163. *The Lattice Dimensions of Zinc Oxide.*

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THE elimination of the chief sources of error in the electron-diffraction determination of crystal-lattice constants by the introduction of the double-shutter method, combined with zinc oxide condensed from the smoke as a reference structure (Finch and Quarrell, *Proc. Physical Soc.*, 1934, **46**, 148), has rendered it desirable to review previous determinations of the lattice constants of this compound. These are given in Table I, where a and c are the basal and the major axis respectively.

TABLE I.

Material.	a, Å.	c, Å.	Axial ratio.	Authority.
Zincite	3·22	5·20	1·608	W. L. Bragg, *Phil. Mag.*, 1920, **39**, 647.
Zincite	3·22	5·20	1·608	Aminoff, *Z. Krist.*, 1921, **56**, 495; 1922, **57**, 204.
Zincite	3·251	5·226	1·6077	Weber, *ibid.*, p. 398.
Zinc oxide ("Merck")	3·242	5·176	1·596	Barth, *Norsk Geol. Tidsskr.*, 1927, **9**, 317.
Zinc oxide ("spectroscopic purity")	3·235	5·209	1·610	Fuller, *Science*, 1929, **70**, 196.

In their study of crystal structure and orientation in zinc oxide films, Finch and Quarrell (*loc. cit.*) referred their measurements to Bragg's values, which, however, had been obtained from zincite; and according to Barth this material is rare in the pure state.

Since the axial ratio, c/a, is a dimensionless number, it can be evaluated by electron diffraction without a knowledge of either the electronic wave-length or the camera dimensions, the only measurements involved being those of ring diameters, provided the indices of the corresponding Bragg planes are known. A correction due to the use of a plane recording surface is easily applied, but is small because the maximum deviation of the diffracted electrons from the main beam is of the order of 3° in the case of the Bragg plane spacings involved. In no case does this correction exceed the equivalent of 0·0015 Å. with 40—60 kv. electrons. The accuracy attainable is thus virtually that with which ring diameters of, say, 2—7 cm. (effective camera length = 50 cm.) can be measured, and thus depends in the main upon sharpness of the rings and upon equality of definition of the inner and the outer edge of each ring. Over-all definition can be greatly improved by suitable beam focusing, combined with suppression of undue beam divergence, and uniformity in ring-edge definition is ensured by the use of a constant current supply to a correctly adjusted cold cathode discharge tube (*Proc. Roy. Soc.*, 1933, **141**, 398). Patterns obtained under such conditions compare favourably with the best X-ray patterns of the Debye–Scherrer type (see *Proc. Physical Soc.*, *loc. cit.*, Figs. 6 and 7). It is essential, however, that wherever the concentrating field extends beyond the specimen it should be uniform in planes at right angles to the beam axis up to the limits of their intersections with the cones or rays of diffracted electrons. The true circularity and the relative diameters of rings produced by a known structure may be used as a check upon the uniformity of the magnetic field (*loc. cit.*, p. 404).

With fields non-uniform in the sense employed, ring distortion results as, *e.g.*, in Fig 1. An even more sensitive check is afforded by means of a suitable single-crystal transmission pattern, such as that shown in Fig. 2, which was obtained from a mica single crystal with the c axis oriented in the direction of the beam. Since the spots are all due to planes parallel to the axis, they should form a pattern reproducing the pseudohexagonal symmetry of the crystal structure about this axis, provided distortion effects due to concentrating and stray fields are absent. The uniformity of the field employed in the experiments of which an account is set forth below can thus be easily verified by applying a straight edge in different directions to the several rows of spots in Fig. 2.

In order to determine a and c for zinc oxide with the desired accuracy by electron diffraction, it is necessary to employ as reference material a substance of a high degree of purity and of which the lattice constants have been measured by the most refined methods of X-ray analysis. Determinations of the length of side of unit cube, a, for gold of a purity exceeding 99·9% have been recently carried out by Sachs and Weerts (*Z. Physik*, 1930, **60**, 481), Wiest (*ibid.*, 1933, **81**, 121), and by Owen and Yates (*Phil. Mag.*, 1933, **15**, 472), and the weighted mean of their results is $a = 4{\cdot}0700 \pm 0{\cdot}0006$ Å. at 20°. For reasons previously pointed out (*loc. cit.*), gold is unsuitable as a general reference material; in view of its simple structure and the high order of accuracy to which a is now known, however, it serves very well as a dimensional reference for comparison with zinc oxide, although the difficulty of obtaining specimens in which the dispositions of the crystals are random renders gold valueless as a ring intensity reference.

For some reason, probably connected with the different conductivities of zinc oxide and gold, the central pattern spots due to the undiffracted beam do not as a rule coincide in double-shutter records of gold–zinc oxide transmission patterns (Fig. 3). If the possibility of overlooking a change in accelerating voltage between exposures be guarded against by bracketing the recording of the one pattern by two under-exposures of the reference material, the pattern displacement due to a shifting of the central beam on changing from one specimen to the other is general, and thus in effect merely results in doubling the number of micrometer readings involved in a single spacing determination. This, however, entails a corresponding increase in the error attached to the final result. For this reason in the following experiments the zinc oxide was deposited on gold. The resulting diffraction patterns then consisted of a pattern due to zinc oxide superimposed upon one due to gold. Double-shutter records, as shown in Fig. 3, of separate gold and zinc oxide specimens were also measured and analysed, and the results not only served to assist in identifying the rings in the composite patterns, but also afforded a check upon the absence or otherwise of pseudomorphic strain effects in the structure of the zinc oxide of the composite specimens (*locc. cit.*). No trace of such structural distortion was observed in the case of films formed by the condensation of the smoke.

EXPERIMENTAL.

Four gold specimens were prepared from leaves beaten by Messrs. Johnson and Matthey out of their purest grade metal. They were thinned down by floating on $N/10$-potassium cyanide, and washed by being transferred on to several changes of distilled water. The gold films, faint bluish-green by transmitted daylight, were then supported on fine-meshed nickel gauze and dried. Zinc oxide smoke, obtained by the combustion in oxygen of fresh granulated zinc of forensic quality, was deposited on the gold specimens. In addition to the smoke, veil-like films of zinc oxide are sometimes formed, but with careful manipulation it is not difficult to avoid their deposition on the specimen. It is essential to do so, because there is a pronounced tendency for the veil crystals to be oriented in such a manner that the corresponding ring-intensity distribution differs from the normal to such an extent as to conduce to error in ring, or even structure, identification (*loc. cit.*, p. 155 *et seq.*).

The electron-diffraction patterns yielded by the composite specimens were recorded in Camera No. 1 (*loc. cit.*, p. 400), which is now fitted with a double shutter of the type previously described (*loc. cit.*, p. 151). The patterns were measured with a Cambridge travelling microscope reading to 0·001 mm.; to within a limit of this order the instrument was free from perceptible back-lash.

Results.—A composite zinc oxide–gold electron-diffraction pattern typical of those obtained from the four specimens is shown in Fig. 4. The ring radii and origins are given in Table II. Radii corrected for flatness of recording field are denoted by an asterisk.

Evaluation of c/a.—The four patterns each contain two sufficiently well-defined and distinct zinc oxide rings of zero third index and one of zero first and second indices. The (0 0 4) zinc oxide ring, though visible in all four patterns, is too faint to permit of accurate measurement. Thus eight independent values for c/a can be obtained directly from the ring radii in Table II, as follows :

In the case of the zinc oxide lattice (close-packed hexagonal)

$$(N/d)^2 = 4(h_1^2 + h_2^2 + h_1h_2)/3a^2 + h_3^2/c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is the diffraction order, d the Bragg plane spacing, and the h's are the Millerian indices. Further,

$$(N/d)^2 = R^2/(\lambda L)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

FIG. 1.

Ovoid ring distortion due to non-uniformity of magnetic fields in the planes normal to the beam.

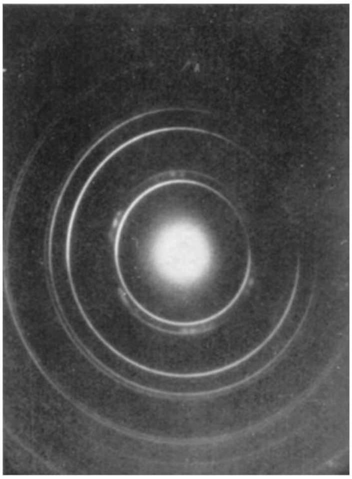

FIG. 2.

Transmission pattern from a mica single crystal, to serve as a test for uniformity of field.

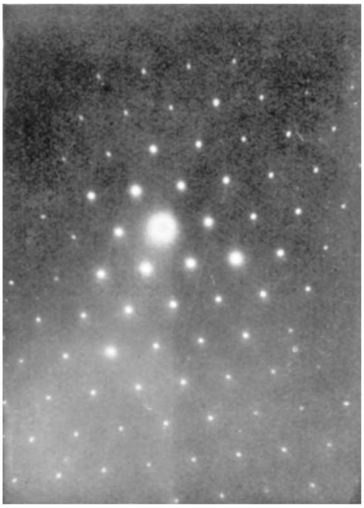

FIG. 3.

Double-shutter transmission pattern of zinc oxide (left) bracketed by two half exposures through gold (right). Although the central spots do not coincide, the definition of the gold pattern shows that the voltage was constant throughout all exposures.

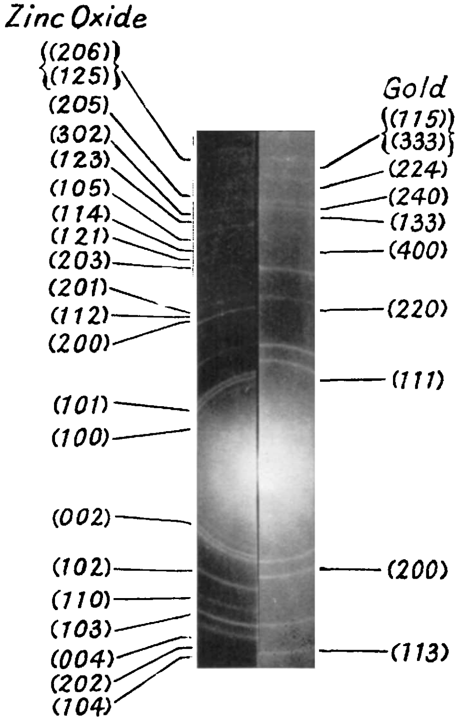

FIG. 4.

Composite transmission pattern of zinc oxide superimposed on gold. The black central spot has been drilled through the emulsion by the undiffracted beam. The rings can be identified by comparison with Fig. 3.

TABLE II.

Ring radii, cm.				Indices.	
Specimen.					
I.	II.	III.	IV.	Gold.	Zinc oxide.
0·883 *0·883	0·884 *0·884	0·885 *0·885	0·878 *0·878	—	(1 0 0)
0·953 *0·953	0·953 *0·953	0·954 *0·954	0·945 *0·945	—	(0 0 2)
1·003	1·003	1·006	0·996	—	(1 0 1)
1·061	1·061	1·064	1·052	(1 1 1)	—
1·225	1·226	1·228	1·215	(2 0 0)	—
1·301	1·300	1·302	1·291	—	(1 0 2)
1·530 *1·529	1·532 *1·531	1·535 *1·534	1·519 *1·518	—	(1 1 0)
1·679	1·682	1·684	1·668	—	(1 0 3)
1·735	1·734	—	1·724	(2 2 0)	—
1·807	1·806	1·805	1·792	—	(1 1 2)
—	—	—	—	—	(0 0 4)
2·031	2·028	2·030	2·015	(1 1 3)	—
—	—	—	—	—	(1 0 4)
2·270	2·270	2·275	2·253	—	(2 0 3)
2·385	2·380	2·382	—	—	(1 2 1)
2·453	2·450	2·451	2·432	(4 0 0)	—
2·540	2·537	2·545	2·522	—	(1 0 5)
2·741	—	2·745	2·722	(2 4 0)	—

where λ and L are the electronic wave and effective camera lengths respectively, and R is the ring radius corrected for flatness of recording field. Equating (1) and (2) for planes of $(h_1\,h_2\,0)$ and $(0\,0\,h_3)$ types, we have

$$R^2_{(h_1\,h_2\,0)}/(\lambda L)^2 = 4(h_1^2 + h_2^2 + h_1h_2)/3a^2$$

and $$R^2_{(0\,0\,h_3)}/(\lambda L)^2 = h_3^2/c^2 \text{ respectively.}$$

Elimination of λL gives c/a in terms of ring radii and the corresponding indices, thus

$$c/a = R_{(h_1\,h_2\,0)} \cdot h_3/R_{(0\,0\,h_3)} \cdot \{4(h_1^2 + h_2^2 + h_1h_2)/3\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (3)$$

Insertion of the appropriate corrected ring-radii values, marked with an asterisk in Table II, leads to absolute values for c/a as set forth in Table III.

TABLE III.

Specimen.	I.	II.	III.	IV.	Mean.
c/a	1·606	1·606	1·606	1·609	1·607 ± 0·002
	1·606	1·606	1·608	1·606	

Evaluation of a.—The d/N values corresponding to the zinc oxide rings were determined by reference to the gold rings for which the corresponding spacings were calculated from the equation

$$d/N = a/(h_1^2 + h_2^2 + h_3^2)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $a = 4{\cdot}070$ Å. These interpolated values for zinc oxide are given in Table IV. In the case of the (1 0 0) or (1 1 0) zinc oxide rings, a equals $2d/\sqrt{3}N$ or $2d/N$ respectively; and the a values in Table IV obtained in this manner independently of the axial ratio are marked with an asterisk. Otherwise a was obtained from the corresponding spacing by equation (1), the mean value of c/a, as given in Table III, being taken.

TABLE IV.

	d/N, Å., for ZnO.				a, Å., for ZnO.			
	Specimen.				Specimen.			
Indices.	I.	II.	III.	IV.	I.	II.	III.	IV.
(1 0 0)	2·826	2·822	2·826	2·818	*3·263	*3·259	*3·263	*3·253
(0 0 2)	2·621	2·618	2·622	2·617	3·255	3·260	3·265	3·260
(1 0 1)	2·488	2·488	2·486	2·483	3·263	3·263	3·260	3·257
(1 0 2)	1·918	1·921	1·920	1·916	3·258	3·261	3·260	3·254
(1 1 0)	1·631	1·629	1·627	1·630	*3·262	*3·258	*3·254	*3·260
(1 0 3)	1·487	1·486	1·483	1·486	3·265	3·260	3·254	3·263
(1 1 2)	1·381	1·382	1·382	1·381	3·255	3·256	3·256	3·255
(0 0 4)	—	—	—	—	—	—	—	—
(1 0 4)	—	—	—	—	—	—	—	—
(2 0 3)	1·099	1·098	1·096	1·098	3·265	3·260	3·256	3·262
(1 2 1)	1·047	1·047	1·047	—	3·263	3·265	3·259	—
(1 0 5)	0·9828	0·9826	0·9809	0·9819	3·262	3·261	3·256	3·259
Mean of a for each specimen					3·261	3·260	3·258	3·258

Thus the asterisked values give as mean $a = 3{\cdot}258 \pm 0{\cdot}005$ Å., whilst that of those values which involve c/a is $a = 3{\cdot}259 \pm 0{\cdot}006$ Å.

Evaluation of c.—In the case of planes of $(0\ 0\ h_3)$ type,

$$c = h_3d/N \qquad \ldots\ldots\ldots\ldots \qquad (5)$$

Four values of the spacing of one such type of plane are given in Table IV, and from these by (5) the mean value of $c = 5{\cdot}239 \pm 0{\cdot}005$ Å. By the less direct evaluation, where $c = a(c/a)$, insertion of the mean values for a and c/a yields $c = 5{\cdot}237 \pm 0{\cdot}006$ Å.

DISCUSSION.

While the value of $c/a = 1{\cdot}607$ obtained from the above experimental results agrees closely with previous determinations, except with that due to Barth (*loc. cit.*), those found by electron diffraction for the close-packed hexagonal zinc oxide axes, $a = 3{\cdot}258$ Å. and $c = 5{\cdot}239$ Å. (referred to gold, $a = 4{\cdot}0700$ Å.), are considerably higher than those obtained with X-rays by other observers. Even in the case of Weber's values the differences certainly exceed the experimental errors of the present determinations. It is to be noted that the product of the independently determined electron-diffraction values of a and c/a is 5·236 Å., whereas the electron-diffraction value of c obtained independently of a and c/a is 5·239 Å.

Since the coefficient of linear thermal expansion of gold is about three times that of zinc oxide, the above discrepancy cannot be ascribed to a differential expansion of the gold and superimposed zinc oxide films due to heating effects of inelastic electronic collisions. The circularity of the composite pattern rings and the close agreement of the values for c/a negative any suggestion that the ring widening is due to charging-up effects. Thus it seems probable that the discrepancy between the values of the lattice constants previously obtained by X-rays and now by electron diffraction is due to a difference in the nature of the zinc oxide examined. This question could probably be settled, and the interests of accurate electron-diffraction analysis materially furthered, by an X-ray examination of pure condensed zinc oxide smoke.

SUMMARY.

A revision of the lattice constants of zinc oxide has been carried out by electron diffraction. For the close-packed hexagonal lattice of zinc oxide, a value for the axial ratio $c/a = 1{\cdot}607 \pm 0{\cdot}002$ has been obtained directly from zinc oxide transmission diffraction patterns. Values for the axes, a and c, have been obtained by reference to a superimposed diffraction pattern due to gold, to the structure of which a value of $a = 4{\cdot}0700 \pm 0{\cdot}0006$ Å. has been assigned. These values are as follows:

$$a = 3{\cdot}258 \pm 0{\cdot}005\text{ Å.};\ c = 5{\cdot}239 \pm 0{\cdot}005\text{ Å.}$$

Whilst the value for c/a is in good agreement with those obtained by most previous workers, the electron-diffraction values for a and c are appreciably higher than the corresponding X-ray values. It is suggested that the discrepancy is probably due to differences in the nature of the materials examined by different investigators.

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