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DEHYDRATION OF SYNTHETIC LEPIDOCROCITE (γ-FeOOH)

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The thermal decomposition of synthetic lepidocrocite, γ-FeOOH, was studied using DTA, infrared and Mössbauer spectroscopy and X-ray diffraction, and the dependence of the phase composition of the dehydration products on the method of preparing the initial γ-FeOOH was described. The results demonstrated that γ-Fe_2O_3 formed by dehydration of γ-FeOOH consists of very small particles with a broad size distribution and that, depending on the method of preparation, the initial γ-FeOOH can contain a large amount of amorphous ferric hydroxide. A preparation method yielding γ-FeOOH which is not contaminated with other ferric oxide-hydroxides is recommended.

From a thermodynamic point of view, lepidocrocite (γ-FeOOH) is unstable ferric oxide-hydroxide; however, it can be quite stable under suitable conditions. It also occurs naturally as the mineral lepidocrocite in mesozoic formations [1]. A layered structure is typical for the compound, where the layers of close-packed FeO_6 octahedra are connected by hydrogen-bonds. Lepidocrocite is isotypical with boehmite (γ-AlOOH) and has an orthorhombic structure [2, 3] with symmetry space group D_{2h}^{17} (CmCm).

On heating in the air, transformation to γ-Fe_2O_3 (maghemite) first occurs, followed on further heating by transformation [4] to α-Fe_2O_3 (haematite):

$$\gamma\text{-FeOOH} \xrightarrow{T_1} \gamma\text{-Fe}_2\text{O}_3 \xrightarrow{T_2} \alpha\text{-Fe}_2\text{O}_3\,.$$

The temperatures T_1 and T_2 at which these reactions proceed are very dependent on the method of sample preparation.

Synthetic lepidocrocite is usually prepared [5] by oxidation of an aqueous solution of $FeCl_2$ with sodium nitrite in a medium buffered with urotropine. This modification can be prepared in the pure form [6] by oxidation of an aqueous solution of $FeSO_4$ with air at pH 7. This work deals with differences in behaviour of the two thus-prepared types of γ-FeOOH on heating, and with some properties of the dehydration products, found by analysis of the Mössbauer and infrared spectra.

Experimental

The initial lepidocrocite was prepared by oxidation of $FeCl_2$ with sodium nitrite in an aqueous medium, according to the method described in the Brauer handbook [5] (samples *A* and *B*). These samples were chosen from a number of repeated procedures; sample *A* was phase purest, while sample *B* contained the least lepidocrocite. Sample *C* was prepared by oxidation of a 0.36 *M* solution of $FeSO_4$ with atmospheric oxygen at 20° and pH 7 ± 0.1; a constant pH value was maintained by continuous additions of an aqueous solution of ammonia by an automatic burette controlled by a pH-stat. A detailed procedure has already been published [6]. All the samples of lepidocrocite prepared are yellow-orange powders with a large specific surface area (ca. 100 m^2/g). It was found [6] using an electron microscope that all three types of γ-FeOOH are morphologically similar and consist of thin leaf-like particles arranged in spherical conglomerates. Only the diffraction lines of lepidocrocite were observed in the X-ray diffractograms; no other crystal modifications of ferric oxide-hydroxides were identified.

DTA of the samples was carried out under the following conditions: sample weight 200 mg, heating rate 5°/min, atmosphere – air. The measurement was carried out in corundum crucibles with a reference Al_2O_3 sample. To determine the phase composition of the sample at a particular temperature, the experiment was interrupted at a given point in the DTA curve by rapid cooling of the sample, which was then stored in a desiccator over dried silica gel.

The X-ray diffraction was measured on a DRON-2.0 diffractometer using the $Co_{K\alpha}$ line.

The Mössbauer spectra were measured on a 612-channel spectrometer with constant acceleration with a ^{57}Co source in a Rh matrix. The measurement was carried out at laboratory temperature and at the boiling point of liquid nitrogen; the sample thickness was about 35 mg/cm^2.

The infrared spectra were measured on a grating double-beam Beckman IR-20 A spectrometer over the range 4000–250 cm^{-1} on pellets. The pellets were prepared by mixing an exactly weighed amount of substance and TlBr (Uvasol, Merck) in a ratio of 1 : 300; the mixture was homogenized by grinding in an agate mortar and pressed into a metal ring 12 mm in diameter at a pressure of 5 MPa.

The specific surface area of the samples was measured by the thermal desorption method of Nelson and Eggertsen on an instrument described by Mangel [7].

The two types of synthetic γ-FeOOH yielded almost indentical X-ray diffraction patterns, characteristic of lepidocrocite in the absence of other crystal phases. It is known, however that X-ray diffraction cannot identify the presence of an amorphous phase or a crystal phase with very small particle dimensions. The infrared spectra are not very useful either for identifying amorphous or poorly crystalline admixtures in lepidocrocite, as the characteristic amorphous ferric gel (e.g. the products of precipitation of $Fe(NO_3)_3$ with alkalies) peaks which lie at 1355, 1485 and 1580 cm^{-1} are relatively weak and the results are subject to a large error in the presence of excess γ-FeOOH (see Fig. 1, curves 4 and 5.)

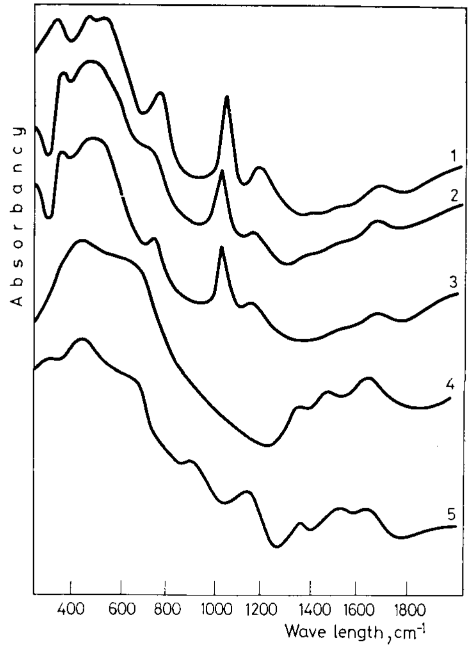

Fig. 1. The infrared spectra of some ferric oxide-hydroxides. (1) γ-FeOOH (sample *A*); (2) γ-FeOOH (sample *B*); (3) γ-FeOOH (sample *C*); (4) amorphous $Fe_2O_3 \cdot nH_2O$ (ferrihydrite), prepared by precipitating a solution of $Fe(NO_3)_3$ with sodium hydroxide; (5) δ-FeOOH prepared by oxidation of $Fe(OH)_2$ at pH 11–12 with hydrogen peroxide

Measurement of the Mössbauer spectra of samples *A*, *B* and *C* at 298 K indicate the presence of lepidocrocite in all the studied samples. The spectrum of sample *C* measured at 298 K is characterized by a doublet with a quadrupole splitting of 562 mm/s and an isomeric shift of 0.262 mm/s. The spectra of samples *A* and *B* could not be completely satisfactorily resolved into a single doublet; analysis of the spectra measured at 298 K indicated the presence of about 20–40% Fe with markedly increased quadrupole splitting ($\Delta = 0.9$ mm/s). It is not possible to interpret these results unambiguously as the presence of a further phase, however, because the deformation of the spectral lines can be caused by other factors. Measurement of the Mössbauer spectra of samples *A*, and *B* and *C* at 77 K did not yield an unambiguous solution either to the problem of the phase purity of the studied samples of γ-FeOOH. At this temperature only the paramagnetic doublet was observed, which was somewhat broader for samples *B* and *C* and less symmetrical. The spectra of samples *A*, *B* and *C* measured at 298 K are given in Fig. 2.

The DTA curves of samples *A*, *B* and *C* are given in Fig. 3. In spite of certain differences, the DTA curves are basically similar. In agreement with the literature

[4], the dehydration involves two steps; the first dehydration peak, with a minimum at 390–410 K, corresponds to the freeing of weakly bound water, probably sorbed on the surface. No observable changes in the γ-FeOOH structure occurred during this process. Freeing of the structurally bound water appears in the DTA curve as an endothermic effect at 540–550 K, when dehydration to γ-Fe_2O_3 occurs. On a further increase in temperature, γ-Fe_2O_3 is transformed at 650–670 K to α-Fe_2O_3. It is apparent from Fig. 3 that, at least for sample *B* and *C*, the peaks corresponding to these processes, i.e. dehydration of γ-FeOOH and transformation of γ-Fe_2O_3 to α-Fe_2O_3, are sufficiently separated to allow collection of the reaction intermediates on interruption of the experiment. For better elucidation of the dehydration of γ-FeOOH, some properties of the γ-Fe_2O_3 samples obtained by interrupting the DTA experiment at the temperatures indicated by the arrows in Fig. 3 (samples A_1, B_1, C_1) were studied.

The Mössbauer spectrum of sample C_1 measured at room temperature is given in Fig. 4. The spectrum consists of a six-line pattern with broadened lines and a paramagnetic doublet in the middle of the spectrum.

The Mössbauer spectra of magnetically ordered materials usually consists of clearly defined six-line patterns. The hyperfine magnetic field is proportional to the magnetization of the sublattice. The situation is different with ultrafine particles. The direction of the resultant magnetization of the particles changes rapidly with thermal motion. This phenomenon is termed superparamagnetism. The superparamagnetic relaxation time changes markedly with temperature and depends

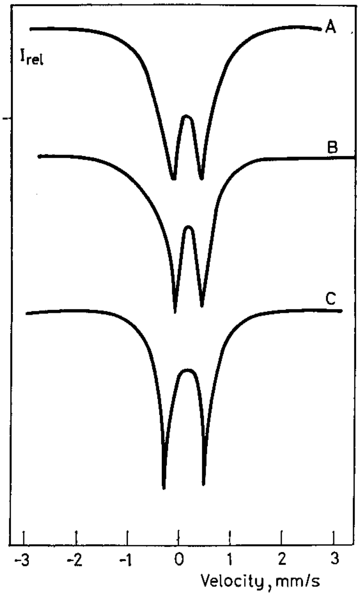

Fig. 2. Mössbauer spectra of the studied γ-FeOOH samples. Temperature 298 K

strongly on the particle volume. The superparamagnetic relaxation time τ is given, according to Neel [8], by Eq. 1:

$$\tau = \tau_0 \cdot \exp (KV/kT) \qquad (1)$$

where τ_0 is the time constant with a value of the order of 10^{-10}, KV is the anisotropic energy for a particle with volume V, k is the Boltzmann constant, and T is the

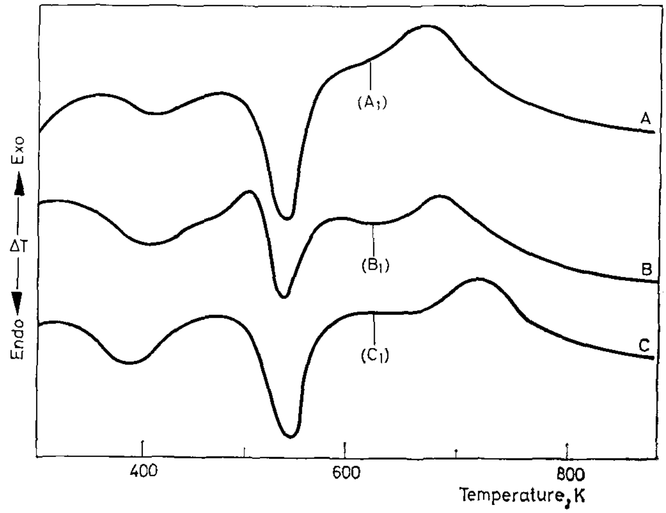

Fig. 3. Recorded DTA curves for the studied samples of γ-FeOOH (lepidocrocite)

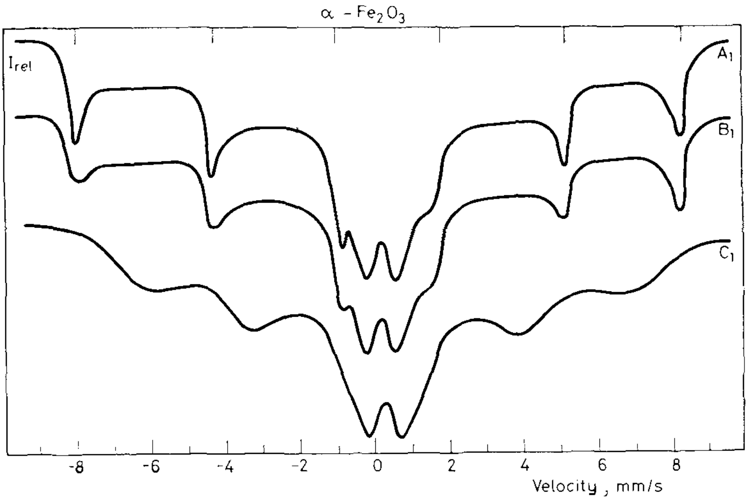

Fig. 4. Mössbauer spectra of the decomposition products of γ-FeOOH. Temperature 293 K

temperature (K). The Mössbauer spectrum is very sensitive to the value of τ, provided that τ is of the same order of magnitude as the value of the nuclear Larmor precession τ_L (10^{-8} s). For $\tau > 10^{-8}$ s the spectrum is magnetically split. For $\tau < 10^{-9}$ s a paramagnetic spectrum is mostly found and the transition region $\tau \sim 10^{-8}$ s is a gradual transition between these two extremes.

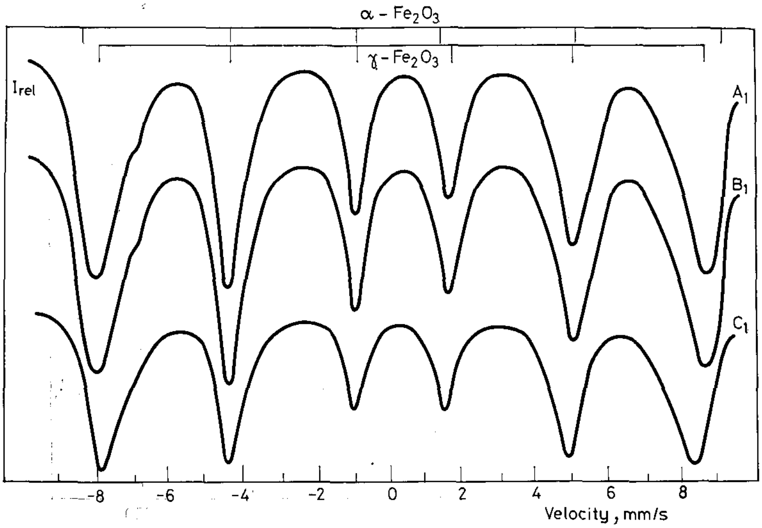

Fig. 5. Mössbauer spectra of the decomposition products of γ-FeOOH. Temperature 77 K

In a given sample with a certain particle size, the relaxation time for a given temperature is sufficiently long compared with the period of the Larmor precession. Then magnetically split spectra are usually obtained. Above this temperature, magnetic splitting disappears as a result of rapid relaxation and paramagnetic spectra are observed, consisting of one or two lines. Close to this "blocking" temperature, spectra with broad lines are observed.

In concrete cases interpretation is also complicated by the particle size distribution in the sample.

The Mössbauer spectrum obtained for sample C_1 can be interpreted as being the result of the presence of very small particles in the sample. The spectrum measured at 298 K consists of superimposed paramagnetic and magnetic components. At 77 K (Fig. 5) the quadrupole lines disappear and the spectrum exhibits only hyperfine splitting. This behaviour of the Mössbauer spectra can be explained by the existence of a critical volume V_{cr}. Particles of smaller volume than V_{cr} are completely paramagnetic at a given temperature, while particles with larger volumes are magnetically ordered. In systems with particleswith a size distribution there can be particles of larger and smaller volumes than V_{cr}, and the Mössbauer spectrum then reflects the presence of both paramagnetically and magnetically ordered components. The intensity of the paramagnetic component is then determined by the relative weight content of the particles with smaller volume than V_{cr}.

To determine the kind of small particles in the sample it is necessary to cool the sample to a temperature at which the relaxation effect is negligible. The spectrum of the sample measured at 77 K is given in Fig. 5. At this temperature there are no traces of paramagnetic lines, and the spectrum consists of a six-line pattern with broadened lines with a hyperfine splitting value of 39.56 MA/m. The parameters of the spectra (Figs 4 and 5) and their changes with temperature are in good agreement with the spectra of small particles of γ-Fe_2O_3 [9, 10]. The relatively large asymmetric line broadening is a result of surface effects (with ultrafine particles the effect of Fe close to the surface is important) and the very broad particle size distribution. The asymmetry can also be emphasized by the presence of structurally bound water in the sample.

Figure 6 depicts the dependence of the content of the superparamagnetic component in sample C_1 on temperature. The Figure indicates the presence of very small particles with a broad size distribution. The literature [11, 12] gives models for transformation of the dependence on the particle size; however, use of these methods here without comparison with another method could lead to erroneous interpretation. It can be stated, however that the sample consists primarily of very small particle with dimensions of 2 – 6 nm. These results are in good agreement with other work [13] dealing with the dehydration of γ-FeOOH.

The Mössbauer spectra of samples A_1 and B_1 measured at room temperature at 77 K are also given in Figs 4. and 5. The spectrum measured at 293 K is a superposition of the relaxation spectrum and the clearly resolved sextet of α-Fe_2O_3. Measurement at 77 K also demonstrated the presence of small particles of maghemite. The relative maghemite content was 60% for sample *A* and 80% for sample *B*. The same results were obtained from the X-ray diffraction data.

It can thus be stated that, on dehydration, the two types of γ-FeOOH yield γ-Fe_2O_3 with similar properties, characterized by very small particles with a broad size distribution. There is, however, a marked difference in the content of α-Fe_2O_3 in the dehydration products at temperatures much lower than the temperature of

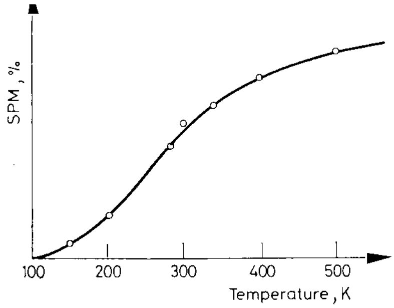

Fig. 6. Temperature-dependence of the content of the superparamagnetic component in sample C_1, found by analysis of the Mössbauer spectra

the transformation γ-$Fe_2O_3 \rightarrow \alpha$-$FeO_3$. γ-FeOOH samples prepared by oxidation of a $FeCl_2$ solution with sodium nitrite (*A* and *B*) always yielded on dehydration a product with a large α-Fe_2O_3 content. In contrast, samples prepared by oxidative precipitation from a $FeSO_4$ solution at pH 7 (sample *C*) always yielded phase-pure γ-Fe_2O_3 on dehydration. The best explanation of this observation is that samples *A* and *B* contained, in addition to γ-FeOOH, another ferric oxide-hydroxide whose dehydration produced α-Fe_2O_3 (haematite). It was not possible to identify this component reliably in the initial samples using any of the methods described (X-ray and electron diffraction, IR and Mössbauer spectroscopy, thermal analysis), and thus it is possible that the substance is either an amorphous or a poorly crystalline ferric oxide-hydroxide of the ferric gel type or δ-FeOOH with very fine particles which are difficult to identify in mixtures with the crystalline phase. This observation is important because the preparation of γ-FeOOH by oxidation of $FeCl_2$ with sodium nitrite in various ways is the method used most frequently, and the possible presence of another, different ferric oxide-hydroxide can distort the results of the study of substances prepared in this way.

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RÉSUMÉ—La décomposition thermique de la lépidocrocite synthétique, γ-FeOOH a été étudiée par ATD, spectroscopies infrarouge et Mössbauer ainsi que par diffraction des rayons X. L'influence de la méthode de préparation de γ-FeOOH initial sur la composition des phases des produits de déshydratation est décrite. Les résultats ont montré que l'oxyde γ-Fe_2O_3 formé par déshydratation de γ-FeOOH est constitué de particules très petites avec une large distribution de taille et que, suivant la méthode de préparation, le γ-FeOOH initial peut contenir un taux élevé d'hydroxyde ferrique amorphe. On recommande une méthode de préparation donnant γ-FeOOH non contaminé par d'autres oxydes ou hydroxydes ferriques.

ZUSAMMENFASSUNG—Die thermische Zersetzung von synthetischen Lepidocrit, γ-FeOOH, wurde durch DTA, Infrarot- und Mössbauerspektroskopie und Röntgendiffraktion untersucht. Die Abhängigkeit der Phasenzusammensetzung der Dehydratisierungsprodukte von der Herstellungsmethode des Ausgangs-γ-FeOOH wurde beschrieben. Die Ergebnisse zeigten, daß das durch Dehydratisierung von γ-FeOOH entstandene γ-Fe_2O_3 aus sehr kleinen Partikeln mit einer breiten Grössenverteilung besteht und daß in Abhängigkeit von der Herstellungsmethode das Ausgangs-γ-FeOOH eine große Menge amorphen Ferrihydroxids enthalten kann. Eine Herstellungsmethode, welche mit anderen Ferrioxid-hydroxiden nicht verunreinigtes γ-FeOOH ergibt, wird empfohlen.

Резюме — Используя ДТА, ИК- и мессбауэровскую спектроскопию, диффракцию рентгеновских лучей, было изучено термическое разложение синтетическото лепидокроцита γ—FeOOH и описан фазовый состав продуктов его дегидратации в зависимости от метода получения исходного γ—FeOOH. Результаты показали, что при дегидратации γ—FeOOH, состоящего из очень малых частиц с широким интервалом их размеров, образуется γ—Fe_2O_3. При этом в зависимости от метода получения, исходный γ—FeOOH может содержать большое количество аморфной гидроокиси железа. Предложен метод получения γ—FeOOH, при котором он не загрязнен другими примесями.