

STUDY OF COPPER FERRITE AGING BY X-RAY SPECTROSCOPY AND THE MÖSSBAUER EFFECT

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Ferrites synthesized by ceramic techniques are frequently nonequilibrium systems which tend toward a more equilibrium state as they age. This behavior is evident, in particular, in the changes of several properties. The transition is complicated. During aging there is presumably a redistribution of ions, a change in the ion valence, a decomposition of the solid solution, etc. [1, 2]. The contributions of each of these processes to the overall mechanism for ferrite aging have not been determined.

We report here a study of copper ferrite subjected to various kinds of heat treatment, including one treatment intended to be equivalent to artificial aging. We measured the Mössbauer effect, certain x-ray structural and x-ray spectral properties, and the saturation magnetization and resistivity of the samples.

The CuFe_2O_4 samples were synthesized by the ordinary ceramic technique from "analytical grade" oxides of the corresponding metals. A preliminary annealing was carried out for 2 h at 700°C in air. The final sintering was at 900°C for 2 h in oxygen. Some of the samples, allowed to cool with the disconnected furnace, were heated to 1100°C and then quenched in water; others were subjected to artificial aging in air

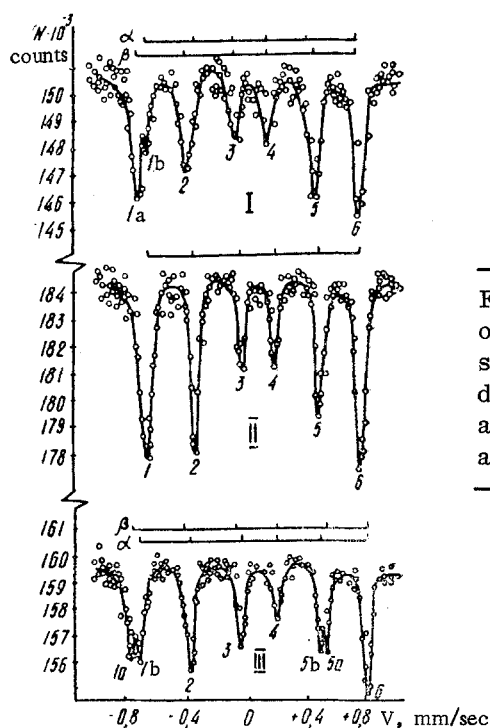


Fig. 1. Mössbauer spectra of quenched samples (I), samples cooled with the disconnected furnace (II), and samples subjected to aging (III).

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TABLE 1. Displacement of the Basic K Lines of Iron and Copper, Lattice Constants (a , c), Magnetic Moment (n_B), and Resistivity (ρ) for the Ferrite CuFe_2O_4 Subjected to Various Types of Heat Treatment

Heat treatment	Displacement of copper lines, ΔE (Cu) eV			Displacement of iron lines, ΔE (Fe) eV			Lattice constants, Å	n_B at 77°K	$\rho, \Omega \cdot \text{cm}$, at 300°K
	K_{α_1}	K_{α_2}	$K_{\beta_{1,2}}$	K_{α_1}	K_{α_2}	$K_{\beta_{1,3}}$			
Quenching from 1100°C	+1,15	+1,35	+0,85	-0,65	-0,65	-0,65	$a=8,3954 \pm 0,0002$	2,17	$8,8 \cdot 10^3$
Cooling with disconnected furnace	0	0	0	0	0	0	$a=8,24 \pm 0,01$ $c=8,65 \pm 0,02$ $c/a=1,051 \pm 0,005$	1,23	$1,7 \cdot 10^3$
Aging at 250°C (300 h)	+1,15	+1,15	+1,50	+0,75	+0,65	+0,85	$a=8,217 \pm 0,001$ $c=8,73 \pm 0,04$ $c/a=1,062 \pm 0,002$	1,08	$1,7 \cdot 10^3$
Error	$\pm 0,20$	$\pm 0,20$	$\pm 0,25$	$\pm 0,35$	$\pm 0,35$	$\pm 0,40$	—	$\pm 3\%$	$\pm 5\%$

at 250°C for 300 h. All the samples were single-phase according to x-ray structural analysis. Mössbauer spectra were recorded on an electrodynamic apparatus with an AI-256 analyzer. The source was a Co^{57} isotope in a stainless steel matrix [3]. The procedures used to measure the other parameters are described in [2].

Tables 1 and 2 show the experimental results. Analysis of these data reveals that by arranging the quantities $\Delta E(\text{Fe})$, a , c/a , n_B , H_A^{oct} , ΔH^{tet} , and Δ^{oct} in the order "quench-cooled with furnace-aging," we find monotonic changes. For the other properties (ρ , H_A^{tet}), there is a tendency toward a monotonic behavior which is "masked" by the fact that the errors involved are comparable to the magnitudes of the quantities themselves; for $\Delta E(\text{Cu})$, δ^{tet} , δ^{oct} , the mean deviations in this order of states are of the same sign.

The Mossbauer spectra shown in Fig. 1 result from a superposition of two six-line spectra having components of various intensities; component 1 in spectra I and III splits into two lines, 1a and 1b.

In interpreting these results it is natural to single out the monotonic changes in most of these properties through this sequence of states as the most general and most clearly defined characteristic. In this case the state of the ferrite cooled with the furnace should be treated as an intermediate state, while the quenched and aged states are further from and closer to equilibrium, respectively.

The monotonic changes in the parameters in Tables 1 and 2 can be explained under the assumption that some of the Fe^{3+} ions convert from B to A positions in the quench-cooled with furnace-aging sequence, while copper ions made the opposite move. This process must be accompanied by a decrease in n_B (according to the Neel model), by an increase in ρ (due to the decrease in the iron content in the B sublattice), and a decrease in lattice constant A (because of $r_A < r_B$ and $r_{\text{Cu}^{2+}} > r_{\text{Fe}^{3+}}$), as is in fact observed experimentally. The shortwave displacement of the $\text{Fe}K_{\alpha_1, \alpha_2, \beta_{1,3}}$ lines implies an increase in the 3d-electron density in the Fe atomic volumes [4], accompanied by an increase in the local magnetic field (H_A) at the Fe^{57} nuclei (Table 2). Since the chemical shifts δ^{tet} and δ^{oct} (Table 2) are characteristic of the Fe^{3+} ions (and not Fe^{2+} ions), and since the ρ values (Table 1) rule out the possibility that Fe^{2+} ions appear after aging, we must apparently attribute the increase in the 3d-electron density in the Fe atomic volumes to an increase in the covalency of the chemical bonds of the Fe^{3+} ions in the tetrahedral positions.

According to Mossbauer measurements [3], a high magnetic field at iron nuclei corresponds to the case of Fe^{3+} ions in the B sublattice, while a low field corresponds to the presence of these ions in the A sublattice. We should therefore associate spectrum α with Fe^{3+} ions in B positions and spectrum β with the same ions in A positions. Comparison of the peak values in the Mossbauer spectra (Fig. 1) on this basis confirms this conclusion regarding the redistribution of Fe^{3+} ions. For the quenched ferrite, the intensity of line 1a of the

TABLE 2. Mössbauer-Spectrum Parameters for Copper Ferrite Samples Subjected to Various Kinds of Heat Treatment

Heat treatment	Magnetic field at ^{57}Fe nuclei, kOe		Quadrupole splitting, mm/sec		Chemical shift mm/sec	
	H_K^{tet}	H_K^{oct}	Δ^{tet}	Δ^{oct}	δ^{tet}	δ^{oct}
Quenching from 1100°C	439	467	0,19	0,06	0,60	0,37
Cooling with disconnected furnace	486	486	0,12	0,12	0,35	0,35
Aging at 250°C	480	493	0,04	0,16	0,66	0,53
Error	± 5	± 5	$\pm 0,01$	$\pm 0,01$	$\pm 0,01$	$\pm 0,01$

first component of the α -spectrum is twice that of the same line in the β -spectrum; in the aged ferrite, these lines are approximately equal in intensity. This result corresponds to a disordered distribution of Fe^{3+} ions among sublattices in the quenched ferrite (a degree of inversion of $\approx 1/3$) and to an ordered distribution of these ions resulting from aging (a degree of inversion of approximately 1).

The Mössbauer spectrum of the ferrite cooled with the furnace (spectrum II in Fig. 1) deviates from the general behavior; it would seem that this spectrum should occupy an intermediate position between spectra I and III, but this is not the case. The lines of this spectrum are not resolved — simple broadened. We cannot completely explain this behavior of spectrum II.

The direction in which the quantities ΔE change (Table 1) show that the 3d-electron density in the copper atomic volumes is greater in the quenched and aged ferrites than in the ferrite cooled with the furnace, according to [4]. This situation may result from an increase in the covalency of the chemical bonds of the Cu^{2+} ions; in the case of the quenched ferrite, this increase is due to the tetrahedral surrounding of Cu^{2+} , while in the case of the aged ferrite, it is due to the Jahn–Teller effect [7], as can be seen from the increase in the ratio of c/a from 1.051 to 1.062 (Table 1). This result is consistent with the changes in the quadrupole splittings Δ^{tet} and Δ^{oct} (Table 2).

CONCLUSIONS

1. Aging of copper ferrite, CuFe_2O_4 , is accompanied by the formation of an inversion structure.
2. The combination of Mössbauer-effect measurements and other types of measurements (magnetic, electric, x-ray spectral, and x-ray structural) can be an effective means for studying the electron structure of ferrites.

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