NONEQUIVALENT POSITIONS OF Fe^{3+} IONS AND
RELAXATION EFFECTS IN Mn—Zn-FERRITES

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A study is made of manganese—zinc ferrites $Mn_{1-x}Zn_xFe_2O_4$ where x varies from 0.3-0.9.
It is established that the variation of the form of the spectra with variation of x is of a re-
laxation nature. In this system the nonequivalent nature of the neighborhood of the ions has
an effect on the relaxation processes and on the character of the magnetic ordering.

The system $Mn_{1-x}Zn_xFe_2O_4$ is a very suitable object for Mossbauer investigations of the nonequivalent
positions of Fe^{3+} ions, since the Zn^{2+} and Mn^{2+} ions occupy exclusively tetrahedral sites. The Fe^{3+} ions
are localized principally in B-sites. The presence of such a cationic distribution (for $x \leq 0.4$) is confirmed
by the neutronographic method [1, 2].

The Mn—Zn-ferrites also possess interesting magnetic properties. In the region of low concentra-
tions of Zn^{2+} ions an increase in the saturation magnetization is observed with increase of x. Here the
collinear model of Néel is satisfied. In the region of high concentrations of Zn^{2+} ions ($x \geq 0.4$) a decrease
in the magnetization is observed during the process of replacement of the Fe^{3+} ions [3]. So far no attempt
at explaining this has been completely successful. We investigated the localization neighborhood of iron
ions by the Mossbauer method in order to obtain information on the nature of the distribution of Fe^{3+} ions
at B-sites of the lattice and on magnetic ordering.

In the works existing in the literature (for example, [2]) it did not prove possible to obtain Mossbauer
spectra of Mn—Zn-ferrites with good resolution. As a rule, spectra were observed with very broadened
lines. In our Mossbauer effect experiments an improved method was used. The source was radioisotope
Co^{57} in a Pd matrix. The spectra were recorded on an electrodynamic type set-up with triangular form of
the reference signal. Motion of the source was effected with the aid of a linear motor from the Finnish firm
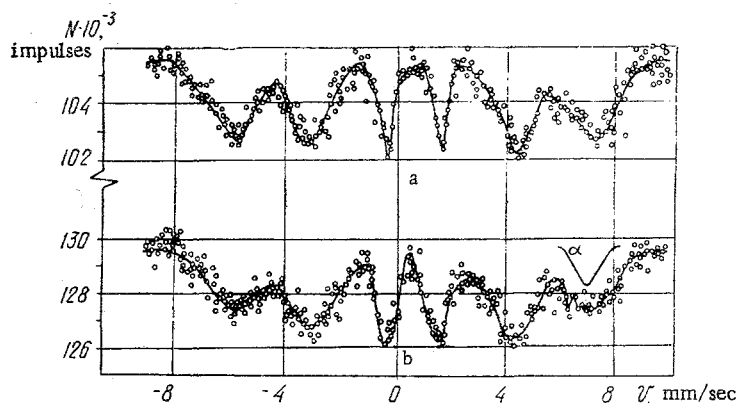

Fig. 1. Mossbauer spectra of Mn—Zn-ferrites, a)
x = 0.4, b) x = 0.5.

TABLE 1. Maximum Probabilities of the Formation of Nonequivalent Positions of Fe^{3+} ions in Mn—Zn-Ferrites

x	$P(1,x)$, $m=1$	$P(2,x)$, $m=2$	$P(3,x)$, $m=3$	$P(4,x)$, $m=4$	$P(5,x)$, $m=5$	$P(6,x)$, $m=6$	No. of most probable first neighbor Zn^{2+} ions
0,5	—	0,22	0,31	0,22	—	—	2,3,4
0,6	—	0,14	0,28	0,31	0,19	—	2,3,4,5
0,7	—	—	0,18	0.324	0,3	0,12	3,4,5,6
0,8	—	—	—	0,24	0,396	0,262	4,5,6
0,9	—	—	—	—	0,35	0,53	5,6

"Nokia." The spectra were recorded by an AI-4096 analyzer. However, in the spectra of the Mn—Zn-ferrites investigated by us no splitting of the extreme components was observed for x = 0.4 and 0.5 either. All six lines were considerably broadened, especially the extreme ones (Fig. 1a and b).

The ratio of the intensities of the components of the spectra turned out to be unusual. For polycrystalline specimens it should equal 3 : 2 : 1. From Fig. 1 (curves a and b) it is seen that the lines corresponding to the transitions $\pm 3/2 \rightleftharpoons \pm 1/2$ are of low intensity, and the ratio of the intensities of the components of the spectrum deviate considerably from 3 : 2 : 1. This peculiarity of the spectrum indicates the presence of relaxation effects in Mn—Zn-ferrites. As the content of Zn^{2+} ions in an Mn—Zn-ferrite increases, the local magnetic field due to magnetic disordering decreases. For sufficiently small dimensions of the regions of magnetic ordering ("superparamagnetic particles") relaxation occurs of the total magnetic moment of the region of ordering with frequency

$$ \nu = \nu_{0} \exp \left(-\frac{Kv}{\kappa T} \right), $$

where K is the effective anisotropy constant, referred to unit volume, and v is the volume of the region of ordering [4, 5].

In the formation of superparamagnetic particles, the long-range order in the ordering of spins breaks down. However, in the particles themselves the short-range order is preserved. Magnetic inhomogeneities of this type arise due to fluctuations of the local neighborhood of the Fe^{3+} ions. As a result, nonequivalent positions of the Fe^{3+} ions are formed.

Using the method described in [6], the spectra of the Mn—Zn-ferrites (Fig. 1) were resolved into a number of sextuplets of Fe^{3+} ions, having in the first cation neighborhood a different number of diamagnetic Zn^{2+} ions. Since each octahedral Fe^{3+} ion has six first neighbor tetrahedral ions, the number of nonequivalent positions of the Fe^{3+} ions equals 7. Table 1 gives the maximum probabilities P(m, x) of formation in the crystal lattice of an Mn—Zn-ferrite of nonequivalent positions of Fe^{3+} ions. For example, for x = 0.5 the maximum probabilities P(m, 0.5) will be 0.22, 0.31, and 0.22. This corresponds to three nonequivalent positions of the Fe^{3+} ions having in the first cation neighborhood, 2, 3, and 4 diamagnetic Zn^{2+} ions respectively. The form of the extreme lines of the experimental spectra corresponds to the form of the lines obtained when the components from the nonequivalent positions of the Fe^{3+} ions are added (line α, Fig. 1). Consequently, the Fe^{3+} ions in Mn—Zn-ferrites are statistically positioned in B-sites.

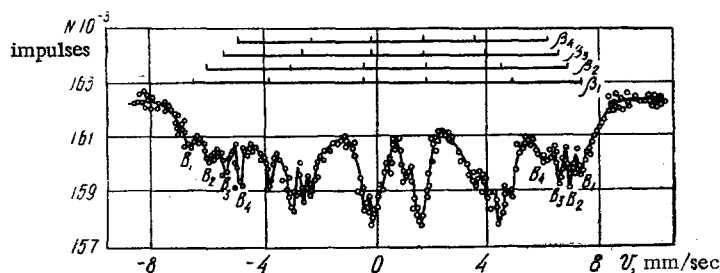The Mössbauer spectrum of $Mn_{0.4} Zn_{0.6} Fe_2O_4$ (Fig. 2) proves to be interesting. Here we observe

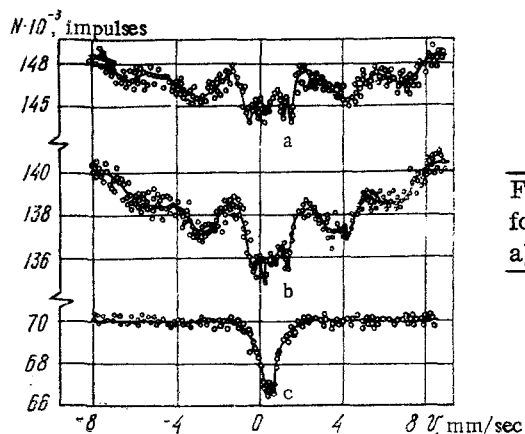Fig. 2. Mössbauer spectrum of Mn—Zn-ferrite (x = 0.6).

350

Fig. 3. Mossbauer spectra
for Mn—Zn-ferrites:
a) x = 0.7, b) x = 0.8, c) x = 0.9.

TABLE 2. Parameters of Moss-
bauer Spectra

Spectrum	$H \wedge$ kOe	$\delta \frac{mm}{sec}$	$\Delta \frac{mm}{sec}$
β_1	435	0,5	0,14
β_2	404	0,5	0,04
β_3	365	0,5	0,04
β_4	333	0,5	0,01

completely clear splitting of the spectrum into four sextuplets, β_1, β_2, β_3, and β_4, of Fe^{3+} ions having in the first cation neighborhood 2,3,4, and 5 diamagnetic Zn^{2+} ions respectively. Table 2 gives the magnetic field on the Fe^{57} nuclei, the chemical isomeric shift δ, and the magnitude of the quadrupole, splitting Δ calculated for the spectra β_1, β_2, β_3, and β_4.

Analysis of these values shows that in a Mn—Zn-ferrite with x = 0.6, the magnetic field depends on the number of exchange interactions. When the number of exchange interactions is reduced by one, the magnetic field on the Fe^{57} nuclei decreases, on the average, by 34 kOe. The spectrum β_4 due to Fe^{3+} ions, whose first cation neighborhood sphere consists of five Zn^{2+} ions and one Fe^{3+} ion, has a hyperfine structure. Consequently, in Mn—Zn—ferrites, even Fe^{3+} ions with one exchange interaction take part in the ordering.

The value of the chemical isomeric shift is practically independent of the first cation neighborhood, and is equal to 0.5 mm/sec. The results of calculating the quadrupole shift of the spectra (Table 2) are unexpected. For spectra β_2, β_3, and β_4, the value of Δ is small. Spectrum β_1 has a large quadrupole shift, in spite of the fact that it is due to Fe^{3+} ions with two Zn^{2+} ions in the first cation neighborhood sphere. Apparently the magnetic moment of such ions Fe^{3+} is not directed along the axis of easy magnetization, i.e., the [111] axis. The deviation of the direction of the magnetic moment from the [111] axis may be connected with the appearance of angular ordering of the spins. It was earlier said that this was the only reason leading to the high value Δ = 0.12 mm/sec. The octahedra in which the Fe^{3+} ions are localized with two Zn^{2+} ions in the first cation neighborhood sphere, may be considerably distorted. However, the effect of the chemical composition of the first cation neighborhood sphere must be excluded, since a change of the number of Zn^{2+} ions from 3 to 5 in the first coordination neighborhood sphere of the Fe^{3+} ions does not lead to significant changes in the quadrupole splitting (Spectra β_2, β_3, β_4, Table 2).

We note that in accordance with the Yafet—Kittel theory for large Zn^{2+} content, the A—B interaction becomes weaker, and B—B interaction between the Fe^{3+} ions begins to become apparent. This can lead to the situation that two magnetic sublattices B' and B" at an angle to each other appear in the B sublattice.

TABLE 3

Speci-men No.	Chemical formula	a, Å	μ_B, error 10%	T_C, °C	ρ, $\Omega \cdot cm^{-1}$
1	$Mn_{0,7} Zn_{0,3} Fe_2O_4$	8,489	5,54	242	$3 \cdot 10^4$
2	$Mn_{0,6} Zn_{0,4} Fe_2O_4$	8,485	6,20	190	$2,4 \cdot 10^4$
3	$Mn_{0,5} Zn_{0,5} Fe_2O_4$	8,480	6,74	150	$7 \cdot 10^5$
4	$Mn_{0,4} Zn_{0,6} Fe_2O_4$	8,468	6,3	80	$8 \cdot 10^5$
5	$Mn_{0,3} Zn_{0,7} Fe_2O_4$	8,457	5,6	40	$6,5 \cdot 10^5$
6	$Mn_{0,2} Zn_{0,8} Fe_2O_4$	8,448	4,05	—	$6 \cdot 10^6$

Remark: For composition 6 the Curie point lies in the room tempera-
ture range.

The angle increases from 0 to 180° as we pass from a pure Mn-ferrite to a pure Zn-ferrite. The theory gives a satisfactory description of the course of the magnetization curve independence on x. It is possible that for large concentrations of nonmagnetic Zn^{2+} ions, a chaotic angular spin structure may occur. In the low Zn^{2+} concentration region, the breakdown of exchange interactions of A—B type does not lead to any deviation from the collinear spin structure.

The lattice parameter a, the magnetic moment μ_B, the Curie point T_C and the specific resistance ρ of Mn—Zn-ferrites are given in Table 3.

More complex spectra were observed for Mn—Zn-ferrites with x = 0.7 and 0.8 (Fig. 3). They are very blurred and compressed. A distinguishing feature of these spectra is their relaxation nature. The disappearance of the hyperfine structure as the Zn content in Mn—Zn-ferrites increases is apparently due to the decrease in intensity of the lines $\pm 3/2 \rightleftharpoons \pm 1/2$ due to relaxation effects and the approach of the lines to each other due to magnetic disordering. The compression and blurring of the spectral lines may also be caused by the presence of a chaotic angular structure in the specimens.

Consequently, the change in the form of the spectra of Mn—Zn-ferrites occurring at room temperature may apparently be explained either by the presence of superparamagnetic regions or else by angular ordering of the spins. Both reasons are associated with a nonequivalent neighborhood of the ions, and hence with variation of the exchange interactions.

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