On the Multiple Orientation Relationships Between Hematite and Magnetite

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Abstract

Lattice fringe and diffraction observations of hematite/magnetite interfaces are described: elongated laths of magnetite, with \((111)_M\parallel(0001)_H\) and, less frequently, \((211)_M\parallel(0001)_H\), were found. General interfaces are incoherent as shown by the presence of steps, which are probably transformation dislocations. The magnetite is invariably multiply twinned, showing steps which may be twinning dislocations. A theoretical analysis of the possible secondary and ternary orientation relationships due to multiple twinning explains one of the two further less-frequent relationships indicated by texture goniometry. Such higher-order relations are not topotaxic and their identification and interpretation is a general problem for texture goniometry.

1. Introduction

Four orientation relationships have been deduced to occur during the low-temperature reduction of a single crystal of hematite \((\alpha-Fe_2O_3)\) to form magnetite \((Fe_3O_4)\). They are (Becker, Heitzmann & Baro, 1977)

1. \((111)_M\parallel(0001)_H\) and \((110)_M\parallel(10\bar{1}0)_H\),
2. \((112)_M\parallel(0001)_H\) and \((110)_M\parallel(10\bar{1}0)_H\),
3. \((113)_M\parallel(0001)_H\) and \((110)_M\parallel(10\bar{1}0)_H\),
4. \((115)_M\parallel(0001)_H\) and \((110)_M\parallel(10\bar{1}0)_H\).

Only (1) has the obvious topotaxic relationships, where the two structures share an approximately close-packed plane of oxygens. This is always the major component in texture goniometer studies. Orientation (2) was found to be a minor component for relatively high-temperature reductions \((773-1273\) K) whereas (3) and (4) were found only in the \(473-673\) K temperature range, where \(CO/CO_2\) gas buffers were used for reduction. Even then (3) and (4) occurred only after orientations (1) and (2) were already well-developed.

The above relationships were established by X-ray texture goniometry and consequently very little is known about the microscopic structure and texture of the phases and interfaces involved. Furthermore, there has been no structural interpretation of relationships (2), (3) or (4). In this paper we describe electron microscopic observations of orientations (1) and (2), found in a sample of naturally deformed hematite ore containing magnetite intergrowths. The magnetite/hematite interface is surprisingly complex and multiple twinning of magnetite occurs. We then give structural interpretations of the topotaxic relations (1) and (2) and show that relation (4) may be simply explained as a secondary relation due to multiple twinning of the magnetite. The texture goniometer evidence for relation (3) is not conclusive and should be re-examined. It is suggested that the complexity of the magnetite/hematite interface is due to the necessity to relieve elastic strain, since the primary topotaxic relations (1) and (2) are far from perfectly coherent, and also due to the kinetic requirement to provide pathways for diffusion of oxygen, for example out from the interface if \(Fe_2O_3\) is being reduced to \(Fe_3O_4\).

2. Experimental

(a) Specimen selection

These were selected from heavily deformed hematite ores collected at Kooyanobbing in Western Australia by Dr C. J. Wilson and Mr A. Griffin of the Department of Geology. The observation of twinning dislocations at rhombohedral twin interfaces in hematite from the same samples has already been reported (Bursill & Withers, 1979a). Fragments were taken from shiny platey crystals which, although apparently lamellar in habit, proved to be difficult to cleave or crush. It has been established from optical and electron microprobe analyses that the hematite contains a small fraction of magnetite and also goethite (Wilson & Griffin, 1978).

(b) Sample preparation and electron optical conditions

Single-crystal fragments were ground in an agate mortar and deposited on carbon lace. They were examined in a JEOL-100C electron microscope using a slightly modified goniometer operating within objective-lens pole-pieces, having spherical aberration coefficient \(C_s=2-4\) mm. The micrographs were recorded using focused illumination (semi-cone angle \(\alpha=1\) mrad) at electron optical magnifications of \(200 000\) to \(740 000\) \(\times\). Under these conditions, the combined effects of spherical aberration and beam diver-

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gence limit the obtainable point-to-point resolution to approximately 3-8 Å (see Bursill & Wilson, 1977). All of the micrographs were recorded using the symmetric Laue case with the transmitted beam along the optic axis. A large objective aperture was used so that all beams out to $2\cdot3^{-1}$ Å$^{-1}$ were used to form the image. The low visibility of the lattice fringes reflects the lack of perfect coherence in the illumination. Thus, most of the defect contrast will come from any diffuse scattering surrounding the transmitted beam. The images were obtained using objective lens defocus approximately $-1000$ Å when, for sufficiently thin crystals, the image contrast is proportional to the projected charge density in the crystal (Lynch, Moodie & O'Keefe, 1975). The image will also contain a significant contribution from aperture contrast due to the exclusion of strong diffracted beams from the effective objective aperture. Complete through-focal series of images were not recorded and we will not attempt a full explanation of the defect-image contrast, which would involve prohibitively large computer calculations using the method of periodic continuation (see for example MacLagen, Bursill & Spargo, 1977; Bursill & Barry, 1978). Nevertheless, much useful in-

(c) Electron microscope observations

Fig. 1 shows a typical area of magnetite intergrown with hematite. The texture is complex, showing laths

Fig. 2. Enlargement of Fig. 1 showing detail of the lattice fringes at the interfaces; note mirror plane at the $M1/M1'$ interface and the $H/M1$ and $H/M1'$ interfaces.

Fig. 3. Enlargement of another area of Fig. 1 showing three further interfaces $J, K$ and $L$; also note interfaces $H/M2$ and $H/M2'$. 

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**Fig. 1.** Micrograph showing hematite/magnetite intergrowth. Note laths of finely-twinned magnetite 200–500 Å wide and 1–2 μm long. Six different interfaces, labelled $A$ to $F$ are indicated. Note the step (S) at interface $C$; this is probably a twinning dislocation.
of finely-twinned magnetite approximately 200–500 Å wide and 1 to 2 μm long. Six different interfaces are labelled A to F. A, B and C appear edge-on over most of their length, but show unit steps (S) having height equal to one (0003)ₜ fringe spacing (4.6 Å). Interfaces D to F show different inclinations to the incident beam. These contain much broader fringes as expected for moiré, interfacial dislocations or simply wedge fringes. Fig. 2 shows an enlargement of part of Fig. 1, where the lattice fringes may be more readily seen. These are parallel to (111)ₘ, (111)ₘ, (200)ₘ and (0003)ₜ. Note the mirror across the M₁/M₁' twin and the change in the fringes across the H/M₁ and H/M₁' interfaces. Fig. 3 shows another enlargement from the same crystal flake. Three further interface types J, K and L appear. Comparison with Fig. 2 shows two distinct magnetite orientations (M₂/M₂') with M₂/M₂' and H/M₂ interfaces. Interface L appears to be a single fault within M₂.

Fig. 4(a) shows a selected-area diffraction pattern from most of the area shown in Figs. 1 and 3. This may be indexed using four reciprocal nets; i.e. the [21.0]ₜ zone [Fig. 4(b)] and three <011>ₘ zones, indicated by M₁, M₂ and M₂' [Figs. 4(c), (d), (e)]. Note that all four zones appear to be parallel to the incident electron beam, since they are all symmetrically excited in Fig. 4(a). However, in fact, there may be some misalignment since the patterns were recorded from thin crystals (say 200–500 Å thick) where the relrods may intersect the Ewald sphere over a significant range of orientations. Nevertheless, we may state that Fig. 4(c) demonstrates orientation relation (1), with (111)ₘ parallel to (0001)ₜ, whereas Figs. 4(d), (e) demonstrate two twin-related forms of relation (2), with (422)ₘ and (422)ₘ' parallel to (0001)ₜ. Close inspection of the fringe spacings and orientations in Figs. 2 and 3 enabled us to identify slabs of hematite (H) and four distinct orientations of magnetite (M₁, M₁', M₂ and M₂'), labelled in Figs. 1, 2, 3. Thus the magnetite is multiply twinned for both orientation relations (1) and (2), indicated by M₁/M₁' and M₂/M₂' interfaces in Figs. 2 and 3 respectively.

Fig. 4. (a) Selected area diffraction pattern from area of Fig. 1. (b), (c), (d), (e) Decomposition of (a) into four reciprocal lattice nets. These index as the [21.0]ₜ and three <011>ₘ zones, indicated by subscripts M₁, M₂ and M₂'.
3. Structural implications of the observed orientations

(a) Structural background for hematite and magnetite

The corundum structure, isomorphous with α-Fe₂O₃, has been thoroughly described by Megaw (1973). It is convenient to use the octahedral representation, shown for the [10.0]ₜ projection in Fig. 5(a). The crystallographic data are given in Table 1. One octahedral layer is shown in Fig. 5(a), small dots indicate Fe atoms lying within a (1120)ₜ plane (the plane of the drawing), whereas thick and thin open circles represent O atoms lying in front of and behind this plane respectively. The corners of the unit cell are indicated. The oxygen atoms form an h.c.p. array if the structural parameter $u$ is idealized to zero. Thus, pairs of face-shared octahedra with (0001)ₜ common are arranged on a rhombohedrally-centred hexagonal lattice. Note that the edges of the shared face are shorter than those of the unshared face opposite. The Fe atoms are further apart than if they remained midway between the oxygen layers. Thus the Fe atoms become puckered about the basal plane whereas the O sheets remain flat. The nature of the O displacements away from ideal h.c.p. are evident in the [00.1]ₜ projection [Fig. 5(b)].

Table 1. Crystallographic parameters for hematite and magnetite

(After Megaw, 1973.)

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<th>Hematite</th>
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<td>Rhombohedrally centred hexagonal lattice with $a_\text{R} = 5.038$, $c_\text{R} = 13.772$ Å and six formula units per cell. Space group $R3c$ (No. 167) with atomic coordinates: Fe in 12(c); 00z, with $z = 0.3553 = \frac{1}{3} + u$, with $u = -0.027$ O in 18(e); x0z, with $x = 0.3059 = \frac{1}{3} + w$, with $w = 0.022$.</td>
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<td>Magnetite</td>
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<td>Face-centred cubic lattice with $a_\text{M} = 8.3963$ Å and eight formula units per cell. Space group $Fd\overline{3}m$ (No. 227) with atomic coordinates: Fe in 8(a); 000 Fe in 16(c); O in 32(e); $x'x'x'$, with $x' = \frac{1}{3} + u'$, where $u' = 0.004$.</td>
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The crystallographic data for magnetite are also listed in Table 1. It has inverse spinel structure (Megaw, 1973). If $u'$ were zero the oxygens would be c.c.p. Writing $\text{Fe}_3\text{O}_4 = \text{Fe}^{3+}(\text{Fe}^{3+}\text{Fe}^{2+})\text{O}_4$ characterizes the inverse spinel, whereby all of the Fe$^{2+}$ and half of the Fe$^{3+}$ are distributed randomly (above 120 K) over certain of the octahedral interstices and the remaining Fe$^{3+}$ occupy tetrahedral interstices. Octahedra share edges forming ribbons parallel to [110]ₜ and [110]ₜ in the (001)ₜ plane [Fig. 6(a)] and in the other four (110)ₜ directions inclined at 45°. Occupied tetrahedral sites link the octahedral ribbons as shown. (Fig. 6a shows only half the unit cell, the remainder may be generated using the translation operation $[1\frac{1}{2}0]ₜ$. The patterns of filled octahedral and tetrahedral sites on (111)ₜ planes are given in Figs. 6(b), (c). Note that two distinct types of (111)ₜ layers occur, one containing octahedra only [Fig. 6(b)] and, alternating with it, one containing some octahedra and some tetrahedra [Fig. 6(c)].

(b) Structural implications of orientation (1)

Relation (1) implies topotaxy across a common O plane which is approximately c.p. In fact, there are four possible (111)ₜ||[0001]ₜ interfaces. If we label the common plane $A$ then the h.c.p. O layers up to this
may be written $ABABA$. Thereafter, the stacking becomes c.c.p. with $ABCABC$. The sequence across $A$
may therefore be either

$$ABABABCABC \quad (5)$$
or

$$ABABACBACB . \quad (6)$$

Using (5) we may fill the interstices between $A$ and $B$
in magnetite using either the octahedral [Fig. 6(b)] or
octahedral plus tetrahedral [Fig. 6(c)] sites. Both lead
to strings of three face-shared polyhedra across the
$H/M$ interface. However, use of (6) leads to only edge-
sharng of octahedra between $H$ and $M$ using Fig. 6(b);
or to strings of three face-shared octahedra for Fig.
6(c). Thus, on electrostatic grounds we expect alterna-

![Figure 6](image)

(a)

(b)

(c)

Fig. 6. (a) $[001]_M$ projection showing two levels of the structure
parallel to $[001]_M$. The first level contains ribbons of edge-shared
octahedra along $[001]_M$ and $[110]_M$ joined together by filled
tetrahedra, the second level being related to the first by a 90
rotation. (b), (c) Patterns of filled octahedral (b) and octahedral
plus tetrahedral (c) interstices parallel to $[111]_M$.

![Figure 7](image)

(a)

(b)

Fig. 7. (a) Model for the $(111)_M[[0001]]_H$ interface, drawn assuming c.p.
oxygen layers: note edge-sharing of octahedra between $H$ and $M$.
(b) Superposition of real atomic coordinates for $(0001)_H$ and $(111)_M$
anion layers showing relaxation required for perfect coherency:
note the dilation of $M$ relative to $H$.
tive three to be preferred. This model for the interface is shown in Fig. 7(a), drawn for ideal c.p. layers. Fig. 7(b) shows a superposition of the real hematite and magnetite O positions for the common layer. Thus considerable relaxation is required for a coherent interface. The mean fractional dilation of magnetite relative to hematite is $\delta_1 = -0.04$.

(c) Structural implications of relations (2), (3) and (4)

Inspection of a model of the hematite structure shows a puckered sheet of O atoms with mean plane $(2\overline{1}0)_H$ which is topologically equivalent to a c.p. O layer. Adjacent $[21.0]_H$ c.p. rows are displaced alternately up and down with respect to the ideal c.p. plane [Fig. 8(a)]. A superposition of $(2\overline{1}0)_H$ and $(\overline{1}11)_M$ O planes [Fig. 8(b)] shows larger misfit than Fig. 7(b), with dilations $\delta_2 = -0.04$ and $\delta_3 = 0.055$ along $[21.0]_H$ and $[00.1]_H$ respectively. Thus $(2\overline{1}0)_H$ could act as a common plane giving rise to relation (2). In this case there is only one distinct way of filling the interstices at the interface which avoids triple face-sharing. The mixed octahedral/tetrahedral layer [Fig. 6(c)] must follow the $(2\overline{1}0)_H$ layer of octahedra. This contains no edge-shared polyhedra and it may be able to distort to match the puckered $(2\overline{1}0)_H$ oxygen net. However, we point out that the observed interface for $H/M^2$ (Fig. 3) does not have this composition plane. Further work is required to identify the equilibrium interface plane.

So far we have not deduced a topological basis for relation (3). However, (4) may be simply derived by first applying (1) then twin the magnetite on $(\overline{1}11)_M$ so that $(11\overline{5})_M$ becomes parallel to $(0001)_H$ [shown in Fig. 9(a)]. Thus we find that (4) is a secondary orientation due to magnetite twinning and does not imply
direct topotaxy. Clearly, it is dependent upon the prior establishment of (1), as was observed by Becker, Heizmann & Baro (1977). Repeated twinning of the magnetite, maintaining \((110)_M\) parallel to \((10\bar{1}0)_H\), leads to only one further distinct relation:

\[
(11,11,1)_{M}||\langle 0001 \rangle_{H} \text{ and } (110)_{M}||\langle 10\bar{1}0 \rangle_{H}.
\]

(7)

This is represented schematically in Fig. 9(a), but it is not required to explain the texture goniometry results; nor was it observed in the present study, presumably because such ternary relations have low probability.

Similarly, allowing for multiple twinning of the magnetite following prior establishment of relation (2) leads to a secondary relation

\[
(1\bar{1}2)_{M}||\langle 0001 \rangle_{H} \text{ and } (110)_{M}||\langle 10\bar{1}0 \rangle_{H}.
\]

(2')

which is indistinguishable from (2). The corresponding ternary relation gives

\[
(1,1,21.8)_{M}||\langle 0001 \rangle_{H} \text{ and } (110)_{M}||\langle 10\bar{1}0 \rangle_{H}.
\]

(8)

Relations (2') and (8) are represented in Fig. 9(b). Again, relation (8) fails to explain relation (3) of Becker, Heizmann & Baro (1977). Close inspection of their Figs. 2 and 3 shows that there is in fact poor agreement between the theoretical and experimental intensity maxima positions for (3); pairs of peaks occur in the experiment, spanning the positions predicted for (3). This evidence needs to be re-examined. It may be that further texture goniometry will reveal evidence for the ternary relations (7) and (8) derived above. Further higher-order relationships may be derived using matrix transformation techniques (Bursill & Withers, 1979b); in addition we may include multiple twinning of both the magnetite and the hematite.

(d) Analysis of electron microscopic results

Fig. 4(c) clearly shows relation (1), with \((\overline{1}11)_{M}||\langle 0001 \rangle_{H}\). Figs. 4(d), (e) show two twin-related forms of relation (2), with \((\overline{2}1\overline{1})_{M2}||\langle 0001 \rangle_{H}\) and \((\overline{2}1\overline{1})_{M2'}||\langle 0001 \rangle_{H}\). Note that orientations \(M2\) and \(M2'\) are related by a mirror operation across the common plane \((\overline{1}11)_{M2,M2'}\) (Fig. 3). Similarly \(M1\) and \(M1'\) are equivalent after a mirror operation across \((\overline{1}11)_{M1,M1'}\).

We also note that \(M2\) may be related to \(M1\) by a rotation of 90° about the common direction \([01\overline{1}]_{M1,M2}\).

Steps in the interface between \(M1/M1'\) could be twinning dislocations, since they are sources of elastic strain attached to the composition plane. Movement of these steps would allow thickening of one twin at the expense of the other. Similar steps have been shown to be twin dislocations at rhombohedral twin composition planes of hematite (Bursill & Withers, 1979a).

At least six other interfaces, some inclined to the electron beam, appear in Fig. 1. These often appear to contain interfacial dislocations. However, such an interpretation is not unique, since wedge fringes, due to inclined boundaries, or moiré fringes, due to rotation or dilation of lattice planes across the interface, are also expected. The fringe spacing is usually too small (10–20 Å) and they are too numerous to correspond to wedge fringes. Then, since the presence of moiré fringes implies that interfacial dislocations also occur, we are justified in claiming that most of the observed interfaces are incoherent, as expected from Figs. 7(b) and 8(b).

The growth of \(\text{Fe}_3\text{O}_4\) at the expense of \(\text{Fe}_2\text{O}_3\), or vice versa, clearly involves a complex reaction zone, with multiple orientation relations between reactant and product, including multiple twinning of the magnetite. \(\text{Fe}_3\text{O}_4\) laths are elongated approximately along the basal plane of hematite, as expected for relation (1), with composition plane shown in Fig. 7(a). \(H/M2\) and \(M2/M2'\) interfaces occur less frequently and it seems unlikely, from Fig. 3, that the composition plane is necessarily \((2\overline{1}\overline{1}0)_H\). Despite the complexity of Figs. 1, 2, 3 and 4(a), we have found no evidence for relations (3) or (4) by electron microscopy.

The 4 to 5–5% dilations required for topotaxy according to (1) or (2) suggest that the complex reaction zone may represent an attempt to reduce coherency strains. Multiple twinning, including deformation twinning, would be expected to reduce elastic strain. The appearance of what are probably interfacial dislocations in the interfaces (Figs. 1, 2, 3) also arise due to relaxation of coherency strain. The nature of the reaction zone will also be determined by kinetic factors. For example, interfacial dislocations and the dagger-like penetration of magnetite into hematite may be required to provide diffusion paths for exchange of oxygen during, for example, a reduction process

\[6\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{O}_2.\]

(9)

Interfacial dislocations between hematite and magnetite should be regarded as 'transformation dislocations' (Bilby, 1953; Christian, 1975). These are simply steps with associated strain fields which are confined to the interface. They are partial dislocations in the sense that the Burger's vector is not a lattice vector. Their movement is necessary for the propagation of one phase at the expense of the other. In this case there must be a stoichiometry change associated with the step.

4. Conclusion

We have provided microscopic evidence for relations (1) and (2) and for multiple fine-scale twinning of the magnetite. Thus the reduction of hematite to magnetite will, in general, involve a complex reaction zone, with lath-like penetration of magnetite into hematite, requiring interfacial transformation dislocations and deformation twinning. We suggest that the complexity follows from the significant lack of coherency and build up of elastic strain.

Whereas the structural considerations we have discussed should be quite general, the experimental observations are not: clearly, the details of the reaction
mechanism will depend on the reduction or oxidation conditions used. Further carefully controlled studies of the reaction mechanisms should prove interesting.

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References


