

## MOSSBAUER SPECTROSCOPY OF Ni-FERRITE AND NON-STOICHIOMETRIC Ni-Zn FERRITES

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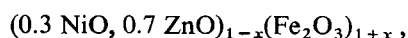
**Résumé.** — Les spectres d'absorption Mössbauer du ferrite de nickel et de ferrites Ni-Zn non-stoichiométriques, dans les compositions  $(0,3 \text{ NiO} \cdot 0,7 \text{ ZnO})_{1-x}(\text{Fe}_2\text{O}_3)_{1+x}$ ,  $x = 0$  et  $x = 0,02$ , ont été obtenus à la température ambiante et à 77 K. Pour le ferrite de Ni, les champs hyperfins associés aux ions ferriques dans les sites octaédriques et tétraédriques ont été résolus, pour les deux températures. Les intensités relatives de ces spectres présentent un comportement particulier en fonction de la température. Dans le cas des ferrites Ni-Zn non-stoichiométriques, les champs hyperfins n'ont pas été résolus. Cependant, ces spectres présentent des caractéristiques différentes, ce qui montre que, même pour des petits écarts par rapport à la composition stoechiométrique, les changements structuraux sont importants.

**Abstract.** — The Mössbauer absorption spectra of Ni-ferrite and non-stoichiometric Ni-Zn ferrites in the compositions  $(0.3 \text{ NiO} \cdot 0.7 \text{ ZnO})_{1-x}(\text{Fe}_2\text{O}_3)_{1+x}$ ,  $x = 0$ ,  $x = 0.02$ , were obtained at room temperature and 77 K. For Ni-ferrite, the hyperfine fields associated to the iron nuclei at the octahedral and tetrahedral sites were resolved, at both temperatures. The relative intensities of these spectra presented a peculiar behavior in temperature. In the case of non-stoichiometric Ni-Zn ferrites, a broadening in the lines did not allow the hyperfine fields to be resolved. However, the Mössbauer spectra presented different features, showing that even for small deviations from stoichiometry, the structural changes are important.

**1. Introduction.** — The behavior of the magnetic properties of non-stoichiometric Ni-Zn ferrites has been interpreted [1] on a qualitative basis. However, the changes in the ionic structures have not been established. These changes are important since for small deviations from stoichiometry, and taking into account the contribution of the variations in granular structure due to non-stoichiometry, the variations of initial susceptibility are near six times.

Mössbauer spectroscopy provides a powerful method for the study of ionic structures. This technique leads to a direct measurement of the hyperfine fields in solids. In this paper, we present some preliminary results on the study of Ni and Ni-Zn ferrites by using Mössbauer spectroscopy, in order to relate the magnetic properties to the changes of the ionic structure, as a consequence of the deviations from stoichiometry.

**2. Experimental results.** — The samples were prepared by the normal ceramic method from reagent grade oxides. Non-stoichiometric Ni-Zn ferrites were prepared by varying the relative content of divalent and trivalent oxides in the initial mixture of oxides, before sintering, accordingly to the formula :



with

$$- 0.02 \leq x \leq 0.02 .$$

The samples were sintered at 1 180 °C in an oxidant atmosphere ( $\text{O}_2$  100 %, 1 atm). The magnetic properties and lattice parameter of these samples presented a systematic behavior [1]. The Mössbauer spectra were obtained with a  $^{57}\text{Fe}$  source, at room temperature and 77 K.

The Mössbauer spectra of Ni-ferrite at room temperature and 77 K are shown in figure 1. Two superimposed hyperfine fields are associated to the iron nuclei at the tetrahedral (A) sites and octahedral (B) sites. The values obtained,  $H_A = 507$  kOe and  $H_B = 543$  kOe

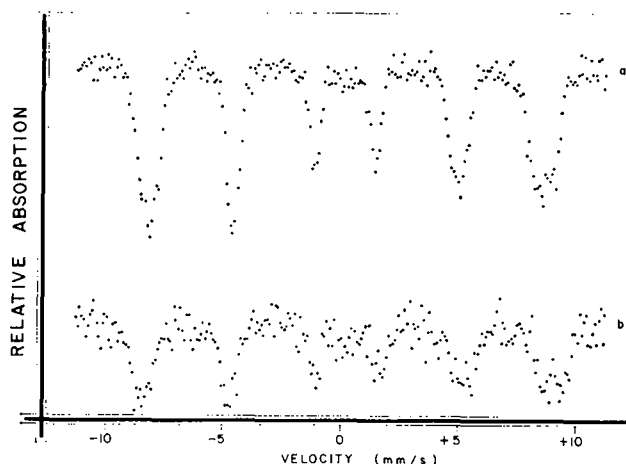


FIG. 1. — Mössbauer absorption spectra of Ni-ferrite: a) At room temperature. b) t 77 K.

for room temperature, and  $H_A = 525$  kOe and  $H_B = 560$  kOe for 77 K, are in good agreement with those reported [3] by other authors. However the relative intensities of the Mössbauer peaks of the two superimposed spectra presented a peculiar behavior. At room temperature, the ratio  $I_B/I_A$  is around 0.3; at low temperature (77 K), the relative intensities have a very similar value, figure 1,  $I_B/I_A \approx 1$ . These facts can be interpreted on the basis of a different thermal dependence of the  $f_A$  and  $f_B$  recoilless fractions [2].

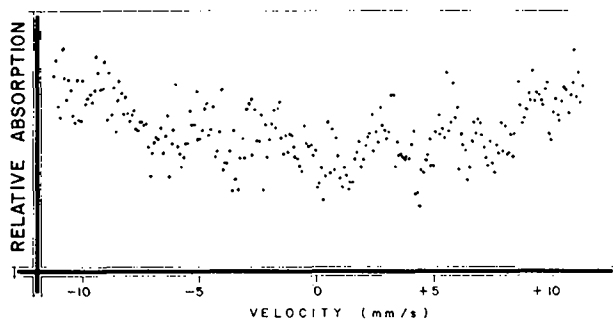


Fig. 2. — Mössbauer absorption spectrum of  $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$  ferrite at 77 K, ( $x = 0$ ).

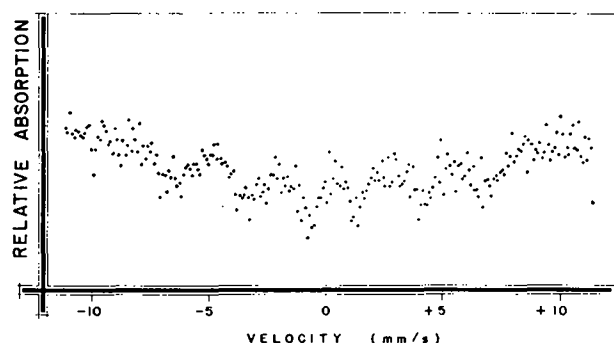


Fig. 3. — Mössbauer spectrum of non-stoichiometric  $(0.3 \text{ NiO}, 0.7 \text{ ZnO})_{1-x} (\text{Fe}_2\text{O}_3)_{1+x}$  ferrite,  $x = 0.02$ , at 77 K.

The Mössbauer spectra of two Ni-Zn ferrites with  $x = 0$  and  $x = 0.02$ , at 77 K, are presented in figures 2 and 3. These spectra show an important line broadening, similar to that reported by other authors [3] for stoichiometric Ni-Zn ferrites. It appears that although the deviation from stoichiometry is small, these spectra are different, and confirm the importance of the deviations from stoichiometry on the ionic structure. The average hyperfine fields obtained are  $H = 427$  kOe for  $x = 0$  and  $H = 410$  kOe for  $x = 0.02$ ; these values are considerably lower than those obtained for Ni-ferrite. These results show the complexity of the problem.

**3. Conclusions.** — In order to explain the different ionic structures produced by the deviations from stoichiometry by using Mössbauer spectroscopy, a very systematic study, is necessary starting from the simpler ferrites. Even for the latter, a comparison between the Ni-ferrite spectra herein reported with others [4, 5] shows small differences. These differences could be explained by taking into account small differences in the preparation technology (sintering temperature and atmosphere, impurities, etc). It seems that it is necessary to specify the conditions during samples preparation, in order to obtain comparative results; to confirm these facts, we have entreprised a systematic study of the influence of technological parameters on the Mössbauer spectra. On the other hand, the results concerning the thermal behavior of the  $I_B/I_A$  intensities ratio, present similar characteristics with those obtained by Sawatzky *et al.* [5, 6], in  $\text{Fe}_3\text{O}_4$ , YIG and  $\text{NiFe}_2\text{O}_4$ . The value of  $I_B/I_A$  reported on the former at 106 K is very near to that obtained by us at 77 K. Finally, a study of the influence of non-stoichiometry on the ionic structure of Ni-ferrite seems more accessible than in Ni-Zn ferrite, where the line broadening does not allow a clear resolution of the two superimposed fields. We have entreprised such a study.

### References

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