It may be interesting to note that a decomposition product from preparation 2, decomposed at 440 °C on the Cahn balance, and measured without ever having been in contact with air, gave a specific surface of only 23.8 $m^2 g^{-1}$. The substance consisted according to x-ray diffraction of α-Fe_2O_3 and the particle size derived from this surface is 480 Å (cube edge or equivalent sphere diameter). This clearly indicates that the subsequent transition of γ-Fe_2O_3 into α-Fe_2O_3 is connected with sintering effects. In other words, two entirely different methods give identical and conclusive evidence of a total disruption of the initial crystals of γ-FeOOH into tiny cubes of γ-Fe_2O_3. This of course eliminates at least for the final stage of the reaction all phase boundary controlled mechanisms, as the rate determining step in this stage is to push the reaction water out of the pore system of the extremely finely divided end product.

9. Electron microscopy

9.1 Electron diffraction. The evidence accumulated so far has only in part been satisfactory. It therefore seemed desirable to look directly at (and into) the γ-FeOOH crystals at various stages of their decomposition. While the initial γ-FeOOH showed the usual Bragg fringe contrast this was not the case in the uniformly grey final γ-Fe_2O_3. Yet the size and shape of the crystals did not alter and the selected area electron diffraction of single crystal changed gradually from that of γ-FeOOH (b* c* zone) into that of apparent γ-Fe_2O_3 single crystals. The orientation of the latter was always that described by previous authors, one axis being [110] in the pseudocubic notation and the other [001] as shown in Fig. 13.

We shall deal with the disappearing Bragg fringes in Section 9.2 and look first into the diffractions. According to our experience, reflections in electron diffraction are sharp if more than about 20 identity periods (unit cells) scatter coherently. Whenever between about 5 and 20 periods contribute to a reflection, it will be broadened and can be treated according to the Scherrer equation. Less than about 5 coherently scattering periods do not produce a reflection. The appearance of such an electron diffraction will be that of an "amorphous" substance.

As we do not find tetragonal supercell reflections in any of our γ-Fe_2O_3 diffractions, and as the other reflections are considerably broadened, we may assume qualitatively that the crystallite size of our γ-Fe_2O_3 produced in vacuo is less than 5 identity periods of the supercell but more than 5 periods of the pseudocubic subcell, i.e., 40–120 Å. This is in excellent agreement with figures in Table 9.

γ-Fe_2O_3 from preparation 2 produced in 1 h at 320 °C under atmospheric pressure shows less broadened reflections in its electron diffractions, not presented here for the sake of brevity. This confirms the already outlined importance of the H_2O partial pressure on the reaction. Figure 14 underlines this point by showing two products, the history of which differs only in the water vapour pressure. In vacuo perfectly pseudomorphous γ-Fe_2O_3 is obtained while under atmospheric pressure but otherwise similar conditions α-Fe_2O_3 with beginning sintering effects occur. The products were checked by x-ray diffraction. Thus the water vapour pressure has allowed nucleation of another phase than that occurring in vacuo. This underlines

one of our aims, namely to show that kinetics and even the mechanism of decomposition reactions with H_2O evolution are subject to the influence of the H_2O partial pressure to such an extent that any mechanisms derived only from formal measure-
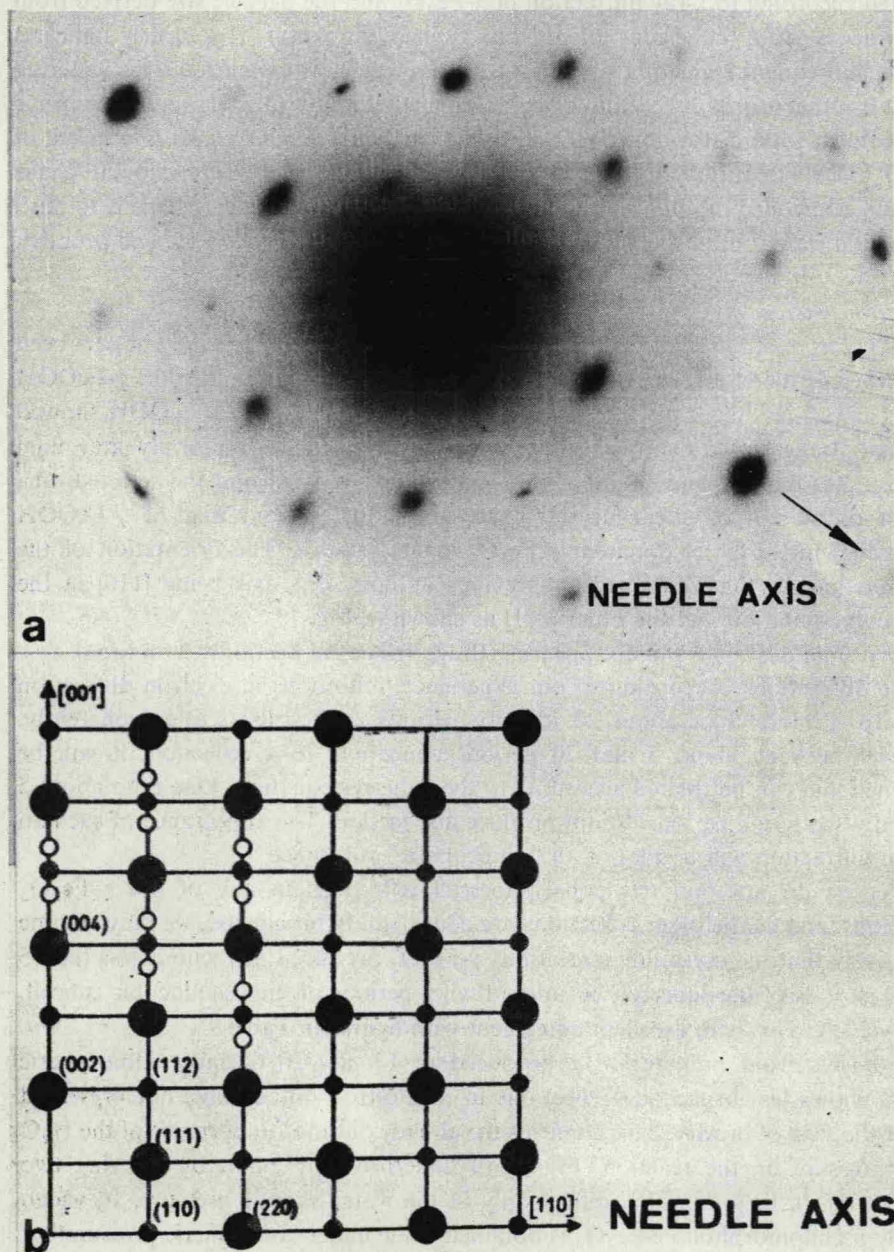

Fig. 13. (a) Selected area electron diffraction of γ-Fe_2O_3 (preparation 2; 1 h, 400 °C, 10^{-4} torr). (b) Idealized indexed diffraction with super cell reflections. The indices refer to the cubic subcell of γ-Fe_2O_3.