

reflection and imaging the crystal in the dark field mode we can, according to the above explanation, produce a dark field picture of the undecomposed γ -FeOOH while an analogous dark field picture in the light of an appropriately selected γ -Fe₂O₃ reflection shows the decomposed parts, i.e. the γ -Fe₂O₃, within the matrix crystal.

From a series of such pictures we conclude that the γ -Fe₂O₃ in Fig. 15 is not a single crystal but a polycrystalline aggregate so perfectly orientated that its texture pattern could be mistaken for a single crystal electron diffraction. Secondly the pictures indicate that the more the reaction proceeds, the smaller are the coherently scattering regions in a crystal (i.e. γ -FeOOH), and the larger become the regions of non-coherently scattering γ -Fe₂O₃ crystallites within the initial platelet.

In the beginning stage of the reaction, γ -Fe₂O₃ forms predominantly at edges, cracks, and other defects even in the interior of a crystal. Later on, these "nuclei" of 70 Å size give rise to formation of further γ -Fe₂O₃ crystallites of the same size, and this proceeds almost exclusively along the needle axis direction. Towards the end of the reaction the growth of a decomposed region proceeds also sideways and very fast. In the end the mentioned pseudomorphous, perfectly oriented aggregation of γ -Fe₂O₃ crystallites fills out the initial space of the γ -FeOOH crystal. The sharp contrast present in the early stage of the reaction fades away and in the end a uniformly grey platelet is visible.

As we were interested to know whether or not these γ -Fe₂O₃ crystallites in the aggregation could grow to a larger size in an appropriately slow decomposition, we ran an isothermal one-month decomposition (heating rate such that the weight loss remained 0.3 mg per day; from ambient temperature to 200°C, 10⁻⁵ torr). The attained fractional decomposition after one month was ca. 77% and the apparent particle size (from a BET surface of 87.9 m² g⁻¹) about 130 Å. This apparent particle size and BET surface correspond entirely to the unfinished reaction; a second run with heating rate ca. 2°C min⁻¹ and otherwise the same conditions has led to $\alpha \sim 0.91$ and a BET surface of 142.1 m² g⁻¹ or particle size 83 Å. This proves that even extremely slow decomposition leads to polycrystalline γ -Fe₂O₃.

CONCLUSION

1. Lattice transformation

The electron micrographs show that the γ -FeOOH crystals decompose—once the decomposition is under way—to γ -Fe₂O₃ of about 70 Å size; i.e. through the entire thickness of the crystal in one event. The γ -FeOOH lattice consists of corrugated layers of (FeO₆) octahedra, separated from each other by fairly strong hydrogen bonds. (Fig. 16a). γ -Fe₂O₃, on the other hand, may be described in terms of a defect spinel, and thus consists of a framework of ccp [FeO₆] octahedra, with edge and corner sharing.

The electron microscopical evidence leads to the following assumption: The γ -FeOOH layers collapse such that by more edge and corner sharing O²⁻ ions become available to form H₂O on the one hand and a ccp of O²⁻ on the other hand.

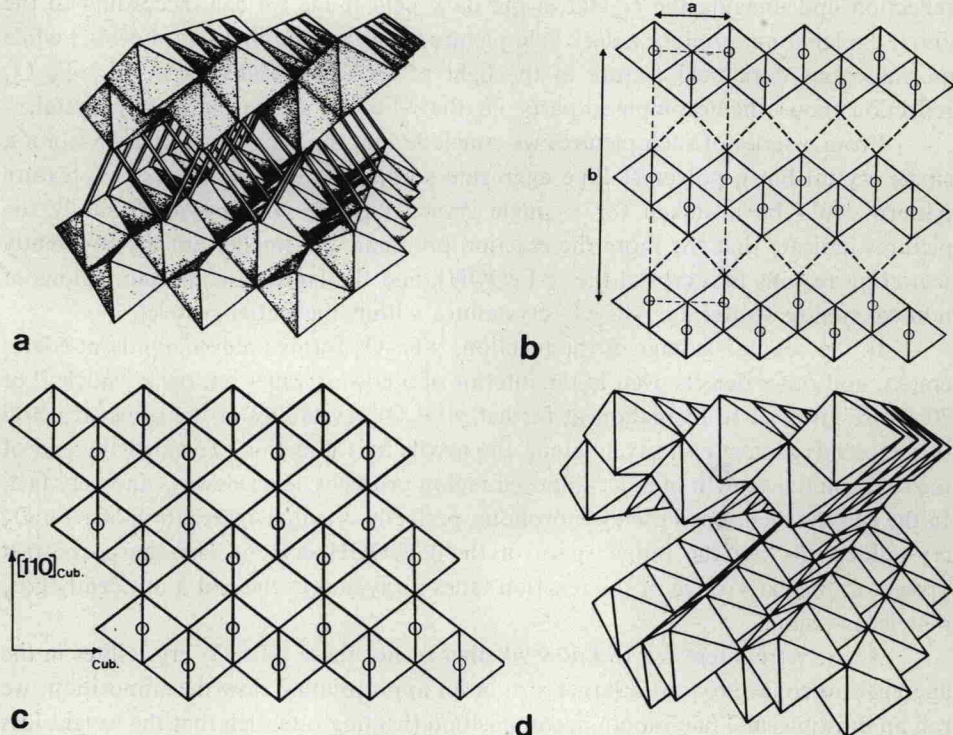


Fig. 16. (a) Lepidocrocite type (γ -FeOOH) with corrugated layers of $[\text{FeO}_6]$ octahedra. (b) Projection of (a) along $[001]$. (c) Collapsed $[\text{FeO}_6]$ layers forming a ccp and new (empty) octahedral sites. (d) Interface between intact γ -FeOOH (foreground) and collapsed layers forming γ -Fe $_2$ O $_3$ (background).

This involves, however, an enormous lattice strain as shown in Fig. 16d. It is out of question that this lattice strain can be accommodated by the crystal, and the part of the γ -FeOOH decomposed must collapse, thus producing the crystallites of 70 Å size and the strong contrast phenomena shown in Fig. 15. It seems likely that the front and sides of such a γ -Fe $_2$ O $_3$ crystallite act as nuclei for the proceeding reaction. If we accept this mechanism for the start of the reaction we also obtain immediately the answer to the otherwise unexplicable fact that by dehydration of γ -FeOOH fully ordered γ -Fe $_2$ O $_3$ of the quality of that obtained by oxidation of Fe $_3$ O $_4$ cannot be attained: Fe $_3$ O $_4$ as a starting material provides the framework that allows diffusion of Fe $^{3+}$ such that these can arrange themselves³. In our case, however, there is no chance that the Fe $^{3+}$ ions find time in the short period of lattice disruption to get in place by a cooperative motion; and once the 70 Å crystallites of γ -Fe $_2$ O $_3$ are formed, there is no longer a coherent matrix available for low temperature diffusion. The reaction water, furthermore, will partly be stuck at the interface between the γ -Fe $_2$ O $_3$ crystallites. This again is all very well in accord with the extremely sluggish end stage of that reaction. The latter fact, taken for itself, might lead to the erroneous conclusion that