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Electron Microscopic Study of Dehydration Transformations. II. The Formation of "Superstructures" on the Dehydration of Goethite and Diaspore*

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It is shown that the satellites observed in the diffraction pattern of the dehydrated single crystal of the mineral goethite, which were previously attributed to a "superstructure," are better interpreted in terms of small angle scattering by a "texture" of the dehydration product hematite. This texture consists of rows of cavities parallel to the H(003) = G(100) planes with an average distance of 30–50 Å, depending on the stage of the transformation, in a highly twinned hematite matrix. In corundum resulting from the dehydration of diaspore a more isotropic texture is formed and the diffraction pattern exhibits "halos" instead of rows of satellite spots.

1. Introduction

It was reported some time ago in several papers (*1–3*) that a "superstructure" is formed on dehydrating goethite, forming in this way hematite. In X-ray diffraction patterns of single crystals of goethite, partly transformed into hematite, Lima de Faria (*3*) found satellites around each hematite spot corresponding with a period of about 34 Å, and which could also be revealed by electron microscopy. These observations were confirmed by electron diffraction and bright field images by Lahousse (*4*). Lima de Faria proposed that these satellites are produced by a superstructure, constituting an intermediate state, resulting from a periodic change in iron concentration. This state could be visualized somewhat like a concentration wave of iron in the hexagonally close-packed sublattice of oxygen ions, which is common to both goethite and hematite. This superstructure could be an intermediate stage between hematite and goethite and would be formed before hematite is actually present. According to Lima de Faria the transformation path should be represented as:

$$\alpha\text{-FeOOH} \rightarrow \text{intermediate superstructure} \rightarrow \alpha\text{-Fe}_2\text{O}_3.$$

However, this is difficult to reconcile with some of the observations to be reported in part III (*5*). In particular, in electron micrographs of partly transformed specimens strictly separated areas consisting either of goethite or of hematite occur and cover completely the whole specimen; no third phase is detected. This seems to suggest that the dehydration reaction might better be

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represented as:

$$\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3,$$

i.e., as a direct transformation of goethite into hematite.

As shown in part I (*6*) the hematite resulting from the dehydration of goethite is a highly oriented polycrystalline aggregate of very small hematite crystals in twin relation. This together with the fact that satellite spots are observed simultaneously with hematite spots suggests that the so-called "superstructure" might be caused by regular aggregates of such microcrystals and would then be better termed a "texture."

A "superstructure" in the usual sense of the word would imply the existence of regular arrangements of iron within the oxygen sublattice and with a unit cell of which one of the dimensions would have to be ~34 Å.

It is the purpose of this second part of the paper to show that the diffraction effects produced by the so-called superstructure can be interpreted in terms of small angle scattering (*7, 8*). This type of diffraction phenomena gives information on the shape, size, and size distribution of the scatterers and is not related to the atomic structure of the scatterers.

The problem is then to distinguish between a genuine superstructure as proposed by Lima de Faria and a texture as suggested here. As we shall see, the use of high-resolution imaging has allowed us to conclude unambiguously that the diffraction effects observed in hematite (α-Fe_2O_3) obtained by the dehydration of goethite (α-FeOOH), and in corundum (α-Al_2O_3), prepared by the dehydration of diaspore (α-AlOOH), are due to small angle scattering of polycrystalline aggregates with a well-defined texture and not to a genuine superstructure. This in turn implies also that the transformation is a direct one, without the formation of an intermediate phase.

2. Observations

2.1. Low-Magnification Images

Due to the scale of the phenomena the so-called superstructure can best be observed at relatively low magnification. Such images are reproduced in Fig. 1. Figure 1 is an underfocused bright field of a partly transformed goethite crystal. The transformed hematite parts appear as white, wedge-shaped, striated areas with a distance of 30–50 Å between striae. The extinction contours can still be recognized in the single-crystal goethite parts. These contours reveal strains at the tips of the wedge-shaped transformed parts. The regularity in spacing of the highly parallel striations is very apparent. The "superstructure" revealed in this image is the subject of this paper; as it will turn out, the term periodical "texture" would be more appropriate for this feature.

2.2 Diffraction due to the Microstructure

Some results for the isostructural system diaspore (α-AlOOH) corundum (α-Al_2O_3) (*9*) will also be taken into consideration for comparison.

The diffraction pattern of a partly transformed area taken along the [001] zone of the initial hydroxide, which is parallel to the [210] zone of the product phase obtained by dehydration, is represented schematically in Fig. 2a; actually observed examples are reproduced in Figs. 2b, c, d, and e. The pattern of fig. 2b was obtained from an area containing goethite as well as hematite whereas fig. 2c was obtained from an area containing only hematite. It is clear that only the hematite spots exhibit satellites, while the goethite spots remain perfectly sharp.

The satellites are formed in a direction perpendicular to the H(003) = G(100) planes; only one satellite on each side of the basic spots is clearly visible, suggesting that the quasi-periodic object giving rise to these satellites has not a strictly defined period.

FIG. 1. Underfocused bright field image of a partly transformed goethite crystal in the G[010] orientation. Note the white striae consisting of rows of cavities which form a grating with a spacing of about 50 Å.

The corresponding diffraction patterns for the transformation of diaspore into corundum are shown in Figs 2d and e. The pattern of Fig. 2d was obtained from an area containing untransformed diaspore as well as the reaction product corundum. The pattern of Fig. 2e on the other hand was produced by an area containing corundum. Also in this case it is clear that diffraction phenomena due to the "microstructure" are only observed around the spots due to the product phase, i.e., corundum.

The features of the diffraction patterns due to the microstructure are different in the two cases, however. In the corundum case an almost circular "halo" of intensity is observed around the corundum spots, the diaspore spots remaining perfectly sharp.

2.3. *High-Resolution Images*

Although the regularity of the superstructure in hematite is lost at large magnifications, it is worthwhile to study the regions exhibiting the superstructure at high

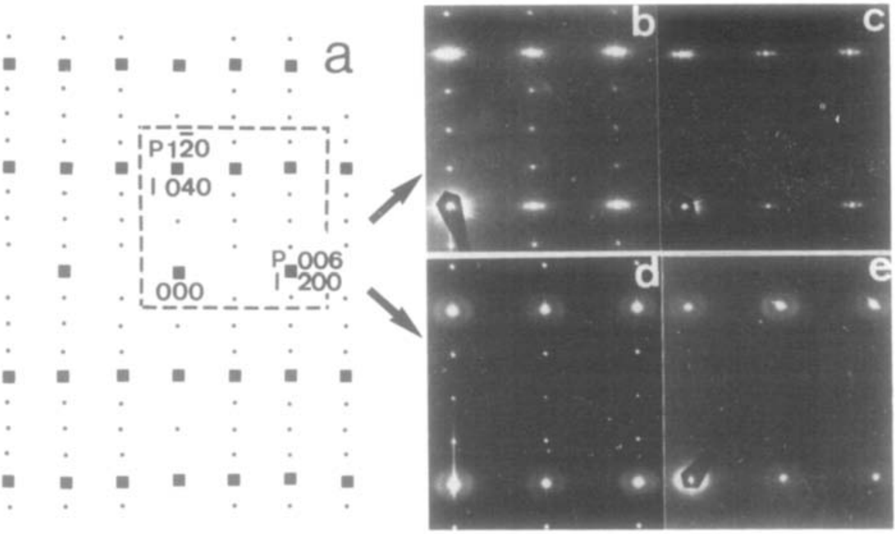


FIG. 2 (a) Schematic representation of the diffraction pattern of partly transformed hydroxide (I) of the goethite structural type along the [001] zone of the hydroxide, which is also the [210] zone of the produced oxide (P). The symbols have the following meaning: (●) spots of the initial hydroxide; (■) spots common to the initial hydroxide and the produced oxide. (b) The selected area contains goethite and hematite. Satellites are formed at common spots only. (c) The selected area contains only hematite. (d) The selected area contains diaspore and corundum. Halos are formed around common spots only. (e) Selected area contains only corundum.

resolution since this allows one to interpret the diffraction patterns in greater detail. In Fig. 3 areas producing the type of diffraction pattern shown in Fig. 2 are imaged at high resolution. Figures 3a and b refer to the system goethite–hematite, whereas c and d refer to the system diaspore–corundum.

Figure 3a shows the contact region between goethite and hematite; the image is taken along [001] zone of goethite (//the [210] zone of hematite). Although the hematite part is a highly oriented twinned polycrystalline aggregate (*6*), the lattice images do not reveal the twinning in this orientation (*5*). Similar conclusions apply to the corundum phase in Fig. 3c.

Figures 3a and b are bright field images respectively taken in overfocus (using tilted illumination) and in underfocus. In the hematite part certain areas look black in overfocus and bright in underfocus. The transition from one type of contrast to the other is apparent along the contact line between the inset (b) and the rest of (a). Such parts have a smaller mass density and therefore have to be interpreted as voids, resulting from dehydration. Moreover they always look darker in dark field images. These arrays of voids have the same general orientation as the striations in the low-magnification images. Finally the average period of the modulation corresponds to the satellite spacing revealed in the diffraction pattern.

Similar observations can be made in the diaspore system. Figure 3c is an overfocused bright field image of the corundum phase, whereas Fig. 3d is underfocused. Modulations are again observed. However, whereas in hematite the modulations are highly oriented (parallel to H(003) = G(100) planes) and reasonably periodic, they are almost randomly oriented and somewhat less periodic in corundum. This is in agreement

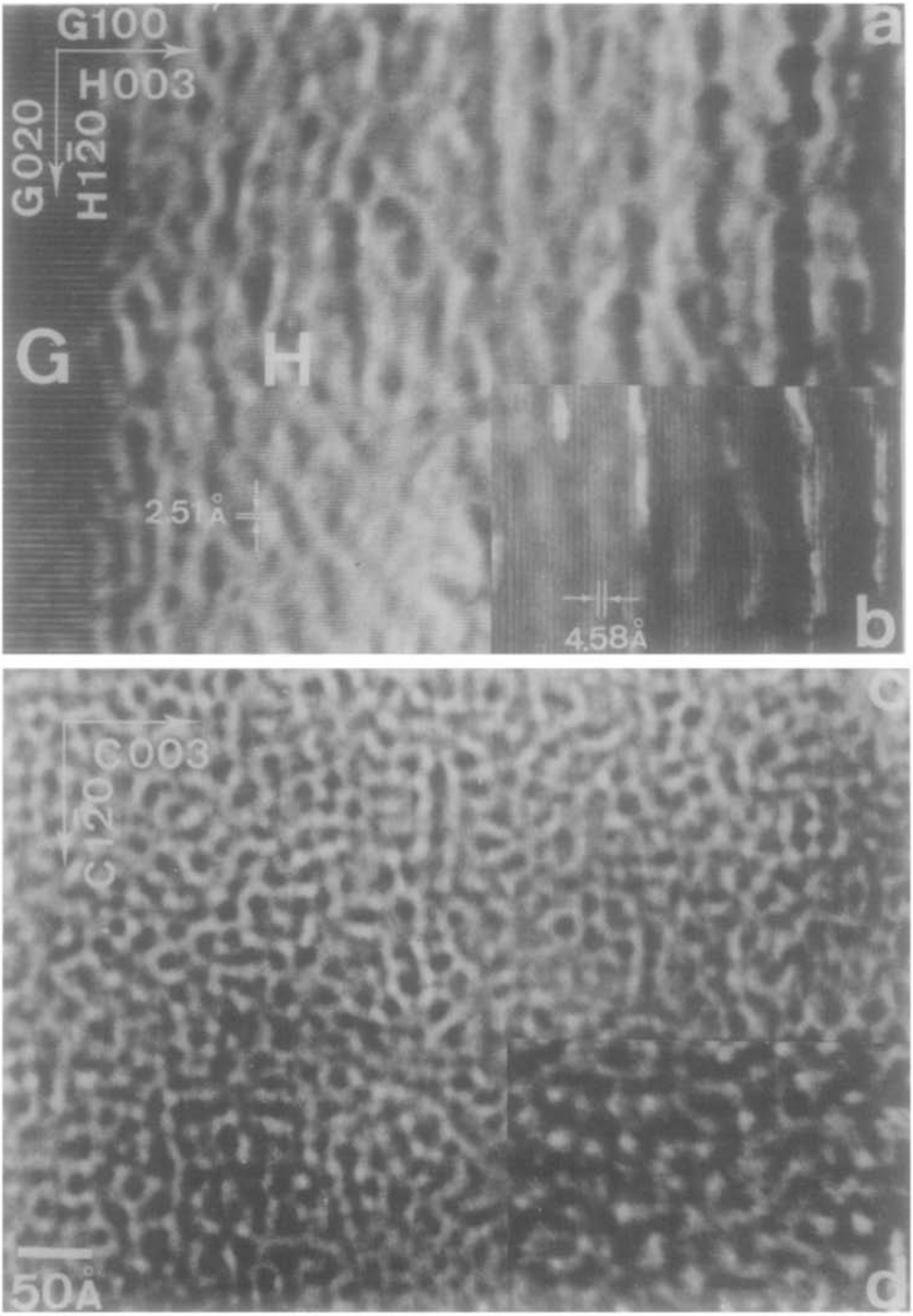


FIG. 3. Bright field high-resolution image of the contact region between goethite and hematite taken along the G[001]//H[210] zone: (a) Overfocused; (b) underfocused. Bright field images of corundum derived from diaspore taken along D[001]//C[210] zone: (c) Overfocused; (d) underfocused. The arrows inside the figure indicate the directions of the diffraction vectors.

with the observation in the diffraction pattern of satellites in hematite and of halos in corundum. The radius of the halo in the diffraction pattern of corundum is again in agreement with the average modulation period in the image.

3. Direct Observation of the Dehydration Process

The electron irradiation and the associated heating produce *in situ* dehydration in the microscope; it is thus possible to follow the formation process of the "line grating" constituting the superstructure, line by line, through successive stages at high resolution.

The sequence of images reproduced in Figs. 4a, b, and c is the result of a contrast experiment on the contact region between hematite and goethite. The diffraction pattern of this crystal area is shown in Fig. 5; the spots used to produce the images of Figs. 4a, b, and c are surrounded by white circles. They can be indexed as shown in Fig. 2a.

Figure 4a is a bright field image along the G[001] zone made by selecting spots belonging to goethite as well as spots common to goethite and hematite. The image contains structural information in the goethite part.

The transformed area is composed of the bright area due to the voids and H (003) fringes. In Fig. 4b the goethite structure is revealed and also H[003] fringes are visible in the transformed part. One can notice that the voids observed in the bright field image of Fig. 4a do not go through the foil but are covered by hematite parts. Also it is now obvious that the transforming area A in Fig. 4a has become more extended approximately parallel to the H(003) = G(100) plane.

At the contact surface of hematite–goethite the lattice image is clearly perturbed. In Fig. 4(c) the hematite part as well as the voids shows up dark since only goethite spots contribute to the image.

The interface between goethite and hematite can clearly be recognized. The irregularity of the lattice fringes in goethite near the hematite region is caused mainly by thickness changes of the goethite part because of the hematite formation along the beam path.

One can conclude from these observations that the white lines in the so-called "superstructure" low-magnification image consist of void arrays, limited by hematite crystals (Fig. 4).

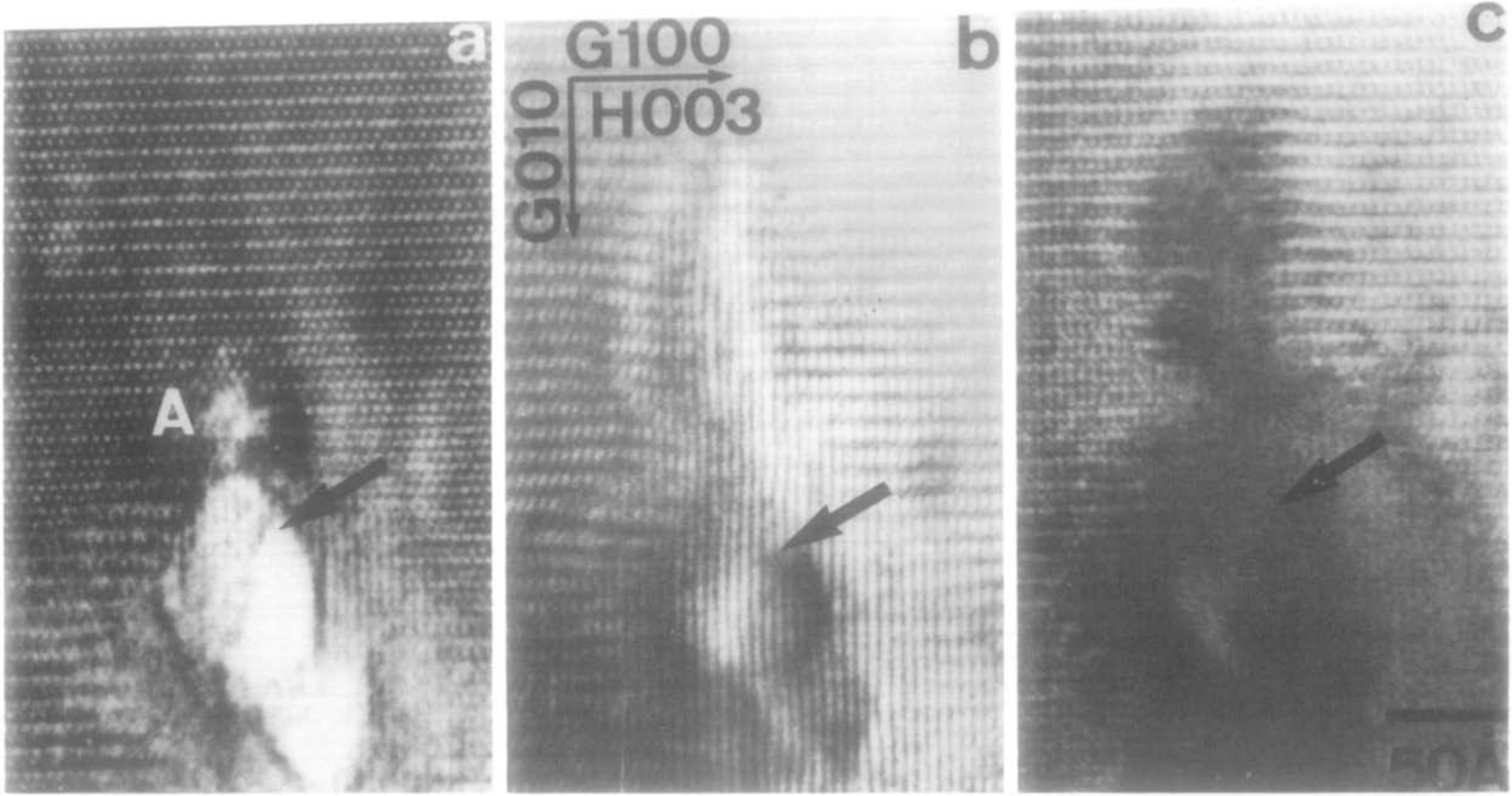
4. Relation among "Superstructure," Texture, and Small Angle Scattering

As mentioned already above, the average modulation period, deduced from the image, corresponds with the period, deduced from the positions of the satellites in the diffraction patterns. Satellites only occur in the diffraction pattern of the transformed part; this is illustrated in Fig. 6.

In Fig. 6a the crystal is still goethite, no transformation has yet taken place, the spots are sharp, and no satellites occur. Just after transformation of the same area (Fig. 6b) the satellite spots are formed. The mean periodicity expected from the satellite distance is indicated on the micrograph. After heating the same area, the crystallites of hematite have grown, but nevertheless the satellites are still present as seen in Fig. 6c. They are now at a smaller distance from the main spots, corresponding with an increase in the average modulation period, which can be well recognized by comparing the modulation in the image with the mean periodicity calculated from the satellite distance as indicated by an inset in Fig. 6c.

The so-called superstructure found by Lima de Faria thus turns out to be a more or less periodic regular texture, rather than a superstructure in the real sense of the word.

The pattern of satellites changes in an interesting manner with the direction of the incident beam. This is illustrated in Fig. 7. In



Fɪɢ. 4. High-resolution bright field image taken along the G[001] zone. (a) The selected spots belong to goethite or are common spots. Note the resolution in the goethite part. (b) Goethite and hematite spots are selected. Note the hematite fringes in the transformed part. The void area has grown compared to (a). (c) Goethite spots only are selected. Hematite area is black.

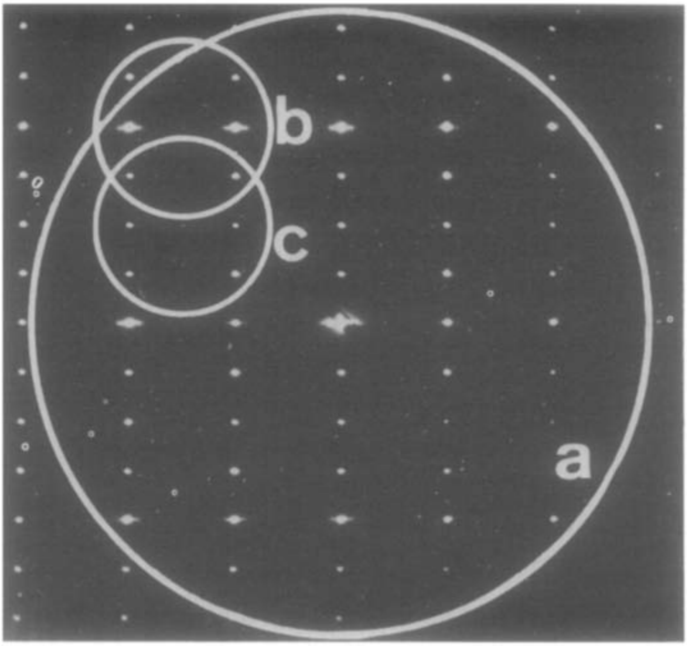


FIG. 5. Diffraction pattern of area used to make the images of Fig. 4. The circles surround the selected spots for (a), (b), and (c). Indexes and symbols are the same as in Fig. 2a.

Fig. 7a the beam is incident along the G[001] zone, which is parallel with the H[210] zone; in this orientation the satellites are clearly visible. Tilting away from this orientation around the G[010] axis, over angles of 20°, 35°, and 58°, which means that the "superstructure" plane, H (003) = G (100) plane, becomes gradually inclined against the beam direction, one obtains the small angle scattering patterns of Figs. 7b, c, and d, respectively.

It is clear that with increasing angle of incidence the features obtained for hematite become more and more similar to the halos obtained from corundum. This is particularly clear from the hematite high-resolution image of Fig. 8 which corresponds to the small angle scattering pattern of Fig. 7d. The image is quite similar to that of Figs. 3c and d for corundum and also the halo in the diffraction pattern is rather similar to that of Figs. 2d and e.

This experiment clearly indicates that the satellite spots are in fact the small angle scattering patterns due to a pronounced texture of parallel linear arrays of voids in hematite, whereas the halo is produced by a texture in which the orientation is random and the period ill defined.

Figure 8 also illustrates that the lattice fringes in hematite are quite straight, without changes in orientation across the crystallite borders.

The sharpness of the diffraction spots in hematite and corundum support this viewpoint that, whatever the texture, regular, at random, or apparently amorphous, as in Figs 3(c) and (d), the basic lattice is common throughout the crystallites. It is the difference in regularity of the crystallites, resulting from the occupation of a common sublattice, that leads to differences in the small angle scattering pattern.

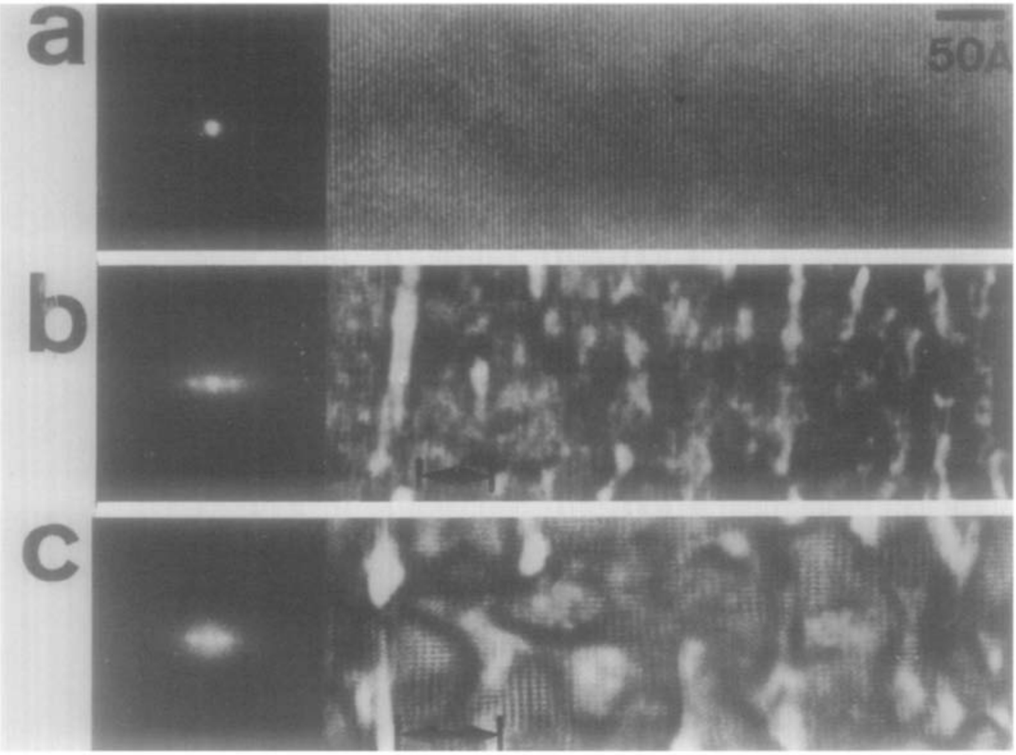


FIG. 6. Origin of satellites. (a) Diffraction spots of goethite part; spots are sharp without satellites. (b) The hematite spots exhibit satellites. The spacing expected from the satellites, which is indicated inside the figure, corresponds to the mean distance between void rows. (c) After crystallite growth the satellite separation has become smaller. The mean distance between void rows is in accord with the satellite spacing.

5. Conclusions

The "superstructure" in dehydrated goethite was studied in great detail by means of electron microscopy and electron diffraction. The satellite spots around hematite reflections are found to be due to small angle scattering by the hematite structure. Whereas in hematite this texture consists of a more or less regular arrangement of void arrays, the corresponding texture in corundum is much more random and gives rise in small angle scattering to "halos" rather than to satellite spots.

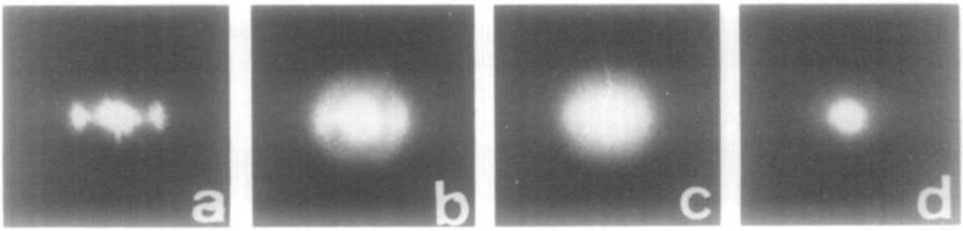


FIG. 7. Change of small angle scattering patterns from the "superstructure" region with direction of incidence of the electron beam. (a) Beam along G[001] zone. (b) Tilting angle 20°. (c) Tilting angle 35°. (d) Tilting angle 58°.

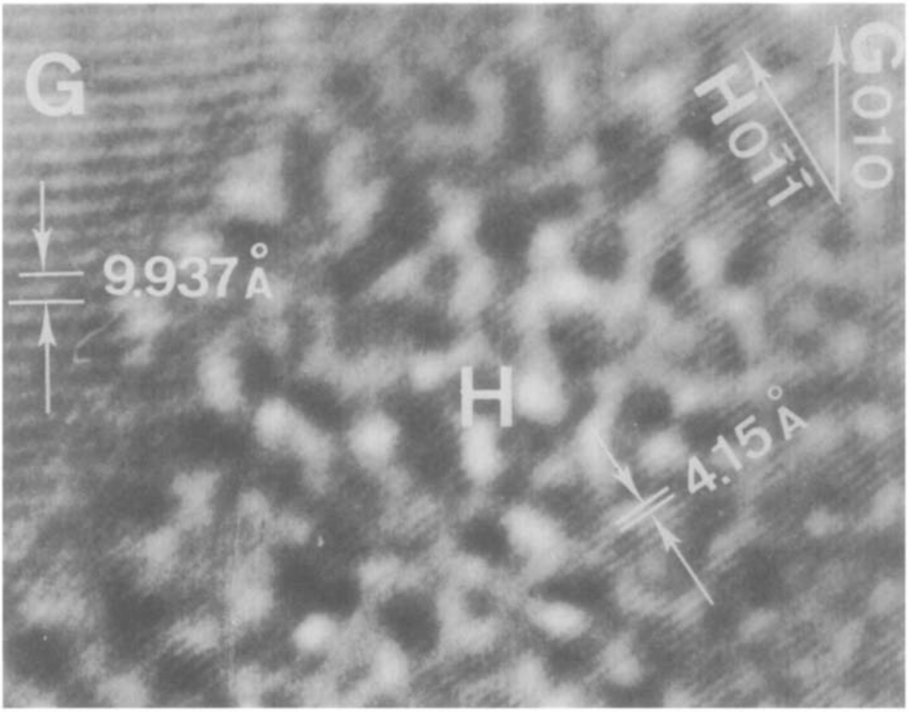


FIG. 8. High-resolution image of hematite and goethite under the diffraction conditions of Fig. 7d. The indexes inside the figure denote the diffraction vectors. Note the aspect of the texture in the hematite region. The lattice fringes in hematite are quite continuous across the crystallite borders.

In high-resolution electron microscopy a sharp boundary is found between goethite and hematite without any evidence for a transition structure. This observation, together with the results of the small angle scattering, provide unambiguous evidence that the so-called superstructure is in fact a peculiar texture of the hematite phase and that the transformation from goethite into hematite and from diaspore into corundum proceeds according to a direct reaction path:

$$2\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O};$$

$$2\alpha\text{-AlOOH} \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{H}_2\text{O}.$$

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