

Electron-optical and electron-diffraction study of a disordered structural state in the transformation goethite-hematite.

(With Plate XX.)

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Summary. Previous X-ray observations by J. Lima-de-Faria and P. Gay on the transformation goethite-hematite indicate that in the process of state change at low temperatures, maxima of scattered X-ray intensity occur as satellites to strong and diffuse Bragg maxima due to hematite. These maxima define a repeat distance of about 32 Å. Corresponding satellite maxima have been observed using electron diffraction technique and satellite maxima flanking the direct beam (000) have been used to obtain a direct electron optical image of the disordered state at high magnification. Such photographs show a mainly regular fringe system with spacing of approximately 30 Å. Dislocation patterns were also observed.

THE present paper contains an account of the direct electron optical resolution of a characteristic repeat in a transitional structural state in the transformation goethite-hematite. The observations on which this paper is based were made subsequent to a detailed study of this transformation by single-crystal X-ray technique (Lima-de-Faria and Gay, in press).

During the latter investigation strong maxima of scattered X-ray intensity were observed as satellites to Bragg maxima due to hematite. Both the intensity of these satellite maxima, and the scale of the periodicity which they defined, about 32 Å., were considered favourable to possible direct-electron optical resolution of the disordered state.

The instrument used for the present experiments was a Siemens Elmskop I, which was operated throughout at 100 kV. A selected-area diffraction aperture defining a specimen area of diameter 0.25 μ was used in the associated diffraction experiments.

The material used in the present study was a single crystal of goethite,

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which was previously heated at 300° C. for 19 hours in air and subsequently examined by single-crystal X-ray oscillation technique. The heat-treated material was then crushed and mounted on a carbon film using a standard electron microscope supporting grid.

On diffraction, fragments of this material were found to yield reciprocal-lattice sections indicating that the crushed fragments had a tendency to lie either on (0001) or (10 $\bar{1}$ 0).¹

A detailed selected-area diffraction study (with 0.25 μ aperture) was made on a flake lying on (10 $\bar{1}$ 0) (i.e. with a and c^* in the plane of the flake). All the selected area diffraction photographs from this flake showed consistent development of satellite maxima along c^* rows through the Bragg maxima. On the original plates weak second order maxima of intensity were also observed. One of the diffraction photographs in this series has been illustrated and indexed in pl. XX, fig. A, and in fig. B the position of the selected area which provided this diffraction pattern has been indicated.

The nature of the off-on high voltage fluctuations on the microscope used does not permit of an accurate determination of absolute values for the cell-dimensions, but, because the reciprocal lattice plots obtained comprise very sharp diffraction maxima and because these plots are effectively undistorted, it has been possible to derive accurate values for the ratios of the reciprocal distances concerned by direct measurement. The c/a ratio of hematite determined in this way was 2.76 ± 0.01 and the ratio of the repeat defined by the first-order satellite maxima with respect to the c^* repeat of hematite was determined in the same way as 2.50 ± 0.02 , corresponding to a true repeat in direct space of $34.4 \text{ \AA}$. in terms of the c -dimension of hematite ($13.75 \text{ \AA}$.). This repeat is equal to approximately 7.5 times the a repeat of goethite. The (10 $\bar{1}$ 0) flake initially used for detailed selected-area diffraction study was also used to obtain a direct electron-optical image at high magnification ($\times 80\,000$). This flake has been illustrated in pl. XX, fig. B. In this case a suitable objective aperture was used to select the direct beam (0000) and its associated satellite maxima for image formation. The resulting photograph showed a well-developed fringe system with spacing of approximately $30 \text{ \AA}$. An enlargement of part of this photograph has been provided as fig. C. On the original plate a well-defined pair of dislocations were observed in this area. These have been drawn out schematically in fig. C.

¹ Throughout the present paper hematite has been referred to hexagonal axes, $a = 5.035$, $c = 13.749 \text{ \AA}$. (Bernal, Dasgupta, and Mackay, 1959).

It is necessary here to state briefly the theory required for the explanation of the fringe formation and its defects. In the diffraction photographs the distribution of scattered radiation is observed as an intensity distribution, which cannot yield any information on the phase of the scattered radiation but only on its amplitude. Accordingly the location of defects cannot be defined. Since in electron-optical resolution, as in an ordinary optical microscope, the scattered electron waves are recombined correctly with regard to both phase and amplitude it is possible to derive an image (with resolution limited only by the objective aperture chosen, and the perfection of the lens system) in which the location of irregularities and defects may be observed directly.

In the present instance the resolution was of the order of 10–15 Å. Study of the present fringe system indicates that the fringes are not all equally spaced. It has also been possible to demonstrate an offset along the length of one particular fringe through a distance corresponding to approximately 10 Å. Apart from indicating the nature of some of the imperfections present, however, the present investigation must be considered to demonstrate conclusively the very high degree of regularity obtaining in the structural state involved. It is obviously not permissible, on the basis of the present experiments alone, to comment in detail on the nature of the inhomogeneity responsible for the well-developed fringe system observed. It is possible only to suggest that a considerable variation in scattering power exists in the direct sequence normal to the fringes, i.e. parallel to c^* , and that this must probably be taken to indicate a corresponding distribution for the heavier iron atoms present in the general structural pattern.

Fringe systems of similar origin have, in the past, been obtained by direct electron-optical resolution of Bragg maxima from suitable crystalline materials (Menter, 1956), and similar resolution experiments illustrating the degree of regularity in antiphase domain patterns have been made by Owaga, D. and H. Watanabe, and Komoda (1958), and by Glossop and Pashley (1959).

The present paper directs attention to the possibility of studying phase transitions of continuous character (i.e. those where a high degree of structural continuity is maintained) by direct electron-optical means, since in this case the nature and distribution of defects may be directly appreciated.

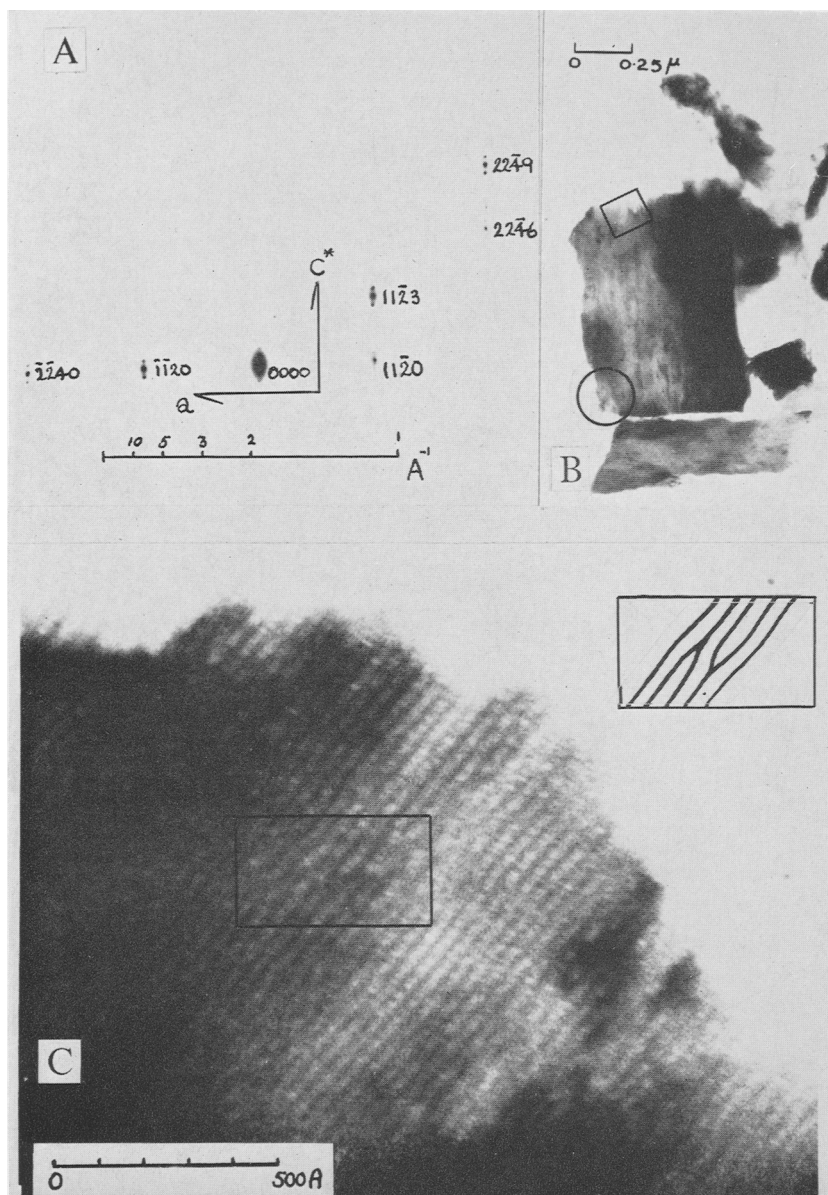
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EXPLANATION OF PLATE XX.

- FIG. A. Indexed electron-diffraction photograph of the $(10\bar{1}0)$ flake studied. The selected area involved has been ringed in fig. B.
- FIG. B. Electron photomicrograph of the flake studied. Original magnification $\times 20\,000$.
- FIG. C. High resolution photomicrograph of the area defined by a square in fig. B. Original magnification $\times 80\,000$. The c -direction in the flake lies normal to the length of the fringes and a pair of dislocations in the pattern have been illustrated.
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GOETHITE-HEMATITE