

Remeasurement of the Structure of Hexagonal ZnO

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The X-ray scattering pattern of hexagonal ZnO at 298°K, within a reciprocal lattice hemisphere of radius $(\sin \theta)/\lambda = 1.02 \text{ \AA}^{-1}$ containing the polar c^* axis as diameter, was measured with PEXRAD. The integrated intensities of 374 reflections, resulting in 141 independent F_{meas} , were determined. The structure was refined by the method of least squares: the final agreement index R was 0.0378. The sole position parameter is $u = 0.3825 \pm 0.0014$. The predicted value is 0.3799, obtained from the measured c/a ratio of 1.602107 and assuming equal Zn–O distances in the ZnO_4 tetrahedra. The characteristic Debye temperature θ , in isotropically vibrating ZnO, is 370°K. The absolute configuration of the ZnO_4 tetrahedra is such as to present a triangular oxygen face normal, directed from the face, toward the positive sense of the piezoelectric polarization as induced by a compressive stress applied along the polar axis. The piezoelectric coefficients are predicted to have a small temperature dependence.

Introduction

Hexagonal zinc oxide was among the very first crystals to be analyzed by X-rays (Bragg & Bragg, 1915), and the resulting description of the crystal structure was in terms of two interpenetrating hexagonal lattices. Numerous investigations of this crystal structure have been made subsequently, of which the most recent appears to be a neutron powder study by Nitts, Papulova, Sosnovskaya & Sosnovskij (1964). The single position parameter u (Zn is at 0,0,0 and O is at 0,0, u) was given by this study as 0.374. An ideal value of $\frac{2}{3}$ is expected for a true tetrahedral nearest-neighbor atom environment around each atom in a unit cell having $c/a = 2\sqrt{2}/\sqrt{3} = 1.63299$.

Among the various relationships between structure and physical properties in polar crystals (see, for example, Abrahams, Kurtz & Jamieson, 1968) one that has not previously been experimentally determined is that between applied electric field and the resulting atomic displacement. By the use of the X-ray method for such a determination, the atomic positions in zero applied electric field should be known with high accuracy. The simple structure of hexagonal zinc oxide, together with the availability of large high purity single crystals (Kolb & Laudise, 1965), led to the present remeasurement and redetermination preparatory to an investigation of the above relation.

Crystal data

Zinc oxide, ZnO. Formula weight (F.W.) = 81.369. Hydrothermally grown, Li⁺-doped (10 p.p.m. Li⁺), crystals with dimensions 20 mm along a and 6 mm along c were available (Kolb & Laudise, 1965). Hexagonal, with lattice constants of $a = 3.249858 \pm 6$ and $c = 5.206619 \pm 2 \text{ \AA}^\dagger$ at 298°K (Barns, 1968), using

[†] In this, and subsequent numerical values, errors listed without decimal points correspond to the least significant digits in the function value.

$\lambda(\text{Cu } K\alpha_1) = 1.540562 \text{ \AA}^*$. Volume of unit cell = $47.622830 \pm 9 \text{ \AA}^3$. $D_m = 5.642 \pm 12 \text{ g.cm}^{-3}$ (measured with a large crystal of regular shape), $D_x = 5.6730 \text{ g.cm}^{-3}$, for 2 F.W. per unit cell. Absorption coefficient for Mo $K\alpha_1$ X-radiation is 25.1 mm^{-1} ; for the sphere used, $\mu R = 2.811$. $F(000) = 76 e$.

The only reflections systematically absent, $hh0l$ for $l = 2n + 1$, taken in conjunction with the piezoelectric properties of hexagonal ZnO, are consistent with the early (Aminoff, 1921) space group assignment of $P6_3mc - C_{6v}^4$.

Experimental

A sphere of hexagonal ZnO of radius $0.112 \pm 3 \text{ mm}$ was ground from a large pale-yellow crystal grown by Kolb & Laudise (1965). The sphere was mounted on a Pyrex capillary of 0.163 mm external diameter and 0.085 mm internal diameter, with an a^* axis parallel to the capillary axis. All measurements of the integrated intensities were made with this sphere, by use of our programmed electronic X-ray automatic diffractometer, PEXRAD (Abrahams, 1962, 1963). The basic experimental conditions have been described elsewhere (Abrahams & Bernstein, 1965; Abrahams & Reddy, 1965): the profile through each reciprocal lattice point was measured, for each member of the balanced pair of filters, at 118 values of ω differing successively by 0.03°. A total of 374 reflections were thus measured, with Mo $K\alpha$ radiation.

Structure factors (F_{meas}) together with the corresponding standard deviations (σF_{meas}) were computed directly from the PEXRAD magnetic tape output, by use of programs similar to those of Cetlin & Abrahams (1963). The integrated intensities were corrected for Lorentz and polarization factors and for absorption. Twenty F_{meas} values, derived from integrated intensities with values less than three standard deviations based only on counting statistics, were omitted from the refinement procedure but are included in Table 1 and marked with an asterisk. Reflections for which the

difference in structure factor magnitude between pairs of a form exceeded ten per cent were excluded from all subsequent calculations. The constant term for the variance due to systematic isotropic sources of error (Abrahams, 1964) was $52 \times 10^{-4} (F_{\text{meas}})^4$. A correction for extinction was made by Zachariasen's (1963) method, the parameter C having a value, on the absolute scale, of 0.793×10^{-5} . The resulting maximum change in F_{meas} is 14.9 per cent, for $F(110)$. The final 141 independent values of F_{meas} and σF_{meas} used in this study are contained in Table 1 on the least-squares derived absolute scale ($K=0.01858$).

Refinement of the structure

The method of least-squares was used to refine the structure of zinc oxide, the initial model being taken with $u=\frac{2}{3}$ and an isotropic temperature factor of 1 \AA^2 for both zinc and oxygen atoms. Busing, Martin & Levy's *ORFLS* (1962) program was used for this calculation. Mean atomic scattering factors for neutral Zn and O were taken from *International Tables for X-ray Crystallography* (1962), after correction to the Zn form factor had been made for dispersion, caused by use of Mo $K\alpha$ radiation, by means of Cromer's (1965) values of $\Delta f'$ and $\Delta f''$.

The initial model thus contained four parameters: the single scale factor, u , B_{O} and B_{Zn} . With the parameter values chosen above, and a scale factor that placed the F_{meas} essentially (within 2 per cent) on the absolute scale, the corresponding value of R was 0.179. Four cycles of least-squares refinement sufficed to reduce changes in each of the four parameters to less than 1 percent of a standard deviation. The final atomic coordinates and temperature factors for ZnO are given in Table 2. The weights used in all refinement are $wF_{\text{meas}} = 1/\sigma^2 F_{\text{meas}}$. The accuracy indicators are given by

$$R=0.0378; wR=0.0518; S=0.865,$$

where R is the usual reliability index based on F_{meas} , wR is the related weighted index and S is the standard deviation of an observation of unit weight, *i.e.*,

$$[\sum (|F_{\text{meas}}| - |F_{\text{calc}}|)^2 / \sigma^2 F_{\text{meas}}] \div (m-n)^{1/2},$$

where m is the number of observations and n is the number of parameters.

Table 2. Final atomic coordinates and temperature factors for ZnO at 298°K

	x	y	z	B
Zn	0	0	0	$0.63 \pm 2 \text{ \AA}^2$
O	0	0	0.3825 ± 14	0.68 ± 7

The corresponding anisotropic motion model contains six variables: the scale factor, u , $\beta_{11}(\text{Zn})$, $\beta_{33}(\text{Zn})$, $\beta_{11}(\text{O})$ and $\beta_{33}(\text{O})$. Symmetry requires that $\beta_{11} = \beta_{22} = 2\beta_{12}$ and that $\beta_{13} = \beta_{23} = 0$ for both Zn and O atoms. The accuracy indicators for the final refined-anisotropic model are:

$$R=0.0378; wR=0.0512; S=0.861.$$

The hypothesis that the atomic motion in ZnO at 298°K is anisotropic rather than isotropic may be tested by use of Hamilton's (1965) \mathcal{R} -ratio. The dimension of this hypothesis is 2, and $\mathcal{P}_{135,2,0.005} = 1.039$. The experimental value is $0.0518/0.0512 = 1.012$. The hypothesis may thus be rejected at the 0.005 significance level. The thermal motions of the Zn and O atoms in ZnO at room temperature may hence be regarded, with confidence, as isotropic.

The standard deviation of an observation of unit weight provides an unbiased indicator of the original estimates of σF_{meas} and of the correctness of the final model. The calculated value of S that would only be exceeded in one per cent of replications of the present experiment, assuming a normal distribution, ranges from 1.155 to 0.848. This range includes the experi-

Table 1. Measured and calculated ZnO structure factors at 298°K†

h	k	l	I_{meas}	σI_{meas}	I_{calc}	h	k	l	I_{meas}	σI_{meas}	I_{calc}	h	k	l	I_{meas}	σI_{meas}	I_{calc}						
0	0	4	26.9	1.2	27.7	3	-1	4	8.6	0.5	6.7	4	-2	8	0.5	7.8	4	-2	8	10.2	0.7	9.8	
0	0	-4	27.1	1.2	28.0	3	1	5	12.9	0.8	12.4	4	0	3	13.7	0.8	13.2	4	-2	-8	10.3	0.7	9.7
0	0	6	23.5	1.0	21.0	2	0	9	6.9	0.5	7.2	3	-1	5	16.9	0.7	16.5	4	-4	4	5.1	0.3	5.2
0	0	-6	13.4	1.0	20.2	2	0	-9	7.1	0.5	7.0	3	1	-5	12.3	0.7	12.6	4	0	4	5.4	0.5	5.3
0	0	8	13.4	0.9	15.8	2	2	0	23.0	1.2	22.3	3	-1	-5	16.6	0.9	16.8	4	0	-4	4.9	0.4	5.4
0	0	10	3.3	0.6	9.5	2	2	2	18.2	1.7	18.3	3	1	6	5.7	0.4	5.5	4	0	5	11.6	0.7	11.0
1	1	0	48.5	1.6	46.8	2	-2	2	15.9	0.9	16.3	3	-1	6	7.3	0.5	7.2	4	0	-5	10.9	0.7	11.2
1	1	2	36.2	2.1	35.7	2	-2	-3	25.3	1.2	26.7	3	-1	-6	6.6	0.5	6.9	4	0	6	5.4	0.4	5.0
1	-1	2	21.9	1.0	22.1	2	2	4	13.0	0.8	12.7	3	-1	7	9.6	0.6	9.6	4	0	-6	4.7	0.3	4.7
1	-1	3	33.1	1.4	36.2	2	-2	4	10.3	0.7	10.3	3	1	7	7.6	0.5	7.7	4	0	7	7.4	0.5	6.7
1	1	4	21.8	2.2	22.0	2	-2	5	20.2	1.3	19.6	3	1	-7	7.6	1.0	8.2	4	0	-7	7.0	0.5	7.2
1	-1	-5	25.5	1.2	24.6	2	2	6	11.2	1.1	11.6	3	-1	-7	10.4	0.7	10.2	4	2	0	6.1	0.4	5.5
1	1	6	17.5	1.0	17.6	2	-2	6	3.1	0.6	8.3	3	-1	8	5.6	0.4	6.0	4	2	1	7.0	0.5	7.4
1	-1	6	10.1	0.6	9.8	2	-2	7	11.3	1.2	11.0	3	-1	-8	6.2	0.4	5.9	4	-2	-1	1.5*	0.07	0.07
1	1	7	13.6	1.8	12.8	2	2	8	10.5	0.9	9.8	3	-1	9	6.9	0.5	6.3	4	2	-1	6.8	0.5	7.1
1	1	8	13.4	0.8	13.9	2	-2	8	6.6	0.6	6.7	3	-1	-9	6.5	0.5	6.1	4	-2	1	1.4*	0.04	0.04
1	-1	8	7.9	0.7	7.5	2	2	-9	8.2	0.6	7.0	3	3	0	9.4	0.6	11.5	4	2	2	5.0	0.4	4.5
1	-1	9	8.1	0.7	8.0	3	1	0	11.2	0.7	10.5	3	-3	-1	0.7*	0.07	0.07	4	-2	2	17.9	0.9	18.3
2	0	0	23.5	1.5	20.9	3	-1	0	15.9	1.0	16.0	3	-3	2	20.1	1.0	22.0	4	2	-2	4.8	0.4	4.7
2	0	-1	27.6	1.2	26.1	3	-1	1	21.4	1.1	20.9	3	-3	-2	9.5	0.6	10.0	4	-2	-2	18.0	0.9	19.0
2	0	1	27.6	1.2	26.7	3	-1	-1	19.6	2.4	20.3	3	-3	3	1.4*	0.08	0.08	4	2	3	8.6	0.6	8.3
2	0	2	17.4	0.9	16.2	3	1	-1	14.0	0.8	13.7	3	-3	4	14.4	0.8	14.9	4	2	-3	8.0	0.6	7.9
2	0	-2	17.8	0.9	16.6	3	1	1	14.5	0.8	14.2	3	-3	5	11.8	0.8	12.6	4	2	0	6.1	0.4	5.5
2	0	3	27.3	1.3	27.3	3	1	-2	9.0	0.6	8.9	3	-3	-5	1.8*	0.06	0.06	4	-2	3	1.7*	0.05	0.05
2	0	-3	27.4	1.3	26.8	3	-1	-2	13.3	0.8	13.1	3	-3	6	12.6	0.8	13.0	4	-2	4	12.8	0.8	12.7
2	0	4	10.9	0.7	10.2	3	-1	3	23.2	1.1	21.8	3	-3	7	2.2*	0.04	0.04	4	-2	-4	12.1	0.7	12.9
2	0	5	20.1	1.0	19.7	3	1	3	15.7	0.9	15.3	3	-3	-7	2.2*	0.04	0.04	4	-2	5	2.3*	0.04	0.04
2	0	-5	20.7	1.0	20.0	3	-1	3	20.8	1.0	21.3	3	-3	8	11.3	0.7	11.2	4	-2	-5	2.4*	0.04	0.04
2	0	6	9.5	0.6	8.3	3	1	-3	14.6	0.8	14.9	4	0	0	9.9	0.6	9.0	4	-2	6	11.8	0.7	11.6
2	0	-6	4.1	0.6	7.9	3	1	4	6.7	0.5	6.0	4	-2	6	12.3	0.7	12.0	4	-2	-6	10.8	0.7	10.9
2	0	7	10.7	0.7	11.1	3	-1	4	8.6	0.6	8.4	4	0	1	11.4	0.7	11.6	4	-2	7	2.3*	0.04	0.04
2	0	-7	11.6	0.7	11.6	3	-1	-4	6.0	0.6	6.1	4	0	2	7.6	0.5	7.4	4	-2	-7	2.6*	0.04	0.04

† Standard deviations in the measured structure factors are given under σF_m . Unobserved values are marked with an asterisk.

mental value of 0.865, indicating the goodness-of-fit to be acceptable at this level.

Characteristic temperature of zinc oxide

Since the thermal vibration of the Zn and O atoms in ZnO at 298°K are isotropic and are not significantly different, the characteristic temperature θ may be computed under the assumption that the optic modes of vibration make a negligible contribution to the value of M in the expression:

$$M = (6h^2T/mk\theta_M^2) \left[\varphi(x) + \frac{x}{4} \right] (\sin^2\theta/\lambda^2)$$

where the various terms have their usual meaning (e.g. see James, 1948). With this assumption (Batterman, 1964), m is taken as the average mass of an atom in the unit cell. For $\bar{m} = 40.685$ and $\bar{B}_{298^\circ\text{K}} = 0.640 \text{ \AA}^2$, the characteristic temperature $\theta = 370^\circ\text{K}$. This value of θ may be too high owing to the presence of a possible but uncorrected thermal diffuse scattering component in the measured structure factors. We have found only two other estimates of θ for ZnO in the literature: a value of 355°K based on electron diffraction experiments (Ehrhardt & Lark-Horovitz, 1940) and 416°K based on a room temperature mean sound velocity of 3.186 kmsec⁻¹ (Robie & Edwards, 1966). The latter value is the elastic Debye temperature: it would be of interest to have a value of θ based on calorimetry for further comparison.

Interatomic distances and angles

The atomic coordinates given in Table 2 were used, together with the lattice constants given under *Crystal data*, to derive the interatomic distances and angles listed in Table 3. These quantities, and the corresponding standard deviations, were computed using Busing, Martin & Levy's (1964) ORFFE program. Corrections have been made neither for the effects of atomic motion on the interatomic distances and angles, nor for such effects on their standard deviations.

Table 3. *Interatomic distances and angles in ZnO*

Zn-O	= 1.992 ± 7 Å [1]*
Zn-O	= 1.973 ± 2 [3]
Zn-Zn	= 3.209 ± 1 [3]
Zn-Zn	= 3.250 ± 1 [4]
O-Zn-O	= 108.1 ± 0.2 ° [3]
O-Zn-O	= 110.8 ± 0.2 [3]

* The value in square parentheses is the number of distances or angles per tetrahedron.

Discussion

In this section, the absolute configuration of the atomic arrangement is related to the polarization of the ZnO crystal under compressive stress, a brief discussion is given of the crystal structure and the characteristic Debye temperature of zincite, and the temperature

dependence of the parameter u is considered. The absolute configuration in a crystal with polar c axis may be determined by comparison of $F(hkl)$ with $F(hk\bar{l})$ terms, if measurable anomalous dispersion is present. The sense of the polar axis adopted in the *Refinement* section resulted in the position parameter $u = 0.3825$, with $wR = 0.0512$. For the opposite polarity, given by $u = 0.3825$, $wR = 0.0630$. The hypothesis that the opposite choice of polarity is correct may be conveniently tested using Hamilton's \mathcal{R} -ratio, for which $\mathcal{R}_{137,1,0.005} = 1.030$: the experimental ratio is 1.230, hence the hypothesis is rejected. Heiland, Kunstmann, & Pfister (1963) have shown that the (00 $\bar{1}$) face develops a positive charge and the (001) face a negative charge under compressive stress along [001], on the assumption that $u = \frac{3}{8}$ *. The tetrahedron of oxygen atoms about each zinc atom is thus oriented so that the normal from Zn to the triangular face which is perpendicular to the polar axis is directed toward the positive dipole end formed under compressive stress along [001], as shown in Fig. 1. An identical absolute orientation has been found for the oxygen tetrahedron surrounding a germanium atom in Bi₁₂GeO₂₀ (Abrahams, Jamieson & Bernstein, 1967). A simple explanation applicable to the present case was given for Bi₁₂GeO₂₀ to account for the absolute dipole sense in terms of the distortions produced within the tetrahedron on compression. Heiland *et al.*, and also Mariano & Hanneman (1963) have pointed out that the (00 $\bar{1}$) face on ZnO may readily be distinguished from the (001) face by its more rapid etching behavior in strong acids.

The recent investigation of the atomic arrangement in ZnO by Nitts *et al.* (1964) was based on nine lines observed by use of a neutron powder diffractometer. By minimizing R as a linear function of u , a best fit was obtained for $u = 0.374$. The uncertainty in this result was not stated, but it may be noted that this value differs from that given in Table 2 by 6.1 of our standard deviations.

The ZnO structure type embraces over twenty binary compounds, a fact that lends additional value to a careful remeasurement of its structure. Each atom in ZnO is tetrahedrally coordinated to four nearest neighbors of the other atomic kind, with two independent distances per tetrahedron. These distances become identical if $4a^2 = (12u - 3)c^2$. For the 'ideal' value of $u = \frac{3}{8}$, equality in these distances requires $c/a = 2\sqrt{2}/\sqrt{3}$. In ZnO, $c/a = 1.602107$, and the value of u hence must be 0.3799 if the two distances are equal. The actual value (see Table 2) is 0.3825 ± 14 , or 1.9 standard deviations greater. The two Zn-O distances in ZnO (Table 3) differ by 0.018 Å, or 2.4 pooled standard deviations.

* From the coordinates in Table 2, we calculate $F^2(002)/F^2(00\bar{2}) = 0.967$ for Cu $K\alpha$ radiation, compared with the value observed by Heiland *et al.* (1963) of 0.96. Similarly for $F^2(006)/F^2(00\bar{6})$, we calculate a ratio of 1.059 for Cu $K\alpha$ and 1.076 for Mo $K\alpha$, compared with observed values of 1.03 and 1.06 respectively.

Table 4. Zn-O distances in 4-, 5-, and 6-coordination (in Å)

Compound	Coordination			Reference
	4	5	6	
ZnO	1.978	—	—	This work
Zn(acetylacetonate) ₂ ·H ₂ O	—	2.015	—	Montgomery & Lingafelter (1963)
Bis(salicylaldehyde)ethylenediamine Zn·H ₂ O	—	2.00	—	Hall & Moore (1960)
ZnMoO ₄	—	2.025	2.078	Abrahams (1967)

The average Zn-O distance in tetrahedral coordination may be compared with the distance found in higher coordination, given in Table 4. It may be seen that each increase in coordination by unity causes an increase in the Zn-O distance by about 0.05 Å.

The characteristic Debye temperature θ of 370°K found in the present investigation provides a useful potential measure by which the accuracy of the F_{meas} may be assessed. Many of the systematic errors, to which sets of F_{meas} are liable, may be compensated for by least-squares fitting of the temperature factors. The only literature θ values for ZnO are 355°K and 416°K; measurement by alternative physical methods, at 298°K, would permit assessment of the magnitude of such systematic error, including that due to thermal diffuse scattering.

A recent note by Khan (1968) gives values of a and c for ZnO over the approximate temperature range 300–900°K. Khan's lattice constants, on correction for thermal expansion, agree with Barns' (1968) values to within one pooled standard deviation. The parameter u calculated from Khan's lattice constants, by the method above, appears to have the very small temperature dependence of $7.25 \times 10^{-7} \text{K}^{-1}$. On the assumption that the piezoelectric dipole originates in the tetrahedral environment of oxygen atoms about the zinc atom, we may predict that the small temperature dependence of u will also correspond to a small temperature dependence in the piezoelectric coefficients, particularly for d_{33} . Measurement of the ZnO piezoelectric coefficients, as a function of temperature, is now in progress (Spencer & Smith, 1968).

Note added in proof:—Soon after this paper had been accepted for publication, we learned that a single-crystal neutron diffraction investigation of BeO and ZnO had been completed by T. M. Sabine and S. Hogg (submitted to *Acta Cryst.*). The values reported therein for the ZnO parameters are: $u = 0.3826 \pm 7$, $B_{\text{O}} = 0.55 \pm 8 \text{Å}^2$ and $B_{\text{Zn}} = 0.31 \pm 6 \text{Å}^2$. The agreement with the results of the present paper are excellent for u and B_{O} : however the B_{Zn} values differ by 5.1 pooled standard deviations. Accepting the two values as from the same population, the mean (based on the stated standard deviations) becomes $B_{\text{Zn}} = 0.60 \text{Å}^2$.

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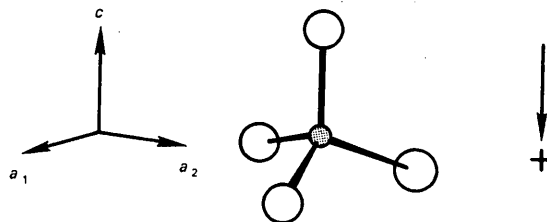


Fig. 1. Absolute spatial relation of a ZnO₄ tetrahedron to the electric dipole induced by compressive stress applied along [001].

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