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Anomalous Orientations of Cubic Close Packing in the Dehydration of Goethite in an Inert Atmosphere*

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Single-crystal X-ray studies of the dehydration of goethite (α -FeOOH) in an inert atmosphere (N_2) at relatively low temperatures (350–500°C) showed that haematite (α -Fe₂O₃) and magnetite (Fe₃O₄) are both formed topotactically. The haematite has the same orientation as when it is formed on dehydration in air, but no satellite reflexions were observed. The magnetite is formed in eight different orientations. Two of these correspond to the normal orientations; for both [111] is parallel to [100] of goethite ($[0001]_{h.c.p.}$); one has (1 $\bar{1}$ 0) parallel to (001) of goethite ($[2\bar{1}\bar{1}0]_{h.c.p.}$), and the other is rotated through 60° from this position. The other six orientations, all with $[11\bar{2}]$ parallel to [100] of goethite ($[0001]_{h.c.p.}$) are interrelated by 60° rotations; one corresponds to (111) parallel to (010) of goethite ($[(1\bar{1}00)_{h.c.p.}]$), and the others are at 60, 120, 180, 240 and 300° from this orientation. General considerations are discussed regarding the mechanisms of transformations in structures based on hexagonal close packing and cubic close packing assemblages of atoms or ions. Normal orientations (first kind) and anomalous orientations (second kind) of close packing are derived from a slipping mechanism of the close-packed layers. Emphasis is put on the distinction between twinning derived from different orientations of the packing of the large ions, and twinning derived from different distributions of the interstitial ions inside the packing.

Introduction

Results for the dehydration of goethite (α -FeOOH) in air have been published by several authors (*e.g.* Goldsztaub, 1935; Francombe & Rooksby, 1959; Lima-de-Faria & Gay, 1962; Lima-de-Faria, 1963). The iron ion being so readily reduced, it was thought that dehydration in an inert atmosphere could give rise to results quite different from the previous ones. Their study is the subject of the following work.

X-ray single crystal work

The main results established for the dehydration of goethite (α -FeOOH) in air were the following: haematite (α -Fe₂O₃) is derived topotactically from goethite, with twinning developing during the transformation; inter-

mediate stages of the transformation are observed before the dehydration is completed. The intermediate stages are characterized by the occurrence of satellite spots and diffuse intensity regions around the strong haematite reflexions. An earlier stage of the dehydration in air with haematite satellites and a few reflexions of goethite still present is obtained on heat-treatment at 350°C for 5 minutes (Lima-de-Faria, 1963). Therefore, the same temperature and time were used for a single crystal of goethite (0.8 mm long), but with a nitrogen atmosphere. A similar stage of dehydration was obtained in that haematite reflexions and some reflexions of residual goethite were observed, but no satellites were detected; on the other hand, extra reflexions were observed which could be ascribed to magnetite (Fe₃O₄). Further heating at 400°C for 1 hour, or at 500°C for 15 minutes, made the goethite reflexions disappear, while haematite and magnetite reflexions were observed. The haematite was in the same twinned orientation as when formed on dehydration of goethite in air.

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General packing considerations

Before tackling the determination of the actual orientations of the magnetite formed, some general considerations on transformations in structures based on close-packed assemblages of atoms or ions may be surveyed. The possible transformations of this type involving the two fundamental close-packed arrangements, *viz.* cubic close packing (c.c.p.) and hexagonal close packing (h.c.p.) are: (a) h.c.p. \rightarrow h.c.p., (b) c.c.p. \rightarrow c.c.p., (c) h.c.p. \rightarrow c.c.p., and (d) c.c.p. \rightarrow h.c.p. A tendency for the preservation of the type of packing has been pointed out by several authors (*e.g.* Ervin, 1952; Dent Glasser, Glasser & Taylor, 1962; Brindley, 1963). If the original structure and the transformed structure have the same type of packing (cases (a) and (b) above), this is preserved throughout the transformation, the small ions only being allowed to move inside the packing. Moreover when there is a change in the type of packing the tendency for the preservation of the close-packed layers determines the possible orientations.

The simplest way of preserving the close-packed layers is for the transformation to proceed by slipping of the layers over one another. Now, there are only two possible ways of placing one layer over another; therefore one is bound to a single new position when moving a layer relative to the layer below. This movement can consist of a single slip along one out of three different directions (spheres will move along valleys, that is, from one hole to the nearest hole) all giving rise to the same final state, and therefore being equivalent. To describe the movements of layers in these transformations it is convenient to consider the $(1\bar{1}0)$ section of the c.c.p. structure and the section of the h.c.p. structure parallel to $(2\bar{1}\bar{1}0)$ (Christian, 1951) (Fig. 1). The advantage of these sections is that the spheres corresponding to the sequences $ABAB \dots$ and $ABCABC \dots$ all lie on the plane of the Figure. With the help of packing models of plastic balls it can easily be seen that to change from h.c.p. the layers have to slip by pairs, as if locked together, in the $[01\bar{1}0]$ direction, and that all the pairs slip in the same direction (Christian, 1951) (Fig. 1, middle part). The necessity for the layers to move in pairs is a consequence of the single new position that can be obtained by slipping, as pointed out above. For instance, if a third layer slips relatively to the layer below which has already slipped, the resulting position of this third layer in relation to the first layer will be the same as initially, the sequence ABA being maintained. Two possible c.c.p. orientations can be derived from h.c.p. as movements of pairs AB or BA take place (Fig. 1), thus twinning is obtained in this transformation. Since there exists a unique set of close packed planes in the h.c.p. structure, only two possible c.c.p. orientations are obtained in the transformation h.c.p. \rightarrow c.c.p.

To transform the c.c.p. into h.c.p. the layers have again to be moved by pairs, slipping in the $[11\bar{2}]$ direction and the two possible orientations derived for h.c.p.

are parallel, not giving rise to twinning (Fig. 1, lower part). Since there are four equivalent sets of close-packed planes in the c.c.p. structure, four different orientations are obtained in this transformation. These results are summarized in Fig. 2.

It is interesting to notice that, given a direction of slipping for pairs of layers in the h.c.p. structure, owing to packing characteristics the pairs BA and AB can move only in opposite directions. On the other hand, both of the two movements for pairs of layers in the c.c.p. structure take place in the same direction.

In Fig. 2, lower part, the various packing orientations developed on transformations involving change from h.c.p. into c.c.p., and *vice versa*, are shown with their packing axial relationships. From it many particular transformations can be derived if the packing characteristics of the original and the transformed structures are known. The axial relationships, which are the same for these two transformations, are the following: $[0001]_{\text{h.c.p.}}$ parallel to $[111]_{\text{c.c.p.}}$, $[01\bar{1}0]_{\text{h.c.p.}}$ parallel to $[11\bar{2}]_{\text{c.c.p.}}$.

Apart from the twinning that comes from the close packing conditions, twinning can also arise from different, non-equivalent distributions of interstitial ions between the close packed layers. This is the case for haematite derived from heated goethite; although the type of packing is the same in haematite and goethite,

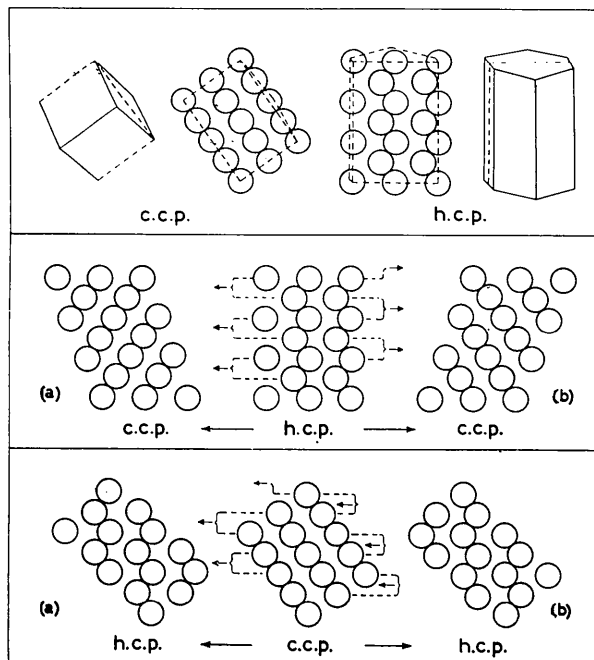


Fig. 1. Mechanism of h.c.p. \rightarrow c.c.p. transformation and *vice versa*. The top part of the Figure shows schematically the sections of close packing models of plastic balls, appropriate for the description of the mechanism of these transformations: $(1\bar{1}0)$ section of c.c.p. and $(2\bar{1}\bar{1}0)$ section of h.c.p. Two different movements are represented, corresponding one to the left-hand arrows and the other to the right-hand arrows, leading respectively to structures (a) and (b). The layers slip by pairs, as locked together.

in haematite the iron ions can have two non-equivalent distributions inside the h.c.p. arrangement of oxygen ions, and this gives rise to twinning. Distinction should therefore be made between these two types of twinning.

Further considerations on the X-ray results

For the transformation of goethite (with h.c.p. of the large ions) into magnetite (with c.c.p. of the large ions), and in the light of these considerations, it was possible to verify that some of the magnetite spots corresponded to the two derived orientations just mentioned. But other spots of magnetite could not be ascribed to these orientations. From the repeat distance corresponding to the extra spots, it was concluded that they could be ascribed to orientations where the $[11\bar{2}]$ direction of magnetite (or of the c.c.p. structure) is parallel to the $[0001]$ direction of the h.c.p. oxygen framework of goethite. Six non-equivalent orientations were observed, all with the (111) face of the c.c.p. parallel to the six prismatic faces of the h.c.p., *i.e.*, interrelated by 60° rotation (Fig.3). This was verified by direct comparison of oscillation photographs of magnetite in these six orientations.

It is interesting to notice that these two kinds of orientation of magnetite crystallites have been observed on reduced haematite (Keeling & Wick, 1963). They are also the same as those described by Sleswyk (1962) for the h.c.p. \rightarrow c.c.p. transformation in relation to the mechanical deformation of certain metals and alloys. However instead of shear on the $(0\bar{3}31)$ plane, as postulated by Sleswyk (1962), this transfor-

mation can be explained by two half slips of close-packed layers (Fig.4). In the first movement alternate layers of the h.c.p. structure (Fig.4) slip half way, giving rise to a structure where two perpendicular sets of close-packed planes exist, one represented as horizontal and another as vertical. From this position the new vertical close-packed layers can now move; if they move half way upwards, the c.c.p. orientation marked (a) is obtained; if they do so downwards, that marked (b) is formed. Therefore, two different orientations of c.c.p. can develop in each prismatic face of the h.c.p. (Fig.3). The physical reason for such anomalous orien-

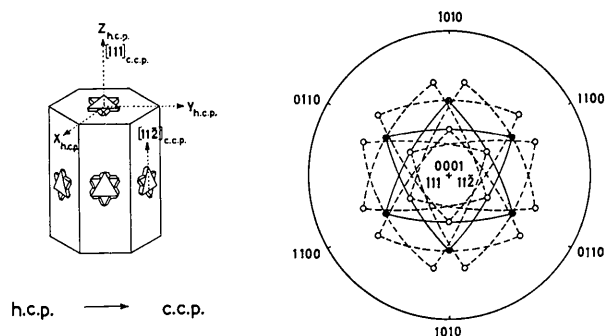


Fig.3. C.c.p. orientations of first and second kinds derived from h.c.p. The c.c.p. is represented by octahedra. On the top of the hexagonal prism are represented the two normal (first kind) orientations, and on the prismatic faces the six anomalous (second kind) orientations of c.c.p. On the right side of the Figure is represented the stereographic projection of the cube poles of these eight orientations (after Sleswyk, 1962).

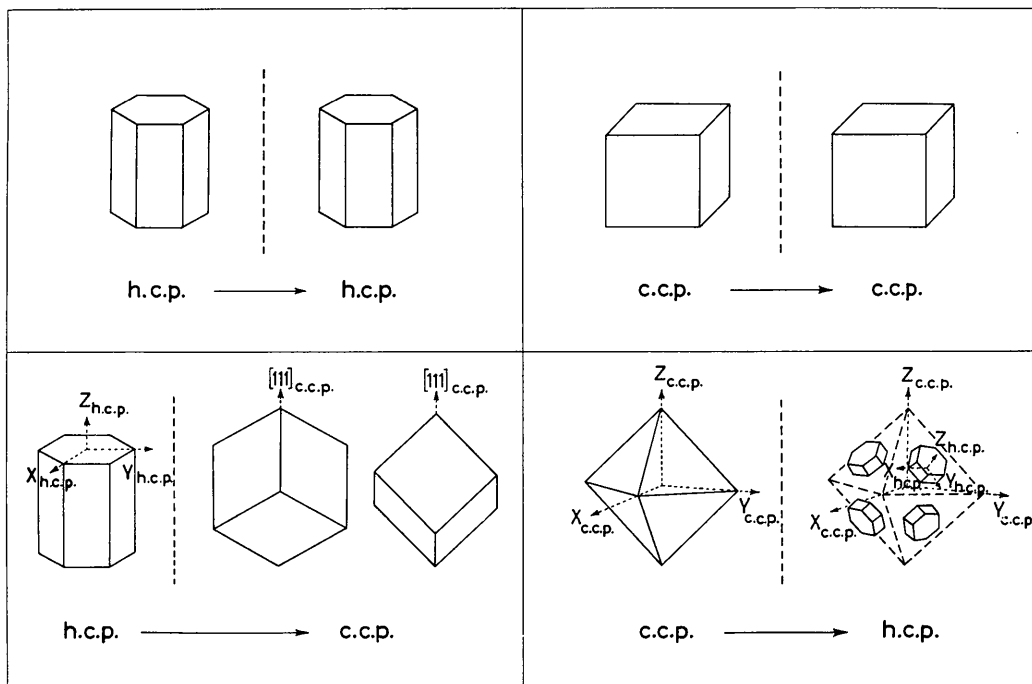


Fig.2. Normal orientations (first kind) derived on transformations involving c.c.p. and h.c.p.

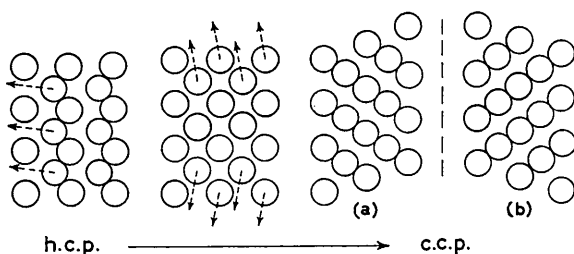


Fig. 4. Mechanism of the h.c.p. \rightarrow c.c.p. transformation giving rise to orientations of the second kind. First (left side) alternate layers slip half way; secondly all the formed vertical close-packed layers slip upwards giving rise to the (a) orientation, or slip downwards giving rise to the (b) orientation.

tations might be sought for in any internal stresses perpendicular to the prismatic faces. These would hamper the development of the normal mechanism of transformation, which involves expansion perpendicular to these faces. On the other hand, the anomalous mechanism would help to compensate for the internal stresses, because of the contraction of the structure along this direction.

The six anomalous orientations observed here might be called orientations of the second kind, as compared with the two normal orientations, which should be referred to as being of the first kind.

The corresponding anomalous orientations of h.c.p. which could be derived on the c.c.p. \rightarrow h.c.p. transformation would produce prismatic faces of the h.c.p.

parallel to the (111) face of the c.c.p. However this does not seem physically probable because it would give rise to expansion in the same direction as the normal orientation, and would therefore be as unfavourable to the relief of any internal stresses as would the normal orientations.

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High Pressure NaAlGeO_4 , a Calcium Ferrite Isotype and Model Structure for Silicates at Depth in the Earth's Mantle

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The high pressure phase NaAlGeO_4 formed at 120 kilobars and 900°C has the calcium ferrite structure, space group $Pnma$, unit-cell dimensions $a = 8.87$, $b = 2.84$, $c = 10.40$ Å and $D_x = 4.73$ g.cm $^{-3}$. The isomorphous silicate NaAlSiO_4 , $D_x = 3.9 \pm 0.1$ g.cm $^{-3}$, should exist in the earth's mantle, being transformed by pressure from nepheline or jadeite.

Introduction

The phases in the earth's mantle at depths between 400 and 900 kilobars are generally believed to be denser polymorphic varieties of common silicate minerals (Birch, 1952). Although it is still not practicable to achieve the experimental pressures and temperatures

which simulate conditions at depths below 600 km and to transform many silicates directly, a technique of particular value is to replace them with their germanium analogues, which undergo transitions at much lower pressures (Ringwood, 1966).

High pressure synthesis is expected to result in an increase in both the density of the phase and the co-