

Mechanically induced structural disordering in spinel ferrites

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Mechanicky indukované štruktúrne neusporiadanie vo feritoch - spineloch

V práci je študovaný charakter mechanicky indukovaného štruktúrneho neusporiadania a metastability feritov so spinelovou štruktúrou. Vysvetlený je pôvod mechanicky indukovaných zmien magnetických vlastností študovaných látok.

Kľúčové slová: mechanická aktivácia, spinel, ferit, kationová redistribúcia, mechanicky indukované neusporiadanie.

Introduction

Over the past 20 years there has been a fairly extensive amount of work directed toward investigation of mechanically induced metastable states formation in substances with close packed structure units. Among the most important contributions made in the 1980s by Russian scientists, the influence of the original structure on the nature of mechanically induced structural disordering in ferrites should be mentioned: if large cations are present in the system (e.g. in CdFe_2O_4 , LaFeO_3 , DyFeO_3 , BiFeO_3), the translation invariance completely disappears and amorphisation takes place. A characteristic feature of spinels containing relatively small cations (Zn, Ni, Co, Mg) is the possibility of preserving the long-range order at stressing (Boldyrev, 1994; Pavljukhin, 1987; Pavljukhin et al., 1984 a 1988; Rykov et al., 1989; Yermakov et al., 1982).

A study of mechanically activated spinel ferrites has revealed that during energy-intensive milling they are transformed into an activated state whose magnetic properties differ essentially from those of the initial polycrystalline ferrites (Pavljukhin, 1987; Pavljukhin et al., 1984; Rykov et al., 1989). A model of mechanically induced structural disordering in both normal and inverse spinel ferrites has been proposed on the basis of Mössbauer spectroscopy measurements and calculations of radial distribution functions of atom densities (Pavljukhin et al., 1982-1988; Rykov et al., 1989; Boldyrev, 1986). According to this model, in the course of mechanical activation of these substances, all the cations that initially occupied tetrahedral (A) sites move into octahedral [B] positions due to the shear deformation of the close-packed anion layers in the $\langle 111 \rangle$ direction. Thus, after the transition into a final activated state only the octa-sublattice remains filled, and the decisive factor determining the modified magnetic properties of mechanically activated spinel ferrites is the interaction of the octa/cation-anion-octa/cation.

Further attempts to explain the origin of mechanically induced changes in magnetic properties of a normal spinel ferrite have been based on analogy with a mechanically induced inversion (Rykov et al., 1989; Yermakov et al., 1982; Yermakov, 1991).

However, the results of previous work do not sufficiently confirm the model of mechanically activated spinel ferrites based on a random distribution of all cations in octahedral sites. In addition, the causes of a total transition of cations into octahedral positions are also unclear, since the shear deformation of the close-packed anion layers in the $\langle 111 \rangle$ direction allows also a reverse transition of cations (Rykov et al., 1989; Petrakovskii, 1981).

It is evident from the discussion of the contradictory views that the character of mechanically induced disordering in spinel ferrites is not yet satisfactorily explained. The present paper summarizes the results of the contract cooperation between the Institute of Solid State Chemistry of the Russian Academy of Sciences (Novosibirsk) and the Institute of Geotechnics of the Slovak Academy of Sciences (Košice) aimed at the study of the formation of metastable states in mechanically activated spinel ferrites.

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Normal spinel ferrite

Application of a sophisticated software for the evaluation of X-ray powder diffraction data opens new ways to get more precise information on the crystal structure of studied solids. In order to get refined information on structural changes taking place during mechanical activation of spinel ferrites, at first, we analysed in detail powder diffraction pattern of mechanically activated zinc ferrite using the powerful Rietveld refinement (Young et al., 1982).

The use of Rietveld analysis for a more precise description of mechanically induced disordering needs a careful selection of the sample. Sample selection was thus based on a compromise between two requirements: first, the mechanically induced disorder should manifest itself by qualitative changes in the magnetic properties, but, second, the fitting of the defect structure by a model diffraction pattern should give reasonable values of crystal structure model indicators, i.e. the errors in determining the refined structure parameters should be as low as possible. These requirements are met by a sample activated in a planetary mill (EI 2x150, Inst. Solid State Chemistry, Novosibirsk) for 5 minutes (Šepelák et al., 1996 and 1993).

It is evident from final results of the Rietveld refinements (Table 1) that in the process of mechanical activation of zinc ferrite mainly the decrease of the occupation factor of both zinc and iron cations in tetrahedral and octahedral positions, respectively, took place, when compared to the as-prepared ferrite. Cations of zinc and iron "interchanged" their positions in the close-packed anion sublattice, i.e. a redistribution of cations took place during mechanical activation of zinc ferrite. Fig. 1 shows graphically the fit obtained between calculated and observed pattern of mechanically activated zinc ferrite.

Table 1. Final results of the Rietveld refinement for the as-prepared zinc ferrite (top) and for mechanically activated (5 min) zinc ferrite (bottom) in space group $Fd\bar{3}m$; x, y, z - positional parameters, g - occupation factor.

| Atom | x | y | z | g |
|---|-------|-------|-------|-------|
| Zn-tetra | 0.125 | 0.125 | 0.125 | 0.984 |
| Fe-octa | 0.500 | 0.500 | 0.500 | 1.953 |
| Zn-octa | 0.500 | 0.500 | 0.500 | 0.000 |
| Fe-tetra | 0.125 | 0.125 | 0.125 | 0.015 |
| O | 0.260 | 0.260 | 0.260 | 3.933 |
| Sys.: cubic, $\alpha/\beta/\gamma = 90^\circ/90^\circ/90^\circ$; degree of inversion: $\delta=0$. | | | | ← |

| Atom | x | y | z | g |
|--|-------|-------|-------|-------|
| Zn-tetra | 0.125 | 0.125 | 0.125 | 0.333 |
| Fe-octa | 0.500 | 0.500 | 0.500 | 1.223 |
| Zn-octa | 0.500 | 0.500 | 0.500 | 0.612 |
| Fe-tetra | 0.125 | 0.125 | 0.125 | 0.666 |
| O | 0.245 | 0.245 | 0.245 | 3.914 |
| Sys.: cubic, $\alpha/\beta/\gamma = 90^\circ/90^\circ/90^\circ$; degree of inversion: $\delta \approx 0.67$ | | | | ← |

The second important result obtained by Rietveld analysis is that mechanical activation leads to the contraction of the ferrite crystal lattice characterized by the decrease of the a value from 0.84432 nm (for the as-prepared sample) to 0.84248 nm. Contraction of the crystal lattice is accompanied by the decrease of oxygen parameter value from 0.385 to 0.3705. Since during

mechanical activation the spinel motif of the structure is retained (cubic symmetry with space group $Fd3m$ does not disappear), it

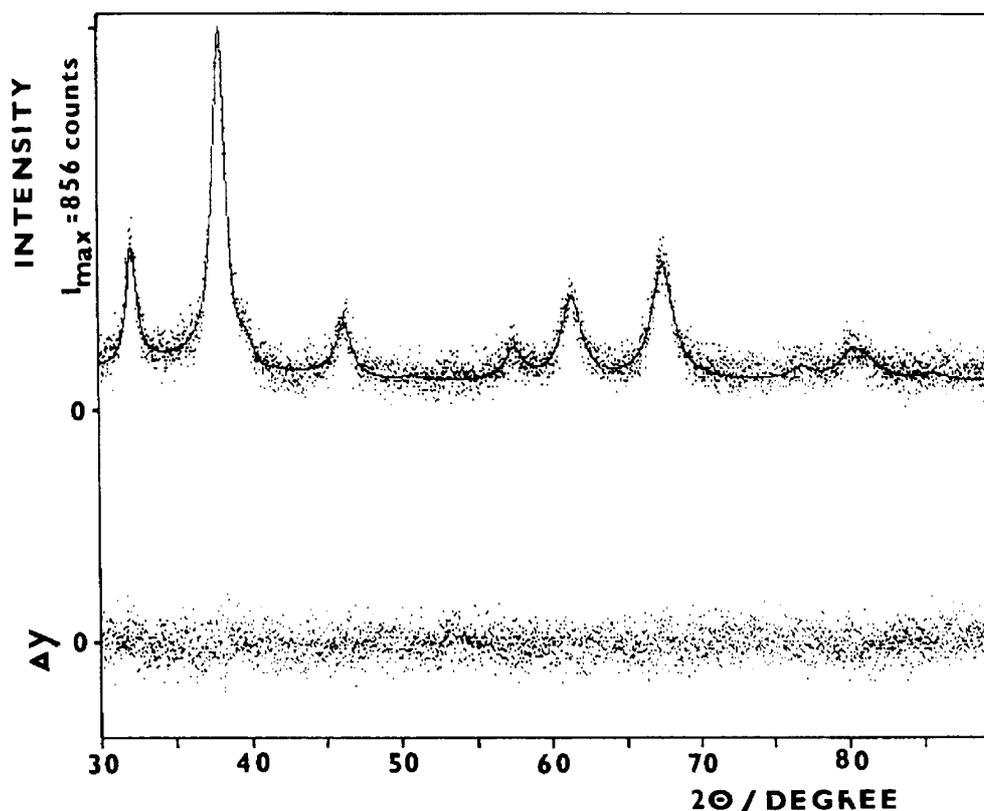


Fig. 1. Rietveld refinement profile of the X-ray powder diffraction data for mechanically activated (5 min) zinc ferrite. Points show observed X-ray diffraction intensities. A difference between the observed and calculated intensities (ΔY) is shown at the bottom; ($NiK\alpha$ radiation); structure model indicators: $R_B = 0.034$, $R_p = 0.029$, $R_{wp} = 0.036$.

may be said, on the basis of the determined interatomic distances (see Table 2) that during mechanical activation of zinc ferrite partial deformation of the anion sublattice takes place. This is manifested, in addition to a small change in the lengths of tetrahedral and octahedral bonds, mainly by the deformation of octahedron: the shared octahedral edges become longer than the unshared ones, contrary to the as-prepared zinc ferrite. Since the distances tetra-tetra, octa-tetra and octa/cation-octa/cation did not change significantly, the change in the octahedron geometry results in the alteration of the octa/cation-anion-octa/cation bond angle.

Table 2. Interatomic distances (in angstroms) for the as-prepared zinc ferrite (top) and for mechanically activated (5 min) zinc ferrite (bottom).

| tetra-tetra cation | tetra-octa cation | octa-octa cation | tetrahedral bond | octahedral bond | tetrahedral edge | shared oct. edge | unshared oct. edge |
|-----------------------|----------------------|---------------------|---------------------|--------------------|---------------------|---------------------|-----------------------|
| 3.656(1) | 3.500(4) | 2.985(1) | 1.996(2) | 2.018(4) | 3.259(8) | 2.710(5) | 2.991(4) |
| 3.648(1) | 3.492(7) | 2.978(6) | 1.758(4) | 2.144(8) | 2.871(4) | 3.085(8) | 2.979(6) |

Increase in magnetic moment in the structure of mechanically activated zinc ferrite creates favourable conditions to study hyperfine magnetic interactions at a temperature of 77 K. With prolongation of milling time the doublet in Mössbauer spectrum disappears and is gradually replaced with a sextet typical for magnetically ordered state of structure (Šepelák et al., 1996 and 1997). Results of Mössbauer spectroscopy indicate the presence of two types of interactions in mechanically

treated structure (Fig. 2). Taking into account the results obtained by Rietveld analysis we can attribute the first component of Mössbauer spectrum, in agreement with (Rykov et al., 1989; Yermakov et al., 1982; Yermakov, 1991), to the intersublattice exchange interaction of the $\text{Fe}^{3+}(\text{A})\text{-O}^{2-}\text{-Fe}^{3+}(\text{B})$ type (with bond angle of 125°), taking place due to the mechanically induced inversion. Interaction typical for the second component may be related to the state of the Fe^{3+} cations in the octahedral sublattice, i.e. to the interaction of the $\text{Fe}^{3+}(\text{B})\text{-O}^{2-}\text{-Fe}^{3+}(\text{B})$ type with deformed bond angles different from 90° ; this interaction is, according to (Pavljukhin et al., 1982-1988; Rykov et al., 1989; Boldyrev, 1986), solely responsible for the changes in the magnetic properties of mechanically activated zinc ferrite.

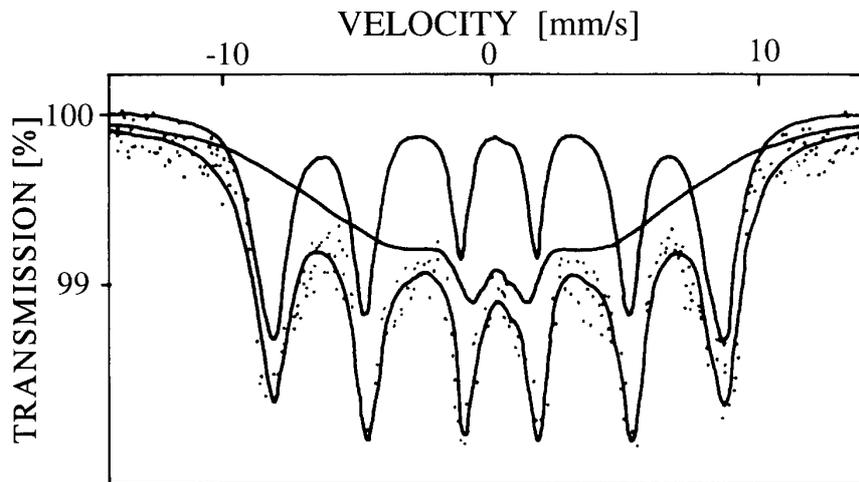


Fig.2. Two components in the Mössbauer spectrum of mechanically activated (24 min) zinc ferrite; temperature of measurement 77 K; velocity scale calibrated relative to $\alpha\text{-Fe}$.

Inverse spinel ferrites

Further powerful way to obtain information on cation distribution in spinel structure of ferrites is the measurements of integrated intensities of XRD lines. This method was applied to the solution of the mechanically induced structural disordering in partly (MgFe_2O_4) and fully inverse (NiFe_2O_4) spinel ferrites (Šepelák et al., 1997).

The intensities, I_{hkl} , may be calculated for different models assuming variable unit-cell content, based on the relation: $I_{hkl} \sim |F_{hkl}|^2$, where $F_{hkl} = \sum f_j A \exp\{2\pi i(hx_j + ky_j + lz_j)\}$. It is well-known that in spinel structure, the integrated intensity of the X-ray (220) reflection depends exclusively on the cations occupying the (A)-sites. On the other hand, the intensity of the X-ray (222) reflection depends on the [B]-site cations only. The calculation of $|F_{hkl}|^2$ for (220) and (222) reflections of spinel structure gives the following expressions:

$$\begin{aligned} |F_{220}|^2 &= 2(f_A + 4f_O A \cos^2 4\pi u)^2, \\ |F_{222}|^2 &= 8(f_B + 2f_O A \sin^3 4\pi u)^2, \end{aligned}$$

where u is the oxygen parameter and f is the atomic scattering factor.

The measured dependencies of the integrated intensity ratio $I(220)/I(222)$ on the time of planetary milling of nickel ferrite and magnesium ferrite are shown in Fig. 3. A decrease of the integrated intensity ratio $I(220)/I(222)$ with the milling time is also evident from the comparison of diffraction patterns for the activated and the as-prepared ferrite (Fig. 4). Apparent change in the integrated intensity ratio $I(220)/I(222)$ indicates that in the process of mechanical treatment of MgFe_2O_4 and NiFe_2O_4 the concentration of cations on (A)-positions decreases and number of cations occupying [B]-positions increases, i.e. the cations filling the tetra-sites pass into octa-sites.

Mössbauer spectroscopy revealed that with the prolongation of the milling time of MgFe_2O_4 and NiFe_2O_4 , the hyperfine magnetic sextets in their spectra disappear and are gradually replaced with a paramagnetic doublet (Šepelák et al., 1997). The measured value of isomer shift of paramagnetic doublet ($IS = 0.35 \text{ mms}^{-1}$) in the spectra of mechanically treated ferrites is characteristic

for trivalent iron cations on octahedral positions surrounded with oxygen anions (Evans, 1968). Therefore, it may be assumed that in a final state of the ball milling of MgFe_2O_4 and NiFe_2O_4 (when their Mössbauer spectra exhibit only the paramagnetic doublet, see Fig. 5) only the octa-sublattice is occupied by Fe^{3+} cations. Thus, in the process of the high-energy ball-milling of the inverse spinel-ferrites, MgFe_2O_4 and NiFe_2O_4 , the cations that initially occupied tetra-sites pass into octahedral positions of the close-packed anionic sublattice.

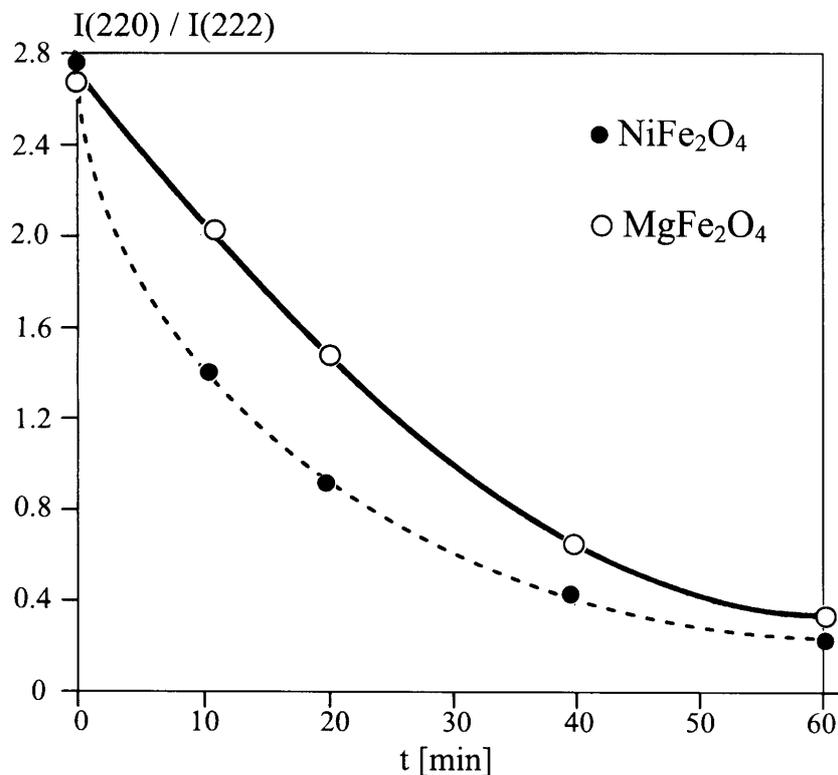


Fig.3. The XRD line intensity ratio, $I(220)/I(222)$, as a function of milling time (t).

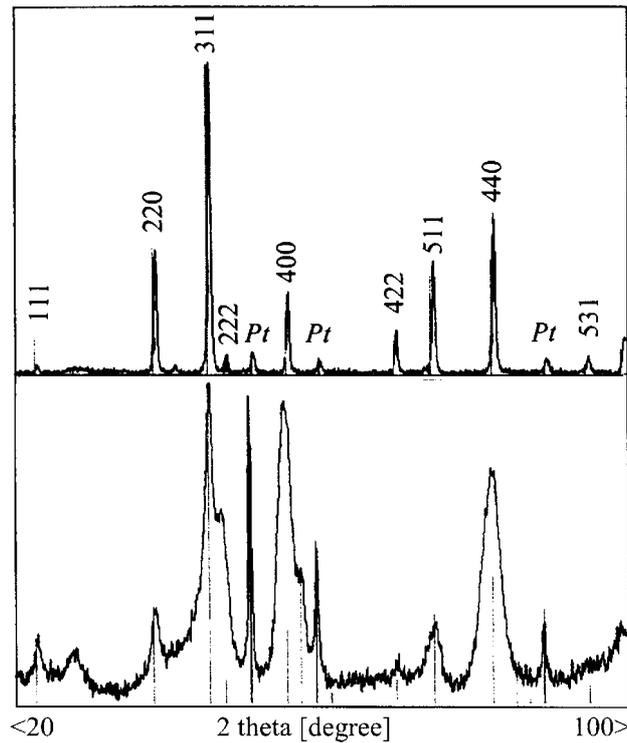


Fig.4. XRD patterns of the MgFe₂O₄ before (top) and after (bottom) milling (60 min); the samples measured on a platinum support.

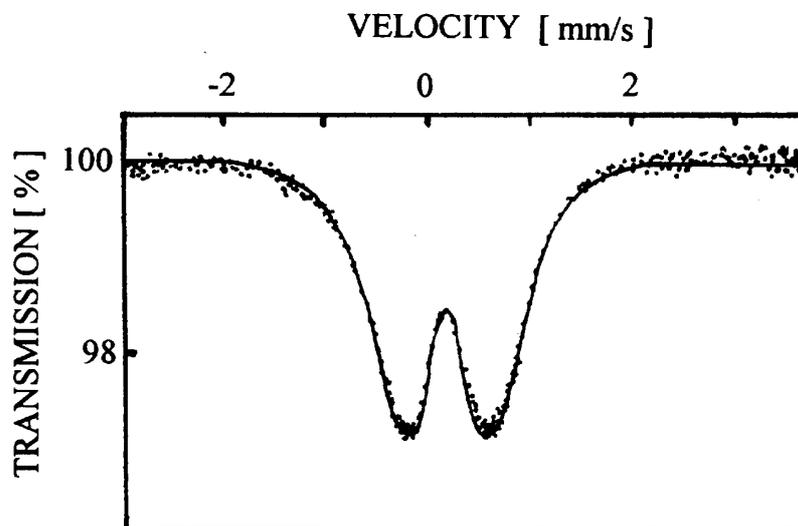


Fig.5. Mössbauer spectrum of the mechanically activated (60 min) nickel ferrite; temperature of measurement 300 K; velocity scale calibrated relative to α -Fe.

Conclusions

The structure of mechanically activated normal and inverse spinel ferrites has been completely solved from the XRD and Mössbauer spectroscopy data.

It was found that mechanical treatment of both partly and fully inverse spinel ferrites leads to the one-directional redistribution of cations into octahedral sites. This is, in this case, a confirmation of the model of the structure of mechanically activated spinel ferrites (Pavljukhin et al., 1982-1988; Rykov et al., 1989; Boldyrev, 1986).

In the process of mechanical activation of normal spinel, two basic structural phenomena takes place: mechanically induced inversion and deformation of octahedron geometry. It is obvious that a suitable combination of modern approaches for the refinement of the structure of mechanically activated normal spinel ferrites leads to the integration of seemingly contradictory views on the nature of mechanically induced changes into a single conception.

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