EXPERIMENTAL EVIDENCE OF THE INFLUENCE OF THE CATION SITE OCCUPANCY AND OF ITS EVALUATION WITH THE TEMPERATURE ON THE MAGNETIC PROPERTIES OF SOFT FERRITES PREPARED BY WET METHODS

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Résumé. — Les ferrites de Mn-Zn préparées par voie humide montrent une haute réactivité : les échantillons pressés atteignent une densité presque théorique à des températures inférieures à celles généralement nécessaires pour fritter les poudres préparées par les techniques céramiques classiques. Elles montrent aussi une occupation des sites cationiques très différente qui évolue avec la température, atteignant celle des ferrites céramiques.

Les spectres Mössbauer sur $MnFe_2O_4$, préparé lui aussi par voie humide, confirment cette évolution qui conduit le moment magnétique mesuré à 0 K à passer de 0,11 à 4,50 μ_B lorsque la température augmente de 25 à 1 350 °C. Les variations thermiques de l'aimantation dues à l'augmentation du contenu de Zn pour les échantillons tels que varient de manière différente de celles des échantillons frittés à 1 350 °C et trempés à l'eau.

Les valeurs des moments magnétiques inférieures à celles prévues par la théorie normale du ferrimagnétisme de Néel sont expliquées assez bien par une certaine évidence phénoménologique d'un effet Yafet-Kittel.

Abstract. — Mn-Zn ferrite prepared by wet methods show high reactivity : pressed samples reach almost theoretical density at temperatures lower than those usually required for sintering powders prepared by common ceramic techniques.

They also show a largely different cation site occupancy which evolves with temperature approaching that of ceramic ferrites.

Mössbauer spectra on $MnFe_2O_4$ also prepared by wet methods confirm such evolution which causes the magnetic moment at 0 K to shift from 4.11 to 4.60 μ_B as the temperature increases from 25 to 1 350 °C.

The temperature dependence of magnetization with increasing Zn content for *as prepared* samples varies in a different way from that of samples annealed at 1 350 °C and quenched in water.

The values of magnetic moments lower than those expected by the normal Neel theory of ferrimagnetism are explained rather well by a certain phenomenological evidence of a Yafet-Kittel effect.

1. **Introduction.** — Wet methods in Mn, Zn ferrites preparation permit a good control of composition and particle size [1], which are of essential importance in telecommunication-filter application [2].

They are much more reactive [3] than those prepared by well known ceramic methods [4, 5].

It is known by neutron diffraction [6] and NMR [7] measurements that $MnFe_2O_4$ prepared by wet methods show a degree of inversion of 50 ÷ 65 % with respect to the 7 ÷ 15 % of ceramic manganese ferrites [8, 9, 10, 11]. $Mn_{(1-x)}Zn_xFe_2O_4$ normally show $m(0, x)$ values (saturation magnetization at 0 K in Bohr magnetons) lower than those predicted by the Néel theory of ferrimagnetism. This was first abscribed to the presence of Mn^{3+}-Fe^{2+} pairs [12, 13] but recent Mössbauer experiments [10, 14, 15] excluded the presence of Fe^{2+} which would account for the previous model.

A Yafet-Kitel [16] arrangement of spins was instead proposed [14, 15] involving the canting of Mn_B^{2+} spins [14, 17] and Fe_B^{3+} spins [10] for $x > 0.5$. For a better understanding of this system we have carried out extensive and systematic magnetic, structural and analytical experiments on (Mn, Zn) ferrites prepared by wet methods.

2. **Experimental.** — Samples of given composition with an average particle size 0.12-0.13 μm and specific surface area of 5 ÷ 9 m^2/g were prepared by slowly adding solutions of $FeSO_4.7\,H_2O$, $MnSO_4.H_2O$, $ZnSO_4.7\,H_2O$ and NaOH in water while stirring and bubbling air and keeping constant pH value of 9.5 and varying the temperature between 60 and 90 °C.

Quenched samples were prepared by loosely pressing powders in 16 × 5 mm disks, heating and annealing in a proper p_{O_2} atmosphere and quenching by dropping them in cold water.

Magnetic moment measurements were carried out by a Vibrating Sample Magnetometer of Foner type. Computer extrapolated data confirmed that also for

(Mn, Zn) ferrites magnetization fell off from 0 K as $T^{3/2}$ as reported in ref. [18] for $MnFe_2O_4$, thus :

$$\sigma_s = (\sigma_s)_0 - \Delta T^{3/2} \quad (1)$$

$$m(T, x) = m(0, x) - \delta T^{3/2} . \quad (2)$$

Mössbauer spectra were obtained at room temperature with a Laben Multi-Channel Analyzer operating in the time mode over 1 024 channels and a numeric constant-acceleration transducer. All calibrations are related to metallic iron and corrected for the ^{57}Co-Rh source employed. The spectra were computer-fitted with Lorentz-shaped lines by the least square method.

Fitting of subspectra where carried out on the basis of the relative intensities of octahedral iron sites following the equation :

$$I(n) = \binom{6}{n} (1 - c)^{6-n} c^n \quad (3)$$

where $I(n)$ represents the relative intensity of the B-peack with n Fe_A nearest neighbours and c is the concentration of Fe_A ($c = 1$ for inverse, $c = 0$ for direct spinel).

After Sawatzky *et al.* [14], a correction has been introduced for the different recoil-free fractions of the A and B sites.

3. **Results and discussion.** — (Mn, Zn_z) ferrites prepared by wet methods show a very high reactivity : they reach in fact density values near to the theoretical ones at relatively low temperatures even for samples loosely packed, in agreement with ref. [3]. This can be seen in figure 1 where percent of theoretical density is plotted versus temperature for samples having different green density.

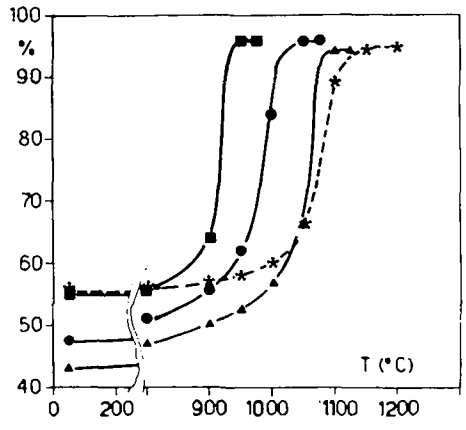

FIG. 1. — Percent of theoretical density vs. Temperature for (Mn, Zn) ferrites of composition Fe_2O_3 = 52.54, MnO = 25.38, ZnO = 22.08 mole percent. (■) = samples prepared by wet method with 55 % green density (●) = same, 48 % green density ; (▲) = same, 43 % green density ; (✱) = samples prepared by fluid bed technique [22] and 56 % green density.

All samples were heated at the same heating rate in a proper argon-oxygen mixture, kept for 2 hours at the given temperature and slowly cooled down to room temperature. Similar results were obtained by sintering in mixtures of CO_2/CO.

Samples quenched from different temperatures and p_{O_2} were analyzed for structure. Results are reported in figure 2 which is a phase diagram in the

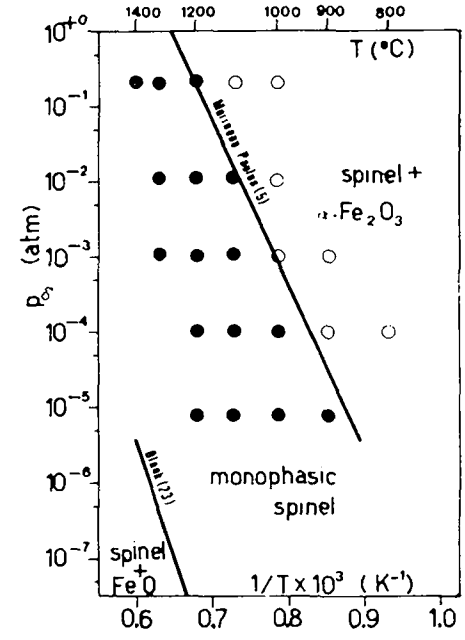

FIG. 2. — Spinel phase boundaries for a ferrite of composition as in figure 1 prepared by wet method. Upper boundary from Morineau & Paulus [19], lower boundary from Blank [20]. (○) = Spinel + α-Fe_2O_3 ; (●) = Monophasic spinel.

log.p_{O_2}/(1/T) space. A comparison with the results of Morineau and Paulus [5, 19] for similar composition is also reported : the fair agreement in phase composition is evident.

There is a large difference in saturation magnetization between *as prepared* and quenched samples, as can be seen in table I and figure 3, where $m(0, x)$ values are

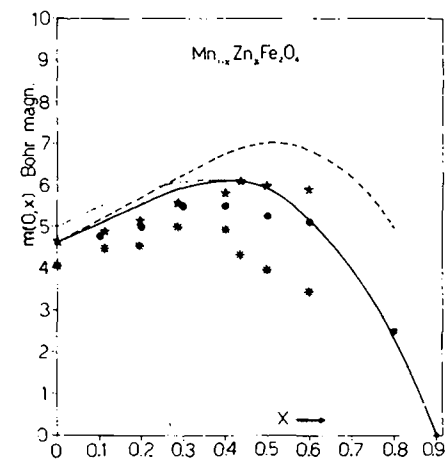

FIG. 3. — Saturation magnetization (in Bohr magnetons) vs. Zn content. (----) = curve from Guillaud [23] ; (....) = curve from Gorter [24] ; (— —) = curve from König [25] ; (●) = data from König [21] ; (✱) = this work, *as prepared* samples ; (★) = this work, quanched samples.

TABLE I

Magnetic properties of Mn, Zn Ferrites as a function of Zn content

Sample No.	x=Zn content	As prepared samples				Samples quenched from 1 350 °C				
		σ_s (293 K) (emu/g)	$m(0, x)$ Bohr magn. (*)	$\Delta \times 10^3$ emu.g^{-1}.K$^{-3/2}$	y=Fe$_A$(**)	σ_s (293 K) (emu/g)	$m(0, x)$ Bohr magn. (*)	$\Delta \times 10^3$ emu.g^{-1}.K$^{-3/2}$	y=Fe$_A$(*)*	T_c(K)
1	0	70.48	4.11 (0.02)	5.54	0.402	80.00	4.60 (0.20)	6.18	0.214	590
2	0.113	76.92	4.50 (0.27)	5.96	(0.332)	79.77	4.93 (0.01)	7.74	(0.192)	567
3	0.194	75.41	4.58 (0.05)	6.98	0.282	76.00	5.15 (0.01)	9.61	(0.160)	511
4	0.286	76.80	5.01 (0.04)	8.62	(0.225)	76.00	5.55 (0.01)	11.29	(0.140)	480
5	0.401	69.09	4.94 (0.07)	9.64	(n. d.)	72.98	5.82 (0.02)	13.23	(0.100)	460
6	0.435	60.00	4.34 (0.10)	8.89	(n. d.)	68.00	6.10 (0.01)	14.00	(0.00)	n. d.
7	0.496	51.40	3.94 (0.15)	8.36	(n. d.)	60.00	5.96 (0.01)	16.36	(0.07)	397
8	0.600	45.62	3.41 (0.17)	6.62	(n. d.)	47.58	5.89 (0.01)	18.06	(0.03)	n. d.

(*) = 95 % affidability of measurements in brackets ;
(**) = Experimental from Mössbauer measurements ; calculated values in brackets ; n. d. means not determined.

reported for 50 mole percent of Fe_2O_3 compositions. Values from König [21] and curves from Guillaud [23], Gorter [24] and König [25] are also reported for comparison.

$m(0, 0)$ is 4.11 μ_B and 4.60 μ_B for *as prepared* and quenched $MnFe_2O_4$ respectively.

For these values of saturation magnetization, Šimša rule [17], which implies a YK arrangement of spins with a canting angle between Mn_A and Mn_B of 53°, gives an inversion degree of 20 and 44.5 % for quenched and *as prepared* sample respectively, which is in good agreement with the value found by Takada *et al.* [7] for a similar material.

$$\text{Šimša rule} : m(0, 0) = 5 - 2\,c(Fe_A) \qquad (4)$$

where $c(Fe_A)$ = Fe ions in tetrahedral A sites.

From our Mössbauer experiments on $MnFe_2O_4$ whose spectra's first lines are reported in figure 4 together with the least-square fit and its Lorentzian components, we obtain a $c(Fe_A)$ value of 0.402 and 0.214 for *as prepared* and quenched samples respectively.

It is possible to show that the low values of $m(0, x)$ of ferrites prepared by wet methods can be abscribed to a YK effect which involves the canting of the angle between Mn_A-Mn_B spins and also between Fe_A and Fe_B spins and that such an angle is a function of the inversion degree and such a structure is energetically stable.

For doing that we followed Sawatzky *et al.* [14] and considered all the molecular fields acting on ions in different cation sites, including exchange interactions for Fe ions in A sites and considering that only AA interactions plus Fe_B-Fe_B and Mn_B-Mn_B can be neglected [26]. By writing the equations of molecular fields, considering the magnetostatic free energy,

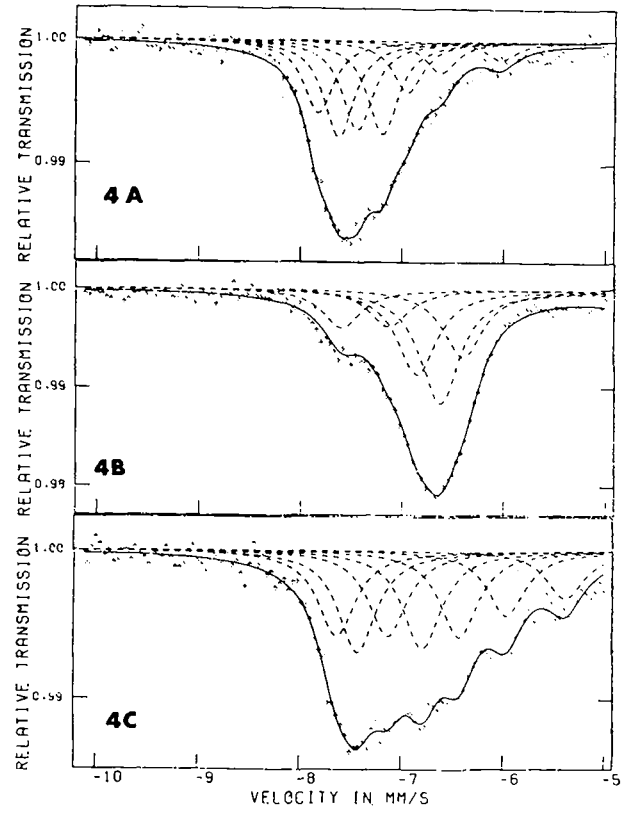

FIG. 4. — Mössbauer spectra of $Mn_{1-x}Zn_xFe_2O_4$. (4A) = $MnFe_2O_4$, as prepared sample ; (4B) = $MnFe_2O_4$, quenched sample ; (4C) = as prepared powder with x = 0.194.

minimizing such energy and dividing and multiplying by k (Boltzmann constant) we obtain :

$$\frac{\sin\theta}{\sin\varphi} = \frac{J_{FF}/k\,|\,\overline{M}_{AF}\,|\,|\,\overline{M}_{BF}\,| + J_{MF}/k\,|\,\overline{M}_{BF}\,|\,|\,\overline{M}_{AM}\,|}{J_{MM}/k\,|\,\overline{M}_{BM}\,|\,|\,\overline{M}_{BM}\,| + J_{MF}/k\,|\,\overline{M}_{AF}\,|\,|\,\overline{M}_{BM}\,|} \qquad (5)$$

where $\overline{M}_{AM}$, $\overline{M}_{BM}$, $\overline{M}_{AF}$, $\overline{M}_{BF}$ are the magnetic moments of Mn_A, Mn_B, Fe_A and Fe_B respectively and J_{MM}, J_{MF}, J_{FF}, J_{BB} the exchange interactions between Mn_A-Mn_B, Mn_A-Fe_B, Fe_A-Fe_B and Mn_B-Fe_B respectively.

θ is the canting angle between Mn_A and Mn_B spins and φ is the canting angle between Fe_A and Fe_B spins.

Indicative values for J_{ij}/k are reviewed by Broese van Groenou *et al.* [26] who report for :

$$J_{FF}/k = -20 \text{ K} ; \quad J_{MF}/k = -11 \text{ K} ; \quad J_{MM}/k = -2.2 \text{ K} .$$

Magnetic moments are given by :

$$| M_i | = g\mu_B S_i c_i N \tag{6}$$

where g = gyromagnetic ratio ($\simeq 2$), S_i = component of the spin (5/2) (for Fe^{3+} and Mn^{2+}), N = number of formula units per mole, μ_B = Bohr magneton and c_i is the quantity of the i ion in the A or B site. With the J_{ij}/k values from ref. [26] and with (6), we can rewrite eq. (5) as follows :

$$\frac{\sin\theta}{\sin\varphi} = \frac{-20(c_{AF}\cdot c_{BF}) - 11(c_{BF}\cdot c_{AM})}{-2.2(c_{AM}\cdot c_{BM}) - 11(c_{AF}\cdot c_{BM})} \tag{7}$$

that leads to a $\sin\theta/\sin\varphi$ value of 26.4 for $c(Fe_A) = 0.214$ and 10.1 for $c(Fe_A) = 0.402$. Considering that $m(0, 0)$ can be expressed by :

$$m(0, 0) = (5\, c_{BF} \cos\varphi + 5\, x c_{BM} \cos\theta) - 5(c_{AF} + c_{AM}) \tag{8}$$

for $m(0, 0) = 4.6\,\mu_B$ and $c_{AF} = 0.214$ we obtain $\varphi = 1^\circ 40'$ and $\theta = 51^\circ$ while for $c_{AF} = 0.402$ and $m(0, 0) = 4.11\,\mu_B$ we have $= 4^\circ 40'$ and $\theta = 55^\circ 12'$. This shows that while it is correct to assume $\varphi \simeq 0^\circ$ for $Fe_A \simeq 0.2$ [14, 17] the same assumption becomes less correct with increasing inversion degree.

The AB interactions are largely affected by temperature [27] depending on the number of A-site magnetic nearest neighbours [26, 25] : the higher the total value of such interactions, the lower the influence of temperature i. e. the value of Δ of eq. (1), as shown in table I.

The fact that Δ increases monotically with x for quenched samples can easily be explained by considering the Curie temperature expression [26] :

$$T_c = [s_i(s_i+1)]^{1/2} [s_j(s_j+1)]^{1/2} \sum_{ij} 2\, J_{ij}/3\, k(n_{ij}\, n_{ji})^{1/2} \tag{9}$$

and plotting the Δ and T_c values as a function of S :

$$S = \sum_{ij} \left(\frac{2}{3}\,\frac{J_{ij}}{k}\right) (n_{ij}\, n_{ji})^{1/2} \tag{10}$$

as we did in figure 5 for quenched samples. From figure 5 in fact, we observe that Δ and T_c are linear functions of S. We also observe that the slope of T_c *vs.* S curve is 33.14 which is in good agreement with the real value of the productory of spins (= 30) that we can obtain from eq. (9), thus confirming that the J_{ij}/k values chosen according to ref. [26] correspond closely to the real values of J_{ij}/k for (Mn, Zn) ferrites.

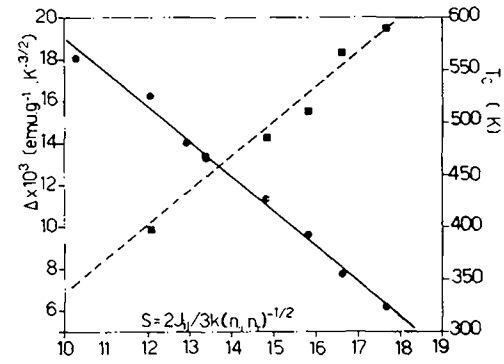

FIG. 5. — Curie temperatures and Δ values (σ vs. $T^{3/2}$ slopes) as a function of the *interaction factor* S (Sum from Eq. 15) (●) = Δ vs. S ; (■) = T_c vs. S.

The behaviour of Δ *vs.* x for *as prepared* samples is instead rather peculiar and cannot be accounted for so easily because of the presence of a maximum for $x \simeq 0.375$.

For these materials, Fe_A-Fe_B interactions certainly play a large role which cannot be explained as easily as for quenched samples.

Some sort of phenomenon, involving cristallite dimensions and interactions, must be taken into account.

Extensive discussion for a less qualitative interpretation of this last point will be given in a future publication.

4. **Conclusions.** — Mn, Zn ferrites prepared by wet methods show a high reactivity which has been shown to be of a great importance during sintering. We have demonstrated, by magnetic and Mössbauer experiments, that in these materials the inversion degree is higher than that of samples prepared at high temperature and that such a difference in inversion degree is responsible for their low magnetic moments. A rearrangement process takes place with temperature, probably between 400 and 700 °C [17] and a situation similar to that of materials prepared by ceramic methods is reached. Phase composition and magnetic behaviour of annealed samples is indeed similar to that reported for ceramic samples.

Our experiments confirm the existence a YK arrangement of spins involving canted Fe^{3+} spins for *as prepared* samples.

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