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On the Consequences of Mechanical Activation of Zinc and Nickel Ferrites

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Mechanical activation of zinc and nickel ferrites was shown to affect their physicochemical properties. For example, the temperature of magnetic transition of activated zinc ferrite sharply increased, while that of activated nickel ferrite decreased. Variation in the magnetic properties of ferrites is not due to their reversal degree, but is caused by transfer of cation from tetrahedral- to the vacant octahedral-sites in the spinel structure. The cations are randomly distributed on the octahedral-sites producing new exchange-bound pairs. The disordering of the anion and cation sublattices, leading eventually to the X-ray-amorphous structure, is thought to be due to the plastic deformations in the course of mechanical activation.

It has been established that the change of reactivity of solids in consequence of intensive mechanical treatment occurs not only because of a simple increase of the surface as a result of specimen fragmentation, but also because of large non-equilibrium defect accumulation (*1–5*). Thus, the change of physicochemical properties of solids and of reactivity, termed mechanical activation, has drawn the attention of researchers. In this paper we studied the nature of activation of some mechanically treated ferrite-spinels. It was natural to expect that the character and the type of mechanical activation would depend first, on crystal–chemical peculiarities of substance's structure and, second, on the character and intensity of mechanical stress in the spinel.

It is known that the main structural feature of spinels is a close-packed cubic oxygen sublattice in which cations are placed in tetrahedral and octahedral interstices. Cations are placed in $\frac{1}{8}$ of tetrahedral-positions and in $\frac{1}{2}$ of octahedral-positions, which correspond to the $8a$ and $16d$ positions for space group $Fd3m$ (*6*). In the normal spinel all divalent cations are in tetrahedral-positions and iron cations are in octahedral-positions. In inverse spinels, divalent cations are in octahedral-positions and iron cations are equally distributed between tetrahedral- and octahedral-positions. In the intermediate case the spinel formula can be specified in the following manner:

$$(Me_{1-\delta}Fe_{\delta})[Me_{\delta}Fe_{2-\delta}]O_4 \qquad (1)$$

where δ is the degree of inverse character of the spinel, which depends on temperature as follows (*7*)

$$\frac{(1-\delta)(2-\delta)}{\delta^2} = \exp(-\Delta p/kT) \qquad (2)$$

Here, Δp is the change of lattice energy when divalent and trivalent cations ex-

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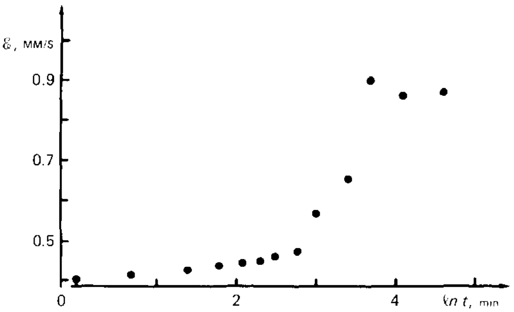

FIG. 1. Quadrupole splitting vs the logarithm of the time of mechanical activation.

change their octahedral and tetrahedral positions. This explains how the cation distribution may be changed by the change of temperatures with the increasing prevalence of the high-temperature distribution, it is possible to state energy in such ferrites. However, the process of altering the equilibrium distribution of cations by mechanical activation, is not sufficient (*8*). Indeed, the equilibrium process demands either a cation distribution in octahedral- and tetrahedral-positions or a corresponding vacancy rearrangement. And this, in turn, is associated with the cation transfer in the sublattice. If one takes into account that a mechanical treatment is usually local and acts for a short time (*9*), then the formation of different types of intermediate non-equilibrium states can be expected. The formation of such states during mechanical deformation is especially great if an intensive energy increase is followed by application of three-dimensional loading and of shear stress. This type of deformation usually occurs in centrifugal mills.

In this paper, the influence of mechanical treatment on cation distribution was studied in zinc ferrite (normal spinel) and in nickel ferrite (inverse spinel). Both ferrites were synthesized by sintering of mixed oxides at 1000–1100°C ($ZnFe_2O_4$) and 1300°C ($NiFe_2O_4$) for several hours using routine ceramic technology. The ferrites so produced were identified with the help of X-ray diffraction and γ-resonance spectroscopy. The mechanical activation was achieved in the centrifugal mill with an acceleration of 400 m/sec^2, its balls and cylinders were made of ceramic so as not to contaminate the specimen. After treatment for sufficient length of time the specimens were analyzed on a Mössbauer spectrometer YGRS-4M. All chemical shifts were determined relative to α-Fe. In those cases where it was necessary to study the influence of mechanical activation, a portion of the probe was dissolved in 3 N H_2SO_4. Chemical analysis established the degree of cation leaching from ferrite by acid.

The mechanical activation of zinc ferrite enhanced the quadrupole splitting of the Mössbauer spectra at room temperature from 0.33 to 0.90 mm/sec (*10*) and the line width increased by approximately a factor of two (Fig. 1). This testifies to the significant change of the crystallochemical structure of the initial substance. At 78 K the spectra of the activated samples, indicate the appearance and an increase with the time of mechanical activation of the magnetically ordered state of the substance (Fig. 2). In this case, the effective magnetic field activity on the iron nuclei is 470 ± 10 kOe, and the quadrupole splitting is 0.00 ± 0.02 mm/sec. The observed doublet (Figs. 2 and 3) has parameters corresponding to those of the initial zinc ferrite. The mechanical activation notably increases the solubility of the substance. After dissolution, the component associated with the magnetically ordered substance, which appears with activation, is no longer present in the spectra (Fig. 3). The difference in the magnetic and chemical properties of the initial and activated substance, permits one to distinguish between these two states and to follow the process of their mutual transformation. The temperature of the magnetic transition in the magnetically ordered states of the activated zinc ferrite is ca. 210 K as compared

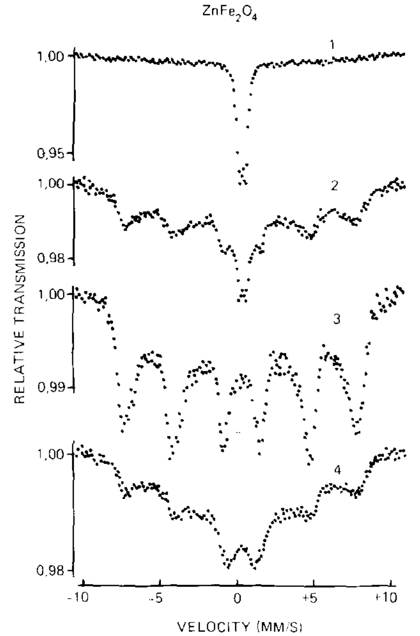

FIG. 2. Mössbauer spectra of zinc ferrite at 78 K. Activation for (1) 0 min (initial), (2) 6 min, (3) 20 min, and (4) 60 min.

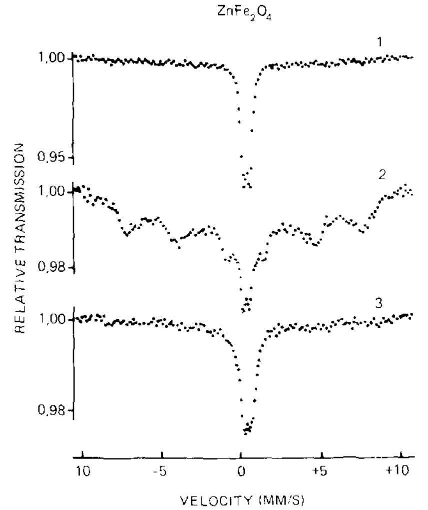

FIG. 3. Mössbauer spectra of zinc ferrite at 78 K: (1) initial, (2) activated for 6 min, and (3) residue after dissolution of the activated ferrite for 6 min.

with 9 K for the initial ferrite. The line width of the magnetically ordered component decreases with increasing time of mechanical activation, and after 40 min, the substance begins to exhibit superparamagnetic properties even at 78 K.

In the case of the nickel ferrite (with a Néel temperature of 858 K) with mechanical activation of short duration it is possible to distinguish the components corresponding to the tetrahedral- and octahedral-cations (Fig. 4). When increasing the time of the mechanical activation a new substance with a magnetic transition at ca. 260 K, is formed. With prolonged activation, nickel ferrite, like zinc ferrite, transforms to the superparamagnetic state. The substance resulting from the mechanical activation processes differs in magnetic properties from those of the classical ferrite spinels, and the resulting magnetic structure tends toward perfection with an increase in the time of activation. A further increase of the temperature of the magnetic transition is quite probable; however, the superparamagnetic phenomenon at this step cannot be detected by the Mössbauer technique. Thus, for zinc and nickel ferrites, a transition to the mechanically activated state with almost the same magnetic properties, is observed. Mechanical activation leads to new exchange reactions different from those of the

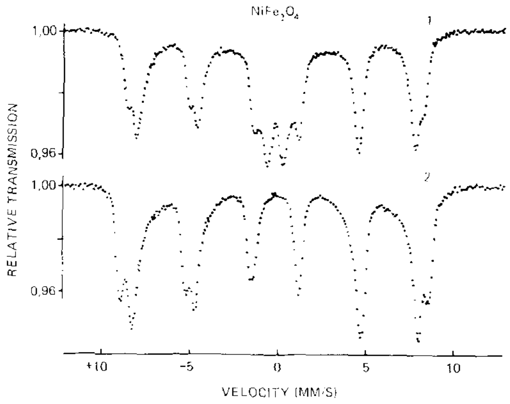

FIG. 4. Mössbauer spectra of nickel ferrite activated for 10 min: (1) at room temperature and (2) at 78 K.

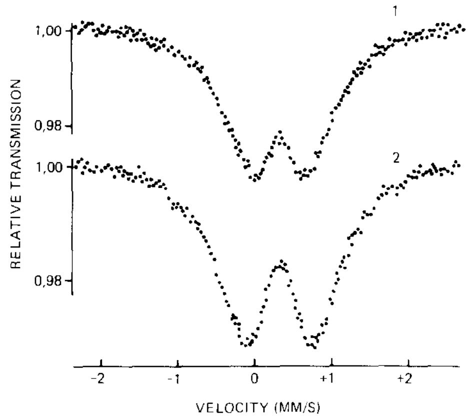

FIG. 5. Mössbauer spectra at room temperature: (1) zinc ferrite activated for 20 min and (2) nickel ferrite activated for 30 min.

ferrite spinels and subsequently lowers the regions where these reactions occur; as a result, the substance exhibits superparamagnetic properties. The study of the properties of activated ferrites made it possible to follow the sequence of transformations of these substances.

Mössbauer spectra of zinc and nickel ferrites activated at room temperature, for which the transition from the initial to the mechanically activated state is almost complete, exhibit only a doublet (the substance can be both in paramagnetic and superparamagnetic states). Measurements at slow rates suggest (Fig. 5) that the parameters of the hyperfine interactions of the activated zinc and nickel ferrites (their chemical shift equals 0.35 ± 0.01 mm/sec) correspond to Fe(III) in octahedral surroundings of the oxygen ions. This result is quite natural for zinc ferrite because the iron cations are located initially on the octahedral-sites. However, in the initial nickel ferrite the iron cations are equally distributed between the octahedral- and tetrahedral-sites. As is known, the chemical shift for the iron on tetrahedral-cations in ferrites with spinel structure is 0.10–0.15 mm/sec less than that of the cations on octahedral sites [II]. Therefore, if the iron cations are on the octahedral- and tetrahedral-sites, the Mössbauer spectrum will contain a superposition of the two doublets. Whenever these latter are poorly resolved and the number of cations on tetrahedral- and octahedral-positions is different, the spectrum will form an asymmetric doublet. If the number of cations on tetrahedral-positions equals that on octa-interstices, the doublet will be symmetric, but the chemical shift is smaller by 0.05–0.07 mm/sec than that for the cations in octahedral interstices. As is seen in Fig. 5, the spectra of activated ferrites are symmetric, and their chemical shift corresponds on a one-to-one basis to Fe(III) on octahedral-sites. This result indicates that during mechanical activation there occurs no shift of cations from octahedral to tetrahedral locations. However, a transition of cations from tetrahedral into the vacant octahedral-sites is possible. Thus, during mechanical activation, a substance with a unique cation distribution is, indeed, formed.

The main structural feature of the crystallochemical transformations during mechanical activation resulting in such cation distribution, seems to be the shear stress of the oxygen planes with respect to each other, which produces imperfections in the packing. The cations located between these planes can be displaced; in particular, cations are moved from tetrahedral interstices into the large octahedral-sites (*12*). We believe that during mechanical activation the close packing of oxygen sublattice is retained, but that the ordering of the sequences of oxygen layers becomes random. Hence, in the activated ferrites the oxygen sublattice exhibits no long-range order, and in the short-range order, cubic packing of oxygen ions (similar to the spinel structure), as well as hexagonal packing and their superposition are possible. One may reasonably suppose that in the course of the mechanical activation of ferrites the cations

TABLE I

THE NUMBER OF THE NEAREST OCTAHEDRAL-SITES FOR OCTAHEDRAL-CATION BETWEEN THE OXYGEN PLANES A AND B AS A FUNCTION OF THE LOCAL POSITION OF OXYGEN PLANES IN THE DENSELY PACKED LATTICE

Local position of oxygen planes in densely packed lattice	Probability of configuration	The number of the nearest octasites corresponding to the angle of the cation–anion–cation bond			
		71°	90°	132°	180°
Cubic, CA(cation)BC	$\frac{1}{4}$	0	12	0	6
Hexagonal, BA(cation)BA	$\frac{1}{4}$	2	6	12	0
Hybrid, BA(cation)BC	$\frac{1}{4}$	1	9	6	3
Hybrid, CA(cation)BA	$\frac{1}{4}$	1	9	6	3

(initial and transferred therein by mechanical activation) are randomly distributed among the octahedral-sites. The number of the nearest octahedral-sites for any cation is given in Table I as a function of the local type of the oxygen sublattice bond for different angles of the cation–anion–cation. The appearance of short-range order in hexagonal packing, as well as in cubic packing, and their hybrid and the random cation distribution on the octahedral-sites leads to the formation of new exchange-bound pairs, with an angle of the cation–anion–cation bonding that is atypical for the spinel structure. Among the new pairs there occur some for which the exchange interactions are more effective, due to the change in the bond angle, than in the structure of the initial zinc ferrite (*13*). In this manner one can account for the temperature change of the magnetic transition of the activated zinc ferrite from 9 K to ca. 210 K. The decrease in the temperature of the magnetic transition of the activated nickel ferrite from 858 K down to ca. 260 K is due to the transfer of cations from tetrahedral- into octahedral-sites, and consequently, to the breaking of the strongest exchange interaction between the octahedrally and tetrahedrally located cations. Thus, in terms of the proposed model of the crystallochemical transformations, ultimately leading to the X-ray-amorphous product, it is possible to explain the variation of such physical constants as the temperature of the magnetic transition.

The proposed mechanism of the mechanical activation of ferrite spinels can also be used to describe related crystalline structures. For example, we have examined the consequences of the mechanical activation of chalcopyrite $CuFeS_2$, the main structural element of which is a closely packed hexagonal lattice composed from the sulfur ions, with cations on tetrahedral-sites. During the mechanical activation of $CuFeS_2$, a new component appears in the Mössbauer spectrum whose chemical shift increases from 0.20 ± 0.02 to 0.33 ± 0.02 mm/sec, which is characteristic of the change of the iron coordination from tetrahedral to octahedral (*14*, *15*). Thus, in this compound, the disordering of the densely packed hexagonal lattice of anions is also accompanied by the cation transition from tetrahedral- to octahedral-sites.

Thus, the results allow us to establish some general consequences of mechanical activation of inorganic solids whose main structural peculiarity is a close anion packing. A pulse of mechanical action produces plastic deformations leading to imperfections in the packing. The cations transfer from tetrahedral to large octahedral-sites. The cations are randomly distributed on the octahedral-sites and, particularly, may occupy sites which were vacant in the initial structure. Evidently, this mechanism of mechanical activation should apply to a great number of inorganic solids.

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