

## Existence of a direct phase transformation from haematite to maghemite

By S. MEILLON†, H. DAMMAK‡, E. FLAVIN§ and H. PASCARD†

† Laboratoire des Solides Irradiés, Commissariat à l'Énergie Atomique,  
Centre National de la Recherche Scientifique, École Polytechnique,  
91 128 Palaiseau Cedex, France

‡ Laboratoire CPS, Centre de Recherche, École Centrale Paris,  
92 295 Chatenay Malabry Cedex, France

§ Direction des Matériaux, Office National d'Études et de Recherches Aéronautiques,  
OM, 29 avenue de la Division Leclerc, 92 322 Chatillon Cedex, France

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### ABSTRACT

The observation of a direct phase transformation from haematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (antiferromagnetic) to maghemite  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (ferrimagnetic) by the mechanical action of grinding is reported. A simple grinding process is used; it is characterized by the presence of a shearing component exerted on the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. All crystallographic and magnetic measurements show existence of a phase transformation  $\alpha \rightarrow \gamma$ . The interpretation is based on a mechanism using two crystallographic concepts: the orientation relationship between the two phases, and movement of the oxygen planes due to a periodic shearing sequence. The results are also consistent with the phenomena related to the inverse transformation  $\gamma \rightarrow \alpha$ .

### § 1. INTRODUCTION

In the field of iron oxides (haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), three phase transformations are well known (Lefever 1970):

- (1) the transformation from rhombohedral (hexagonal)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to cubic (spinel) Fe<sub>3</sub>O<sub>4</sub> at about 1300°C in inert gas;
- (2) the transformation from cubic (spinel) Fe<sub>3</sub>O<sub>4</sub> to cubic (spinel with vacancies)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at about 200°C in air;
- (3) the transformation from cubic (spinel with vacancies)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> to rhombohedral (hexagonal)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at about 400°C in air.

Here, we report the observation of the direct phase transformation from haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) (antiferromagnetic) to maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) (ferrimagnetic) by the mechanical action of grinding. Previously, such a transformation was partially observed (with other phases) only by hydrogen reduction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Aharoni, Frei and Schieber 1962). In our case, we use a simple grinding process characterized by the presence of a shearing component exerted on the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles.

### § 2. GRINDING EXPERIMENTAL PROCESS

The technological process (Globus 1977) is based on the following principles: the haematite powder to be ground was put in suspension in a liquid (ethanol), and this liquid was made to pass in a continuous and repeated manner between two rubbing surfaces. One of the rubbing surfaces forms part of a horizontal disc driven by a vertical

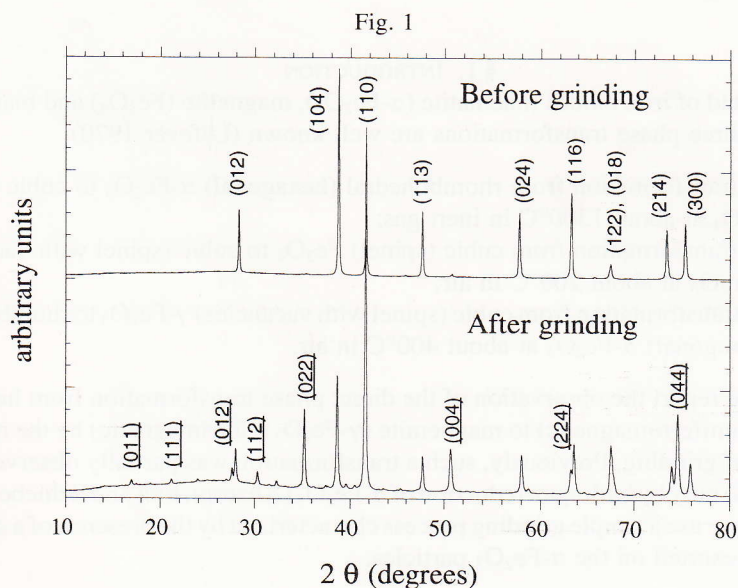
shaft; the disc is a conventional diamond-set grinding wheel whose surface has been rendered smooth by preliminary wear. The other rubbing surface comprises four stationary shoes resting on the disc; these shoes are made from very dense polycrystalline blocks of haematite whose surface has been polished.

In such a process, the surface which face each other are smooth and haematite grains (size about  $15\ \mu\text{m}$ ) are subjected to an action comprising two stress components: compressive stress due to the pressure applied vertically (roughly  $1\ \text{kg cm}^{-2}$ ), and shearing stress due to the rotating motion of the disc surface. Then the grains are crushed and thus progressively reduced to smaller and smaller sizes. At the end of the grinding procedure, the ethanol was evaporated by heating at  $80^\circ\text{C}$  and the ground powder was collected: ultra-fine particles were obtained. The grain sizes (from microns to submicrons) depend on the duration of the experiments (three grindings were made, with different durations: 25, 40 and 55 days).

### § 3. CRYSTALLOGRAPHIC AND MAGNETIC RESULTS

The most striking phenomenon was the appearance of magnetism after grinding, directly observed by the strong attraction of the powder by a magnet. So, the powder ground for 55 days was investigated by X-ray diffraction; in addition to the X-ray pattern of the haematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) phase, we have discovered the existence of additional lines due to another crystallographic phase (fig. 1). These new diffraction lines correspond exactly to the diffraction pattern of the maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) phase.

The same powder was investigated by magnetic measurements. The saturation magnetization at 300 K was  $J = 0.26\ \text{T}$ . This value corresponds to the magnetization of the mixture of  $\gamma$  and  $\alpha$  ferric oxides and is directly proportional to the percentage of  $\gamma$

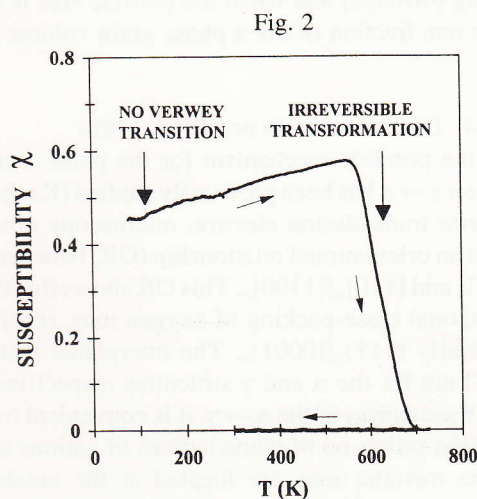


X-ray diffraction patterns of  $\alpha\text{-Fe}_2\text{O}_3$  before grinding corresponding to  $a_\alpha = 0.504\ \text{nm}$  and  $c_\alpha = 1.379\ \text{nm}$  (top), and after grinding for 55 days (bottom). After grinding, additional lines appear, which correspond exactly to the diffraction pattern of the maghemite  $\gamma\text{-Fe}_2\text{O}_3$  phase, with the lattice parameter corresponding to that phase:  $a_\gamma = 0.836\ \text{nm}$ . Furthermore, from the analysis of the line intensities, the percentage (in mass) of the maghemite phase can be measured; it is found to consist of 58% of the  $\gamma\text{-Fe}_2\text{O}_3$  phase.



phase since  $\alpha\text{-Fe}_2\text{O}_3$  is antiferromagnetic (resulting magnetization  $J_\alpha = 0$ ) and  $\gamma\text{-Fe}_2\text{O}_3$  is ferrimagnetic ( $J_\gamma = 0.46$  T). Thus the percentage of  $\gamma$  phase deduced from magnetic measurements is  $J/J_\gamma = 57\%$ , in remarkable agreement with the value found from X-ray diffraction (fig. 1).

The magnetic susceptibility  $\chi$  was measured as a function of temperature from 77 to 750 K and then from 750 to 300 K (fig. 2); the main observation was the existence of an irreversible magnetic transition in the temperature range of 700 K in which it is known that  $\gamma\text{-Fe}_2\text{O}_3$  is transformed to  $\alpha\text{-Fe}_2\text{O}_3$  in air. The disappearance of the magnetic



Initial magnetic susceptibility  $\chi$  of the powder after grinding for 55 days as a function of temperature, first at increasing temperature from 77 to 750 K and then at decreasing temperature from 750 to 300 K. Measurement is made on a toroidal sample obtained by packing the powder under pressure. The sample is used as a transformer core at low frequency; the secondary voltage is proportional to the magnetic susceptibility  $\chi$ . Around 120 K (the Verwey transition temperature of magnetite), a flat variation in  $\chi$  is observed; hence it can be concluded that no magnetite is present in the investigated powder.

Variations in particle size, saturation magnetization and percentage of  $\gamma$  phase.

Grinding duration <sup>†</sup> (days)	Particle size $D_m$ <sup>‡</sup> ( $\mu\text{m}$ )	Magnetization $J$ <sup>§</sup> (T)	Amount of $\gamma\text{-Fe}_2\text{O}_3$ <sup>  </sup> (%)
0	10–20	0	0
25	1–5	0	0
40	0.25–0.6	0.035	8
55	0.04–0.06	0.26	57

<sup>†</sup> Duration of three different lots of powders ground using the same procedure.

<sup>‡</sup> Mean value  $D_m$  of the powder particle size obtained from the observation of the granular structure by scanning electron microscopy.

<sup>§</sup> Saturation magnetization measured with a magnetic field up to 1.5 T to saturate the  $\gamma\text{-Fe}_2\text{O}_3$  particles.

<sup>||</sup> Percentage of  $\gamma\text{-Fe}_2\text{O}_3$  phase for the differently ground powders, deduced from the magnetization  $J$  which is directly proportional to the percentage of  $\gamma$ -phase (since  $\alpha\text{-Fe}_2\text{O}_3$  is antiferromagnetic ( $J_\alpha = 0$ ) and  $\gamma\text{-Fe}_2\text{O}_3$  is ferrimagnetic with  $J_\gamma = 0.46$  T).

$\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase was confirmed both by the cancellation of  $\chi$  (from 750 to 300 K), and by X-ray diffraction (all  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> diffraction lines disappeared after heating at 750 K). Finally, in the case of extended-period grinding, all crystallographic and magnetic measurements are consistent with the existence of a phase transformation from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

Furthermore, we have studied the phenomena as a function of the grinding duration, in two other intermediate cases: grinding for 25 and 40 days. The variations in the particle size, the saturation magnetization and the percentage of  $\gamma$  phase are given in the table. The main result is the appearance of the  $\gamma$  phase both when the grinding duration is sufficiently long (40 days) and when the particle size is sufficiently small (roughly submicron); then one fraction of the  $\alpha$  phase grain volume is transformed to  $\gamma$  phase.

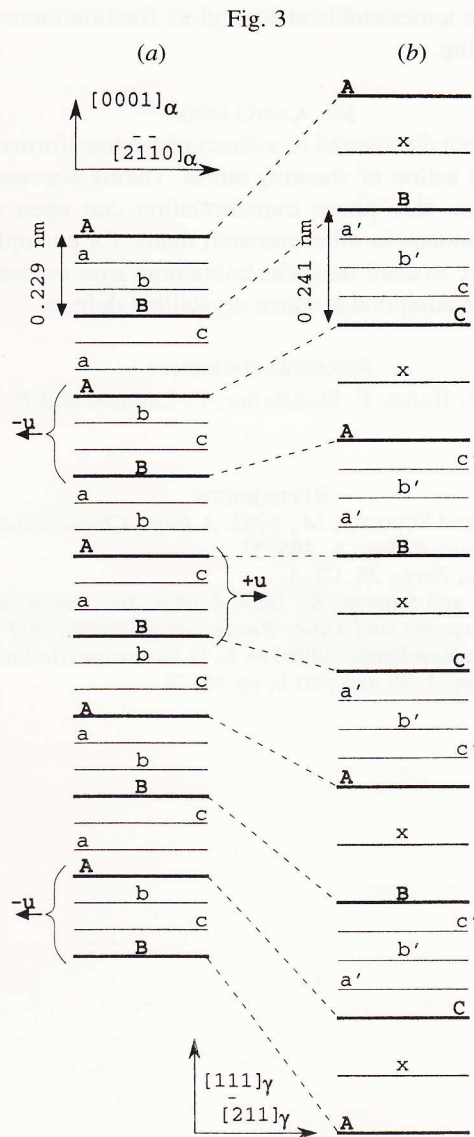
#### § 4. DISCUSSION AND INTERPRETATION

Now, let us consider the possible mechanism for the phase transformation. The inverse phase transformation  $\gamma \rightarrow \alpha$  has been previously studied (Kachi, Momiyama and Shimizu 1963), using *in-situ* transmission electron microscopy observations; it was pointed out that there exists an orientational relationship (OR) between the phases when they coexist:  $(111)_\gamma // (0001)_\alpha$  and  $[\bar{1}10]_\gamma // [1\bar{1}00]_\alpha$ . This OR shows that there is a common plane, containing the hexagonal close-packing of oxygen ions, remaining undistorted and unrotated which is clearly  $(111)_\gamma // (0001)_\alpha$ . The interplanar distances of oxygen planes are 0.229 and 0.241 nm for the  $\alpha$  and  $\gamma$  structures respectively.

When we consider the mechanism of the  $\alpha \rightarrow \gamma$ , it is convenient to describe the two structures as composed of the piling-up of plane lattices of cations and anions. In the hexagonal structure  $\alpha$ , the metallic ions are located at the octahedral interstices. The stacking sequence of close-packed oxygen planes is AB... Between each two oxygen planes, there are two sheets of cations (fig. 3(a)). The period along the  $[0001]_\alpha$  direction repeats each six oxygen planes. The  $\gamma$  structure is a spinel defect, that is cation vacancies in an oxygen framework. The stacking sequence of oxygen planes is ABC... The metallic ions are present in their interstices. They themselves form two kinds of two-dimensional trigonal lattice. The first, denoted  $x$  and called 'kagome', is one in which all interstices are octahedral sites. The second is made up of three hexagonal planes with the stacking sequence  $a'b'c'$ ... (fig. 3(b)). All interstices are tetrahedral sites, except for the middle plane  $b'$ , where the site is octahedral.

A mechanism to change the stacking sequence AB... into ABC... has been proposed in cobalt metal (Christian 1951), for the h.c.p  $\rightarrow$  f.c.c. transformation. From that description, the mechanism for the  $\alpha \rightarrow \gamma$  transformation can occur by a periodic sequence shear, where two oxygen planes move together with the same shearing stress. Two oxygen planes AB become BC by moving  $+a_\alpha/3$  along one of the  $\langle 2\bar{1}\bar{1}0 \rangle$  directions, where  $a_\alpha$  is the lattice parameter. In the same way, the next two oxygen planes AB become CA by moving  $-a_\alpha/3$ . The following planes AB remain unchanged. Repeating this scheme with the period of six oxygen planes, fig. 3 is easily constructed. During this shearing sequence, we note the following two cases: in case (1), the two cation planes between two neighbouring oxygen planes AB are assumed to move together with them; in case (2), the two cation planes between two neighbouring oxygen planes BA undergo shearing stress in the opposite direction. The cations have to be organized to minimize their energy (Christian 1951), leading to the formation of the  $x$  plane or the  $a'b'c'$  planes. We note in fig. 3 that, in case (1), the collapse of the two cation planes followed by a coherent diffusionless movement as previously





Schematic diagram of the mechanism of the  $\alpha \rightarrow \gamma$  phase transformation in  $\text{Fe}_2\text{O}_3$ , describing the piling-up of atomic planes of cations  $\text{Fe}^{3+}$  (thin lines) and anions  $\text{O}^{2-}$  (thick lines) for (a) the  $\alpha$  phase and (b) the  $\gamma$  phase. The transformation is obtained by a shear sequence of planes, followed by a rearrangement of the cations and an expansion of about 5.2% parallel to  $[0001]_\alpha$  and about 1.37% perpendicular to  $[0001]_\alpha$ . The displacement vector  $\mathbf{u}$  is equal to  $(a_\alpha/9) [\bar{2}110]$ .

described (Kachi *et al.* 1963) lead to the x plane and, in case (2), the two planes divide into three ion planes  $a'b'c'$  which belong to the  $\gamma$  structure. However, this re-stacking may just be opposite, that is a collapse in case (2), and a division in case (1).

One can imagine that the grinding induces a shearing of the  $(0006)_\alpha$  oxygen planes in the  $\alpha$  grains. In one grain, the shearing is randomly induced, which implies stacking faults. As the grains are dividing, the density of stacking faults increases, until the domains of the  $\gamma$  phase appear. This is coherent with the experimental results, because

the  $\gamma$  phase is formed in a metastable state, and its fraction increases when the grain size decreases by grinding.

#### § 5. CONCLUSION

The existence has been discovered of a direct phase transformation from haematite to maghemite under the action of shearing stress. Taking account of the importance of iron oxides in nature, this phase transformation can open up the way to the comprehension of phenomena in other research fields, for example in geomagnetism where high pressures are exerted on rocks containing iron oxides, or for example in nuclear science where irradiations produce crystalline defects.

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