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1935 Proc. Phys. Soc. 47 835

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THE LATTICE-DIMENSIONS OF ZINC OXIDE

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Received March 16, 1935. Read in title June 21, 1935

ABSTRACT. The lattice-dimensions of pure zinc oxide condensed from the smoke have been determined to a high degree of accuracy by means of X-ray powder photographs. Bradley and Jay's lattice-dimensions of quartz⁽⁴⁾ and Siegbahn's X-ray wavelengths⁽⁵⁾ being accepted as standards, the lattice-dimensions of zinc oxide are found to be:

$$\left. \begin{aligned} a_0 &= 3.2426_5 \pm 0.0001 \\ c_0 &= 5.1948 \pm 0.0003 \end{aligned} \right\} \text{at } 18^\circ \text{ C.}$$

$$\text{Axial ratio } c_0/a_0 = 1.6020_0 \pm 0.0001$$

Both the lattice-dimensions themselves and the axial ratio are lower than Finch and Wilman's electro-diffraction values⁽²⁾ which are based on the X-ray lattice-dimension of gold, by amounts larger than the combined errors of both methods. There are thus real discrepancies, which are of the order of $\frac{1}{2}$ to 1 per cent.

In view of these discrepancies, Finch and Wilman's assumption that the apparent lattice-dimension of gold is the same for 40–60 kV. electrons as for X-rays may not be correct. The discrepancies therefore represent the combined possible discrepancies shown by gold and zinc oxide.

This does not apply to the axial ratio, which is independent of any reference substance. The difference between the axial ratios determined by electrons and by X-rays appears to point to a real difference in axial ratio between the surface and the interior of zinc oxide crystals.

§ 1. INTRODUCTION

PURE zinc oxide condensed from the smoke has been selected by Finch and Quarrell⁽¹⁾ as a reference substance in electron-diffraction determinations of crystal-lattice dimensions, and Finch and Wilman have recently determined its lattice-dimensions by reference to gold⁽²⁾ using 40 to 60 kV. electrons. The values obtained in this way are considerably higher than those obtained previously by X-ray methods. The figures are collected in table 1, which includes a set of X-ray results that have appeared since Finch and Wilman's work.

Although the X-ray values differ considerably among themselves, they are consistently lower than the electron-diffraction values. Finch and Wilman conclude that the difference between the X-ray and electron-diffraction figures is due to a difference in the nature of the zinc oxide examined, and state that "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." This has now been done.

Table 1

Material	a_0 (Å.)	C_0 (Å.)	Axial ratio	Reference
<i>X-ray method</i>				
Zincite	3·22	5·20	1·608	W. L. Bragg ⁽⁹⁾
Zincite	3·22	5·20	1·608	Aminoff ⁽¹⁰⁾
Zincite	3·251	5·226	1·6077	Weber ⁽¹¹⁾
Zinc oxide (Merck)	3·242	5·176	1·596	Barth ⁽¹²⁾
Zinc oxide (spectroscopically pure)	3·235	5·209	1·610	Fuller ⁽¹³⁾
Zinc oxide	3·248	5·202	1·602	Ivannikov, Frost, Shapiro ⁽¹⁴⁾
<i>Electron-diffraction method</i>				
Zinc-oxide smoke	3·258	5·239	1·607	Finch and Wilman ⁽²⁾

§ 2. EXPERIMENTAL

Zinc-oxide smoke was made by the combustion of pure granulated zinc of forensic quality supplied by Prof. Finch. X-ray powder patterns were obtained by the Hull-Debye-Scherrer method, using a camera 9 cm. in diameter of the type described by Bradley and Jay⁽³⁾. The camera was improved by the addition of brass screens which trap the primary beam soon after it has passed the specimen at the centre of the camera, the dimensions being such that none of the scattering which occurs inside the trap can possibly reach any part of the film; among other things, this has the effect of reducing the general background intensity, thus increasing the contrast of the lines and materially aiding the attainment of the highest accuracy of measurement.

In Bradley and Jay's type of camera, the exposed portion of the film is brought to an abrupt end by a knife edge, which thus registers a constant angle on every film. In the present instance this angle corresponds to a Bragg angle of 82° . For accurate determinations of lattice constants, only the reflections at large Bragg angles of 60 to 80° , which are well resolved into α_1 and α_2 doublets, are used. The distances between pairs of corresponding lines and the total length of the exposed portion of the film are measured, the angles being obtained by simple proportion. This eliminates errors due to shrinkage of the film.

The constant camera-angle is found by taking powder photographs of a substance whose lattice-dimensions are accurately known; Bradley and Jay have shown⁽⁴⁾ that quartz is by far the best for this purpose. A sample of pure quartz, similar to that used by Bradley and Jay, was kindly supplied by Dr H. E. Buckley. Four powder photographs were taken with copper $K\alpha$ radiation, four separately mounted specimens being used so that the corrections should be different. The camera angle θ_k was found by calculating a value from each reflection in the range 60 to 80° , plotting these values against $\sin 2\theta/2\theta$, and extrapolating to $\sin 2\theta/2\theta = 0$. The mean value of θ_k from the four films was found to be $82.125^\circ \pm 0.005^\circ$. This error of ± 1 in 16,000 in the value of θ means that if the above value of θ_k is assumed, the lattice-dimensions of quartz can be obtained by the following method with an error of ± 1 in 60,000.

The lattice constants of a hexagonal crystal are found by first calculating an approximate value for the axial ratio c from several pairs of reflections by means of the equation

$$(d_{hkl})^2 \left\{ \frac{4}{3} (h^2 + k^2 + hk) + l^2/c^2 \right\} = (d_{h_1 k_1 l_1})^2 \left\{ \frac{4}{3} (h_1^2 + k_1^2 + h_1 k_1) + l_1^2/c^2 \right\}.$$

This axial ratio is then used to calculate a_0 from all the reflections at large angles, thus

$$a_0 = d_{hkl} \sqrt{\left\{ \frac{4}{3} (h^2 + k^2 + hk) + \frac{l^2}{c^2} \right\}}.$$

These values of a_0 are plotted against $\cos^2 \theta$, and a linear extrapolation is made to $\cos^2 \theta = 0$. Bradley and Jay have shown that errors due to absorption of X-rays, thickness of specimen, and eccentricity of mounting are eliminated in this way. If there is any systematic one-sided deviation from the line on the part of values derived from reflections with large l indices, the axial ratio is in error, and another value must be tried.

In the present instance two powder photographs were taken with copper $K\alpha$ radiation and two with cobalt $K\alpha$ radiation, all with separately mounted specimens so that the corrections should be different. The zinc-oxide smoke gave very good photographs, with strong sharp lines.

There is no sign of line-broadening, and the crystals are therefore larger than 1000 Å. in diameter. It so happens that with both radiations there is one strong doublet very near the end of the film at an angle of over 80° , and there are several more between 60° and 80° ; this makes for great accuracy.

The films were measured on a Pye travelling microscope reading to 0.001 cm. Values of d/n were calculated from the Bragg equation $d/n = \lambda/2 \sin \theta$ for each line. The pairs of values from α_1 and α_2 wave-lengths were averaged, the α_1 value being given twice the weight of the α_2 value on account of its greater intensity. A correction for refraction of X-rays was then made by means of Siegbahn's formula⁽⁵⁾:

$$\text{True } d = d(\text{observed}) \times \left(1 + 5.4 \frac{d^2 \rho}{n^2} \cdot 10^{-6} \right),$$

where ρ is the density of the crystal (5.68 for ZnO).

The indices of the reflections were found in the usual way, by means of a chart of the Hull and Davey type. The lattice constants were then found in the way already described. Details are given in tables 2 and 3. The value of the axial ratio c which best fitted all the films was found to be 1.6020. The error here is not likely to be greater than ± 0.0001 .

The temperature near the camera was about 18°C . for all the films.

It may be noted that the final cobalt values are higher than the final copper values. The cobalt values could be reduced to the same level as the copper values by adopting a slightly higher axial ratio (1.6021), since the value from 213, which chiefly determines the final cobalt value, would be reduced by about the right amount; but a higher axial ratio would throw some of the other values too far out, and therefore has not been adopted.

Table 2. Powder photographs of ZnO taken with copper K α radiation $\alpha_1 = 1.537395 \text{ \AA.}$ $\alpha_0 = 1.541232 \text{ \AA.}$

Re- flection	Intensity	Film I					Film II				
		θ (deg.)	$\frac{d}{n}$ (Å.)	$\frac{d}{n}$ average	$\frac{d}{n}$ corrected	a_0	θ (deg.)	$\frac{d}{n}$ (Å.)	$\frac{d}{n}$ average	$\frac{d}{n}$ corrected	a_0
213 α_1	Very strong	58.247	0.90401	0.90405	0.90408	3.2396	58.226	0.90421	0.90419	0.90422	3.2401
α_2		58.464	0.90415					58.463	0.90416		
302 α_1	Strong	60.884	0.87988	0.87987	0.87989	3.2400	60.880	0.87992	0.87998	0.88000	3.2403
α_2		61.145	0.87986					61.117	0.88009		
006 α_1	Weak	62.676	0.86524	0.86524	0.86526	3.2407	—	—	—	—	—
205 α_1	Strong	67.075	0.83462 ₀	0.83465 ₇	0.83467 ₂	3.2407 ₀	67.211	0.83485 ₅	0.83485 ₉	0.83487 ₆	3.2414 ₉
α_2		67.398	0.83472 ₆					67.375	0.83486 ₄		
106 α_1	Medium weak	68.372	0.82691 ₈	0.82691 ₈	0.82693 ₂	3.2409 ₈	68.364	0.82696 ₃	0.82700 ₁	0.82701 ₆	3.2413 ₁
α_2		—	—	—	—	—	—	68.712	0.82707 ₅		
214 α_1	Medium	69.355	0.82145 ₆	0.82144 ₆	0.82145 ₆	3.2411 ₄	69.350	0.82147 ₆	0.82149 ₉	0.82151 ₄	3.2413 ₇
α_2		69.743	0.82142 ₁					69.720	0.82154 ₄		
220 α_1	Strong	71.552	0.81034 ₁	0.81036 ₁	0.81037 ₉	3.2415 ₂	71.547	0.81036 ₄	0.81040 ₃	0.81041 ₈	3.2416 ₇
α_2		71.971	0.81040 ₇					71.955	0.81048 ₁		
310 α_1	Strong	80.776	0.77877 ₀	0.77876 ₆	0.77877 ₉	3.2423 ₁	80.761	0.77880 ₂	0.77878 ₀	0.77879 ₈	3.2423 ₇
α_2		81.711	0.77875 ₈					81.728	0.77871 ₇		
		Extrapolated a_0					3.2426 ₂				

Table 3. Powder photographs of ZnO taken with cobalt K α radiation $\alpha_1 = 1.78529 \text{ \AA.}$ $\alpha_2 = 1.78919 \text{ \AA.}$

Re- flection	Intensity	Film III					Film IV				
		θ (deg.)	$\frac{d}{n}$ (\AA.)	$\frac{d}{n}$ average	$\frac{d}{n}$ corrected	a_0	θ (deg.)	$\frac{d}{n}$ (\AA.)	$\frac{d}{n}$ average	$\frac{d}{n}$ corrected	a_0
211 α_1	Strong	59.269	1.03847	1.03852	1.03855	3.2384	59.227	1.03803	1.03892	1.03895	3.2396
α_2		59.468	1.03860				59.440	1.03890			
114 α_1	Medium strong	61.843	1.01246	1.01255	1.01258	3.2394	61.817	1.01271	1.01280	1.01283	3.2402
α_2		62.051	1.01271				62.023	1.01297			
212 α_1	Medium strong	65.409	0.98168 ₂	0.98171 ₄	0.98174 ₃	3.2400 ₄	65.375	0.98105 ₀	0.98199 ₇	0.98202 ₆	3.2409 ₇
α_2		65.672	0.98177 ₆				65.631	0.98209 ₄			
105 α_1	Strong	66.461	0.97366 ₇	0.97371 ₃	0.97374 ₂	3.2404 ₆	66.425	0.97393 ₃	0.97392 ₆	0.97395 ₅	3.2411 ₇
α_2		66.731	0.97380 ₆				66.716	0.97391 ₅			
204 α_1	Weak	69.544	0.95272	0.95272	0.95275	3.2404	69.496	0.95302	0.95302	0.95305	3.2415
300 α_1	Strong	72.564	0.93563 ₆	0.93569 ₂	0.93571 ₀	3.2414 ₃	72.535	0.93578 ₅	0.93581 ₃	0.93583 ₀	3.2418 ₄
α_2		72.934	0.93586 ₂				72.921	0.93586 ₇			
213 α_1	Very very strong	80.592	0.90481 ₆	0.90483 ₄	0.90485 ₇	3.2424 ₀	80.577	0.90485 ₅	0.90486 ₀	0.90488 ₂	3.2424 ₈
α_2		81.358	0.90487 ₀				81.358	0.90487 ₀			
		Extrapolated a_0									
		3.2427 ₄					3.2427 ₂				

The discrepancy is probably due to refraction effects which cannot be precisely evaluated. Siegbahn's correction formula is for symmetrical reflection, i.e. the incoming and outgoing rays make equal angles with the crystal surface. This condition is usually not fulfilled on account of the development of a limited number of faces on the crystals; each line in a powder photograph is made up of many individual reflections which undergo varying deviations, the resultant of which may not correspond with that given by the formula (6). The last line on the cobalt films is from a totally different plane from that on the copper films, and the refraction corrections may not be quite right for either of them. However, since the extrapolated values of a_0 lie within the expected limits of error, this question need not be considered further; any inaccuracies due to these refraction effects are not likely to throw the final average value outside the limits given.

In the films taken with copper radiation, the last two reflections are from prism planes (310 and 220), and hence the extrapolated value of a_0 depends very little on the axial ratio adopted. These values have therefore been allowed double weight in taking a final average of a_0 , which is found to be as follows:

$$a_0 = 3.2426_5 \pm 0.0001 \text{ A.}$$

Combining this with the axial ratio 1.6020 ± 0.0001 , we get

$$c_0 = a_0 c = 5.1947 \pm 0.0004 \text{ A.}$$

In giving a possible error of ± 1 in 30,000 in the value of a_0 , Bradley and Jay's lattice-dimensions of quartz are taken as standards. These in turn rest on Siegbahn's X-ray wave-lengths. Any error here will, of course, increase the absolute error of the present results. But for the present purpose of comparison with Finch and Wilman's electron-diffraction results, this does not enter into the problem, since those workers used as standard the lattice-dimension of gold, which rests on the same X-ray wave-lengths.

The c_0 dimension can be obtained with a little more precision by following the same procedure as for a_0 , by means of the equation

$$c_0 = d \sqrt{\left\{ \frac{4}{3} (h^2 + k^2 + hk) c^2 + l^2 \right\}}.$$

The results are given in table 4.

Table 4. Powder photographs of ZnO. Determination of c_0

Reflection	c_0 (A.)		Reflection	c_0 (A.)	
	Film I	Film II		Film III	Film IV
213	5.1898	5.1906	—	—	—
302	5.1904	5.1910	211	5.1879	5.1899
006	5.1915	—	114	5.1895	5.1908
205	5.1916	5.1928 ₈	212	5.1905 ₅	5.1920 ₄
106	5.1920 ₈	5.1925 ₈	105	5.1912 ₂	5.1923 ₆
214	5.1923 ₀	5.1926 ₇	204	5.1911 ₈	5.1928 ₀
220	5.1929 ₁	5.1931 ₆	300	5.1927 ₇	5.1934 ₄
310	5.1941 ₉	5.1942 ₉	213	5.1943 ₁	5.1944 ₆
	5.1946 ₃	5.1946 ₈		5.1949 ₂	5.1948 ₆

The results from films III and IV, taken with cobalt radiation, depend on the axial ratio to a smaller extent than the other results. Allowing them therefore double weight in taking a final average, we obtain

$$c_0 = 5.1948 \pm 0.0003 \text{ \AA}.$$

The limits of error for c_0 are wider apart than for a_0 ; this is because the lines nearest to the ends of the films are not basal-plane reflections.

§ 3. DISCUSSION

The lattice-dimensions found by the X-ray method differ from those found by the electron-diffraction method for similar material by amounts larger than the combined errors of both methods.

Table 5

	a_0	c_0	Axial ratio
X-ray method	$3.2426_8 \pm 0.0001$	5.1948 ± 0.0003	$1.6020_0 \pm 0.0001$
Electron-diffraction method	3.258 ± 0.005	5.239 ± 0.005	1.607 ± 0.002

There is thus a real difference between X-ray and electron-diffraction values; and not only are the lattice-dimensions themselves different, but also the axial ratios are different.

It must be remembered, however, that the electron-diffraction values for the lattice-dimensions rest on the assumption that the electron-diffraction lattice-dimension of gold is the same as the X-ray value. It now appears that this assumption may not be correct; if zinc oxide shows a discrepancy, gold may do the same. The discrepancies found here represent the combined differences of gold and zinc oxide. This does not apply to the axial ratio, which is independent of the reference substance.

The discrepancies recall the much larger discrepancies (up to 30 per cent) found by Davisson and Germer⁽⁷⁾ who used slow electrons with metallic crystals. On that occasion the apparent lattice-contraction was at first thought to indicate a real contraction on the crystal surface, which is revealed by electron waves on account of their very small penetration. But according to the calculations of Lennard-Jones and Dent⁽⁸⁾ the surface contraction on ionic crystals of the NaCl type is only of the order of 5 per cent, and is practically confined to the first layer of atoms; if the same applies to metal crystals, this explanation seems unlikely to be correct. It was considered that a more likely explanation of the apparent lattice-contraction was to be found in the refraction of electron waves by the crystal.

Here we have to account for apparent expansions of the order of $\frac{1}{2}$ to 1 per cent when fast (40 to 60-kV.) electrons are used. It is not very profitable to carry the discussion further at present, for there is insufficient evidence to point to a definite conclusion. Even the sign of the change in ZnO is uncertain, since the behaviour of gold is unknown. One fact, however—the difference between the axial ratios

measured by the two methods—does appear to point to a difference in the crystalline material encountered by X-rays and by electrons. Since the penetrating power even of fast electrons is very much less than that of X-rays, this indicates a change of axial ratio at the surface. Any surface change of lattice dimensions would, of course, affect the a and c axes in different ratios.

§ 4. ACKNOWLEDGMENT

The author wishes to express his thanks to the Directors of Imperial Chemical Industries Limited for permission to publish this work, which was carried out in the Research Laboratories of their subsidiary company I.C.I. (Alkali) Limited.

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