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Nature of Ageing of Some Mixed Ferrite Spinels

T. A. KHIMICH, V. F. BELOV, S. S. GORELIK, L. M. LETYUK, M. N. SHIPKO, AND V. V. KOROVUSHKIN

Institute of Crystallography, USSR Academy of Sciences

Moscow Institute of Steel and Alloys

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A report is given of a comprehensive investigation of ageing processes in nonstoichiometric mixed ferrites. It is shown that investigations of the Mössbauer effect yield valuable information on the influence of nonstoichiometry on the ageing of magnetic properties of ferrites. Electrical, magnetic, x-ray, and Mössbauer studies show that the process of ageing of complex compositions is determined by changes in the valence state of ions, a redistribution of cations, and a partial precipitation of solid solutions.

A description is given of an investigation of the ageing of mixed nonstoichiometric ferrites of the following compositions: 1) $Mg_{0.406}Mn_{0.633}Zn_{0.272}Fe_{1.69}O_{3.984}$; 2) $Mg_{0.812}Mn_{0.289}Ni_{0.062}Fe_{1.837}O_{3.998}$. Mössbauer, x-ray structure, and x-ray spectroscopic measurements were supplemented by studies of magnetic, electrical, and microwave properties.

Investigations were made of three effects which may give rise to changes in the properties of ferrites with time: a) changes in the valence states of ions; b) precipitation in solid solutions; c) redistribution of cations between tetrahedral and octahedral sublattices in such a way as to achieve a distribution closer to equilibrium.

Table I lists the shifts of the K_{α_1} and K_{β_1} x-ray lines of manganese and iron of composition 1 relative to Mn and Fe. The K_{α_1} and K_{β_1} manganese lines are shifted toward longer wavelengths along the quenching–initial state–ageing sequence, which indicates that the density of the 3d-electrons in the atomic volume of Mn decreases.[3] This shift cannot be explained by an increase in the atomic volume because ageing reduces the lattice parameter (Table II), i.e., it compresses the voids. Consequently, the observed reduction in the density of the 3d-electrons must be due to oxidation of Mn^{2+} and Mn^{3+} ions to Mn^{3+} and Mn^{4+}. This increase in the valence is accompanied by a rise in the number of Mn ions at the B sites.[4]

The K_{α_1} and K_{β_1} lines of iron in composition 1 are also shifted by ageing toward longer wavelengths. These changes in the positions of the K_{α_1} and K_{β_1} lines indicate an increase in the valence of the iron ions in accordance with the scheme $Fe^{2+} \rightarrow Fe^{3+} + e$. This scheme is valid if quenched samples of composition 1 contain Fe^{2+} ions which are oxidized to the Fe^{3+} state during ageing. Similar results have been reported for an Mg ferrite.[2]

The results of neutron and x-ray diffraction studies, carried out on the same samples, show that ageing reduces the fraction of Mn and Mg ions at the A sites, i.e., these ions are transferred to the B sites. The same number of Fe^{3+} ions should be transferred from the B to the A sites. Since the magnetic moments of the Mn^{2+} and Fe^{3+} ions are equal, such an interchange of sites should not alter the net magnetic moment. On the other hand, the replacement of the Fe^{3+} ions at the B sites with the nonmagnetic Mg ions during ageing should alter the net magnetic moment. The transfer of some of the Fe^{3+} ions from the B to the A sites and of the same number of the Mn and Mg ions from the A to B sites should reduce strongly the net magnetic moment. However, our experiments showed that the magnetization n_B of sample 1 did not change along the quenching–ageing sequence. Consequently, the model based on a redistribution of cations fails to explain satisfactorily the ageing of composition 1.

The Mössbauer spectra of the investigated ferrites are shown in Figs. 1 and 2. An interesting feature of the spectra of composition 1 is a low intensity of the components. The outer lines are split by the inequivalence of the positions of the Fe^{3+} ions, which leads to superposition of three sextuplets: $\alpha_1, \alpha_2, \alpha_3$. The exceptionally low intensity of the components of the Mössbauer spectrum and their asymmetry are evidence of the presence of superparamagnetic particles characterized by different fields at the nuclei. The Mössbauer effect in the quenched samples is somewhat stronger than in the aged samples, suggesting the presence of fewer superparamagnetic particles in the quenched state.

It follows from these results that the ageing of composition 1 involves a redistribution of the Mn, Mg, and Fe ions between the A and B sublattices, a change in the valence states of the Mn and Fe ions, and—evidently—precipitation of the solid solution resulting in the formation of finely dispersed particles which are not recorded by the x-ray method. This is supported by measurements of the coercive force, the electrical resistivity, and the width of the ferromagnetic resonance line. These parameters are sensitive to the structure. Since ageing is accompanied by the precipitation of the solid solution, the gain size decreases. The number of layers between grains in-

Table I

State	Mn (K_{α_1})	Mn (K_{β_1})	Fe (K_{α_1})	Fe (K_{β_1})
Quenching	+3.5	+3.5	+1.1	+1.9
Initial	+1.4	+1.9	+0.5	+1.8
Ageing	−0.85	0.0	−0.4	0.0
Error	±0.3	±0.4	±0.3	±0.3

Table II

Parameters of investigated samples after different heat treatments

	Quenching						Initial state						Ageing at 320°C, 25 h					
	a, A	n_B, (300° K)	T_C, C	H_c, Oe	ρ, Ω·cm	2ΔH, Oe	a, A	n_B (300° K)	T_C, C	H_c, Oe	ρ, Ω·cm	2ΔH, Oe	a, A	n_B (300° K)	T_C, °C	H_c, Oe	ρ, Ω·cm	2ΔH, Oe
Ferrite 1	8.443	1.96	176	0.15	$7.5\cdot10^5$	—	8.453	2.16	180	0.30	$3\cdot10^6$	118	8.498	1.87	180	0.42	$2\cdot10^7$	135
Ferrite 2	8.408	1.98	275	3.26	$2\cdot10^6$	—	8.394	1.21	330	6.21	$2.8\cdot10^8$	835	8.390	1.07	342	6.7	10^9	1080
Error	±0.001	±3%	±3° C	±10%	±5%	—												

Note. Ferrite 1 quenched from 1250°C, ferrite 2 quenched from 1150°C; a is the lattice parameter; n_B is the magnetic moment; T_C is the Curie temperature; H_c is the coercive force; ρ is the electrical resistivity; 2ΔH is the width of the ferromagnetic resonance line.

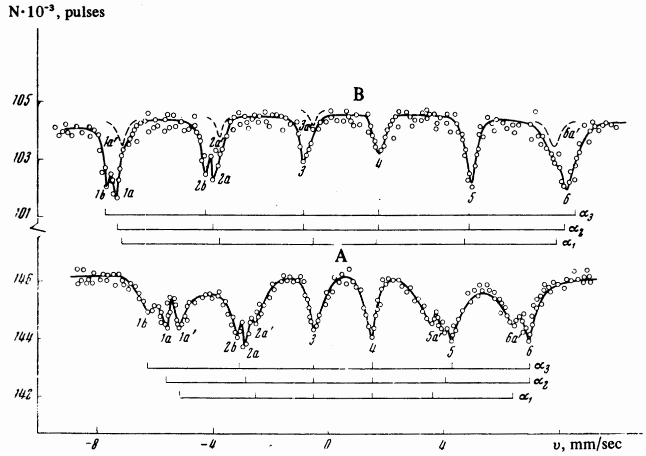

FIG. 1. Mössbauer spectra of a sample of composition 1 subjected to ageing: A) at room temperature; B) at T = 196°C. The components denoted by a (continuous curve) and a′ (dashed curve) represent inequivalent tetrahedral Fe^{3+} ions.

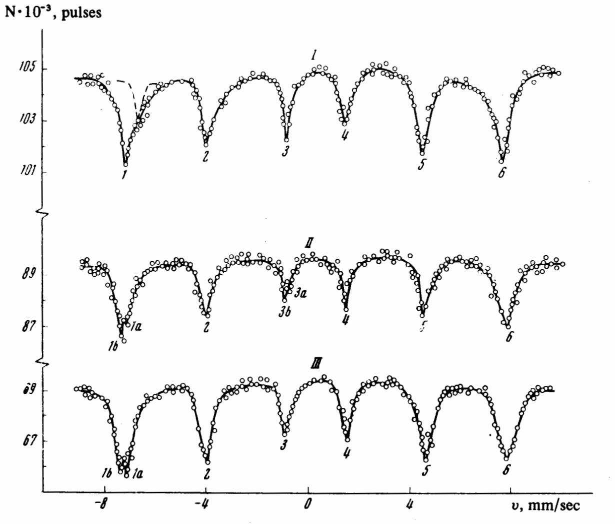

FIG. 2. Mössbauer spectra of a sample of composition 2 subjected to various heat treatments: I) quenching; II) cooling in a switched-off furnace; III) ageing.

creases. Displacements of domain boundaries are hindered by these layers and by second-phase particles and therefore the coercive force of an aged sample is three times as high as that of a quenched sample (Table II). Ageing of composition 1 also increases the width of the ferromagnetic resonance line because of the excitation of spin waves at magnetic inhomogeneities. These inhomogeneities may be due to the presence of second-phase particles and of layers between grains. Consequently, ageing increases the electrical resistivity (Table II).

Thus, an analysis of the experimental data on ferrite 1 shows that the ageing of this compound includes the following processes: i) oxidation of the Mn^{2+} ions to Mn^{3+} and Mn^{4+}, as well as localization of these ions at the octahedral sites; ii) transfer of the Mn and Mg ions from the A to the B sublattice; iii) partial precipitation of the solid solution.

We shall now consider changes which occur in the Mössbauer spectra of composition 2 as a result of various heat treatments (Fig. 2). The spectra of a quenched sample (curve I), a sample cooled in a switched-off furnace (curve II), and a sample aged at 320°C for 25 h (curve III) can be separated into two Zeeman sextuplets representing the tetrahedral and octahedral Fe^{3+} ions. The ratio of the areas under peaks 1b and 1a in the spectrum of the quenched sample is 2.1. The corresponding ratio for the spectrum of the sample cooled in a switched-off furnace is 1.4. Ageing (spectrum III) reduces this ratio to unity. This strong "pumping" of the intensity from peak 1b to peak 1a can be explained by the transfer of the Fe^{3+} ions from the octahedral to the tetrahedral sites along the quenching-initial state-ageing sequence. This is in agreement with a reduction in the net magnetic moment from 1.98 to 1.07 μ_B. It should be stressed that ageing at 320°C for 25 h is accompanied by a greater transfer of the Fe^{3+} ions from the B to the A sites than the transfer observed in[5].

The local magnetic fields H_l^{tet} and H_l^{oct} and the chemical isomeric shifts δ^{tet} and δ^{oct} of the octahedral and tetrahedral Fe^{3+} ions are listed in Table III. Here, as in the case of simple Cu ferrites,[1] ageing increases the magnetic fields H_l^{tet} and H_l^{oct} because of an increase in the number of exchange bonds (this number increases because of a reduction in the number of diamagnetic ions in the immediate cation environment of the iron ions).

Calculations show that Fe^{3+} ions, with a single magnesium ion and five iron ions in the immediate

Table III

Mössbauer parameters of composition 2

Treatment	Quenching Initial state	H_l^{oct}, kOe	δ^{oct}, mm/sec	δ^{tet}, mm/sec
Quenching	466	466	0,39	0.42
Initial state	474	461	0,39	0.39
Ageing	479	459	0,39	0.37

cation environment, predominate in the octahedral sublattice of the quenched sample. Ageing of composition 2 results in the replacement, in the same cation environment, of a magnesium ion with an iron ion. This increases by one the number of exchange bonds between the octahedral and the tetrahedral ions. Therefore, the magnetic field H_l^{oct} increases by 13 kOe along the quenching–ageing sequence.

Since the magnetic field at the Fe^{57} nuclei is proportional to the local magnetic moment of the Fe^{3+} ions, an increase in H_l^{tet} and H_l^{oct} after ageing is evidence of an increase in the strength of the A–B exchange interaction. This is in agreement with an increase in the Curie temperature (Table II).

Although the Mössbauer spectra do not exhibit second-phase lines (Fig. 2), formation of second-phase particles may still occur along the quenching–ageing sequence. Composition 2 is evidently in the pre-precipitation state during ageing, as indicated by rises of such structure-sensitive parameters as the coercive force and the width of the ferromagnetic resonance line (Table II). The same nature of changes in the properties of ferrites 1 and 2 suggests that their ageing mechanisms are identical. The presence of a small amount of nickel in composition 2 cannot exert a significant influence on the behavior of its properties during ageing. If we ignore the presence of the Mn and Ni ions because of their low content, we find that composition 2 is similar to a simple Mg ferrite in which a redistribution of ions and a change in valence states $Fe^{2+} \rightarrow Fe^{3+} + e$ takes place during ageing.[2] Similar processes evidently occur also in composition 2.

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