Disordered structural states in the dehydration of goethite and diaspore.

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Summary. Single crystal X-ray studies of the dehydration of goethite to hematite at low temperatures show that satellite reflections occur close to the hematite diffraction spots. At higher temperature these satellites are replaced by diffuse intensity regions, which disappear on further heating. The satellites are situated on each side of hematite spots on reciprocal lattice lines parallel to the c^*-axis of the hematite; their spacing corresponds to a periodicity in direct space of about 32 Å. A similar phenomenon is observed on the dehydration of diaspore to corundum, with a spacing for the satellites of about 39 Å.

The mode of occurrence of the satellites, both in position and intensity, could correspond to a sinusoidal or square-wave structure amplitude modulation along the c-axis of the hematite and corundum crystallites, before dehydration is complete.

THE dehydration of goethite (α-FeOOH) and diaspore (α-AlOOH) has been the subject of many previous investigations (Deflandre, 1932; Goldsztaub, 1935; Rooksby, 1951; Ervin, 1952; Francombe and Rooksby, 1959, etc.). It was clearly established by these workers that the hematite and corundum were derived from the goethite and diaspore in an oriented manner, with twinning developing from the change in symmetry.

In the present investigation, these transformations have been studied in more detail by single-crystal and powder X-ray methods. By variation of the temperature of dehydration and the duration of heating, it has been possible to observe intermediate stages in the process, not previously reported. The most important characteristics of these intermediate stages are illustrated in fig. 1 (a), which shows part of a rotation photograph of a goethite crystal taken about the a-axis; this crystal had

(*a*)

(*b*)

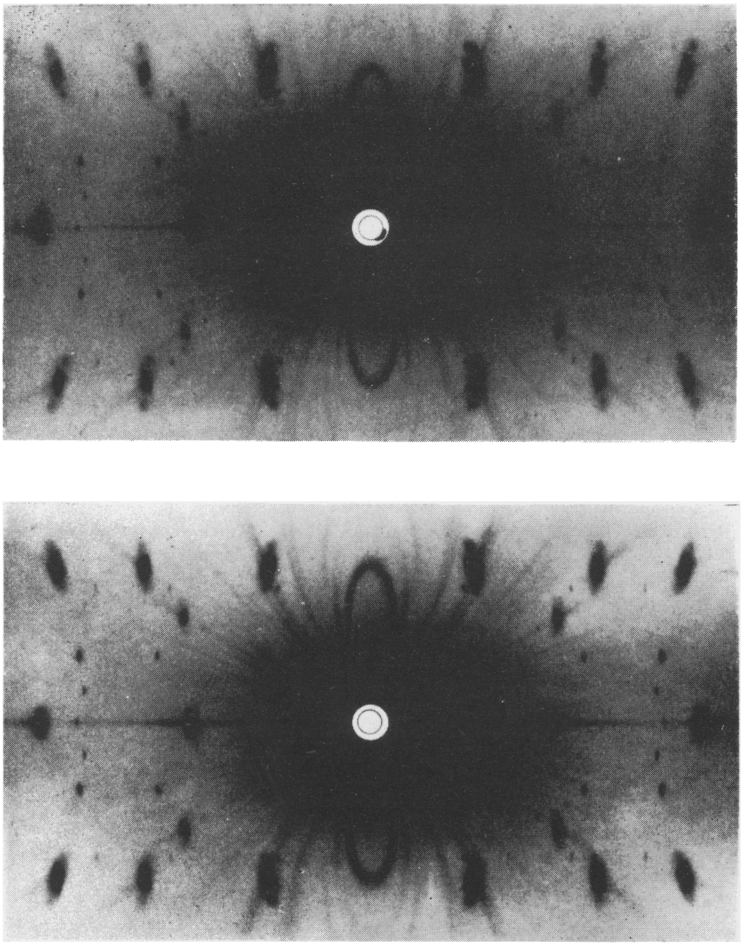

FIG. 1. Rotation photographs of goethite crystal after heating for: (*a*) 19 hours at 300° C; (*b*) 1 hour at 350° C. Axis of rotation, *a*. Fe-$K\alpha$ radiation.

been heated for 19 hours at 300° C. Hematite, in twinned orientations. has been formed, but about hematite spots there are satellite reflections. Examination of such photographs shows: that the satellites lie on lines in reciprocal space parallel to the *c*-direction for hematite (i.e. in fig. 1 (*a*) they are on curves of constant ξ); that the separation of the pairs of satellites about hematite maxima is constant at all points in reciprocal space; that they are observed about all hematite spots of sufficient intensity, even on the zero layer; and that the satellites of each pair are of equal intensity, and their intensity relative to the corresponding hematite maximum seems constant. The last two observations suggest that the satellites are present for all hematite maxima, but cannot be observed for those of lowest intensities for which the satellites are obscured by the general background level of scattered radiation. A zero

FIG. 2. Weissenberg photograph of goethite crystal after heating for 19 hours at 300° C. Axis of rotation *b*, zero layer. Fe-$K\alpha$ radiation.

layer Weissenberg photograph of the same crystal, taken about the *b*-axis, shows a similar distribution of the satellites (fig. 2).

The development of these satellites depends on the conditions of dehydration, e.g. heating goethite at a higher temperature, 350° C for a much shorter time of about 20 minutes produces a specimen whose diffraction pattern is similar to fig. 1 (*a*). However, the separation of the satellites is independent of the conditions of dehydration. Measurement for partially dehydrated goethite shows that this separation corresponds to a periodicity in direct space of about 32 Å. If this distance is compared with the *c*-dimension of hematite (13·75 Å), a ratio of about 2·3 is obtained; a more accurate value of this ratio of 2·50±0·02 was found using electron-diffraction methods by McConnell and Lima-de-Faria (1961).

The relatively well-defined satellites may be made to disappear by further heat-treatment. Fig. 1 (*b*) shows the diffraction pattern from a goethite crystal dehydrated for 1 hour at 350° C. In this are seen diffuse intensity regions, elongated parallel to the *c*-axis of hematite, surrounding the hematite maxima. Prolonged heat treatment (19 hours at 350° C) removes all traces of the diffuse regions, leaving only the hematite pattern.

Similar effects have been found with diaspore, although the dehydration conditions necessary to produce them are somewhat different. For example, satellites comparable with those illustrated for goethite in fig. 1 (*a*) are produced by heating diaspore at 400° C for 20 days, whilst dehydration conditions of about 20 minutes at 550° C produced the diffuse regions around corundum spots comparable with those for goethite in fig. 1 (*b*). Further it is found that the separation of the satellites is slightly but significantly different in diaspore. Measurements give a direct space periodicity of about 39 Å, which when compared with the *c*-dimension of corundum gives a ratio of about 3.

These observations for both goethite and diaspore suggest the formation of intermediate structural states during their dehydration. With well-developed satellites present, the patterns could be interpreted in terms of sinusoidal or square-wave modulation of the structure amplitude along the *c*-axis of the hematite or corundum (e.g. Hargreaves, 1951; Willis, 1957); the occurrence of diffuse regions replacing the satellites at later stages in the transformation would then be due to the breakdown in the regularity of this modulation. Although these effects are clearly related to incomplete removal of water from the structure, the physical significance is not clear, and further work is in progress.

Powder photographs have been taken with a standard camera, and filtered radiation, of goethite specimens dehydrated to the various stages recognized by the single-crystal studies. The patterns show that the lines are equally well defined and that the weak satellites and diffuse regions cannot be observed. However, when a fragment of fibrous natural goethite is heated (1 hour at 350° C), there is non-uniform broadening of the lines of the powder pattern similar to that described by Francombe and Rooksby (1959) for synthetic acicular goethite; a similar effect occurs when a fragment of cryptocrystalline diaspore is heated at 550° C for 1 hour. If the sharp lines of these patterns are indexed in terms of the normal hexagonal cell, it is found that they obey the conditions $h–k = 3n$ and $l = 3n$, which indicates a sub-cell of height one-third of the normal height of the hematite cell, the same as that used by Francombe and Rooksby (1959). It is clear therefore that the non-uniformity of line broadening for certain specimens is not connected to the other diffraction effects observed in this work; it is dependent on the perfection of the material used and would appear to be a stacking disorder effect similar to those observed in cobalt, graphite, and the micas.

The present experiments emphasize the need for complete and careful description of the experimental conditions during transformation studies of this kind; it is essential that not only the temperature and duration of the heat treatment should be specified, but also the size and texture of the material used.

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