the molecule are more stable than those with a five- and six-membered ring. Smith (1944) states that glucuronolactone is probably one of the few examples of crystalline furanose sugar derivatives.

Grünling (1883) measured crystals of glucuronolactone which he reported as monoclinic with apparent point-group symmetry $2/m$. He found

$$a : b : c = 1{\cdot}289 : 1 : 1{\cdot}233; \quad \beta = 91^\circ\ 35'.$$

Cleavage was parallel to (101) and (100).

Oscillation and Weissenberg photographs were taken using Grünling's axes. No reflections were observed for (hkl) with $(h+l)$ odd, which indicated a B end-centered lattice. Photographs taken about a new set of axes chosen to give a primitive cell showed absent reflections only for $(0k0)$ with k odd. This characterized the space group as either C_{2h}^2-$P2_1/m$ or C_2^2-$P2_1$. A positive piezoelectric effect was observed in the crystals and was kindly verified for us by Dr R. G. Stokes of the Naval Research Laboratory, Washington, D.C. This definitely established $P2_1$ as the correct space group.

The unit-cell dimensions were found to be

$$a = 6{\cdot}81, \quad b = 7{\cdot}50, \quad c = 6{\cdot}64\ \text{A.}; \quad \beta = 93^\circ\ 16'.$$

The density, measured by the flotation method, is 1·75 g.cm.$^{-3}$ at 25° C., which requires two (calc. 2·03) molecules in the cell. The refractive indices are

$$\alpha = 1{\cdot}548, \quad \beta = 1{\cdot}578, \quad \gamma = 1{\cdot}588\ (\|b).$$

Cleavage occurs parallel to $(\bar{1}01)$ and (001).

The above results were obtained in a preliminary study of the crystal in the course of an investigation of the structure of glucuronolactone. This investigation was made possible through a fellowship grant by the Corn Products Refining Company, Argo, Illinois, U.S.A.

References

Grünling, F. (1883). *Z. Krystallogr.* **7**, 586.

Haworth, W. N., Owen, L. N. & Smith, F. (1941). *J. Chem. Soc.* p. 88.

Pryde, J. & Williams, R. T. (1931). *Nature, Lond.*, **128**, 187.

Pryde, J. & Williams, R. T. (1933). *Biochem. J.* **27**, 1197.

Reeves, R. E. (1940). *J. Amer. Chem. Soc.* **62**, 1616.

Smith, F. (1944). *J. Chem. Soc.* p. 584.

Smith, L. W. & Stavely, H. E. (1950). *Chem. Engng News*, **28**, 3335.

Acta Cryst. (1951), **4**, 474.

Structure transition and antiferromagnetism in magnetite.*

By N. C. Tombs and H. P. Rooksby, *Research Laboratories of the General Electric Company Limited, Wembley, England*

(*Received* 24 *April* 1951)

Introduction

It has long been known that magnetic and specific-heat anomalies are shown by magnetite, Fe_3O_4, in the region of 125° K. A rise in magnetic susceptibility at about this temperature was reported by Weiss & Forrer (1929), and in the same year Millar detected an apparently associated increase in the specific heat. Li (1932) found that single crystals of magnetite developed a strong magnetic anisotropy when cooled below 114·5° K.

More than one attempt has been made to detect any change in crystal structure associated with these low-temperature phenomena, but without success. Ellefson & Taylor (1934) by powder methods, and Shôji (1935) by means of Laue photographs, studied the crystal structure, and concluded that there was no alteration of symmetry, although Ellefson & Taylor's measurements indicated that anomalous changes in the cubic structure cell constant occurred. Snoek (1947, p. 24) discussed the difficulty of explaining the existence of a symmetry of the magnetic anisotropy lower than that of the crystal anisotropy; he suggested the formation of an ordered arrangement of $3d$ electrons at 114·5° K.

The purpose of this note is to report the results of a new investigation of the crystal structure of magnetite at temperatures down to that of liquid air (approximately 95° K.). By means of X-ray powder photographs it has been possible to show that a structure transition occurs at low temperature, and that this comprises a rhombohedral deformation of the ideal cubic lattice.

Results of X-ray examination

The technique employed was similar to that adopted in our studies of monoxides of the transition elements (Tombs & Rooksby, 1950). A 19 cm. diameter X-ray powder camera was modified so as to allow liquid air or a suitably cooled liquid to stream over the rod-type powder specimen during a photographic exposure. The use of either Co $K\alpha$ or Fe $K\alpha$ radiations yielded good definition of a wide range of reflexions of significance in the disclosure of changes in crystal structure. Various samples of both natural and synthetic magnetite were examined, and notable differences in the definition of the X-ray powder lines were observed; oxides prepared synthetically at low temperatures suffered particularly from line-broadening of a magnitude sufficient to spoil resolution of the $K\alpha$ doublet. A well-crystallized, strain-free material was obtained by firing at 1350° C. in nitrogen a pressed plug of magnetite produced by reduction of a Turkey red pigment α-Fe_2O_3. Although sintering occurred in the high-temperature firing the material could be broken down to a powder of suitable particle size without the introduction of any appreciable lattice distortion. One or two per cent of α-Fe_2O_3 was detectable in the material, but the structure-cell constant of 8·394 A. for the Fe_3O_4 itself corresponds well with published data.

The accompanying figure shows in direct comparison parts of the Co $K\alpha$ powder photographs of magnetite at approximately 295 and 95° K. The line-splitting which is manifest at 95° K. for all recorded reflexions, except 800, is consistent with a deformation of the cubic structure cell along a [111] direction, so that the symmetry becomes rhombohedral. Consideration of displacements and relative

---

* Communication No. 473 from the staff of the Research Laboratories of the General Electric Company Limited.

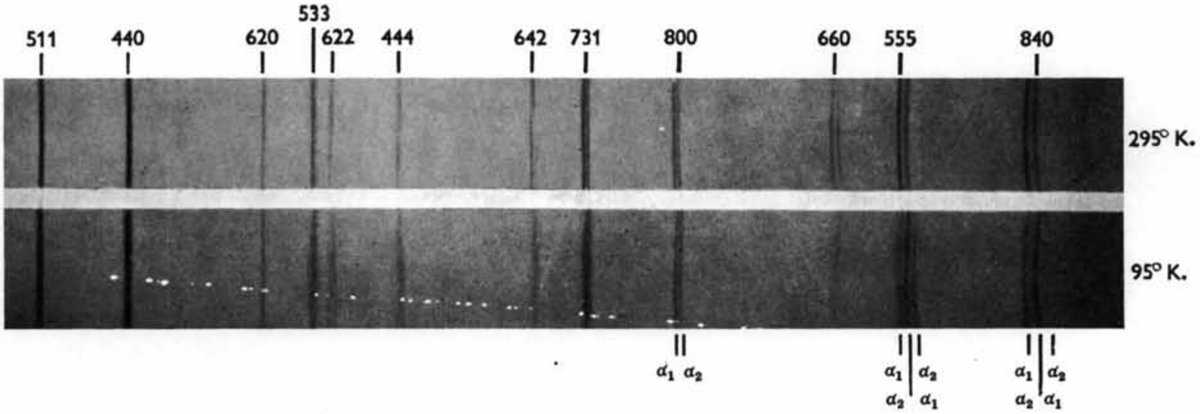

Fig. 1. Parts of X-ray powder photographs (Co $K\alpha$ radiation) of Fe_2O_3 at 295 and 95° K.

Table 1. *Crystal-structure data*

		Data for unit cell referred to rhombohedral symmetry		
Temp. (°K.)	Symmetry	a_R (A.)	α	Unit-cell volume (cm.^{3})
295	Cubic $a_0 = 8{\cdot}3940 \pm 0{\cdot}0005$ A.	$5{\cdot}9370 \pm 0{\cdot}0005$	60°	$24{\cdot}96 \times 10^{-24}$
165	Cubic $a_0 = 8{\cdot}3905 \pm 0{\cdot}0005$ A.	$5{\cdot}9345 \pm 0{\cdot}0005$	60°	$24{\cdot}89 \times 10^{-24}$
95	Rhombohedral	$5{\cdot}938 \pm 0{\cdot}001$	59° 50′	$24{\cdot}90 \times 10^{-24}$

intensities of components of the split reflexions indicates that the rhombohedral angle becomes less than the 60° required for cubic symmetry. This type of structure change is analogous to that found in the monoxides of iron, nickel and manganese (Rooksby & Tombs, 1951). No departure from cubic symmetry is evident in powder photographs of Fe_3O_4 at 165° K., so that the deformation of the structure occurs between 165 and 95° K.

Closely similar effects were obtained using a specimen of natural magnetite.

The crystal-structure data calculated from the X-ray patterns for Fe_3O_4 at 295, 165 and 95° K. are shown in Table 1.

It is noteworthy that the structure cell shows only very small changes in volume below room temperature.

The failure of others to observe the structure transition decisively may be partly due to the use of unsuitable material. Residual lattice strain, very small crystal size, or lack of homogeneity may produce sufficient line-broadening to mask the splitting of the powder reflexions, especially if other experimental conditions are unfavourable. Alternatively, with very small crystallites or in the presence of lattice strain it is possible that the structure transition may be suppressed over the temperature range investigated.

Discussion

It now seems that the structure transition in magnetite at low temperature is associated, like the specific-heat anomaly, with an antiparallel orientation of the spins of the magnetic atoms. Such an arrangement facilitates the development of the condition generally referred to as antiferromagnetism, and in terms of this condition the so-called lower Curie temperature has been explained by Néel (1948, 1950).

In the structure cell of magnetite the iron atoms, whether at fourfold or sixfold co-ordination positions, may be regarded as arranged in sheets perpendicular to the [111] direction. There is then an analogy with the arrangement of magnetic atoms in substances such as manganous oxide and ferrous oxide. In these oxides an antiferromagnetic condition has been postulated in which the spins of the magnetic atoms in a given (111) plane are parallel, but the spins in successive planes are antiparallel. If a similar antiparallel orientation of neighbouring (111) planes of magnetic atoms holds for magnetite, a deformation of the structure cell may well be expected by expansion or contraction along a direction perpendicular to these planes, i.e. along [111]. This is exactly the observed form of the structure transition in magnetite at low temperature.

Fe_3O_4 is thus added to the growing list of substances for which structure transitions have been observed in association with the development of antiferromagnetism (Rooksby & Tombs, 1951; Smart & Greenwald, 1951). Other spinels containing magnetic atoms are being studied.

References

Ellefson, B. S. & Taylor, N. W. (1934). *J. Chem. Phys.* **2**, 58.

Li, C. H. (1932). *Phys. Rev.* **40**, 1002.

Millar, R .W. (1929). *J. Amer. Chem. Soc.* **51**, 215.

Néel, L. (1948). *Ann. Phys., Paris*, **3**, 137.

Néel, L. (1950). *C.R. Acad. Sci., Paris*, **230**, 190.

Rooksby, H. P. & Tombs, N. C. (1951). *Nature, Lond.*, **167**, 364.

Shôji, H. (1935). *Sci. Rep. Tohoku Univ.* **24**, 250.

Smart, J. S. & Greenwald, S. (1951). *Phys. Rev.* **82**, 113.

Snoek, J. L. (1947). *New Developments in Ferromagnetic Materials*. New York and Amsterdam: Elsevier.

Tombs, N. C. & Rooksby, H. P. (1950). *Nature, Lond.*, **165**, 442.

Weiss, P. & Forrer, R. C. (1929). *Ann. Phys., Paris*, (10), **12**, 279.

Acta Cryst. (1951). **4**, 475

The crystal structures of some α-amino acids. A preliminary X-ray examination.

By B. Dawson and A. McL. Mathieson, *Chemical Physics Section, Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia*

(*Received* 14 *June* 1951)

As part of the work of this laboratory on the structure of proteins, the crystal structures of the α-amino acids and simple peptides are being studied. The results here recorded are for compounds representative of amino acids with straight (I) and branched (Ia) aliphatic chains, dicarboxylic (II) and heterocyclic (III) amino acids. The crystal structures of glycine (Albrecht & Corey, 1939) and of alanine (Levy & Corey, 1941; Donohue, 1950) have been studied in detail. The analysis of the copper salt and DL-α-aminobutyric acid (Stosick, 1945) has been completed for one projection only. The cell dimensions and space groups of DL-valine, DL-norleucine and DL-methionine have been recorded by Albrecht, Schnackenberg, Dunn & McCullough (1943), but their data have been proved unreliable by the present work and by the recent study of threonine (Shoemaker, Donohue, Schomaker &