

STUDY OF FERRITE BY RESONANT NUCLEAR SCATTERING MANGANES- IRON : NOTSTOICHIOMETRIC

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Abstract

The Resonant Nuclear Scattering has revealed the directional order that forms in the spinelferrites due to anisotropic distribution of Fe^{2+} and Fe^{3+} to the local direction of magnetization. We undertook to conduct a study on ferrites of composition: $M_{n_{1-\alpha}}^{2+}Fe_{\alpha}^{2+}[M_{n_{\alpha}}^{2+}Fe_{2-\alpha}^{3+}] \diamond_{\alpha} O_4$; $\diamond =$ vacancies, $0 < \alpha \leq 0.2$

These compounds are then called lacunar spinel's. Generally the gaps are located in the octahedral sites, however their presence in tetrahedral sites is reported. For example, the oxidation of Fe_3O_4 magnetite leads to the formation of $\gamma-Fe_2O_3$ and to the appearance of cationic vacancies according to the following charge equilibrium:

$3 Fe^{2+} \rightarrow 2 Fe^{3+}$. The spectra were made on two kinds of samples: quenched and slowly cooled at different temperatures. The results show that it is possible to distinguish at least three sites according to the values of α : an octahedral site (O) occupied by the Fe^{3+} and Mn^{2+} ions, which will be designated by $(Fe^{3+})_O$, a tetrahedral site (T) or $(Fe^{2+})_T$, and a tetrahedral site (T) or $(Fe^{3+})_T$. The variation of intensity of the octahedral site according to α , and the differences of variation according to the cooling conditions suggest the existence of a partial order among the nearest neighbours of the site $(Fe^{3+})_O$ of an ion $(Fe^{3+})_T$, which will make good account of the directional order.

Results

Resonant Nuclear Scattering spectra were performed on ferrites characterized by X-ray Debye-Scherrer camera with iron K_{α} radiation, the composition of the samples was determined by scan chemical and obeys the formula $M_{n_{1-\alpha}}^{2+}Fe_{\alpha}^{2+}[M_{n_{\alpha}}^{2+}Fe_{2-\alpha}^{3+}] \diamond_{\alpha} O_4$; $\alpha < 0.2$.

The values of the three hyperfine parameters H, δ , Δ does not vary at a given temperature as a function of α . Their values according to temperature are given in Tables (1), (2) and (3).

1- The intensities of the $(Fe^{3+})_O$ and $(Fe^{2+})_T$ sites vary with α independently of the treatment undergone by the material at $T = 300K$, where an increase in $(Fe^{3+})_O$ ions accompanied by a decrease in the cations $(Fe^{2+})_T$. (see Figure.1).

2 - The intensities of sites $(Fe^{3+})_T$ and $(Fe^{2+})_T$ vary with α independently of the treatment undergone by the material whatever the temperature, while this is not the case for the other intensities of tetrahedral sites to 300 K. (see Figure. 2). These behavioral differences disappear at 173 K (see Figure. 3).

3- If the change in the intensity of the site $(Fe^{3+})_O$ with α is not affected by the temperature change, that of the site $(Fe^{3+})_T$ is more important than 173 K to 300 K.

On the other hand the intensities according to the total amount of iron present in the sample varies with α as follows: (see Figure. 1)

4 - The decrease of the intensity with α in site $(Fe^{3+})_T$ seems independent of the temperature, while its increase with α is transformed to 173K in a decrease reflecting a change affecting the site $(Fe^{3+})_O$.

Site	δ (mm/s)		
	80 K	173 K	300 K
$(Fe^{2+})_T$	0.29 ± 0.02	0.26 ± 0.02	0.22 ± 0.02
$(Fe^{3+})_T$	0.48 ± 0.02	0.44 ± 0.02	0.40 ± 0.02
$(Fe^{3+})_O$	0.90 ± 0.02	0.81 ± 0.02	0.84 ± 0.02

Site	Δ (mm/s)		
	80 K	173 K	300 K
$(Fe^{2+})_T$	-0.01 ± 0.02	-0.02 ± 0.02	-0.01 ± 0.02
$(Fe^{3+})_T$	-0.01 ± 0.01	-0.02 ± 0.02	-0.01 ± 0.01
$(Fe^{3+})_O$	0.30 ± 0.02	0.20 ± 0.15	0.15 ± 0.15

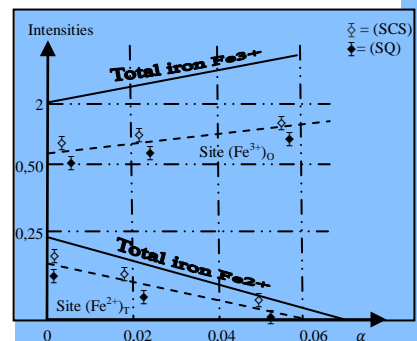


Figure (1): Intensities (normalized to the total quantity of iron) of sites $(Fe^{3+})_O$ and $(Fe^{2+})_T$ at 300 K.

Site	H (T)		
	80 K	173 K	300 K
$(Fe^{2+})_T$	512 ± 1.05	507 ± 1.80	497 ± 2.00
$(Fe^{3+})_T$	549 ± 1.06	546 ± 1.80	530 ± 2.00
$(Fe^{3+})_O$	525 ± 2.04	512 ± 3.00	489 ± 3.00

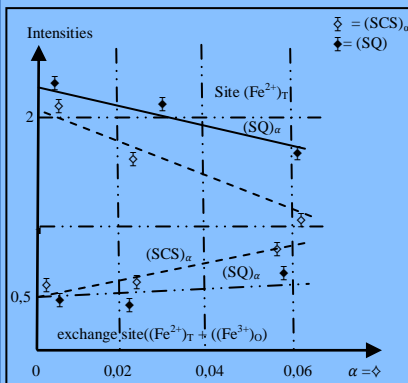


Figure (2): Intensities (normalized to the total quantity of iron) of sites $(Fe^{3+})_O$, $(Fe^{2+})_T$ and $(Fe^{3+})_T$ at 300 K.

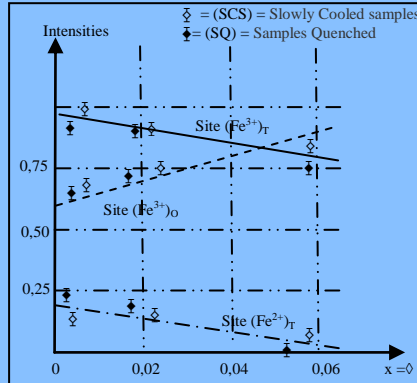


Figure (3): Intensities (normalized to the total quantity of iron) of sites $(Fe^{3+})_O$, $(Fe^{2+})_T$ and $(Fe^{3+})_T$ at 173 K.

Conclusion

We have could highlight by Resonant Nuclear Scattering the electronic exchange $Fe^{2+} \leftrightarrow Fe^{3+}$ by its partial blockade obtained at 80 K. It is expected to make a spectrum at about 4K where the electronic exchange to be completely blocked. The rate of increasing gaps favours the rearrangement ionic therefore directional order. In addition we observe by Resonant Nuclear $Fe^{3+} \leftrightarrow Fe^{2+}$ content in when Scattering a decrease of the electronic exchange the vacancies increases for temperatures lower than 300 K.

This is in accordance with results previously obtained on magnetite¹¹, and with other results obtained by some authors on irradiated ferrites.

Discussion

the vacancies tend to block the exchange Fe^{3+} , Fe^{2+} in tetrahedral site (T) at temperature 173K and in proportion to the rate vacancies. Furthermore at 77 K there is a significant decrease in the intensity of exchange between ions of sites (O) and (T), which corresponds to a partial blockage of the electronic exchange between Fe^{2+} and Fe^{3+} . The decrease in the intensity of the site $(Fe^{3+})_T$ with x whatever the temperature, seems to indicate that it occurs at the octahedral sites of increasing ionic rearrangements with content in vacancies at the temperature 300 K. These rearrangements are also function of the constitution of the material, from which we can remark that it is the quenched material that admits the fewest rearrangements, in view of the phenomenon of rearrangement existing between 300 and 400°C was cancelled remains that only to room temperature.