L-phase follows a kind of Vegard's law. As the L-phase ($\text{Fm}3\text{m}$) is identical with the M-phase, except for the fact that all 16c octahedral sites are occupied in a pure the L-phase (while the 8a tetrahedral sites are empty), it is easy to understand that the appearance of the L-phase in these materials comes from the displacement and reduction of Fe^{3+} in A-sites of the magnetite to neighbour 16c empty sites of the unit cell, in accordance with the results of Ref. [4].

As the magnetic order in magnetite at room temperature is essentially due to the strong superexchange interaction between A and B sites, this displacement has as a result the consequent destruction of the local magnetic order, leading to the appearance of paramagnetic sites as seen by Mossbauer spectroscopy. In Fig.5 it is shown the relative contribution of the paramagnetic phase as a function of the Li concentration. The extrapolation of these results for $x=1$ indicates that at this limit all M-phase would have completely disappeared and we should have only the paramagnetic compound LiFe_3O_4 . This prevision is essentially the same

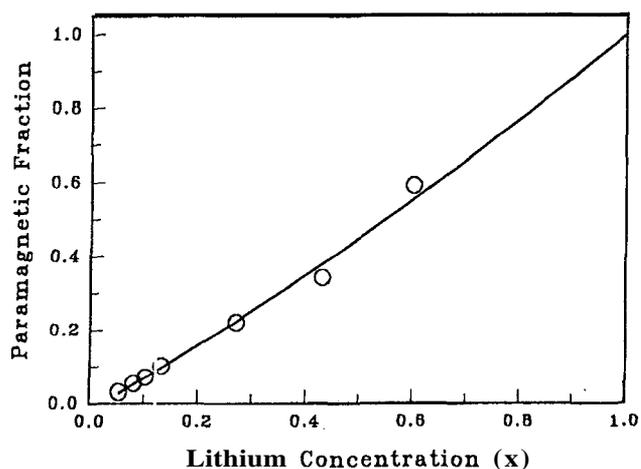


Figure 5: Relative contribution of the L-phase (paramagnetic) obtained from the Mossbauer spectra in low velocity.

as that from x-rays diffraction, Fig.2^[16]. It was also observed that for $x \geq 0.27$ the ratio between Fe^{3+} and $\text{Fe}^{2.5+}$ in the low velocity spectrum of magnetite begins to increase suggesting an interruption of the electron-hopping between the octahedral sites 16d.

IV. Conclusions

It was shown with x-ray and Mossbauer spectroscopy that when lithium enters interstitially into the unit cell of magnetite (spinel) occupying octahedral vacant 16c sites, it displaces and reduces Fe^{3+} ions originally present in sites 16d, generating new planes of reflection corresponding to the phase $\text{Fm}\bar{3}\text{m}$. This displacement breaks the superexchange interaction path between A and B sites and leads to the appearance of paramagnetic sites at room temperature. It was shown that the insertion of lithium by ceramic methods without annealing, as well as electro-chemical methods, leads essentially to the same results. The results from both Mössbauer spectroscopy and x-rays experiments in the annealed materials indicate that the L-phase increases linearly with the lithium concentration pointing in the limit $x=1$ to the paramagnetic compound LiFe_3O_4 . The Mossbauer analysis of the relative intensities of the doublets of magnetite in annealed material recorded in low velocity, shows evidences that the lithiation mechanism affects somewhat the electron hopping between B sites, which is evidenced by the

existence of sites of Fe^{3+} in the fitted paramagnetic spectra^[17].

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