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Morphological and magnetic changes during mechano-chemical transformation of lepidocrocite to hematite

E. MENDELOVICI
Materials Physico-Chemistry Laboratory, IVIC Apartado 1827 Caracas 1010-A, Venezuela
S. NADIV, I. J. LIN
Depts. of Materials and Minerals Engineering Technion, Israel Institute of Technology, Haifa 32000, Israel

The changes taking place during the grinding of lepidocrocite (γ-FeOOH) powder are investigated by means of transmission electron microscopy and Mössbauer effect spectroscopy. The study has shown that small comminuted particles transform directly to superparamagnetic hematite, and that during prolonged grinding they agglomerate to form partially-developed antiferromagnetic larger particles of hematite. A theoretical explanation is suggested, which emphasize also the importance of active molecular surface groups formed on newly exposed surfaces to the process of mechano-chemical agglomeration and crystallization.

1. Introduction

The mechano-chemical transformations undergone by pure synthetic iron oxyhydroxides like goethite (α-FeOOH) or lepidocrocite (γ-FeOOH) were studied by infrared (IR) absorption spectroscopy and X-ray diffraction by Mendelovici *et al.* [1, 2]. It was established that dry comminution processing of these oxyhydroxides leads to topotactic structural modifications associated with changes in surface properties: in both cases, the final product after specified periods of mortar grinding in air was a stable hematite variety; no intermediate maghemite (γ-Fe_2O_3) was detected (unlike in thermochemical process) and no regeneration occurred on overnight exposure to water vapour. In order to learn more about these solid-state transformations, the gradual morphological changes were followed in the present study by means of transmission electron microscopy (TEM). The present contribution concentrates on the lepidocrocite only.

2. Experimental details

The production and comminution of the synthetic crystalline lepidocrocite used in this study are described elsewhere [3]. For TEM (Hitachi F-500, 20 kV) observations, specimens of different grinding times were prepared by dispersing a few milligrammes of the ground product ultrasonically in aqueous ethanol solution; a few drops of the suspension were deposited on a carbon film previously applied by condensation to specimen-holding grids, and slowly evaporated. All micrographs, of the comminuted material from zero up to 48 h grinding, were taken at the same magnification (x 35 000) for easy comparison of the morphology and size variation of the products; the micrograph for the 64 h sample was taken at a somewhat lower magnification (x 30 000) in order to facilitate detailed observation. The comminuted products were also subjected to X-ray diffraction analysis (Fig. 1) and to Mössbauer effect spectroscopy carried out on an Elscint computerized spectrometer, using a 25 mCi source of Co^{57} (Pd) for the 14.4 keV γ-line of the Fe^{57} nuclei, and α-iron was used for calibration.

3. Results

The original tubular morphology of the synthetic lepidocrocite (in uniform-sized bundles) is seen in

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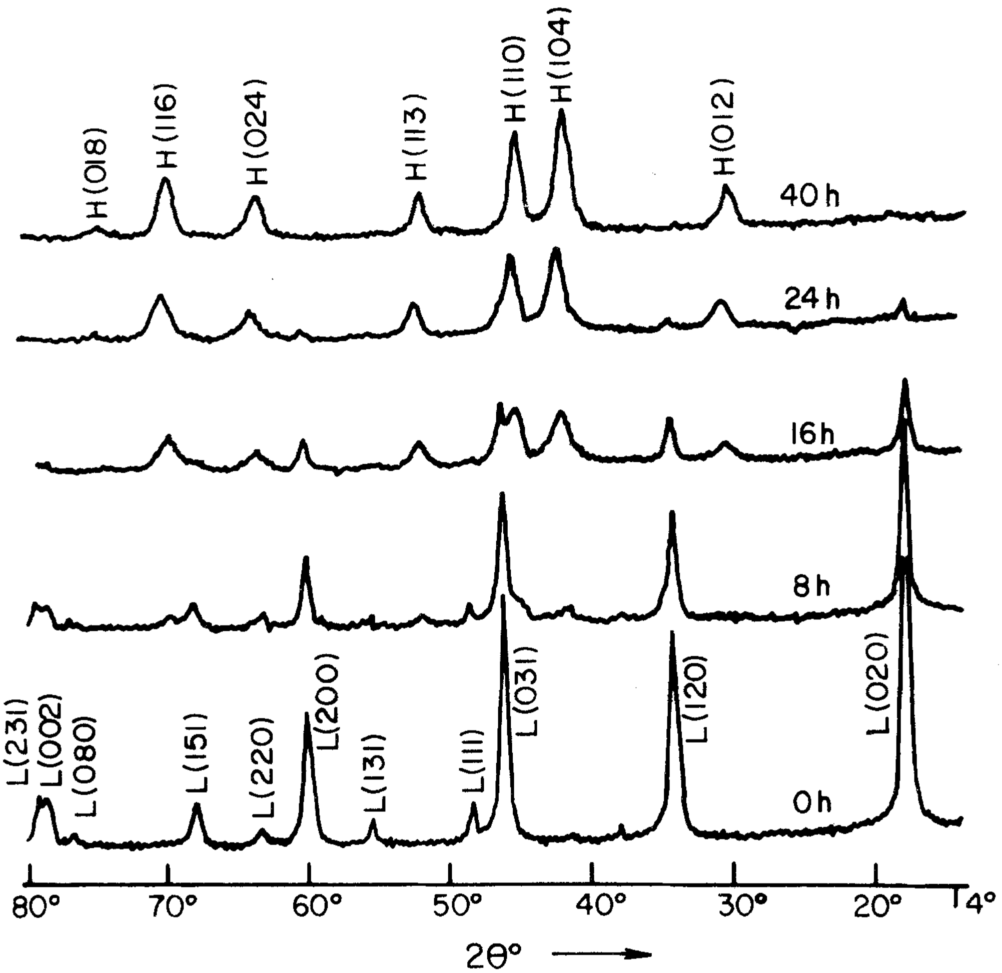

Figure 1 X-ray diffraction patterns (Fe*K*α-radiation) of lepidocrocite powder ground for the times shown. L = γ-FeOOH, H = α-Fe_2O_3.

Fig. 2. The gradual size reduction and associated morphological changes are reflected in Figs. 3 to 6, which represent the 4, 8, 16 and 32 h ground samples, respectively. In the first sample of the series, the tubular configuration is still intact. In the second, small spherical particles make their appearance (indicating traces of hematite, confirmed by XRD); in the third, they become predominant, and in the fourth the original morphology (of the lepidocrocite) is no longer detectable. The 40 h sample (Fig. 7) is shown by XRD to consist exclusively of hematite. The 48 h sample (Fig. 8) shows the onset of aggregation, due to the dispersion meaning, water added to the ethanol acts as a dispersant and ultrasonic vibrations, ceased to be effective (presumably due to the hydrophilic nature of the free surfaces, see below). The 64 h sample (Fig. 9), whose XRD patterns contain well-developed sharp peaks of hematite,

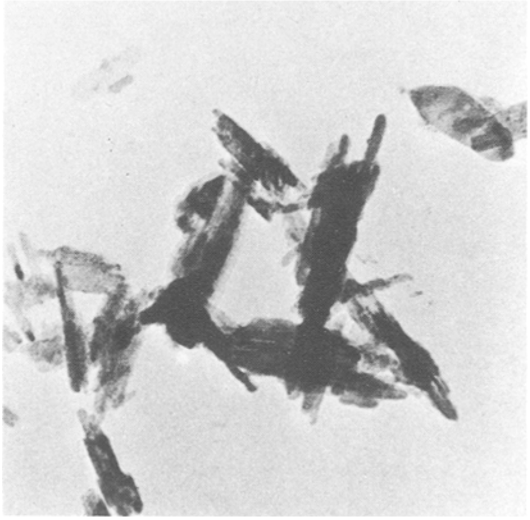

Figure 2 Transmission electron microscopy of original synthetic lepidocrocite powder (magnification × 35 000).

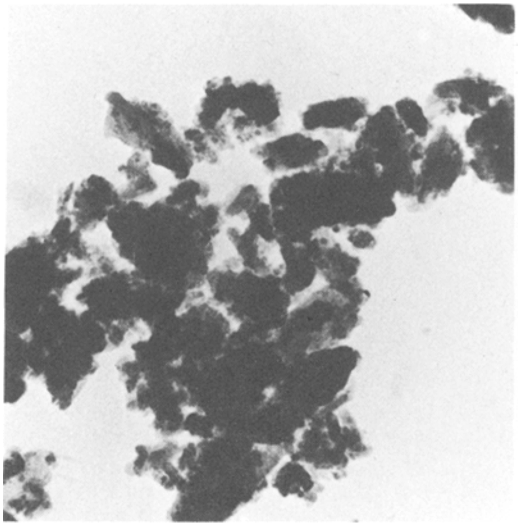

Figure 3 TEM of the lepidocrocite powder (as in Fig. 2) ground for 4 h (magnification × 35 000).

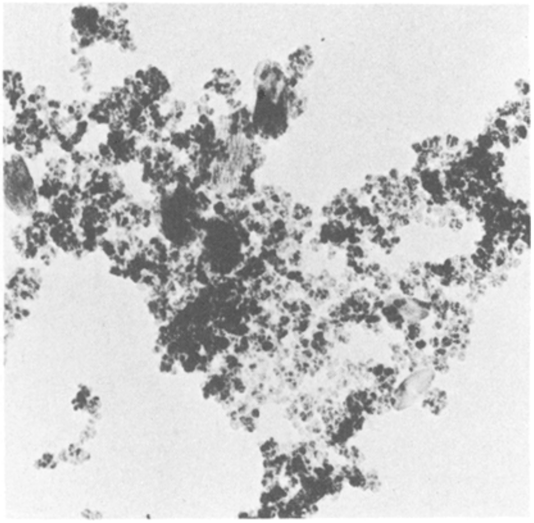

Figure 5 Same as Fig. 2, but ground for 16 h.

demonstrates a further major change, i.e. agglomeration. The resulting agglomerates include particles with irregular linear edges, which are in fact large single hematite crystallites. Further confirmation of the existence of a mechano-chemical crystallization process was obtained by Mössbauer spectroscopy. Figs. 10a and b represent the quadropole spectra of the original lepidocrocite and the 40 h sample, respectively. The first spectrum (isomer shift (IS) = 0.36 mm $\sec^{-1}$, apparent quadrupole splitting (QS) = 0.75 mm $\sec^{-1}$) reflects probably a pair of overlapping doublets, in accordance with the Murad–Schwertman proposition [4]. The second, characteristic of superparamagnetic hematite, (IS = 0.36 mm $\sec^{-1}$ apparent QS = 0.70 mm $\sec^{-1}$) reflects in accordance with the Van der Kraan proposition [5], a partially overlapping pair: the inner one for the core ions and the outer for the free-surface ions. The QS for the core ions is higher than its counterpart in fully crystallized bulk hematite [6]. This is presumably due to uniform expansion of the lattice in the small particles, affected by the action of adjoining surface – an effect analogous to negative hydrostatic pressure,

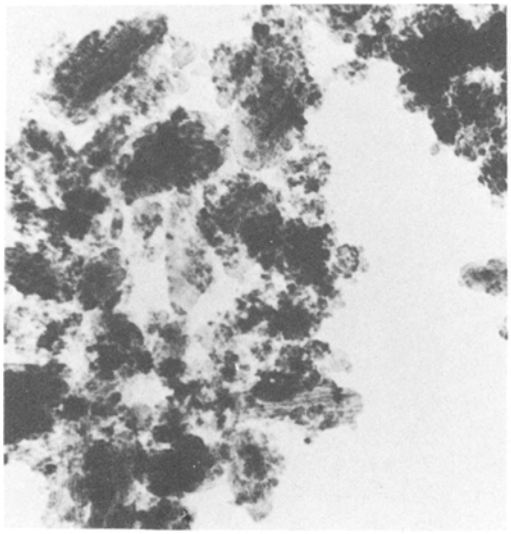

Figure 4 Same as Fig. 3, but ground for 8 h.

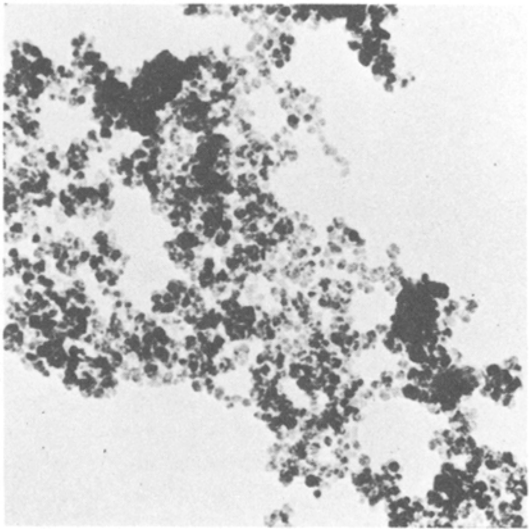

Figure 6 Same as Fig. 2. but ground for 32 h.

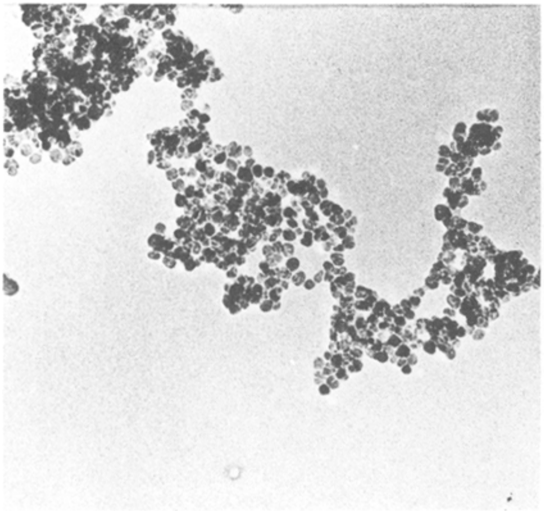

Figure 7 Same as Fig. 2, but ground for 40 h.

counteracting the capillary surface forces [7]. The marked contribution of the free-surface ions is responsible for the high value of QS, attributed by the high specific surface value of the particulate sample [5].

The effect of agglomeration and crystallization upon the Mössbauer spectroscopy can be appreciated in Figs. 11a to c. The first of these refers to the 48 h sample, showing an unresolved hyperfine-split pattern of weak ferromagnetic material together with a centrally superimposed doublet of residual superparamagnetic hematite. The 64 h sample (Fig. 11b) shows a better resolution in the hfs spectrum, which actually comprises a set of overlapping six-line patterns for the core ions, each representing a somewhat different near-neighbour atomic configuration. This heavily distorted material underwent apparently complete recovery after heat treatment for about 1 h at 1000° C, since its subsequent room-temperature Mössbauer spectrum resembled exactly that of the fully crystallized hematite (Fig. 11c).

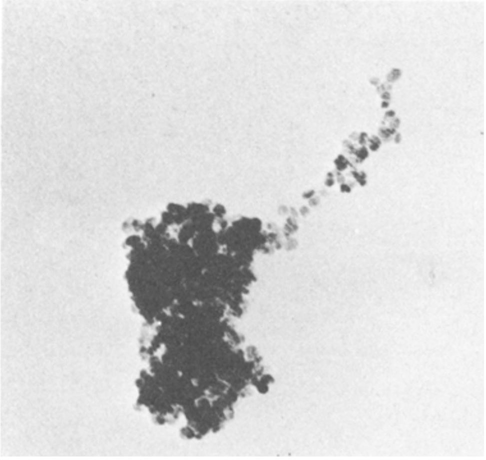

Figure 8 Same as Fig. 2, but ground for 48 h.

Figure 9 Same as Fig. 2, but ground for 64 h (magn. X 30 000 only).

4. Discussion

The mechano-chemical reactions which occur during comminution are the consequence of a relaxation process, i.e. release of accumulated activation energy in the material. This energy has two forms: the specific surface-energy component, reflecting the smallness of the particles; and the retained elastic-strain energy component, reflecting the highly strained and defective crystalline structure [8]. It is thus associated with a "reaction-triggering dimensionality" (RTD) and depends largely on the nature of the relaxation mechanism. Topotactic transformations and syntheses have relatively higher RTD, otherwise microcrystallinity (XRD-observed "amorphization") is a necessary step within a sequence of metastable processes. Another factor favouring higher RTD is a low shear rigidity in certain crystallographic planes.

The observed absence of the intermediate maghemite (or any other metastable forms) in the mechano-chemical sequence – in contrast to its thermochemical counterpart – brings to mind the

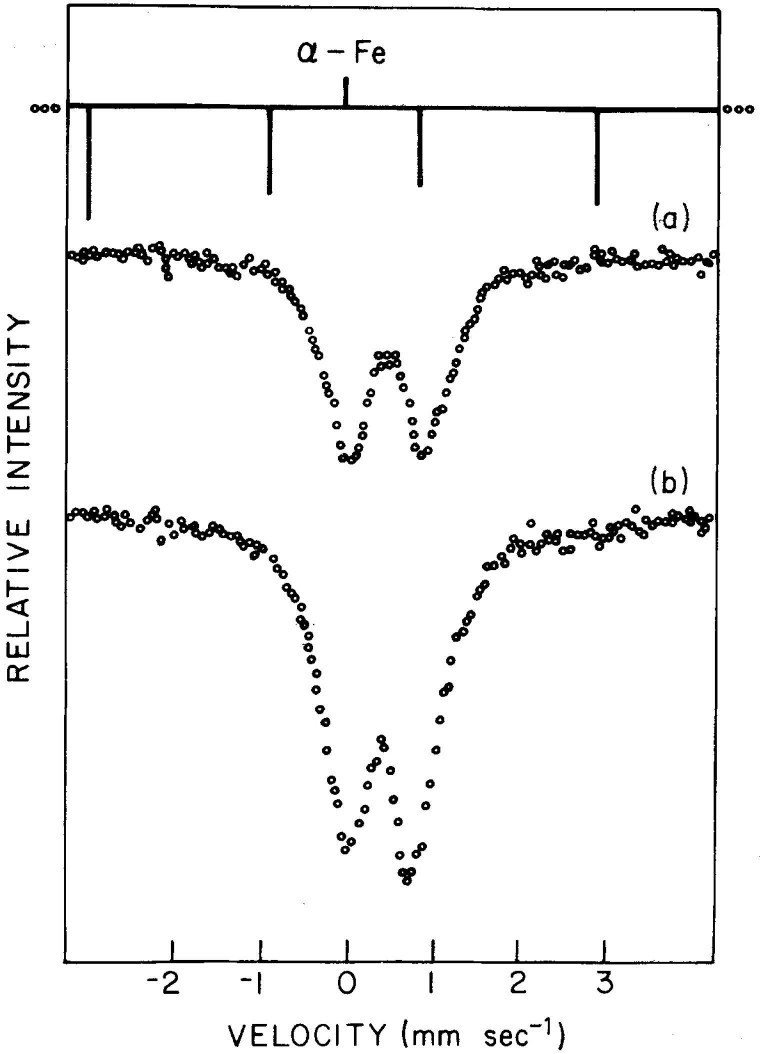

Figure 10 Mössbauer effect absorption spectra (Fe^{57}/Pd). (a) Quadropole-splitted spectrum of original synthetic lepidocrocite powder. (b) Quadropole-splitted spectrum of the lepidocrocite powder ground for 40 h. Resembles superparamagnetic hematite.

well known resemblance of the topotactic reactions in iron and aluminium oxyhydroxide and oxide systems [9]. In aluminium-based systems, the series of intermediate metastable aluminas known to form during thermochemical transformation from the starting phase (γ-AlOOH) to the end product (αAl_2O_3) are probably due to pseudomorphism [10]; the latter cannot exist in mechano-chemical reactions, in which only amorphous alumina (or rather microcrystalline γ-Al_2O_3 [11]) was observed without any of the above mentioned metastable forms. However, this amorphous form was absent in the iron-based systems. The difference in RTD between the two sets of systems was not explained, but was also observed by Nakatani *et al.* [12] in the mechano-chemical transformation of maghemite to hematite. This transformation always takes place to completion, whereas in other mechano-chemical polymorphic transformations dynamic two-phase equilibrium (depending on the comminution regime) is asymptotically approached [13]. However, when some γ-Al_2O_3 is added before grinding to the γ-Fe_2O_3, it makes for its partial stabilization.

Topotaxy refers, by definition [9], to chemical solid-state reactions in which much of the near-neighbour atomic coordination and configurations is conserved. The phases involved in our study have the same basic structure unit, i.e. the octahedral group. According to Murad and Schwertmann [4], as particle size decreases in the microcrystalline range, the individual Mössbauer-effect and XRD characteristics of the oxides and oxyhydroxides gradually disappear until finally only that of the common basic group remains. In hematite, six oxygen atoms form an octahedral

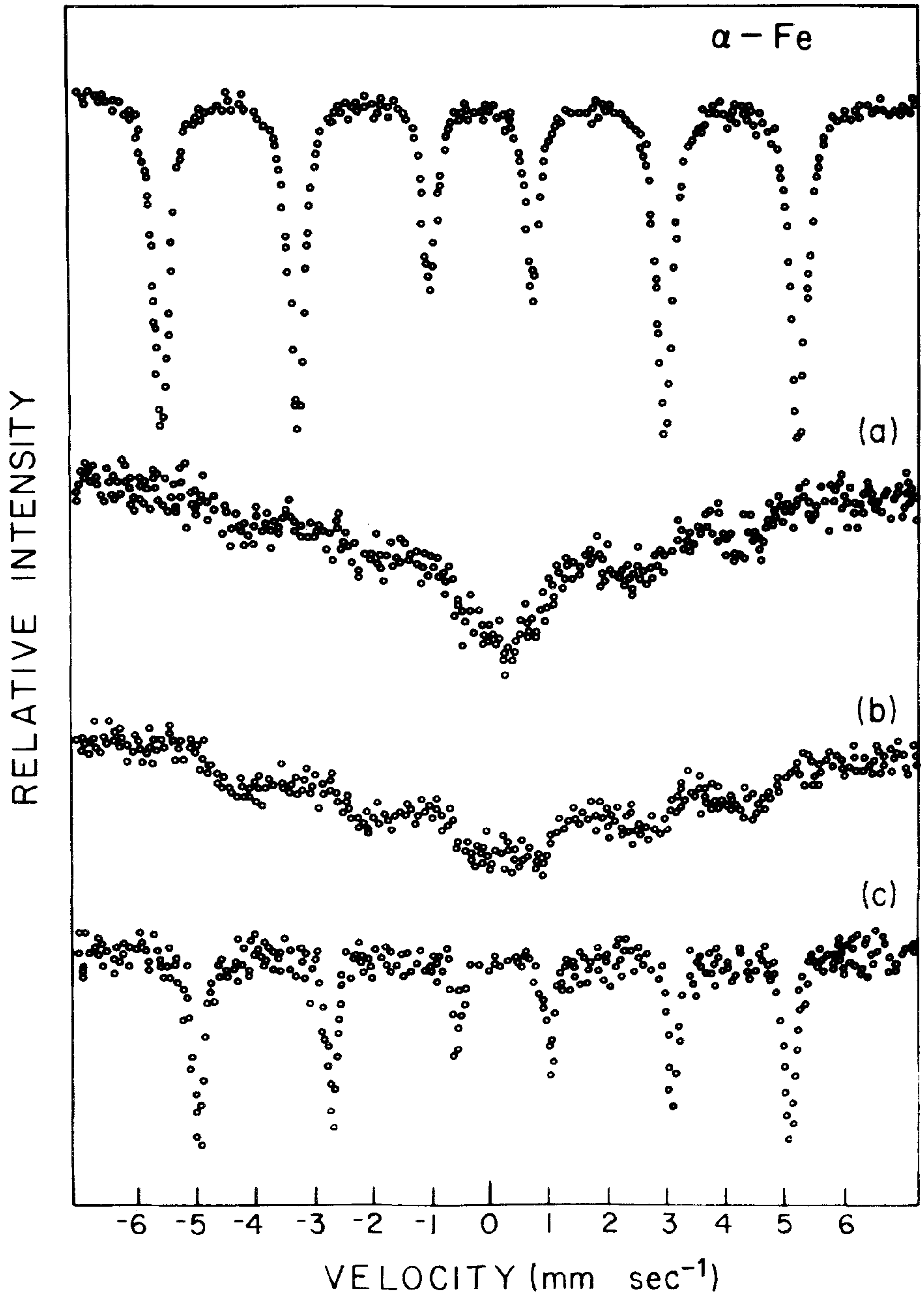

Figure 11 Mössbauer effect absorption spectra (Fe^{57}/Pd). (a) Unresolved hyperfine-splitted spectrum of the lepidocrocite powder ground for 48 h. Resembles undeveloped antiferromagnetic hematite. (b) Partially-resolved hfs spectrum of the lepidocrocite powder ground for 64 h. Resembles partially-developed antiferromagnetic hematite. (c) Fully-resolved hfs spectrum of the same powder as in Fig. 11b, followed by heat-treatment of 1 h at 1000° C (taken at room temperature). Resembles typical antiferromagnetic hematite. (The spectrum of α-Fe is given for comparison and calibration).

group around the iron atom, and each oxygen atom is surrounded by four iron atoms. This structure can best be regarded as a close-packed array of oxygen atoms with iron atoms occupying the octahedral sites at different elevations (for details see Figs. 44 and 45 in [14]). In lepidocrocite, every iron atom is surrounded by a distorted octahedral group of oxygen atoms, and the groups are linked into complex "corrugated" layers connected through hydrogen bonding. Thus every oxygen atom within the layers is nearly equidistant from four iron atoms, whereas each of those on the bonding surfaces of the layers is linked to two iron atoms only and associated with the hydrogen atoms to form O–H–O directed bonds between the layers; the oxygen atoms of adjoining layers are not exactly in the close-packed position, because of the hydroxyl groups in between them (for details see Fig. 195 in [14]).

During comminution of lepidocrocite, there is intralayer-cleavage fracturing by severing of the hydrogen bonds. Simultaneously, hydrogen delocalization and stress-associated diffusion (prototropy) may also take place within the particles, followed by rearrangement of the octahedra. As comminution progresses, the following steps are believed to take place in the hematite particles [15], as suggested by infrared spectroscopy studies:

1. Cleavage along the close packed oxygen layers, yielding surfaces of oxygen atoms. These oxygens are bound to inner iron atoms, forming non-active Fe–O–Fe surface groups, hydrophobic in nature.

2. Fracturing of crystal units off the cleavage planes breaks up the inner Fe–O–Fe groups and produces highly active $Fe–O^-$ and $O–Fe^+$ surface groups, which are hydrophilic in nature.

During the aggregation and agglomeration of the particles, the active surface groups combine into intercrystalline non-active Fe–O–Fe groups, thereby accounting for the mechano-chemical crystallization phenomenon. (Occasional formation of Fe–OH surfaces groups by water chemisorption on the active surfaces does not change the overall picture). When the hematite crystallites have attained their natural geometry, their free surfaces attain non-active characteristics. The importance of the active surface groups in the process of mechano-chemical agglomeration was emphasized also in previous publications [16, 17].

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