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Limonite is goethite.* By W. T. Holser, *Department of Geology, Cornell University, Ithaca, N.Y., U.S.A.*

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With reference to the note by Dasgupta & Maitra (1952) the elementary textbooks of Hurlbut, Miers, or Rogers & Kerr cannot be taken as authority that the structure of 'limonite' is amorphous. It is to be regretted that this name continues to be perpetuated as anything other than '... a field or generic term to refer to natural hydrous iron oxides whose real identity is unknown' (Palache, Berman & Frondel, 1944, p. 685). Since the earliest days of X-ray diffraction (Posnjak & Merwin, 1922, p. 1971) it has been known that most mineral specimens labeled 'limonite' are goethite, $HFeO_2(\alpha Fe_2O_3.H_2O)$, some are lepidocrocite, $HFeO_2(\gamma Fe_2O_3.H_2O)$, and a few are hematite, Fe_2O_3. Most are only very finely crystalline and hence tend to retain considerable adsorbed water; some are so finely divided that X-ray patterns are diffuse. A brief survey of the A.S.T.M. X-ray diffraction cards indicates that the strong lines of the subject material are within the variations previously reported for goethite (e.g. card 1–0406).

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Palache, C., Berman, H. & Frondel, C. (1944). *Dana's System of Mineralogy*, 7th ed. New York: Wiley.

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* *Editorial note.*—Similar views on the same paper were expressed previous to this note in letters received by the Editor from Prof. Duncan McConnell (Columbus, Ohio, U.S.A., 15 December 1952) and Prof. A. Pabst (Berkeley, Cal., U.S.A., 20 December 1952); these letters contain further references (e.g. Böhme, 1928) in support of the view that limonite is identical with goethite.

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The low-temperature crystal structure of magnetite.* By H. P. Rooksby and B. T. M. Willis, *Research Laboratories of The General Electric Company Limited, Wembley, England*

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In a recent communication Abrahams & Calhoun (1953) have presented new evidence concerning the low-temperature structure of magnetite, Fe_3O_4. They conclude that the structure cell deforms on cooling below 115° K. to give an orthorhombic arrangement rather than the rhombohedral arrangement previously proposed by Tombs & Rooksby (1951).

Since Tombs & Rooksby's paper was written we have obtained additional results that support a rhombohedral deformation. It is the purpose of this note to record these results, and to indicate the difficulties of reconciling them with an orthorhombic low-temperature structure for magnetite.

If Abrahams & Calhoun's evidence for an orthorhombic change is carefully studied, it is found to rely principally on the detection of a splitting of the cubic 800 line into two components at liquid-nitrogen temperature. This line should remain unsplit for a rhombohedral transition. Because the 800 doublet separation, measured by Abrahams & Calhoun with a Norelco spectrometer, was so small, viz. 4 min. of arc (Fe $K\alpha$ reflection), and the general fit of all our earlier data with the rhombohedral interpretation so close, we undertook further studies by photographic methods. Powder photographs were taken at liquid-air (95° K.) and liquid-nitrogen (80° K.) temperatures using Co K and Cr K radiations. In this way we examined the splitting of a wide range of reflexions, including 440, 444 and 840, in addition to the 533, 731 and 800 lines studied by Abrahams & Calhoun.

Through the courtesy of Dr Abrahams we were able to examine a specimen of his magnetite powder. Results were in every respect similar to results obtained with our own preparations, so that possible ambiguities arising from use of materials of different origins are eliminated.

Planar spacing values for components of split reflexions gave in every instance the separations predicted by a rhombohedral structure cell with dimensions

$$a_R = 5\cdot940 \text{ Å}, \ \alpha = 59^\circ\, 47\cdot5' \text{ at } 80^\circ \text{ K}.$$

Making the assumption that the atomic co-ordinates correspond with those in the cubic arrangement, the calculated and observed relative intensities of resolved components agree better with the rhombohedral than with the orthorhombic interpretation. The evidence on lines 440, 533, 444, 800 and 840 is summarized in Table 1.

It may be noted that we have not been able to detect any splitting of 800 photographically, though noticeable broadening might have been expected with a separation of the magnitude indicated by Abrahams & Calhoun. Attention, however, may be drawn particularly to the manner of splitting of 440. The splitting is disclosed clearly in either liquid-air or liquid-nitrogen temperature photographs taken with Cr radiation. Two equally strong components, with a separation of approximately 13 min., occur for the α doublet wave-length, and a corresponding splitting is seen with the β reflexion, in which any intensity ambiguity due to overlaps is naturally absent.

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* Communication No. 543 from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.

Table 1.

Throughout the table lines are referred to in order of increasing θ

Cubic *hkl*	Form of splitting observed below transition temperature	Expected result for rhombohedral interpretation	Expected result for orthorhombic interpretation
440	Two components of approximately equal intensities	Split into two components, 208 and 220 (hexagonal indices). Ratio of multiplicity factors 1 : 1	Split into three components, 040, 224 and 400. Multiplicity factors 1 : 4 : 1
533	Three components, the two outer ones (highest θ values) being just resolved. Inner component considerably weaker than the combined outer components	Split into three components, 1,0,11, 315 and 401; the last two nearly coincide. Multiplicity factors 1 : 2 : 1	Split into four components, 143, 035, 305 and 413. Multiplicity factors 2 : 1 : 1 : 2
444	Two components, the inner one considerably weaker than the outer one	Split into two components, 0,0,12, and 404. Multiplicity factors 1 : 3	Split into two components, 044 and 404. Multiplicity factors 1 : 1
800	No splitting or broadening noticeable down to 80° K.	No splitting	Split into two components, 008 and 440. Multiplicity factors 1 : 2
840	Two components of approximately equal intensities	Split into two components, 2,2,12 and 244. Multiplicity factors 1 : 1	Split into four components, 260, 444, 228 and 620. Multiplicity factors 1 : 2 : 2 : 1

The relevant section of the photograph is reproduced in Fig. 1. (This photograph also contains the 511α reflexion. Since this line originates from planes making a relatively small angle with planes of the {100} form, separation between the components of the split reflexion at 80° K. is small and only slight broadening is noticeable.)

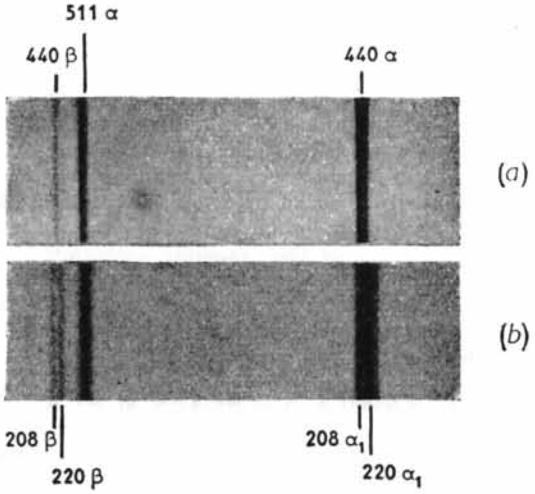

Fig. 1. Sections of powder photographs (19 cm. camera, Cr *K* radiation) at ×2 magnification showing splitting of cubic 440 line into two components at 80° K. (*a*) 295° K.; (*b*) 80° K.

This simple splitting of 440 is exactly that to be expected for the rhombohedral deformation along [111]. For the orthorhombic change we expect three components with the middle one approximately four times as strong as the other two. We believe that the behaviour of 440 is thus of utmost importance when deciding between the two proposed low-temperature structures.

In this connexion it is perhaps relevant to mention results on FeO, for which a substantial rhombohedral deformation at 95° K. has been observed (Rooksby & Tombs, 1951). Line-splitting effects in low-temperature powder photographs of FeO are closely analogous to those found for Fe_3O_4. Owing to the greater magnitude of the deformation of FeO, however, the separation of the two components of line 220 is much larger than in the case of the 440 line for Fe_3O_4, but line 400 remains unsplit. It is hoped to publish the results on FeO in more detail in the near future.

Summarizing, the additional experimental evidence obtained by photographic methods appears to provide adequate confirmation of the original interpretation of the transition in magnetite at low temperatures as a rhombohedral structural deformation. It is admitted that this interpretation does not explain the small splitting of 800 observed by Abrahams & Calhoun. On the other hand we have not been able to detect such splitting by photographic means.

Ultimately, when the structure change is studied in very precise detail, it may be found that the symmetry is lowered to monoclinic or triclinic, but a principal dilatation along [111] appears to be reasonably consistent with the present evidence. It will probably require investigations on single crystals at temperatures below 80° K. to settle the issue unequivocably.

We should like finally to express our thanks to Dr Abrahams for allowing us to see his paper before publication.

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