

STUDY BY MÖSSBAUER SPECTROSCOPY OF NEW SPINEL COMPOUNDS CONTAINING Fe³⁺ AND Sb⁵⁺ IONS

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Résumé.- Nous avons étudié par spectroscopie Mössbauer du ⁵⁷Fe, de nouveaux composés contenant des ions Fe³⁺ et Sb⁵⁺ et dérivant de la structure spinelle. Deux types de structures cristallographiques existent : cubique et orthorhombique, deux types de spectres Mössbauer y correspondent. Dans les composés cubiques, les ions Fe³⁺ occupent les sites B; dans les orthorhombiques, ils occupent les sites A et B dans le rapport de population 2/1. Nous donnons aussi des informations magnétiques déduites des spectres Mössbauer.

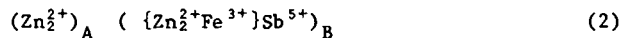
Abstract.- New compounds with Fe³⁺ and Sb⁵⁺ ions deriving from the spinel structure are studied by Mössbauer spectroscopy on ⁵⁷Fe. Two kinds of crystallographic structures cubic and orthorhombic exist for these compounds and two kinds of Mössbauer spectra are observed. In the cubic compounds, Fe³⁺ ions occupy B sites; in the orthorhombic one, they occupy A and B sites in the population ratio 2/1. Magnetic informations are also given from the Mössbauer spectra.

1. Introduction.- We have studied by Mössbauer spectroscopy the compounds with chemical formula $Y_4^{2+} Fe^{3+} Sb^{5+} O_8$ (1) where Y²⁺ is one or several of the following ions; Mg²⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺. Table I gives the list.

Two kinds of crystallographic structures appear in this series. The first one is cubic like the spinel structure, with or without an order 1/3 on the octahedral (B) sites. This is the case for the compounds with Zn²⁺ (first part of table I). The second one is orthorhombic with a triple unit cell deriving from the spinel. It is the case of Mg₄FeSbO₈ and the compounds of the second part of table I. No details are known about that structure, except that an order 2/1 probably exists on the tetrahedral sites (A).

The question was : where are situated the Fe³⁺ ions in these two structures ?

According to the usual sites occupations in spinels, we expected for Zn₄FeSbO₈ (cubic)



and for Mg₄FeSbO₈ (orthorhombic)



2. Room temperature Mössbauer spectra.- At room temperature, two kinds of Mössbauer spectra are observed (figure 1) corresponding to both kinds of crystallographic structures.

For the cubic compounds (figure 1.a), one symmetric

cal doublet appears. The isomer shifts reported in table I are characteristic of Fe³⁺ ions in B sites of the spinel structure /1/ as expected in distribution (2).

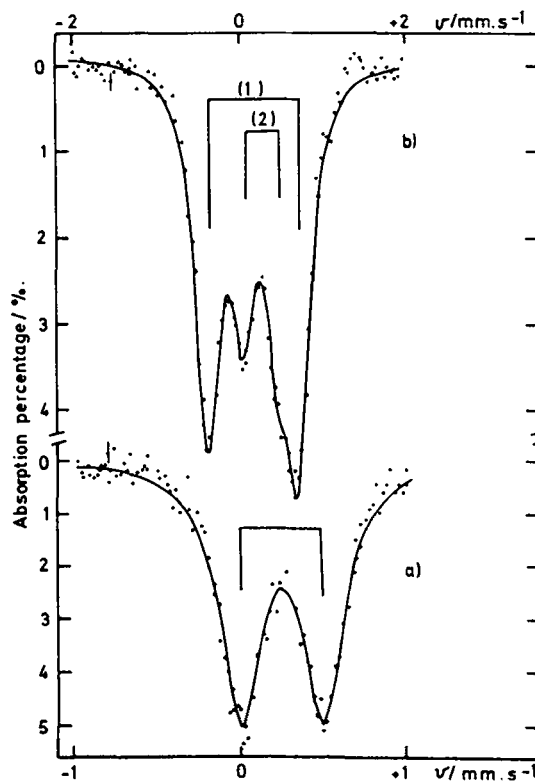


Fig. 1 : Room temperature Mössbauer spectra of (a) Zn₄FeSbO₈ (b) Ni₃CoFeSbO₈. The solid lines are the results of least-squares fits.

Table I

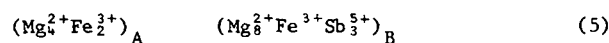
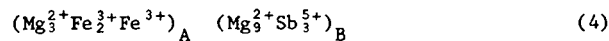
| Compound | Site I | | Site II | | T_c (K) | H_{max} (kOe) |
|---------------------------|---------------------|-------------------|---------------------|-------------------|----------------------|-----------------|
| | ϵ_1 (mm/s) | δ_1 (mm/s) | ϵ_2 (mm/s) | δ_2 (mm/s) | | |
| Zn_4FeSbO_8 (SC) | | | 0.50 | 0.32 | ord. $T < 4$ K | 450 |
| Zn_4FeSbO_8 (Q.1300) | | | 0.61 | 0.32 | not magn. at 77 K | |
| $Zn_2Co_2FeSbO_8$ | | | 0.62 | 0.33 | | |
| $Zn_2Cu_2FeSbO_8$ | | | 0.59 | 0.32 | | |
| Mg_4FeSbO_8 | 1.11 | 0.25 | 0.45 | 0.35 | | |
| $Mg_3CoFeSbO_8$ | 1.04 | 0.22 | 0.44 | 0.34 | | |
| $Mg_3NiFeSbO_8$ | 1.09 | 0.22 | 0.43 | 0.33 | | |
| $Mg_2Ni_2FeSbO_8$ | 1.00 | 0.22 | 0.41 | 0.32 | 190 \pm 5 | 390 |
| $MgNi_3FeSbO_8$ | 1.10 | 0.24 | 0.41 | 0.33 | 175 \pm 10 | 450 |
| $Ni_3CoFeSbO_8$ | 1.09 | 0.23 | 0.42 | 0.33 | 230 | 450 |
| Co_4FeSbO_8 | 0.87 | 0.23 | 0.35 | 0.30 | 210 | 480 |

SC=slow cooling ± 0.01 ± 0.02
Q.T=quenched ± 0.01 ± 0.02
from $T^\circ C$ \overline{Fe} . Fe \overline{Fe} . Fe

The quadrupole couplings are larger than the one observed in usual spinels /1/ but may be due to the presence of the antimony atoms.

The spectra of the orthorhombic compounds (figure 1.b) are the result of the superposition of two doublets with the hyperfine parameters given in table I. The intensity ratio, site I/site II, of these two doublets is 2/1. Thus, we conclude that we have two kinds of Fe^{3+} ions in the population ratio 2/1; but we do not know yet on which sites, they are situated.

In a chemical formula triple of (3), we have two possibilities



Distribution (4) is in agreement with the expected one (3) with two different A sites for Fe^{3+} ions, but (5) is in agreement with an order 2/1 on A sites predicted by X-rays measurements.

From the hyperfine parameters, we are able to choose between (4) and (5). In table I, the differences $\delta_2 - \delta_1$ are around 0.1 mm.s^{-1} , which is very close to the difference between the isomer shifts on B and A sites of classical spinels /2/. This is in favour of (5).

Another argument is given by the substitution of Cr^{3+} instead of Fe^{3+} , Cr^{3+} occupying B sites /3/. In the spectra of the solid solutions $Mg_4Fe_{1-x}Cr_xSbO_8$,

the intensity of doublet (2) decreases with x increasing from 0.1 to 0.4, indicating that doublet (1) is due to Fe^{3+} in A sites which are thus characterized by a large quadrupole splitting.

From room temperature Mössbauer spectra, we conclude that distribution (5) is the correct one. We are going to see that magnetic spectra are also in agreement with that distribution.

We have no indication about an order on B sites and several types are still possible. X-rays spectra on single crystals are necessary to determine that order.

3. Magnetic Mössbauer spectra.- Here, we give the first magnetic informations on these compounds.

The last four compounds of table I are attracted by a magnet at 77 K and are likely to be ferrimagnetic. Figure 2 shows the Mössbauer spectrum of Co_4FeSbO_8 at 77 K. It was fitted by two six-lines Zeeman patterns in the ratio 2/1 with the following parameters given by a Karyagin's treatment of the nuclear levels /4/

$$H_1 = 430 \pm 5 \text{ kOe} \quad \epsilon_1 = \begin{matrix} +1.1 \pm 0.1 \\ -1.1 \pm 0.1 \end{matrix} \text{ mm.s}^{-1} \quad \eta_1 = \begin{matrix} 0.9 \pm 0.1 \\ 0.5 \pm 0.5 \end{matrix} \quad \theta_1 = \begin{matrix} 66 \pm 3^\circ \\ 51 \pm 1^\circ \end{matrix}$$

$$\phi_1 = \begin{matrix} 60 \pm 20^\circ \\ 10 \pm 10^\circ \end{matrix} \quad \delta_1 = 0.2 \pm 0.02 \text{ mm.s}^{-1}$$

$$H_2 = 480 \pm 5 \text{ kOe} \quad \epsilon_2 = \begin{matrix} +0.3 \pm 0.1 \\ -0.3 \pm 0.1 \end{matrix} \text{ mm.s}^{-1} \quad \eta_2 = \begin{matrix} 0.5 \pm 0.5 \\ 0.8 \pm 0.2 \end{matrix} \quad \theta_2 = \begin{matrix} 53 \pm 1^\circ \\ 72 \pm 4^\circ \end{matrix}$$

$$\phi_2 = \begin{matrix} 8 \pm 8^\circ \\ 15 \pm 15^\circ \end{matrix} \quad \delta_2 = 0.3 \pm 0.02 \text{ mm.s}^{-1}$$

There still remains a single line with $\delta = 0.18 \text{ mm.s}^{-1}$ which is probably due to a small amount of impurity non visible in the paramagnetic spectrum.

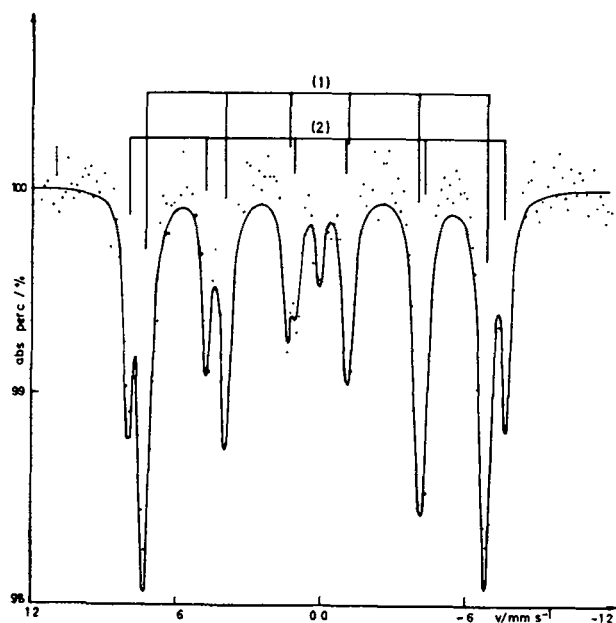


Fig. 2 : Mössbauer spectrum of $\text{Co}_4\text{FeSbO}_8$ at 77 K. The solid line is the result of a least-squares fit.

The most intense subspectrum, attributed to A sites from paramagnetic spectra, has the smallest internal field. This is in agreement with previous observations on classical spinels, where the internal fields on A sites are smaller than the one on B sites (2). Again, this is in favour of distribution (5).

The internal magnetic fields of $\text{Co}_4\text{FeSbO}_8$ do not exactly follow a Brillouin curve for $S=5/2$. This will be discussed in the future.

Table I gives also the transition temperatures of the compounds which are ordered at 77 K and the maximum internal field observed.

4. Conclusions.—We have studied by Mössbauer spectroscopy new compounds deriving from the spinel structure with Fe^{3+} and Sb^{5+} ions.

From the Mössbauer spectra, we can conclude that in the cubic compounds, the Fe^{3+} ions are situated on the B sites and in the orthorhombic compounds, they are distributed between A and B sites in the ratio 2/1.

Furthermore, we give the first magnetic informations about these compounds.

References

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