JOURNAL OF MATERIALS SCIENCE 33 (1998) 2845–2850

A temperature-dependent Mössbauer study of mechanically activated and non-activated zinc ferrite

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The changes of $ZnFe_2O_4$ caused by mechanical activation as well as the structural evolution of non-activated and mechanically activated zinc ferrite occurring during heating, have been investigated by *in situ* Mössbauer spectroscopy. Attention is directed to mechanically induced changes in magnetic properties of zinc ferrite, the variation of nuclear quadrupolar interactions, the thermally induced changes of the Mössbauer shift, and also to the structural response of mechanically activated zinc ferrite to changes in temperature.

1. Introduction

Mechanical activation (high-energy ball-milling) is a solid-state powder processing technique which allows the development of novel crystal structures and microstructures, leading to enhanced physical and chemical properties [1]. Owing to the versatility of spinel-ferrites ($MeFe_2O_4$), combined with the physical flexibility of their structure providing a wide range of physical behaviour, they have been considered as very convenient model systems for the investigation of processes induced by mechanical action.

In previous work, the crystal structure of the mechanically activated zinc ferrite ($ZnFe_2O_4$) has been studied using X-ray powder diffraction (XRD) [2, 3]. On the basis of a Rietveld analysis, the exact coordinates of atoms, the unit-cell dimension, oxygen parameter, atom occupation factors as well as the interatomic distances in mechanically activated zinc ferrite have been determined [2, 3]. Even though considerable progress has been made in the description of the structure of mechanically activated zinc ferrite, a number of questions connected with the explanation of the mechanically induced changes in its structure and properties, still persist [4–7].

Another problem, which was studied only to a limited extent until now, is related to the thermal stability of mechanically induced structural defects in zinc ferrite and the mechanism of their relaxation on heating. From the small amount of available data the results of an *in situ* X-ray diffraction analysis [8, 9] and differential scanning calorimetry (DSC) [10] may be mentioned. *In situ* X-ray diffraction analysis revealed that thermal relaxation occurs in the mechanically activated zinc ferrite in the temperature range 600–1000 K [8, 9]. By DSC it was found that, during heating of zinc ferrite, the amount of released heat, stored in the mechanically disturbed structure, amounts to 40–60 kJ mol^{-1} [10]. During the process of relaxation of mechanically induced metastable states, the advantageous properties of the activated zinc ferrite are mostly lost, thus an understanding of the relaxation mechanism is necessary. This understanding would be of principal importance for, from the scientific point of view, the development of an atomistic and microscopic theory of the mechanochemical processes, as well as for, from the practical point of view, the application of mechanically activated zinc ferrite at elevated temperatures.

One of the most promising applications of zinc ferrite is its use as an absorbent material in high-temperature coal-gas desulphurization [11–14]. An interesting observation is that the mechanical activation leads to a substantial increase of its sulphur absorption capacity in the high-temperature coal-gas desulphurization process [15]. Subsequent high-temperature oxidation (regeneration) of sulphurized zinc ferrite is also favourably influenced in an indirect way by the mechanical pre-activation of the sorbent [15]. In spite of these favourable effects of mechanical activation on the high-temperature reactivity, little is known of the structure–reactivity relationship at high temperatures. The industrial utilization of mechanical activation in the field of environmental protection and further intensification of the high-temperature desulphurization, therefore requires a detailed study of the structure of mechanically activated zinc ferrite at elevated temperatures.

In an attempt to contribute to the solution of the problems mentioned above, this experimental work is devoted to a comparative Mössbauer study of mechanically activated and non-activated zinc ferrite at liquid nitrogen temperature and in the temperature range from 293–1473 K.

2. Experimental procedure

2.1. Material

Zinc ferrite (Franklinite, JCPDS 22-1012) occurs as a mineral of metamorphic rocks and can also be synthesized by solid-state reactions. The ferrite investigated in the present work was prepared in polycrystalline form by a solid-state reaction (further referred to as the non-activated sample). Stoichiometric mixtures of powdered reactants containing 66.34% alpha-Fe_2O_3 and 33.76% ZnO by weight were homogenized in a ball mill. Powdered mixtures were pressed into tablets under a pressure of 30 MPa in a steel mould in order to obtain a high degree of compaction of the reactants. The tablets were 20 mm diameter and 4 mm thick. The reaction tablets were heat-treated isothermally: heating was carried out in a preheated electric furnace, which was maintained at 1220 ± 5 K for 5 h. At the completion of the heat-treatment period, the samples were removed from the furnace and cooled rapidly by air quenching. The single-phase nature of prepared samples was confirmed by XRD analysis and by Mössbauer spectroscopy.

2.2. Mechanical activation

Zinc ferrite was activated by grinding in a planetary ball mill EI 2×150 (made by the Institute of Solid State Chemistry, Novosibirsk, Russia). Non-activated sample (2 g) was ground for 5, 12 and 24 min in a ceramic-covered grinding chamber. The volume of the grinding chamber was about 150 cm^3. Balls made of α-Al_2O_3 ceramics with diameters of 3–5 mm were used. The ball-to-powder weight ratio was 50 : 1. Grinding experiments were performed in air at 750 r.p.m.

2.3. Mössbauer spectroscopy

Mössbauer experiments have been made in transmission geometry using a conventional microcomputer-controlled spectrometer in constant acceleration mode. A $^{57}Co/Rh$ γ-ray source was used. The velocity scale was calibrated relative to α-Fe (or ^{57}Fe in Rh). A proportional counter was used to detect the transmitted γ-rays. All Mössbauer measurements were carried out in a slightly flowing air stream and in thermal equilibrium. At elevated temperatures, samples were measured on quartz glass plates. Non-activated zinc ferrite was measured at 13 different temperatures from room temperature to 1473 K. The sample activated for 24 min was measured from room temperature to 773 K. The spectra of non-activated zinc ferrite were fitted with Lorentzian functions (Table I). The spectra of activated samples were fitted allowing for a distribution of quadrupole interactions [16]. The Mössbauer spectra at 77 K were measured at the Institute of Solid State Chemistry in Novosibirsk, Russia.

TABLE I Mössbauer parameters of the non-activated zinc ferrite at various temperatures. All Mössbauer shifts are referred to ^{57}Fe in Rh at room temperature

Temperature T (K)	Mössbauer shift, δ (mm s^{-1})	Quadrupole splitting, Δ (mm s^{-1})	Linewidth, Γ (mm s^{-1})
293	0.242	0.330	0.308
373	0.176	0.331	0.306
473	0.102	0.337	0.305
573	0.031	0.333	0.268
673	− 0.058	0.353	0.312
773	− 0.116	0.369	0.282
873	− 0.197	0.384	0.319
973	− 0.251	0.399	0.292
1073	− 0.352	0.404	0.326
1173	− 0.401	0.390	0.310
1273	− 0.471	0.412	0.301
1373	− 0.529	0.387	0.323
1473	− 0.613	0.405	0.302

3. Results and discussion

3.1. Mechanically induced structural changes in zinc ferrite

At low temperatures, zinc ferrite adopts the normal spinel structure, in which the diamagnetic Zn^{2+} cations occupy (A)-sites tetrahedrally coordinated by oxygen, while the octahedrally coordinated [B]-sites are occupied by the Fe^{3+} cations. Accordingly, the so-called degree of inversion, x, which characterizes the distribution of cations on the two different sites of the structure, $(Zn_{1-x}Fe_x)[Zn_xFe_{2-x}]O_4$, takes values near zero. According to the Néel theory [17] of ferrimagnetism, there are, in addition to the dominant antiferromagnetic coupling between magnetic ions on tetrahedral (A) sites and on octahedral [B] sites, weaker (A)–(A) and [B]–[B] interactions. Because the (A)–[B] coupling is absent in zinc ferrite, this compound exhibits antiferromagnetism at sufficiently low temperatures. Zinc ferrite undergoes a transition from the paramagnetic into a magnetically ordered state at 9 K [18]. In agreement with this fact, the Mössbauer spectrum of the non-activated zinc ferrite at liquid nitrogen temperature consists of a paramagnetic doublet with a quadrupole splitting $\Delta = 0.346$ mm s^{-1}, a linewidth $\Gamma = 0.356$ mm s^{-1} and an isomer shift $\delta = 0.327$ mm s^{-1}, see Fig. 1a. With the prolongation of the mechanical activation time, the paramagnetic doublet in the spectrum disappears and is gradually replaced by a sextet typical of the magnetically ordered state of the structure, see Fig. 1.

In order to interpret the formation of a magnetic hyperfine sextet during mechanical activation of zinc ferrite, the results of the Rietveld analysis of mechanically activated zinc ferrite, reported in previous work [2, 3], should be taken into consideration. From these results it was concluded that the mechanical activation results in a substantial displacement

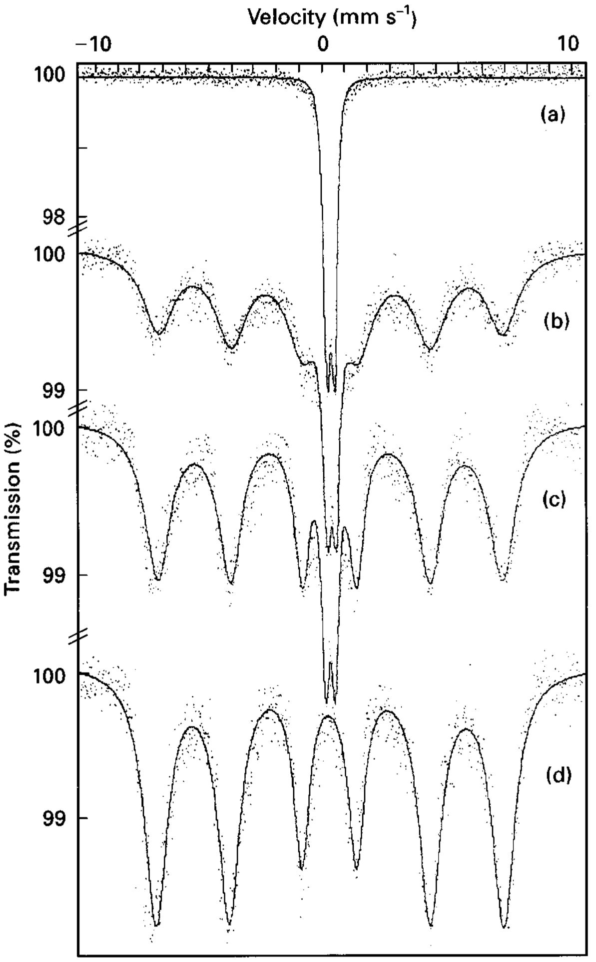

Figure 1 Mössbauer spectrum of (a) the non-activated sample of zinc ferrite, and of samples mechanically activated for (b) 5 min, (c) 12 min, (d) 24 min. Spectra taken at 77 K; velocity scale calibrated relative to α-Fe.

of Zn^{2+} cations to octahedral sites and of Fe^{3+} cations into tetrahedral sites of the cubic close-packed anionic sublattice (i.e. mechanically induced inversion takes place). In fact, it was found from the Rietveld analysis that the degree of inversion changes from $x \approx 0$ to $x = 0.67$ as a consequence of mechanical activation. This considerable change is accompanied by a decrease of both unit-cell dimension and oxygen parameter [2]. In addition to a small change in the lengths of tetrahedral and octahedral bonds, it was also found that the mechanically induced contraction of the crystal lattice is accompanied mainly by the deformation of the octahedron: the shared octahedral edges become longer than the unshared ones. Because the tetra–tetra, octa–tetra and octa–octa cation distances do not change significantly, the change in the octahedral geometry results in the alteration of the octa/cation–anion–octa/cation bond angle [3].

It is known that the presence of cations with nonzero magnetic moments on the tetrahedral as well as on the octahedral sublattice of ferrite-spinels may cause an exchange interaction of the $(A)–O^{2-}–[B]$ type. In the mechanically activated $ZnFe_2O_4$ the induced considerable redistribution of Zn^{2+} and Fe^{3+} cations brings about the onset of these $Fe^{3+}(A)–O^{2-}–Fe^{3+}[B]$ interactions. Mechanically induced changes in the magnetic properties of zinc ferrite are also closely connected with the changes of geometrical factors in its structure. Therefore, another factor determining the modified magnetic properties of mechanically activated zinc ferrite may be related to the change in the octahedral geometry. The alteration of the octa/cation–anion–octa/cation bond angles leads to the onset of the $Fe^{3+}[B]–O^{2-}–Fe^{3+}[B]$ interaction with deformed bond angles different from 90° (typical for the non-activated zinc ferrite). Thus, we attribute the formation of magnetic spin arrangements in the mechanically activated material observed by Mössbauer spectroscopy at 77 K, either to the onset of intersublattice exchange interaction of the $Fe^{3+}[A]–O^{2-}–Fe^{3+}[B]$ type (with bond angle of 125°) taking place due to the mechanically induced inversion and/or to the onset of intrasublattice exchange interactions of the $Fe^{3+}[B]–O^{2-}–Fe^{3+}[B]$ type with deformed bond angles different from 90°.

Information on the structure of mechanically activated zinc ferrite obtained by Mössbauer spectroscopy at liquid nitrogen temperature was complemented by measurements at room temperature. Mössbauer spectra of the non-activated zinc ferrite taken at room temperature are characterized by a paramagnetic doublet, see Fig. 2. As can be seen, mechanical activation leads to a considerable broadening of the doublet when compared to the non-activated sample. The broadening of the doublet provides clear evidence of considerable changes in the quadrupolar interaction. The large extension of the wings of the signal as well as weak indications of magnetic structure in the spectrum clearly show that in the activated material, even at room temperature, some form of magnetic interaction is still present. The superposition of the magnetic and quadrupole interactions and the broadening appearing in the spectra at room temperature cannot be resolved by lineshape fitting. Only at temperatures of 473 K and above, these indications of magnetic interactions have disappeared, see Figs 2 and 3. The broad distribution of the quadrupole splitting, typical for the activated sample, (Fig. 3), is clear evidence of the presence of a wide distribution of electric field gradients at the Fe^{3+} nuclei. Changes of the cation distribution cannot be detected in the Mössbauer spectra, either at room temperature or at higher temperatures, because the broadened lineshapes are highly symmetrical, see the discussion of the spectra of non-activated zinc ferrite in the next section. In particular, the results from X-ray diffraction of mechanically activated zinc ferrite can neither be confirmed nor excluded by the Mössbauer spectra.

3.2. Structural response of zinc ferrite to changes in temperature

Mechanically induced complex structural changes in zinc ferrite cause its transition into an excited metastable state. Return into the low-energy crystalline state is usually a thermally activated process. *In situ* Mössbauer spectroscopy was employed at elevated temperatures, in order to compare thermally induced structural evolution of mechanically activated zinc

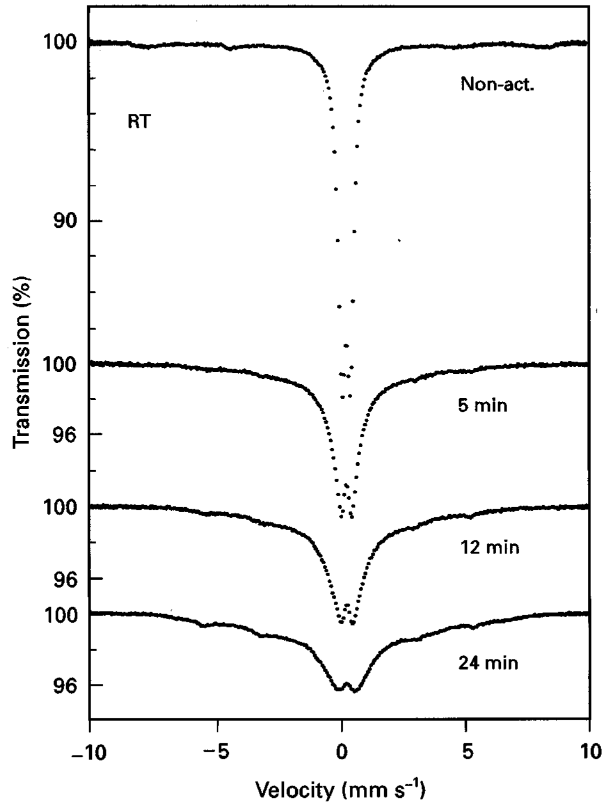

Figure 2 Mössbauer spectrum of the non-activated sample of zinc ferrite and of samples mechanically activated for 5, 12 and 24 min taken at 293 K; velocity scale calibrated relative to iron in rhodium.

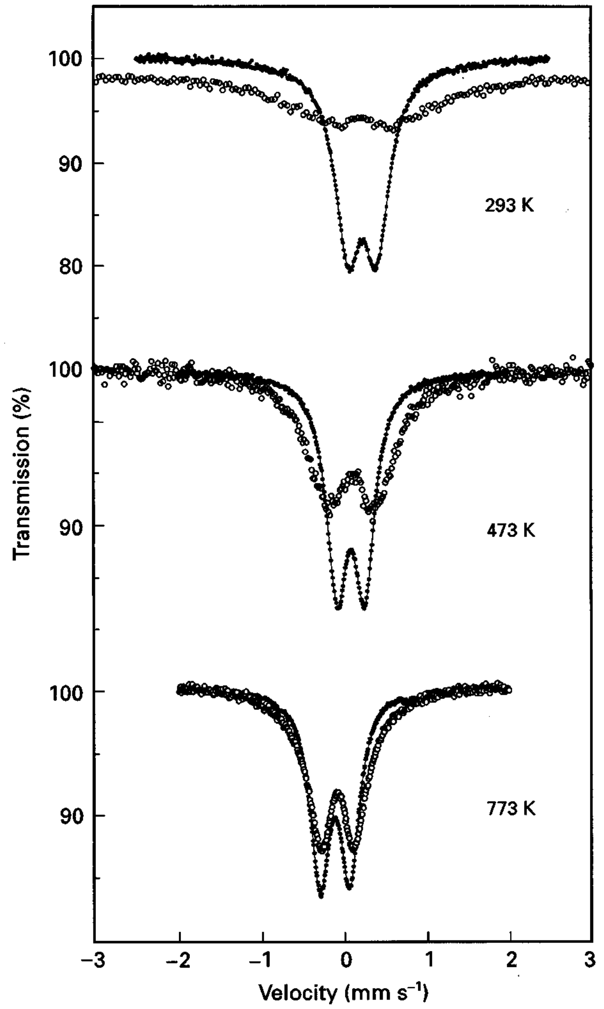

Figure 3 Comparison of Mössbauer spectra of (●) the non-activated and of (○) the mechanically activated (24 min) zinc ferrite taken at 293, 473 and 773 K; velocity scale calibrated relative to ^{57}Fe in Rh.

ferrite with changes occurring during heating of the non-activated zinc ferrite.

Parameters of the Mössbauer spectrum of zinc ferrite at room temperature have been determined by a number of authors [5–7, 19–21]. The values of the Mössbauer shift, δ, the quadrupole splitting, Δ, and the linewidth, Γ, which we obtained at 293 K (Table I), are in good agreement with those reported in the literature. However, the temperature dependence of the parameters has not yet been studied for $ZnFe_2O_4$ at high temperatures. Our temperature-dependent Mössbauer measurements revealed that the linewidth, Γ, of the spectra of the non-activated zinc ferrite, remains practically constant over the considered temperature range (77–1473 K). The evaluation of the high-temperature spectra, however, is complicated due to a loss of zinc by evaporation from the spinel and the accompanied formation of iron(III) oxide, Fe_2O_3. Such iron-rich phases have been detected by electron microscopy and microprobe analysis. A slight increase of the quadrupole splitting, Δ, see Table I, is probably caused by the existence of a spurious signal due to Fe_2O_3 or by a change of the cation distribution. A change of the cation distribution in zinc ferrite at high temperatures is not obvious. Therefore, as a first attempt, the data were fitted by a single doublet for the spinel and a second doublet for Fe_2O_3 where necessary.

The Mössbauer shift, δ, of the spinel doublet (Table I) is a function of temperature. Its temperature dependence is shown in Fig. 4. To a good approximation, it may be described by the following linear dependence

$$\delta(T) = (0.444 \pm 0.007) - (7.19 \pm 0.07)\ 10^{-4}T \qquad (1)$$

The experimental Mössbauer shift, δ, is given by the sum of the chemical shift, δ_C and of the temperature-dependent second-order Doppler shift, δ_{SOD} [22, 23]

$$\delta(T) = \delta_C + \delta_{SOD}(T) \qquad (2)$$

The chemical contribution depends on the electron density at the ^{57}Fe nucleus, while the second-order Doppler shift reflects the dynamic vibrational motion of the nucleus about its lattice site, i.e. it depends on the phonon spectrum of the solid but not directly on chemical bonding. The general evaluation of the second-order shift requires a detailed knowledge of the phonon population (frequency distribution) of the solid, which is not usually available, and has therefore to be approximated. However, in the high-temperature limit, the general result for a harmonic solid is a linear temperature dependence of the SOD-shift with a slope of $-7.307 \times 10^{-4}\,\mathrm{mm\,s^{-1}\,K^{-1}}$. Good agreement is observed between the experimentally determined slope of $-(7.19 \pm 0.07)10^{-4}\,\mathrm{mm\,s^{-1}\,K^{-1}}$ and the theoretical one, see Fig. 4.

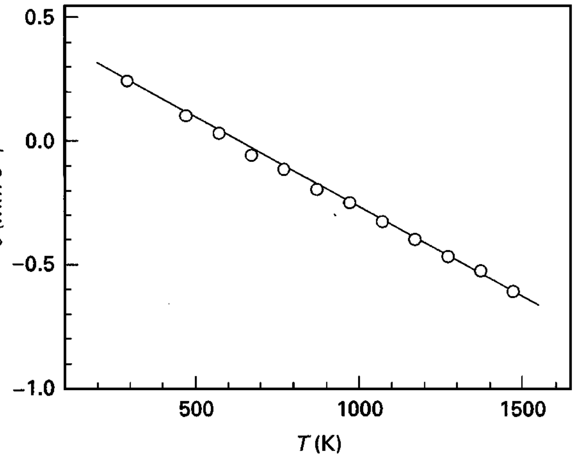

Figure 4 The temperature dependence of the Mössbauer shift for the non-activated zinc ferrite. The solid line represents the theoretical slope of 7.307×10^{-4} mm s^{-1} K^{-1}. Isomer shifts are referred to ^{57}Fe in Rh.

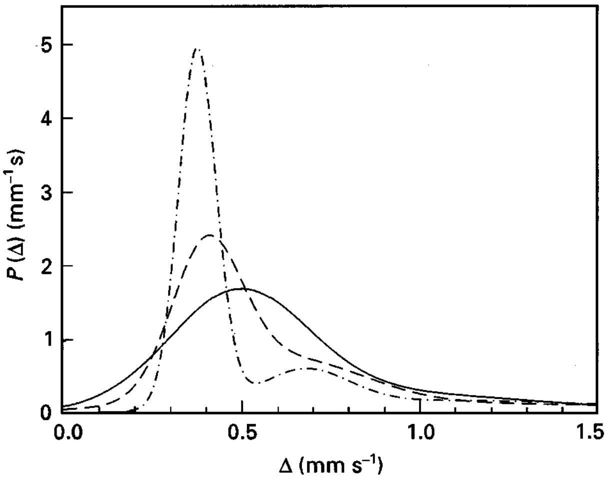

Figure 5 Quadrupole splitting distributions calculated from the *in situ* Mössbauer spectra of mechanically activated (24 min) zinc ferrite taken at (—) 573, (- -) 673 and (—•—) 773 K.

O'Neill [24] studied the temperature dependence of the cation distribution in zinc ferrite by powder XRD structural refinement. He found degrees of inversion between $x = 0.019$ and $x = 0.151$ for samples quenched from 773 and 1073 K, respectively. On the other hand, Mössbauer spectra at room and liquid nitrogen temperature seem to indicate that zinc ferrite is an almost perfectly normal spinel [25]. Regarding the Mössbauer parameters of Fe^{3+} containing spinels AFe_2O_4, the difference of the isomer shift of Fe^{3+} in tetrahedral and octahedral coordination is usually given by 0.12 mms^{-1} [19], but the quadrupole splittings for the tetrahedral and the octahedral site often differ more or less [25, 26]. Under these conditions, it can happen that the spectra appear highly symmetric, especially if the quadrupole splittings are similar and the degree of inversion is small. Keeping in mind the noise of experimental spectra, the separation of iron on the two sites may be very difficult – or even impossible by means of conventional Lorentzian fits.

Using the sophisticated fitting routine of Afanas'ev and Chuev [27] we discovered some tetrahedrally coordinated iron in zinc ferrite above 773 K. The quadrupole splittings for the tetrahedral and the octahedral sites are found to be similar, while the differences in the Mössbauer shifts are as expected. Now it is obvious that the subspectra of tetrahedral iron are hidden because of strongly overlapping lines. However, a similar analysis of the spectra of the activated samples fails, due to the additional quadrupolar broadening of the lines.

In situ high-temperature Mössbauer experiments of the mechanically activated zinc ferrite were undertaken in order to detect how the locally deformed surroundings of the Mössbauer nuclei relax toward its equilibrium configuration. The very slight differences obtained for the Mössbauer shifts of the non-activated and activated samples, which were smaller than 0.01 mm s^{-1}, can be attributed to the above-indicated problems with the lineshape. The dependence of the Mössbauer shift on temperature is similar to that of the non-activated sample. The most apparent change in the spectra taking place during heating is the decrease of the experimental width of the Mössbauer spectra which is directly related to the distribution of quadrupole splittings, see Fig. 3.

In the temperature range 373–773 K, differences between the shapes of Mössbauer spectra of the activated and of the non-activated sample gradually disappear, see Fig. 3. Partial narrowing of the spectral lineshape in the range 373–600 K, where no changes in the structure are registered by XRD analysis [8, 9], gives evidence of the fact that the quadrupole-sensitive Mössbauer nuclei provide a very sensitive probe for changes in local configurations. In line with this, at first the magnetic hyperfine interaction vanishes, and then the wide distribution of quadrupole splittings disappears with heating, see Fig. 3. Fig. 5 shows the results for the distribution of quadrupole splittings, $P(\Delta)$, obtained from the spectra using the method described elsewhere [16]. A Lorentzian linewidth of 0.28 mm s^{-1} resulting from fits of the spectrum at 773 K was chosen for all spectra, taking thickness effects and instrumental broadening into account. The probability densities, $P(\Delta)$, reflect the inhomogeneity of the quadrupolar interactions at the iron nuclei. As can be recognized from Fig. 5, $P(\Delta)$ changes gradually with temperature towards the quadrupole splitting of non-activated samples.

At room temperature, parameters of the Mössbauer spectrum of the mechanically activated zinc ferrite after annealing at 873 K are close to the non-activated ones. Fig. 6 shows a comparison of the quadrupole splitting distribution for the non-activated sample and for the activated sample after annealing. The calculations reflect the remaining slight differences in the lineshapes of the two spectra. Thus, on heating the mechanically activated zinc ferrite has returned to a state that is similar to the initial one, and its properties are gradually restored.

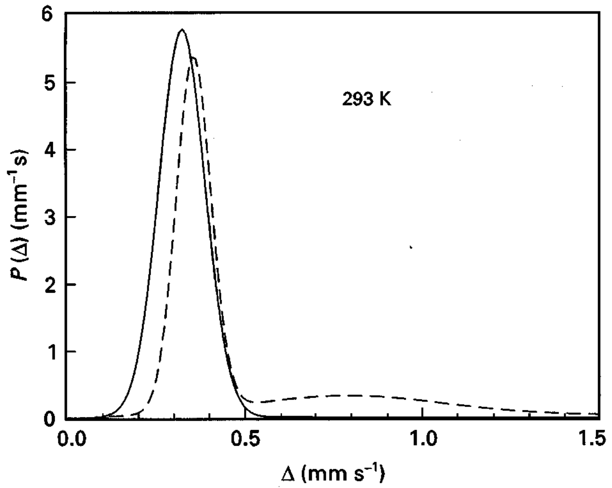

Figure 6 Quadrupole splitting distributions for the (——) non-activated and the (– – –) activated (24 min) zinc ferrite after annealing at 873 K (Lorentzian linewidth 0.28 mm s^{-1}).

4. Conclusion

With prolonged time of mechanical activation, zinc ferrite is transformed into a metastable state whose magnetic properties differ essentially from those of the initial polycrystalline material. The formation of spin arrangements in mechanically activated zinc ferrite at liquid nitrogen temperature is caused by the mechanically induced changes of the local geometry in the deformed structure. Structural metastability of mechanically activated zinc ferrite is manifested by the gradual recrystallization terminating at 900 K by an almost complete recovery of the relaxed, ordered structure. This is sensitively monitored by the quadrupolar interaction of the Mössbauer nuclei which clearly demonstrates that re-equilibrium already starts at temperatures as low as 400 K.

Acknowledgements

The authors are indebted to Professor H. Schmalzried for his supporting interest in their work and to the Deutsche Forschungsgemeinschaft (DFG) for financial support of one of the authors (V. Š.) during his stay at the Institute of Physical Chemistry and Electrochemistry of the University of Hannover.

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Received 20 May 1997
and accepted 27 January 1998