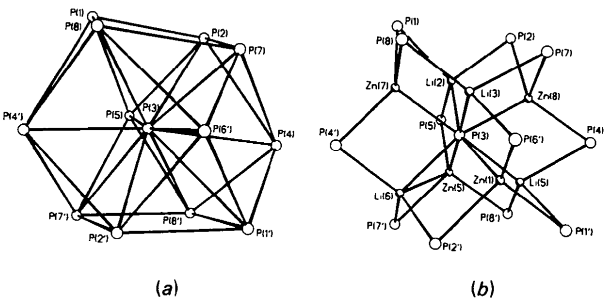

(a) (b)

Fig. 3. (a) Cuboctahedral surroundings of the P(3) atom in the cubic closest packing of PO_4 tetrahedra. (b) Occupation of the tetrahedral voids of the PO_4 packing by Li and Zn.

We are greatly indebted to Dr Müller-Vogt for permitting the crystal growth in his laboratory and to Dr J. Durant for making the SHG test available to us. Special thanks are extended to Professor Dr H. Wondratschek, Professor Dr W. Depmeier, Dr E. Hovestreydt and Dr W. F. Kuhs for fruitful discussions. One of the authors (LE) wishes to thank the DAAD for a grant which made his stay in Karlsruhe possible.

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u Parameters for the Wurtzite Structure of ZnS and ZnO using Powder Neutron Diffraction

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(*Received* 10 *September* 1988; *accepted* 31 *March* 1989)

Abstract. The crystal structures of hexagonal ZnS [$M_r = 97{\cdot}44$, $P6_3mc$, $a = 3{\cdot}8227\ (1)$. $c = 6{\cdot}2607\ (1)$ Å, $V = 79{\cdot}23$ Å^3, $Z = 2$, $D_x = 4{\cdot}08$ Mg m^{-3}, $R_{wp} = 0{\cdot}058$, $R_B = 0{\cdot}017$] and ZnO [$M_r = 81{\cdot}38$, $P6_3mc$, $a = 3{\cdot}2501\ (1)$, $c = 5{\cdot}2071\ (1)$ Å, $V = 47{\cdot}63$ Å^3, $Z = 2$, $D_x = 5{\cdot}67$ Mg m^{-3}, $R_{wp} = 0{\cdot}078$, $R_B = 0{\cdot}012$] at 295 K have been refined by Rietveld analysis of 1·500 (1) Å neutron powder diffraction data containing 50 and 33 independent reflections respectively. Zinc atoms occupy the special position 2(*b*) with coordinates $\frac{1}{3}$, $\frac{2}{3}$, 0. Oxygen and sulfur also occupy special position 2(*b*) with coordinates $\frac{1}{3}$, $\frac{2}{3}$, u. For ZnS, $u = 0{\cdot}3748\ (2)$ and for ZnO $u = 0{\cdot}3817\ (3)$. Both compounds have u and $\frac{c}{a}$ which conform to the known correlation between these parameters. It is shown that this correlation is equivalent to $\frac{uc}{a}$ remaining constant at or near its ideal value $(\frac{3}{8})^{1/2}$. The JCPDS file No. for ZnS is 10-434 and for ZnO is 21-1486.

Introduction. Hexagonal ZnS is the prototype for the wurtzite structure ($P6_3mc$, Zn at $\frac{1}{3}, \frac{2}{3}, 0$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$, and S at $\frac{1}{3}, \frac{2}{3}, u$ and $\frac{2}{3}, \frac{1}{3}, u + \frac{1}{2}$), the high-temperature polymorphic modification of zincblende. Surprisingly, a thorough literature search has failed to reveal a precisely determined value for u which is often taken to have the ideal value $\frac{3}{8}$. A recent NMR study (Bastow & Stuart, 1988) proposed a value of 0·373 for ZnS. In materials with the wurtzite structure, there is an approximately linear relationship between the value of u and the $\frac{c}{a}$ ratio as shown in Fig. 1. This figure has been used to estimate u for ZnS from published $\frac{c}{a}$ ratios. $\frac{c}{a} = 1{\cdot}6407$ (*Handbook of Physics*

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and Chemistry, 1976) gives $u = 0{\cdot}3732$, and $\frac{c}{a} = 1{\cdot}637$ (Lawaetz, 1972) gives $u = 0{\cdot}3742$. Since Rietveld analysis of good high-resolution powder data can provide atomic coordinates to better precision than the scatter of these estimates, it was decided to determine u as accurately as possible so that a good reference value is available.

ZnO has had its u parameter reported as 0·3825 (14) by Abrahams & Bernstein (1969), and 0·3826 (7) by Sabine & Hogg (1969). The ZnO structure was refined to provide a measure of the success of the ZnS determination.

Experimental. The fine ZnS (Leuchstoffwerk GmbH, Heidelberg) powder was supplied, and tested for the presence of non-hexagonal material using X-ray powder diffraction and transmission electron microscopy by CSIRO Division of Materials Science and Technology. The ZnO used was J. T. Baker *ULTREX* (99·9% pure).

The neutron powder data at 1·500 (1) Å fixed wavelength were collected on the High Resolution Powder Diffractometer (HRPD, Howard, Ball, Davis & Elcombe, 1983) at the Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights Research Laboratories. The powders were contained in a rotating thin walled 16 × 50 mm high vanadium can. Intensities were recorded at 295 K as a monitor timed step scan from 0 to 156° 2θ in 0·05° steps. Data from up to eight contributing counters were averaged and given appropriate weight during subsequent refinements. The ZnS pattern contains 50 independent reflections covering the $\sin\theta/\lambda$ range 0–0·652 Å^{-1} whilst that of ZnO contains 33 reflections in the same range.

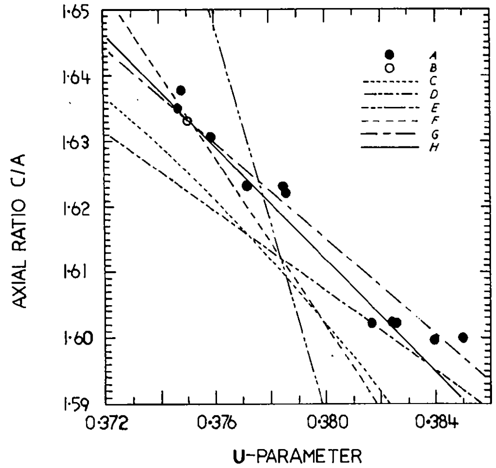

Fig. 1. The u, $\frac{c}{a}$ correlation. (A) All available experimental data including this study; (B) ideal value; (C) curve predicted by the best model of Brown (1967); (D) line predicted by zero electric field at the atom sites, and (E) line predicted by zero electric field gradient due to monopoles (Bastow & Stuart, 1988); (F) line ensuring equal near neighbour distances; (G) prediction of equation 8 of O'Keeffe & Hyde (1978); (H) relation resulting from $\frac{uc}{a} = (\frac{3}{8})^{1/2}$.

The program *LHPM*1 (Hill & Howard, 1986) was used for Rietveld (1969) refinements of the data. A Voigt function was chosen to model the peak shapes as it has been found to be very suitable for this instrument. The half-widths of the Gaussian component are determined by the Caglioti, Paoletti & Ricci (1958) function

$$\mathrm{FWHM}^2 = U\tan^2\theta + V\tan\theta + W \qquad (1)$$

with refineable parameters, U, V and W. The Lorentzian component is given a width $\gamma\sec\theta$ to model particle size effects, where γ is a refineable parameter. A Howard (1982) sum of five peaks asymmetry correction was used with one refineable parameter A. Background was modelled by refining coefficients of the polynomial $B_m\theta^m$ where m has integer values -1 to 3 inclusive. Both the Rietveld (1969) and March model (Dollase, 1986) preferred orientation corrections were used for ZnS. A $(1/\sigma_{\mathrm{obs}})^2$ weighting scheme was chosen and the contribution of calculated peaks was set to zero beyond three half-widths from the calculated positions. The atomic scattering lengths used were $0{\cdot}5680 \times 10^{-12}$, $0{\cdot}2847 \times 10^{-12}$ and $0{\cdot}5805 \times 10^{-12}$ cm for Zn, S and O respectively. Both compounds show negligible absorption of the neutron beam. Refinements were considered to have converged when all parameter shifts were less than 10% of their respective e.s.d.'s.

In all, 11 pattern parameters [scale, zero, four background coefficients, half-width parameters (U, V, W), Lorentzian component width (γ) and profile asymmetry (A)] were refined for both compounds. Calculated FWHM's were checked against the width of individual reflections in the ZnS pattern (measured by fitting Gaussian peaks) and found to be in excellent agreement.

ZnS. The agreement factor R_B of 3·3% after refinement of the unit-cell dimensions, u and individual thermal parameters, was considered unsatisfactory. Tests for the presence of coherently scattering face centred cubic (zincblende) regions, stacking faults and large anharmonic thermal motion failed to account for the observed intensities.

Refinement of a Rietveld (1969) preferred orientation parameter (P) gave a large improvement (R_{wp} $6{\cdot}25 \rightarrow 5{\cdot}78\%$, R_B $3{\cdot}3 \rightarrow 1{\cdot}4\%$) for $(01\bar{1}0)$ orientation and significantly less good results for other orientations. When the March function was used (Dollase, 1986), slightly worse agreement resulted ($R_{wp} = 5{\cdot}84\%$, $R_B = 1{\cdot}7\%$) and the sensitivity to orientation was lessened with (0001), $(10\bar{1}0)$, $(11\bar{2}0)$, $(11\bar{2}1)$ and $(24\bar{6}3)$ all giving equally good results. Orientations like $(11\bar{2}2)$ and $(10\bar{1}1)$ gave poorer fits. The presence of preferred orientation was confirmed by analysis of the relative intensities of various orders of like reflections. It was markedly reduced in a test run when mixed with 44 wt % of Al_2O_3 powder. Structure results quoted are for the March model, which has a sound physical basis, with (0001) preferred orientation as this is a prominent growth face for wurtzite crystals.

Refinements were tested for a false minimum near $u = 0{\cdot}375$ by starting with different u values in the range 0·373–0·377 but convergence back to $u \sim 0{\cdot}3748$ was always rapid. Refined values for all structural and peak shape parameters, their estimated standard deviations and appropriate R values are given in Table 1. A plot of the ZnS refinement result is given in Fig. 2.*

Table 1. *Refined parameters and agreement indices*

Space group $P6_3mc$; Zn, S and O on 2(*b*).

Parameter	ZnS	ZnO
a*	3·8227 (1)	3·2501 (1)
c*	6·2607 (1)	5·2071 (1)
$\frac{c}{a}$	1·6378 (1)	1·6021 (1)
u	0·3748 (2)	0·3817 (3)
B_{Zn} (Å^2)	0·90 (1)	0·55 (2)
B_S, B_O (Å^2)	0·72 (2)	
U	0·046 (2)	0·053 (2)
V	−0·108 (4)	−0·120 (5)
W	0·103 (2)	0·112 (3)
γ	0·033 (1)	0·037 (2)
A	0·145 (3)	0·135 (5)
P	0·966 (2)	Not used
R_p (%)†	4·75	6·53
R_{wp} (%)†	5·84	7·75
R_{exp} (%)†	4·94	6·98
R_B (%)†	1·74	1·21
$(b_{ij})_{max}$‡	73%, a–c	79%, a–c
$(b_{ij})_{max-1}$§	−14%, B_{Zn}–B_S	−4%, a–B

* From Rietveld refinements, affected by neutron wavelength error. $\frac{c}{a}$ is unaffected.

† Defined by Wiles & Young (1981).

‡ Largest structural correlation matrix element.

§ Next largest structural correlation matrix element.

ZnO. Unit-cell dimensions, u and an overall isotropic thermal parameter were refined. Individual thermal parameters could not be refined.† This refinement proceeded directly to a good fit. The final parameters are shown in Table 1.

Discussion. ZnS is known for its many polytypes (153 were reported by Steinberger, Kiflawi, Kalman & Mardix, 1973) and the ease with which the stacking of close packed layers up the c axis becomes disordered (Lawaetz, 1972; Fleet, 1976). Neither extra reflections nor broadening of the reflections with $h - k \neq 3n$ were observed, from which it can be deduced that polytypism and stacking faults are essentially absent from this ZnS sample. Hence the accuracy limiting factor is the preferred orientation correction. Using the Rietveld model with $(01\bar{1}0)$ u was 0·3744. For the March model, u ranges from 0·3746 to 0·3749. The uncertainty in u may therefore be slightly greater than that suggested by the refinement e.s.d. (0·0002).

Stevenson, Milanko & Barnea (1984) and Stevenson & Barnea (1984) have shown that an anharmonic

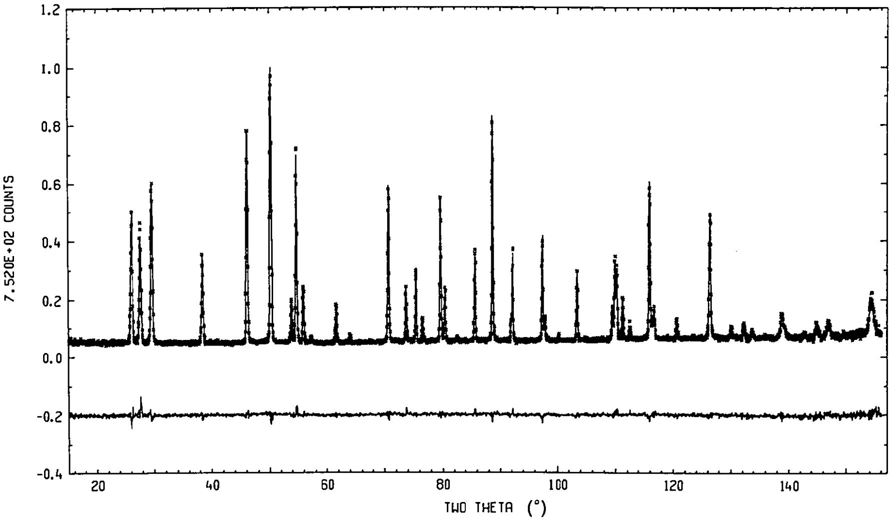

Fig. 2. Rietveld plot of the ZnS refinement. Data points are shown as crosses, the calculated and difference profiles as solid lines on the same scale and reflection markers as vertical bars.

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* A list of numerical values corresponding to Fig. 2 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52402 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The neutron scattering lengths for Zn and O are nearly equal. Isotropic thermal parameters are reported to be very close (Abrahams & Bernstein, 1969). The very low intensities observed for reflections with $l = 4$ confirm this. Structure factor calculations indicate that the other reflections are insensitive to the difference in B_{Zn} and B_O, hence they cannot be refined independently.

model for thermal motion influences the refined value of u for CdS and CdSe. The best models give u values ~0·0003 lower than with no anharmonic thermal motion. With the thermal parameters from our refinement and the known Debye temperature, similar anharmonic effects should be occurring in ZnS. An attempt to detect such anharmonic effects in ZnS using a third order anharmonic model of thermal motion (Whiteley, Moss & Barnea, 1978) was unsuccessful.

The value of u obtained for ZnO (0·3817) is within one combined e.s.d. of the previously published single-crystal X-ray (Abrahams & Bernstein, 1969) and neutron (Sabine & Hogg, 1969) results. High purity ZnO was used and the data showed no evidence of extinction or preferred orientation effects. Polytypism and stacking disorder are not common in ZnO and no evidence for their presence was observed. As ZnO has a higher Debye temperature than CdS and CdSe, the influence of anharmonic thermal motion is expected to be very small and the accuracy of the refined parameters may be taken to be close to that suggested by the refinement e.s.d.'s.

When the results of this study are plotted onto Fig. 1 the agreement to the overall u, $\frac{c}{a}$ correlation is good. The point B is the ideal position [$u = \frac{3}{8}$, $\frac{c}{a} = (\frac{8}{3})^{1/2}$]. The line C used calculated values from the model of Brown (1967) where, in the interionic potential, the repulsive term contains only nearest neighbour (cation–anion) contributions. This model appears to have the correct slope but is displaced negatively by a constant amount. The lines D and E represent the u, $\frac{c}{a}$ relationships which give zero local electric field at the atom sites and zero field gradient due to monopoles as defined by Bastow & Stuart (1988). The line F is simply the locus of u values which would result from the maintenance of equal near neighbour distances. A good fit is given by the lines G and H, where G is from equation 8 of O'Keeffe & Hyde (1978) calculated from bond lengths and non-bonded radii, and H is the empirical constant $\frac{uc}{a}$ [$= (\frac{3}{8})^{1/2}$] discovered during this study. The anharmonic correction to u of 0·0003 would displace the lines horizontally by this amount giving an equally good fit. No successful model for the energy or bonding of these structures which predicts constant $\frac{uc}{a}$ has yet been conceived. The theoretical study of partial polar binding by Kefer & Portis (1957) and subsequent testing by Motida (1983) gives fair agreement between calculated and observed $\frac{c}{a}$ ratios without reference to u values.

The experimentally observed correlation would be more clearly defined if a greater number of structures had experimentally determined u parameters. Lawaetz (1972) reports five measured from 20 binary compounds. Villars & Calvert (1985) contains more than 80, including ternary and quaternary compounds, which have no measured u.

The support of a Commonwealth of Australia – National Research Fellowship (for EK) is gratefully acknowledged.

Many thanks to Dr Tim Bastow and Dr Steven Stuart for providing the ZnS sample and for helpful discussions.

Note added in proof: A recent single-crystal neutron diffraction study of ZnO [J. Albertsson, S. C. Abrahams & Å. Kvick (1989). *Acta Cryst.* **B45**, 34–40] reports $u = 0{\cdot}3819\,(1)$ at 300 K. This is in excellent agreement with our determination.

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