An Experimental Study of the Anomalous Scattering of Mo Kα Radiation by Single Crystals of ZnO

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The relationship between the bond structure and lattice distortions found in the light-atom wurtzite-type structures, BeO and AlN, prompted a similar investigation for ZnO. Here the X-ray analysis failed on account of a quantitative discrepancy between the experimental data and those calculated using Hönl's corrections for anomalous scattering. The form of these discrepancies and the experimental measurements upon which they are based are described. The extension of Hönl's theory to the case where there is more than one anomalous scattering atom in the primitive unit cell is discussed. The concept of the anomalous crystal structure factor is introduced.

Introduction

Zinc oxide is a wurtzite-type structure with a c/a ratio of 1·600, as compared with the ideal value of 1·633, and a u parameter generally assumed to be close to 0·375. Previous studies with X-ray and electron diffraction techniques by Yearian (1935), Johnson & Nordheim (1937), Ehrhardt & Lark-Horovitz (1940), and Johnson (1940), have sought to explain discrepancies between the theoretical and experimental intensities in terms of an ellipsoidal distribution of valence electrons in the ZnO bonds. More recent work by Jeffrey, Mozzi & Parry (1956) and by Keffer & Portis (1957) on the lighter-element wurtzite-type structures, BeO and AlN, has shown that there is a correlation between the departure from the ideal c/a ratio and the u parameter. Since any interpretation of the X-ray or electron diffraction data in terms of electron-density distributions, which did not take into account the precise value of the u parameter and the thermal-motion parameters, was likely to lead to erroneous conclusions, this present investigation originated in an attempt to use the modern technique of single-crystal structure analysis to determine these parameters more precisely. That this attempt was unsuccessful was due to an unexpected divergence between the experimental observations and the anomalous scattering effects predicted from the theoretical treatment of Hönl (1933). The purpose of this paper is to report the experimental work upon which these observations were based and the nature of this divergence with the current theory.

The experimental measurements

Small colorless untwinned crystals of ZnO, elongated about the hexagonal axis and hexagonal in cross-section, were obtained from specimens supplied by the St Joseph Lead Company, Pa., U.S.A. All the crystals used in this investigation were 0·5–1 mm. long and less than 30 microns in diameter. The intensity measurements were made on a General Electric XRD-3 or XRD-5 diffractometer equipped with a prototype single-crystal orienter. Mo K radiation was used with an aluminum filter placed in front of the proportional counter. The reflections were scanned using the θ, 2θ coupling of the diffractometer at the rate of 0·2° min.$^{-1}$. The integrated intensities were obtained from a linear speedomax record by planimetry of the area under the peak after background subtraction. During the course of the investigation the intensities of fifty reflections were measured in addition to those given in Table 1 from which the direct comparison of hkl with $hk\bar{l}$ was obtained.

From an analysis of the intensity measurements of equivalent reflections (with the same sign in l) and the correlation of results from different crystals, it was found that the standard deviations for each measurement varied from 1·3% for medium and strong intensities (which included 65% of all measured intensities) to 5% for the weakest intensities.

The lattice parameters of the crystals were checked and gave

$$a = 3·250 \pm 0·001, \quad c = 5·207 \pm 0·001 \text{ Å}, \quad c/a = 1·602$$
$$(\text{Mo } K\alpha_1, \ \lambda = 0·7093; \ \text{Mo } K\alpha_2, \ \lambda = 0·7135 \text{ Å}),$$

in agreement with the more precise values of Archard (1953).

The corrections for anomalous scattering

On the short wave side of the absorption edge the atomic scattering factor is given by

$$f = f° + \Delta f' + i\Delta f'' . \tag{1}$$

For the scattering of Mo $K\alpha$ radiation by the Zn K electrons ($\lambda/\lambda_k = 0·555$), the values of $\Delta f'$ and $\Delta f''$ predicted by Hönl (1933) and tabulated by James (1954) are 0·21 and 1·31. The latter correction term, although small compared with $f°$ at small $\sin \theta/\lambda$, is by no means always negligible since theoretically

Table 1. *Experimental and theoretical data for $\Delta I/I$*
for two crystals of ZnO

Crystal diameters 29·4 and 28·1μ; Mo $K\alpha$ radiation

Crystal No. 1

				$\Delta I/I$ (%)	
hkl	2θ (°)	I for $\varphi = 268 \cdot 0°$	I for $\varphi = 88 \cdot 0°$	Exp.	Theor., $u = 0 \cdot 375$
006	48·24	2·360	2·510	6·0	8·2
106	50·68	1·715	1·805	5·0	8·7
116	55·20	1·898	2·049	7·4	9·4
206	57·38	1·220	1·340	9·0	9·8
306	67·62	2·00	2·27	11·9	12·2
406	80·88	0·603	0·680	12·8	21·2
416	90·00	1·555	1·781	6·91	16·9
606	118·42	1·018	1·010	−0·79	20·8
008	66·04	2·325	2·400	3·12	0
108	68·00	1·435	1·595	10·0	0
208	73·78	1·022	1·168	12·5	0
308	83·02	1·340	1·495	10·4	0
408	95·82	0·497	0·558	10·9	0
118	71·88	1·983	2·192	10·5	0
418	105·06	1·914	1·987	3·7	0
0,0,10	85·86	1·93	1·735	11·2	21·4
1,0,10	87·78	0·74	0·57	30·0	22·3
1,1,10	91·32	1·626	1·445	26·4	23·2
2,0,10	93·14	0·487	0·388	25·5	23·9
3,0,10	102·30	1·34	1·21	10·7	27·0
2,2,10	107·96	1·380	1·282	7·6	27·7
4,0,10	115·80	0·387	0·338	13·7	29·7
4,1,10	126·42	1·417	1·198	18·3	32·1
200	29·20	1·376	1·379	0	0
400	60·48	1·765	1·755	0	0
410	70·94	1·881	1·884	0	0

Crystal No. 2

				$\Delta I/I$ (%)
hkl	2θ (°)	I for $\varphi = 181°$	I for $\varphi = 1°$	Exp.
006	48·24	1·6502	1·7978	7·65
306	67·62	2·0330	2·2860	11·10
336	100·98	1·2520	1·2965	3·43
606	118·42	1·069	1·0915	2·0
526	124·02	1·065	1·0815	1·5
0,0,10	85·86	1·9980	1·8450	8·3
1,0,10	87·78	0·6120	0·4600	33·0
3,0,10	102·30	1·3370	1·2125	10·3
338	116·76	1·437	1·4675	2·08

φ is the angle of rotation about the polar axis of the
single-crystal orienter.

$\Delta f'$ and $\Delta f''$ are nearly independent of scattering angle;
for example, at $\sin \theta/\lambda$ of 1·0, $\Delta f''$ is 10% of $f°$ for
zinc. For the oxygen atoms with $\lambda/\lambda_k = 0·03$, the
values of $\Delta f'$ and $\Delta f''$ are negligible over the whole
range of $\sin \theta/\lambda$.

To include the effect of the anomalous scattering
on the crystal structure factors it is usual simply to
introduce the expression for f given in (1) into the
geometrical structure-factor expression.

The reduced structure-factor expression for the
ZnO crystal is

$$A = Mf_{Zn} + f_0 (M \cos 2\pi lu + Q \sin 2\pi lu) \,,$$
$$B = Qf_{Zn} + f_0 (Q \cos 2\pi lu + M \sin 2\pi lu) \,,$$

where

$$M = 1 + (-1)^l \cos 2\pi \{(h + 2k)/3\}$$

and

$$Q = (-1)^l \sin 2\pi \{(h + 2k)/3\} \,. \tag{2}$$

Introducing the complex form of the atomic scattering
for the zinc atoms alone we obtain

$$\Delta F_{hkl} = \frac{2M}{F_{hkl}} [\Delta f'_{Zn} (f_{Zn}^° + f_0^° \cos 2\pi lu) + \Delta f''_{Zn} f_0^° \sin 2\pi lu] \tag{3}$$

if $\Delta f'_{Zn}$ and $\Delta f''_{Zn}$ are small and higher powers can be
ignored. ΔF_{hkl} is the difference between the structure
factors with and without the corrections for anomalous
scattering, and F_{hkl} is the structure factor with l
positive.

Since the correction factors are combined with the
trigonometric functions of the u parameter, their
omission can lead to systematic errors affecting the
determination of u by the usual methods of crystal-
structure analysis. This was particularly obvious in
this analysis. With $u \approx 0·375$, the $hk6$ and $h,k,10$
structure factors are respectively decreased and in-
creased with a small increase in u. Therefore the
systematic trend for the $h,k,10$ data to lie below that
of the $hk6$ reflections in the log $|F_c|/|F_o|$ plot shown in
Fig. 1(a) could be removed by increasing u, as in
Fig. 1(b); (a uniform isotropic temperature, B, has
also been included to remove the slope). Fig. 1(c)
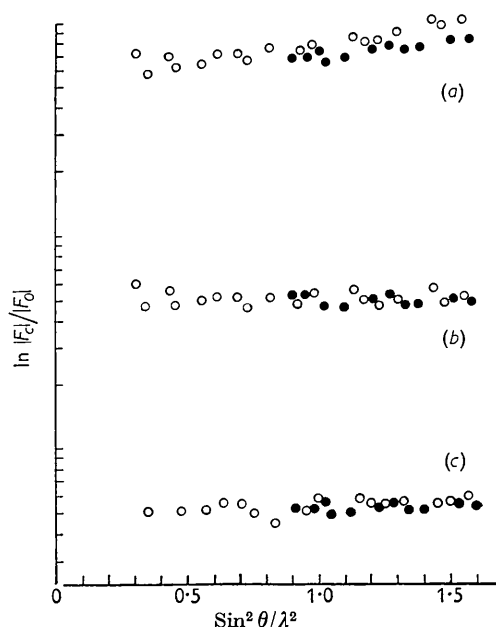shows the same systematic change brought about solely

Fig. 1. Plots of log $|F_c|/|F_o|$ versus $\sin^2 \theta/\lambda^2$ for $hk6$ and $h,k,10$
reflexions of ZnO; Mo $K\alpha$ radiation. Open circles: $hk6$;
closed circles $h,k,10$. (a) $B = 0$, $u = 0·375$; (b) $B = 0·420$
Å², $u = 0·385$; (c) $B = 0·420$ Å², $u = 0·375$, corrected for
dispersion.

by including Hönl's correction factors in the calculated structure factors.

From equation (3), we have

$$F_{hkl}-F_{hk\bar{l}} = \frac{4M}{F_{hkl}}\Delta f''_{\mathrm{Zn}}f^{\circ}_{\mathrm{O}}\sin 2\pi lu \ . \qquad (4)$$

This equation suggested that the comparison of $|F_{hkl}|$ and $|F_{hk\bar{l}}|$ would give a sensitive means for determining u, at the same time providing a more direct experimental check on Hönl's values of $\Delta f''_{\mathrm{Zn}}$. It is more convenient experimentally to measure $(I_{hkl}-I_{hk\bar{l}})/I_{hkl}$, where I refers to the direct relative intensity measurements. Then under the conditions of our measurements, in which the absorption and angle factors for the hkl and $hk\bar{l}$ reflections are equivalent,

$$\frac{\Delta I}{I_{hkl}} = \frac{I_{hkl}-I_{hk\bar{l}}}{I_{hkl}} = \frac{8M}{F^2_{hkl}}\Delta f''_{\mathrm{Zn}}f^{\circ}_{\mathrm{O}}\sin 2\pi lu \ , \qquad (5)$$

ignoring only $\Delta f'_{\mathrm{O}}$ and $\Delta f''_{\mathrm{O}}$.

For particular values of u, $\Delta I/I$ calculated with Hönl's constant values of $\Delta f''_{\mathrm{Zn}}$ rises with increase of $\sin\theta$, as shown by the full lines in Fig. 2. Our experimental measurements diverge significantly from this type of relationship, as shown by the data given in Table 1 and Fig. 2. Up to a value of $\sin\theta/\lambda$ of about 1·0, the $hk6$ data could be fitted to a u parameter between 0·375 and 0·380, but beyond this value the points fall to an apparent minimum at $\sin\theta/\lambda \sim 1·3$, which is quite inconsistent with the theory. With $u = 0·375$, the discrepancy with the theoretical value for the 606 reflections, for example, is about 20% in $\Delta I/I$ and at least five times the standard deviation of the measurements. The $hk8$ data show a maximum and minimum at approximately the same values of $\sin\theta/\lambda$. The $h,k,10$ points appear to oscillate even more rapidly over the limited range of $\sin\theta/\lambda$ which could be observed. In general the discrepancies between the experimental and theoretical values at $\sin\theta/\lambda > 1·0$ were well outside the estimates of the experimental errors, arrived at from the consistency of the intensity measurements from different settings of the same crystal and from different crystals, which agreed within 3% of $\Delta I/I$. It is clearly impossible to determine the u parameter on the basis of this comparison between theory and experiment.

Discussion of the results

A review of the theory upon which the calculated values of $\Delta I/I$ in Table 1 and Fig. 2 are based has shown that the usual method of accounting for anomalous dispersion in a crystal is a poor approximation, except under very special conditions. Calculations making use of a modified atomic scattering factor in the usual crystal-structure formulae, as in equations (1)–(5), are likely to be invalid for two reasons:

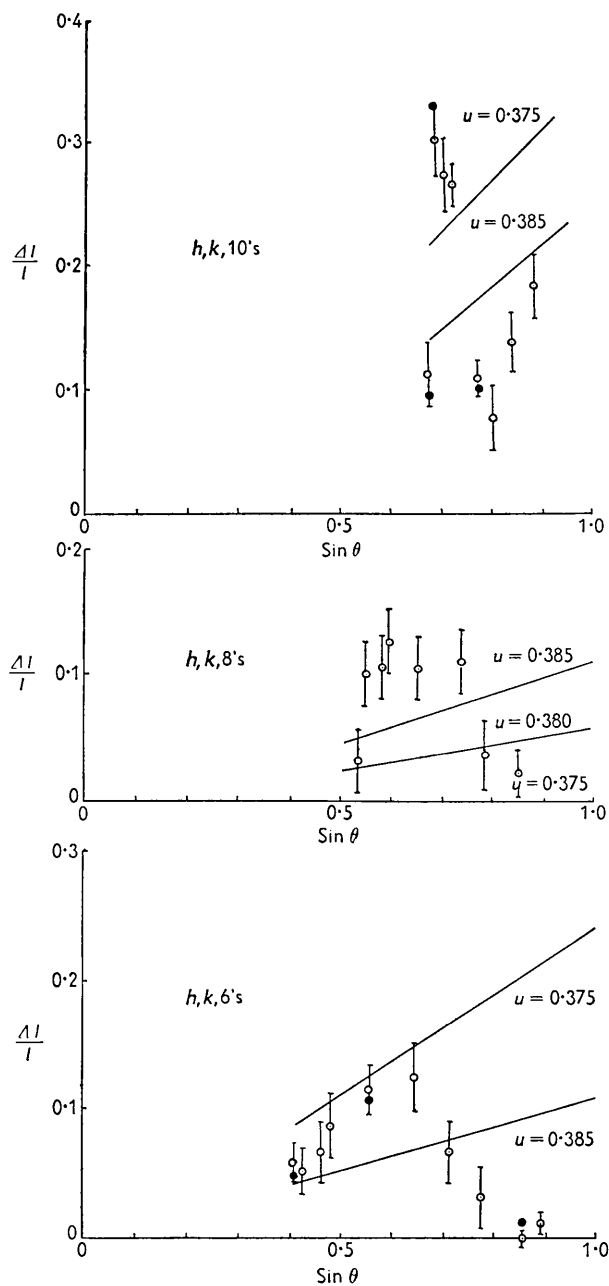(i) Efforts such as Hönl's to produce an anomalous

Fig. 2. Plots of $\Delta I/I$ versus $\sin\theta$ for $hk6$, $hk8$ and $h,k,10$ reflexions for two crystals of ZnO (29·4 and 28·1 μ diameter); Mo $K\alpha$ radiation. Open circles: crystal No. 1; closed circles: crystal No. 2.

atomic scattering factor suitable for all crystals containing a given type of atom appear to have oversimplified the problem. The calculations of anomalous scattering involves a detailed knowledge of the excited electronic state wave functions, which will differ widely from one crystal structure to another. (Conversely the experimental study of anomalous scattering by crystal lattices provides a tool for the exploration of excited electron state wave functions.)

This complication applies to all calculations of $\Delta f'$, and also to $\Delta f''$ if the radiation wavelength is close to the absorption-edge wavelength of the atom.

(ii) When the primitive unit cell* contains more than one anomalously scattering atom, additional details arise which would seem to further limit the use of the concept of the anomalous atomic scattering factor. One must instead directly seek the *anomalous crystal structure factor* instead of finding first the atomic scattering factor and then constructing the crystal structure factor in the usual way.

The second type of failure in the usual theory appears to be the cause of the discrepancies shown in Table 1 and Fig. 2. It is known (e.g. Bouman, 1957) that $\Delta f''$ depends only upon excited states very near where energy would be conserved if the incident photons were absorbed. For the case of Mo $K\alpha$ radiation incident on zinc, these states would be 7·8 keV. above the zinc K absorption edge. It is expected that the crystal lattice potential will have very little effect on such energy states; consequently calculation of $\Delta f''$ should be largely unaffected by the lattice. Hence if the usual concept of the anomalous atomic scattering factor is valid the usual method of calculation should be satisfactory; our experimental observations show clearly that this is not the case.

To study the effect of having more than one anomalously scattering atom per cell, a simplified calculation was carried out comparing the results obtained with one atom and then with two atoms per unit cell. The ground-state wave functions for the K shell of zinc were found by the tight-binding approximation, which should be very satisfactory. The excited-state wave functions were taken as plane waves corresponding to free electrons. This is a very crude approximation for zinc compounds unless the energy is in excess of 5 keV. or so. However, the plane-wave approximation has proven satisfactory to bring out effects of interest, at least in a qualitative way. The calculation was first carried out for one atom per unit cell. Here it is evident that the change produced by anomalous dispersion in the crystal structure factor F is the same as the change in the atomic scattering factor; thus we find

$$\Delta F_1 = \Delta f' + i\Delta f'',$$

where the subscript on F denotes the number of anomalous scatterers per unit cell. The calculation of $\Delta f''$ using plane waves gave 1·52 electrons compared with 1·6 electrons given by Dauben & Templeton (1955) and 1·31 electrons given by Hönl, showing the expected agreement.

A second atom was now introduced in the unit cell at fractional coordinates (x, y, z) relative to the first atom. The usual procedure for calculating ΔF_2 by introducing the complex atomic scattering factor into

the structure-factor formula amounts to the use of ΔF_1 in the usual structure factor formula

$$\Delta F_2(hkl) = \Delta F_1\{1 + \exp[i2\pi(hx + ky + lz)]\}. \quad (6)$$

The calculations using plane waves for the excited state showed this expression to be incomplete. It was found instead that

$$
\begin{aligned}
\Delta F_2 = {} & \Delta F_1\{1 + \exp[i2\pi(hx + ky + lz)]\} \\
& - \exp[i\pi(hx + ky + lz)] \sum_j \cos[\pi(hx + ky + lz) \\
& - 2\pi\mathbf{b}_j\mathbf{R}_0] \int_{V_j} f_1(K_e).dV_{K_e}, \quad (7)
\end{aligned}
$$

where

K_e is the wave vector of the excited state,

$\mathbf{R}_0$ is the vector position of the second atom relative to the first,

$\mathbf{b}_j$ are vectors joining the lattice points of reciprocal space to the origin,

V_j denotes the Brillouin zone in K_e space surrounding the vector $2\pi\mathbf{b}_j$,

$f_1(K_e)$ has both real and imaginary parts and is a function of K_e and the X-ray wave vectors (see Harrison, Jeffrey & Townsend (1957) for details).

The magnitude of the correction terms in (7) which are not present in (6) should be comparable with the first term, judging by the magnitude of $f_1(K_e)$.

No detailed evaluation of these correction terms has been attempted for it is found that the states of small positive energy play a dominant role in their evaluation. With the form of $f_1(K_e)$ based on plane waves, the numerical results would not be reliable. However, if more detailed wave functions had been used, the correction terms would still persist in a more complicated form. These terms would depend upon the crystal symmetry through the vectors $\mathbf{b}_j$, upon the relative positions of the atoms through $\mathbf{R}_0$, and upon the scattering angle 2θ through (h, k, l) and through $f_1(K_e)$. They could therefore give rise to a variation of the anomalous scattering effect with $\sin\theta/\lambda$ such as we have observed experimentally, since in the ZnO lattice there are two Zn atoms in the unit cell. However, it is to be emphasized that the form of (7) was deduced assuming plane waves for the excited electronic states. This cannot be correct for the low-energy states, so the numerical value of the correction terms cannot be found except by a much more elaborate theoretical treatment. The main result obtained from the plane-wave approximation is that additional correction terms in the anomalous crystal structure factor will be necessary. Therefore, knowledge of the anomalous atomic scattering factors (even when corrected for crystal-lattice effects) is likely to be insufficient for deducing the anomalous crystal structure factor when two or more atoms of the

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* Hereafter 'unit cell' will always refer to a primitive unit cell.

anomalous scattering element are present in the unit cell.

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The Crystal Structure of β-Naphthol

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The non-centrosymmetric structure of β-naphthol has been determined with the aid of optical transforms and refined by two-dimensional Fourier methods. Every molecule is attached by hydrogen bonds to two neighbours, and in this way the molecules are linked into chains; adjacent molecules in any chain are crystallographically non-equivalent. Each chain runs throughout the crystal with its length parallel to the *a* axis of the monoclinic unit-cell.

1. Introduction

The crystal structure of β-naphthol has been examined by several research workers. In a paper which includes a review of previous investigations (Hargreaves & Watson, 1957) the authors show that the space group is almost certainly *Ia* and that the unit cell contains two sets of non-equivalent molecules. It was previously assumed that the length of the *c* axis is only half that now established, and that the unit cell contains only one set of equivalent molecules arranged in the space group $P2_1/a$; with these assumptions Kitaijgorodskij (1945, 1947) derived details of the structure of β-naphthol based partly on X-ray evidence and partly on geometrical considerations. The structure determination described in this paper is based wholly on X-ray evidence and confirms that the correct space group is *Ia*.

Wherever possible use has been made of optical-transform methods, and the considerable help afforded by these methods in determining the orientations of the non-equivalent molecules is emphasized in the following sections of the paper.

2. Experimental data

The determination of the space group and unit-cell dimensions are described in the earlier paper (Hargreaves & Watson, 1957) and only the results will be quoted here:

$$a = 8\cdot185 \pm 0\cdot015, \quad b = 5\cdot950 \pm 0\cdot003, \quad c = 36\cdot29 \pm 0\cdot01 \text{ Å};$$
$$\beta = 119° 52' \pm 7'.$$

X-ray data show that the space group is either *Ia* or *I2/a*. Pyroelectric tests and statistical tests on the X-ray intensities indicate that the crystals are almost certainly non-centrosymmetric; this suggests that the centrosymmetric space group *I2/a* should be rejected and that the correct space group is *Ia*. There are 4 equivalent general positions in *Ia* and therefore the 8 molecules in the cell will occupy 2 non-equivalent sets of general positions.

Reflexions *h0l* and *0kl*, recorded in zero-layer-line Weissenberg photographs using unfiltered Cu *Kα* radiation, provided the data from which the final atomic positions were deduced. The intensities of the