Acta Cryst. (1953). **6**, 105

The low-temperature transition in magnetite*.

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(*Received* 20 *October* 1952)

Introduction

In a recent communication, Tombs & Rooksby (1951) reported the transition of magnetite, Fe_3O_4, with decreasing temperature at 119° K. to be from the cubic to the rhombohedral system. This observation was based on a careful study of the X-ray diffraction pattern below the transition, using photographic methods. Measurements made in this laboratory (Calhoun, to be published) on the magnetic anisotropy and conductivity of magnetite at temperatures below 119° K. strongly support the view proposed by Verwey *et al.* (1947) that the transition is to the orthorhombic system. Further weight is lent to this proposal by recent strain-gauge measurements on single crystals of magnetite (Bickford, 1952).

A redetermination of the X-ray data, recorded with the Norelco Geiger-counter spectrometer, confirmed the low-temperature form of magnetite as orthorhombic, and the pattern has been successfully indexed assuming the space group to be *Imma*. The thermal expansion coefficient of the *c* axis becomes negative below 119° K., and at about 95° K. there is no appreciable difference in the spacings of (440) and (008). This appears to be the reason which led Tombs & Rooksby to the assignment of a rhombohedral system.

Experimental

A simple adaptation (Calhoun & Abrahams, to be published) of the Norelco Geiger-counter spectrometer has been devised for use at low temperatures, with the sample in thermal contact with a bath of liquid nitrogen. The temperature of the specimen is measured to within 2° K. by means of a thermocouple in close contact with the sample holder. Fe $K\alpha$ radiation was used throughout ($\lambda = 1{\cdot}93597$ Å). The profiles of the X-ray diffraction lines were obtained by multiple counts of the intensities at intervals of not less than 0·05° in 2θ across the reflection. At background level, about 1000 counts were recorded at each angle. Using the relation $P_f = 0{\cdot}67/N^{\frac{1}{2}}$, the probable error in the intensity is 2·1%, which decreases at angles near the peaks.

The magnetite sample was prepared by reducing very pure, 325-mesh Fe_2O_3 in an atmosphere of 3·2 volume % CO in CO_2 at 1000° C. (Smiltens, 1952). The sample was kept at this temperature for 6 hr. and annealed by cooling at a rate of 100° C. per hour, increasing the CO content as described by Smiltens. No sintering was observed in the product, the entire sample being passable through a 325-mesh screen. The X-ray powder pattern of this magnetite showed no trace of Fe_2O_3 or FeO, and the widths of the peaks at half height was less than 0·15° in 2θ at all angles, thus indicating little or no residual strain.

Crystal data

The unit-cell side of cubic magnetite at 295° K. was measured as $8{\cdot}3940 \pm 0{\cdot}0005$ Å, in exact agreement with Tombs & Rooksby (1951). On cooling through the transition to 78° K., the cubic lines (800), (731) and (533), which are the three strongest high-angle reflections ($2\theta_{hkl} > 90°$) obtained with Fe $K\alpha$ radiation, each split into several lines. The best fit for these observed spacings and intensities corresponds to the orthorhombic unit cell

$$a = 5{\cdot}912,\ b = 5{\cdot}945,\ c = 8{\cdot}388 \pm 0{\cdot}005 \text{ Å},$$

with space group $Imma$–D_{2h}^{28}. This space group was arrived at by a consideration of the resulting symmetry if the electrons order in the manner proposed by Verwey *et al.* (1947). The *a* and *b* axes are half the face diagonals of the cubic modification. Increased accuracy could probably be obtained at liquid-helium temperatures, which would require little modification of this technique. The observed and calculated spacings and intensities based on this cell are collected in Table 1. The intensities were calculated assuming the same atomic positions as in the cubic form, making due allowance for the transformation to the orthorhombic unit cell, and keeping an oxygen parameter of 0·375, since this atom contributes very little to the planes concerned.

Table 1. *Intensities and spacings in orthorhombic magnetite*

hkl	d_o (Å)	d_c (Å)	I_o	I_c‡
143	1·2804	1·2812	weak	65
035	*	1·2804	*	
305	1·2765	1·2774	medium	97†
413	*	1·2762	*	
053	*	1·0942	very faint	20
251	1·0938	1·0937	faint	40
145	*	1·0933	*	40
343	1·0919	1·0923	faint	90†
127		1·0922		
217	*	1·0916	*	59†
433	1·0909	1·0909	faint	59†
415	1·0901	1·0902	weak	80†
521	1·0897	1·0894	medium	100†
503	*	1·0890	*	
008	1·0481	1·0485	weak	50
440	1·0476	1·0481	medium	100

* Resolution was insufficient to permit location of these lines.

‡ Calculated intensities were normalized on the basis $I(440) = 100$.

† This intensity includes an a_2 component, assuming $Ia_1 = 2\,Ia_2$.

Thermal expansion

The dimensions of the magnetite unit cell were measured at 295°, 128° and 78° K. The resulting volumes, 591·4, 589·1 and 589·6 Å^3 respectively, referred to the cubic cell, are in excellent agreement with those given by Tombs & Rooksby (1951). From these data, and a determination of the *c*-axis length at 108° K., the coefficients of thermal expansion above and below the transition may be com-

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* Sponsored by the ONR, the Army Signal Corps and the Air Force under ONR Contracts N5ori-07801 and N5ori-07858.

Table 2. *Thermal expansion coefficients for magnetite*

Temp. (°K.)	Method	Direction	Coefficient	Observer
295–128	X-ray	Any	$7{\cdot}7\times10^{-6}$	Present authors
295–165	X-ray	Any	3·5	Tombs & Rooksby (1951)
323–290	Interferometric	Any	8·6	Sharma (1950)
173–123	Dilatometric	Any*	7·7	Domenicali (1950)
108–78	X-ray	[001]	−20	Present authors
106–93	Dilatometric	[001]	−10	Domenicali (1950)

* Domenicali quoted different values for the [100], [110] and [111] directions; $7{\cdot}7\times10^{-6}$ is the average of these.

puted. These values are compared in Table 2 with those reported by others.

We wish to thank Prof. A. von Hippel for his interest and J. Smiltens for a sample of pure Fe_2O_3 and the use of his specially constructed furnace.

References

Bickford, L. R. (1952). Paper presented at Office of Naval Research Conference on Magnetism, Washington, D. C., September 1952. Abstract in *Rev. Mod. Phys.* (in press).

Domenicali, C. A. (1950). *Phys. Rev.* **78**, 458.

Sharma, S. S. (1950). *Proc. Indian Acad. Sci.* A, **31**, 261.

Smiltens, J. (1952). *J. Chem. Phys.* **20**, 990.

Tombs, N. C. & Rooksby, H. P. (1951). *Acta Cryst.* **4**, 474.

Verwey, E. J., Haayman, P. W. & Romeijn, F. C. (1947). *J. Chem. Phys.* **15**, 181.

Acta Cryst. (1953). **6**, 106

The crystal structure of osmium tetroxide.

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(*Received* 14 *October* 1952)

We have investigated the structure of solid osmium tetroxide by X-ray diffraction. Crystals, grown by sublimation, were sealed in Pyrex capillaries for the X-ray exposures because of their high vapor pressures. Rotation, oscillation, and Weissenberg photographs were taken with Cr $K\alpha$ and Cu $K\alpha$ radiation ($\lambda = 2{\cdot}2909$ and 1·5418 Å).

The structure is monoclinic, with

$$a = 8{\cdot}66,\ b = 4{\cdot}52,\ c = 4{\cdot}75\ \text{Å},\ \beta = 117{\cdot}9^\circ,\quad U = 164{\cdot}3\ \text{Å}^3\,.$$

With $Z = 2$, $D_x = 5{\cdot}14$; $D_m = 4{\cdot}95$ (Krauss & Schrader, 1928). The extinctions show the lattice to be C centered. The fact that all spots allowed by the C lattice are nearly equally intense, except for systematic variations due to absorption and angle factors, confirms that there are only two heavy atoms in the unit cell and shows that the oxygen atoms cannot be located by the present diffraction data.

The diffraction data permit space groups $C2$, Cm and $C2/m$. Only with $C2$ is it possible to find a reasonable arrangement of the oxygen atoms. The OsO_4 molecule must be approximately tetrahedral. If it is taken as perfectly tetrahedral with the Os–O bond distance 1·66 Å (Brockway, 1936), then the structure which gives the best intermolecular distances is:

Space group $C2$–C_2^3.
$(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0)+$
2 Os in $2(a): (0, y, 0)$ with $y = 0$;
4 O_{I} in $4(c): (x, y, z;\ \bar{x}, y, \bar{z})$
with $x = 0{\cdot}13$, $y = 0{\cdot}21$, $z = -0{\cdot}07$;
4 O_{II} in $4(c)$ with $x = 0{\cdot}11$, $y = -0{\cdot}21$, $z = 0{\cdot}31$.

In this structure, each oxygen atom has three oxygen neighbors in the same molecule, at 2·71 Å, and six (for O_{I}) or seven (for O_{II}) neighbors in adjacent molecules at distances ranging from 2·90 to 3·25 Å. The molecule is situated on a twofold axis, so that deviations from tetrahedral symmetry are possible. For example, a twist of the O_{I} pair with respect to the O_{II} pair by 9° results in more nearly equal intermolecular distances (minimum distance 3·00 Å) but with a simultaneous decrease in some of the intramolecular O–O distances to 2·59 Å. Any change in the Os–O distance, of course, results in an inverse change in the minimum intermolecular O–O distances.

Except for the above structure, or small distortions of it, no structure could be found which gives reasonable interatomic distances. Therefore the X-ray data imply that the OsO_4 molecule is tetrahedral or nearly tetrahedral, even though oxygen positions cannot be derived from the observed intensities.

The crystals show twinning corresponding to reflection in the (001) plane. The shortest intermolecular O–O distances are between molecules whose centers are in this plane, and the structure can be visualized as a layer structure. The twinning then involves only the method of stacking layers and does not disturb the shortest intermolecular contacts.

Some of the crystals were provided by Dr C. R. Hurley. This research was done under the auspices of the U.S. Atomic Energy Commission.

References

Brockway, L. O. (1936). *Rev. Mod. Phys.* **8**, 260.

Krauss, F. & Schrader, G. (1928). *Z. anorg. Chem.* **176**, 391.