Table 5. *Experimental atomic scattering factors*

$\sin\theta/\lambda$	Hg	Cu
0·1	78·0	28·5
0·2	71·0	24·0
0·3	58·6	18·0
0·4	40·8	12·5
0·5	38·5	8·4
0·6	22·0	7·5

doubt that the stereochemistry of the $[Hg(SCN)_4]$ $[Cu(en)_2]$ structure is essentially what we have described it to be.

I wish to express my thanks to Prof. J. D. Bernal for providing working facilities and for his continued encouragement, and to Dr C. H. Carlisle for his close supervision and valuable advice throughout the course of the work. Grateful acknowledgements are made to Prof. W. Wardlaw, Prof. C. A. Coulson, Dr D. C. Bradley and Dr A. D. Booth for valuable discussions. I am also indebted to the British Council for the award of a scholarship which enabled me to undertake part of this work.

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Anomalous Lattice Constants of Zinc Oxide

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(*Received* 9 *March* 1953)

Samples of zinc oxide examined by X-ray diffraction were found to exhibit (1) axial ratios 1 part in 5000 lower than normal, and (2) significant discrepancies in the lattice spacings determined from different reflexions. The same samples exhibited abnormal electrical conductivities.

With a view to explaining the observations, two hypothetical lattice distortions were considered. It was found that a small change in the nominally 120° angle of the hexagonal cell could be confused with a change in axial ratio, and that changes in the nominally 90° angles together with mutual translations of the atoms could explain the discrepancies in the lattice spacings. Certain samples changed from 'regular' to 'anomalous' behaviour after exposure to the atmosphere, thus suggesting a possible cause for the phenomenon.

Introduction

In a recent report on a series of measurements of the lattice constants of zinc oxide (Rymer & Archard, 1952) it was mentioned that certain samples, excluded from the results given, behaved in an anomalous fashion; for example, their axial ratios fell considerably below the average value, and the lattice spacings deduced from various reflexion planes appeared markedly different, even when the effects of absorption

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in the specimen were taken into consideration. As zinc oxide may be regarded as a convenient standard substance for precision measurements, it is desirable that these effects should be understood, so that 'anomalous' samples may be detected and excluded.

The purpose of this paper is to describe the behaviour observed, to correlate it with other abnormal properties of the samples, and to suggest a possible explanation.

Experimental procedure

A 19 cm. powder camera kept at a constant temperature of 20±0·2° C. was used to determine the lattice spacing a and axial ratio C (= c/a) of samples of zinc oxide. The uncertainty in a due to camera calibration and temperature measurement should not exceed 1 part in 10^5. Between eight and seventeen clearly resolved Cu $K\alpha_1\alpha_2$ doublets were measured on each film.

Method of calculation

Interplanar spacings d_{hkl} may be deduced from the Bragg angles of the various reflexions. In the case of cubic crystals, the lattice spacing a would be immediately calculated from a knowledge of the indices hkl, according to the equation

$$a = d_{hkl}(h^2+k^2+l^2)^{\frac{1}{2}} . \qquad (1)$$

The effects of absorption in the specimen would then be removed by plotting the apparent values of a deduced from (1) against a suitable function of the Bragg angle and extrapolating to 90°; according to Bradley & Jay (1932), this function is $\cos^2\theta$, but more recently Nelson & Riley (1945) have demonstrated the advantages of using the function

$$\tfrac{1}{2}(\cos^2\theta/\theta+\cos^2\theta/\sin\theta) . \qquad (2)$$

In the case of hexagonal crystals such as zinc oxide, the apparent values of a cannot be deduced directly from the values of d_{hkl} as the connecting equation takes the form

$$a = d_{hkl}((4/3)(h^2+k^2+hk)+l^2/C^2)^{\frac{1}{2}} = f.d_{hkl} , \qquad (3)$$

in which the axial ratio C is not known. The difficulty may be removed in various ways, for example that of Cohen (1935) or that of Butler (1946). In the present work a modification of the latter method was used, as follows. First, a reasonable value for the axial ratio C was assumed; apparent lattice spacings a were then calculated from equation (3). These were plotted against the function (2), and the variance of the least-squares straight line through them was calculated. The assumed value of C was then altered until a minimum variance was obtained; in effect, this involved adding to the apparent values of a certain quantities $aA\delta C$, where

$$A = (df/dC)/f = -l^2/f^2C^3 . \qquad (4)$$

Observations

For most of the samples examined, the foregoing procedure led to good straight-line extrapolations, but for a few samples it was not possible to straighten the extrapolations by the addition of functions of the form $A\delta C$; there was, however, a considerable improvement if quantities of the form $(A+pA^2)\delta C$ were added, p generally being of the order of 2. This may be seen in Fig. 1, in which the residuals of the extrapolations

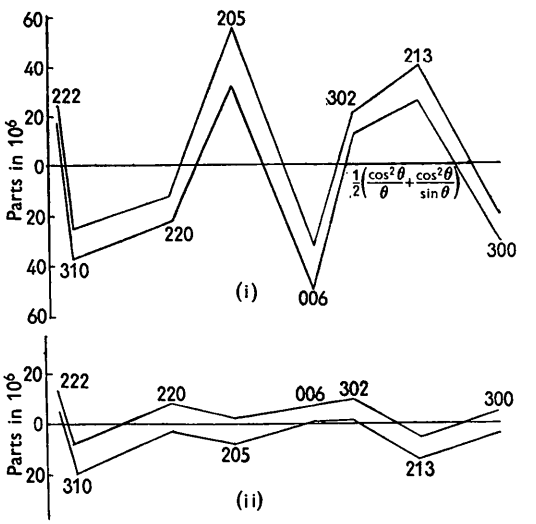

Fig. 1. Residuals of the straightest extrapolations averaged over nine 'anomalous' samples (i) by using function A, (ii) by using A and A^2.

of minimum variance are averaged for a group of nine 'anomalous' samples, first as obtained by the use of the function A only, then as obtained by the use of A together with A^2. The distances between the lines represent twice the standard deviations of the groups of residuals, from which it is clear that the effect is in no way due to random errors in measurement. By inclusion of A^2, the mean variance has been reduced from 760 to 46 units.

It was decided to investigate whether the 'anomalous' samples were abnormal in any other way. To this end, a cylindrical condenser was constructed and made to form part of a resonant circuit. Samples of zinc oxide were employed as 'dielectric', and their conductivity and its temperature coefficient were found by a resonance method (Hartshorn, 1942). The samples examined contained small quantities of cadmium, and it was found that the axial ratios and conductivities of the regular samples were linear functions of cadmium content. On the other hand, 'anomalous' samples had conductivities of the order of 50% higher than their cadmium content would have predicted had they been 'regular'. More striking was the comparison of temperature coefficients of conductivity: Fig. 2 shows that the 'regular' samples of low cadmium content had a small negative coefficient, whereas the

'anomalous' samples, though low in cadmium content, had extremely high positive temperature coefficients.

It seemed desirable to discover whether a 'regular' sample could be made 'anomalous' both in respect of

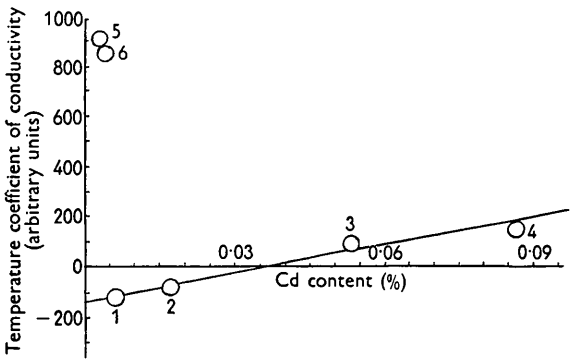

Fig. 2. Temperature coefficient of conductivity *v.* cadmium content. Samples 1, 2, 3, 4 were 'regular', samples 5, 6 were 'anomalous'. Diameters of circles indicate estimated error.

conductivity and axial ratio. This was achieved as follows. It had been the practice to fill specimen tubes in a manipulating box under dried nitrogen, afterwards sealing the tubes with wax. A container of a sample which had already been examined was left open to the air for some hours. Fresh specimens taken from it were found to have changed their characteristics in both respects (Table 1).

Table 1

	Earlier	Later
Axial ratio	1·602186 1·602262	1·601989 1·601972
Temperature coefficient of conductivity	−125	325

The same change in axial ratio was exhibited by another sample when loaded under nitrogen which had not been dried, but in this case conductivities were not measured (Table 2).

Table 2

	Loaded in dry N_2	Loaded in damp N_2
Axial ratio	1·602163 1·602203	1·601987 1·601964

Several samples were made in the laboratory from zinc arcs: two in particular were prepared in very carefully dried oxygen, while two others were made with the minimum of precautions in the open air. The results were as shown in Table 3.

Table 3

	Made in dry O_2	Made in damp air
Axial ratio	1·602335 1·602429	1·601700 1·601720

The correlations summarized in Tables 1, 2 and 3 supplement the evidence of Fig. 1 in attesting to the real existence of the reported discrepancies, and point very clearly to the probability of their being associated with atmospheric contamination.

A distortion theory

If the zinc oxide were contaminated in such a way as to distort its lattice, there might well be expected to follow (1) changes in electrical conductivity, and (2) anomalous lattice constants. Hypothetical lattice distortions will now be examined with a view to discovering what effect they would have on the appearance of the extrapolations.

(*A*) Consider the effect of a small change in the angles of the unit cell. The cell would become triclinic, though still nearly hexagonal. The centres of the lines corresponding to the 24 cooperating planes of a hexagonal lattice would move slightly apart. If the movement were not sufficient to resolve the separate lines, the centre of the compound line might appear to shift. Rymer has shown (private communication) that the recorded position of a compound line would always be the mean of the positions of its components weighted by their intensities.

Now for a triclinic lattice with spacings a, b, c and angles λ, μ, ν we have

$$d_{hkl} = \frac{(1-\cos^2\lambda-\cos^2\mu-\cos^2\nu+2\cos\lambda\cos\mu\cos\nu)^{\frac{1}{2}}}{(\Sigma(h/a)^2\sin^2\lambda-2\Sigma(kl/bc)(\cos\lambda-\cos\mu\cos\nu))^{\frac{1}{2}}} = \frac{1}{\varphi_{hkl}} . \quad (5)$$

Differentiate φ_{hkl} with respect to the angular parameters and then insert the values for a hexagonal lattice, namely $\lambda = \mu = 90°$, $\nu = 120°$. The mean of these may be written

$$\partial f/\partial\lambda = \partial f/\partial\mu = 0 ,$$
$$\partial f/\partial\nu = f(1/2\sqrt{3})(C^{-1}+A)C . \quad (6)$$

This means that the effect of a change in the nominally 120° angle is to a first order the same as that of a change in axial ratio, save for a constant added to all the points of the extrapolation. If such an angular shift exists and the ordinary extrapolation procedure is followed, abnormal values of axial ratio will be found. Numerically, if the nominally 120° angle differs from normal by 1′, the axial ratio will appear to have changed by 1 part in 10,000. For comparison it may be noted that the final 'regular' axial ratio deduced by Rymer & Archard (1952) was 1·60220 ±0·00004, whereas the 'anomalous' axial ratios were of the order of 1·6018 or 1·6019. Again, the value obtained by Bunn (1935) was 1·6020±0·0001, and it may be noted that Bunn did not record taking precautions against contamination by the atmosphere.

On the other hand, changes in the nominally 120° angle do not explain extrapolation discrepancies. The same may be said of the nominally 90° angles—to a

first order—for the lines move symmetrically and the centre of the compound line stays fixed (equation (6)). To a second order the 90° angles would have an effect, for if the values of $\partial^2\varphi/\partial\lambda^2$, $\partial^2\varphi/\partial\mu^2$ are calculated they are found to contain A^2 terms. However, insertion of numerical values shows that if these are required to explain the extrapolation discrepancies the angular shift must be so large that the lines due to cooperating planes would be resolved.

(*B*) The zinc oxide lattice may be considered to comprise two interpenetrating hexagonal lattices bearing zinc atoms, and two others bearing oxygen atoms. The separations of corresponding atoms in the two lattices may be expressed in terms of the cell sides as $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. Now suppose that the two lattices are shifted with respect to one another so that the separations of corresponding atoms become $(\frac{2}{3}+x, \frac{1}{3}+y, \frac{1}{2}+z)$. At the same time, let the angles be distorted as before. Then it may easily be shown that the two kinds of distortion interact to produce instead of A^2 an extrapolation discrepancy of the form:

$$M \propto f^2(1+AC)A \cdot \frac{\cos(2\pi|k-h|/3)\cos\pi l}{1+\cos(2\pi|k-h|/3)\cos\pi l}. \quad (7)$$

This function has very nearly the form $A+CA^2$ for the eight reflexions chiefly considered in the present work, namely 300, 213, 302, 006, 205, 220, 310, 222. Fig. 3 shows the result of using A and M to straighten

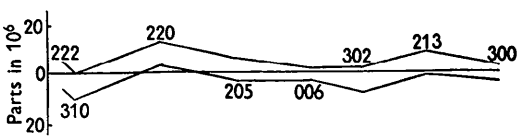

Fig. 3. Residuals of the straightest extrapolations averaged over nine 'anomalous' samples (same as in Fig. 1), using A and M.

the extrapolations of the same group of films as those considered in Fig. 1. For comparison the variances are:

With A only	760 units
With A and A^2	46
With A and M	13

However, in the case of the 204 reflexion the sign of M changes, so that it predicts a discrepancy in a sense opposite to that predicted by $A+CA^2$. In the 204 therefore lies a crucial test to distinguish between the theories. The 204 was a very faint line, but could be measured on good films. Extrapolations were carried out with the eight former reflexions together with the 204. This time the variances were:

With A only	2380 units
With A and A^2	2370
With A and M	45

distinctly favouring the M function.

For comparison, the results of nine 'regular' samples are set out in Fig. 4. It will be noticed that the use of

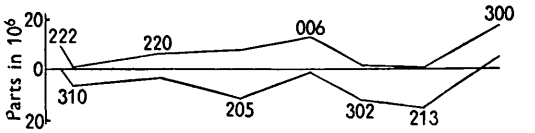

Fig. 4. Residuals of the straightest extrapolations averaged over nine 'regular' samples, using A only.

the M function has reduced the final variance of the 'anomalous' group rather below that of the 'regular' group, i.e. 13 as compared with 30 units.

Calculation shows that a change in the lattice angles of 4′ together with values of x, y and z of the order of 0·1 would explain the extrapolation discrepancies without appreciably separating the cooperating reflexions.

Conclusion

The real existence of 'anomalous' samples of zinc oxide has been demonstrated, and it has also been shown that a certain kind of lattice distortion (M) would produce extrapolation discrepancies of the form observed. The theory is not regarded as final, but it may well form a starting point for the understanding of the discrepancies.

The existence of the discrepancies is not without importance, for they show that the lattice constants of zinc oxide can only be regarded as reproducible if certain chemical precautions are taken—in particular, that the sample be kept at all times away from atmospheric air.

I wish to thank Prof. R. W. Ditchburn for laboratory facilities, Dr T. B. Rymer for constant encouragement and many helpful discussions, Amalgamated Oxides (1939) Ltd for supplying samples of specially prepared zinc oxide, and the Department of Scientific and Industrial Research for a grant operative at the time when the observations were made.

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