

# THREE NEW POLYMORPHS OF ZINC SULFIDE\*

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## ABSTRACT

Three new polymorphs of zinc sulfide are described. All are related structurally to wurtzite but differ in that they represent stacking sequences of hexagonal closest-packing of higher periodicity than that of the basic wurtzite structure. The latter structure may be designated 2H in the nomenclature of Ramsdell (1947). The new polymorphs correspond to 4H, 6H and 15R, and are isotypic with the corresponding polymorphs of silicon carbide. A tabulation of the crystallographic properties follows.

	Wurtzite-2H	Wurtzite-4H	Wurtzite-6H	Wurtzite-15R
$a_0$	3.811 <i>kX</i>	3.806	3.813	3.822
$c_0$	6.234	12.44	18.69	46.79
$a_0:c_0$	1:1.6358	1:3.268	1:4.902	1:12.242
Cell contents	Zn <sub>2</sub> S <sub>2</sub>	Zn <sub>4</sub> S <sub>4</sub>	Zn <sub>6</sub> S <sub>6</sub>	Zn <sub>15</sub> S <sub>15</sub>
Space group	<i>C6mc</i>	<i>C6mc</i>	<i>C6mc</i>	<i>R3m</i>

The crystals of the several polymorphs are steep pyramidal in habit and are doubly terminated with the basal pinacoid present at the analogous pole only. Parallel intergrowths were observed of 15R with 4H and of 15R with 6H. In physical properties the new polymorphs are identical with wurtzite-2H. The new polymorphs occur as tiny crystals in clay-ironstone concretions embedded at certain horizons in carbonaceous black shale of the lower Conemaugh formation over a wide area in southwestern Pennsylvania and eastern Ohio. Associated minerals are barite, sphalerite, chalcopyrite, pyrite and calcite. The concretions and the minerals therein apparently formed during the diagenesis of the sediment at essentially ordinary conditions of temperature and pressure.

## INTRODUCTION

The writers recently were asked by Mr. David M. Seaman of the Carnegie Museum, Pittsburgh, to identify some tiny but perfectly de-

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veloped hexagonal-hemimorphic crystals found by him and Mr. Howard Hamilton of Vandegrift, Pennsylvania, in clay-ironstone (siderite) concretions from near Shelocta, Pennsylvania. The crystals had the general appearance of wurtzite. Goniometric measurements on one of the crystals, however, afforded angles which deviated somewhat from those expected and it was decided to verify the tentative identification by an  $x$ -ray rotation photograph about [0001]. The photograph revealed the surprising fact that the [0001] period was exactly three times that of wurtzite. 0- and 1-layer Weissenberg photographs around the same axis proved that the lattice was hexagonal and that the length of the horizontal cell edge was identical with that of wurtzite. A study was then made of about 50 crystals available from the original specimens and from a considerable amount of additional material, in part from new localities, that had been loaned by Mr. Seaman and Mr. Hamilton. Three distinct kinds of crystals were found: (1) Crystals morphologically of dihexagonal pyramidal habit with a  $\rho$  angle of  $79^{\circ} 59'$  for the dominant pyramid  $\{10\bar{1}1\}$  and identical with the tripled-cell type of wurtzite mentioned above. Crystals of this type, which comprised about two-fifths of the studied material, are hereafter designated wurtzite-6H. The significance of this nomenclature, in which ordinary wurtzite is designated as 2H, is explained beyond. (2) Crystals morphologically of dihexagonal pyramidal symmetry, and very similar in habit to the preceding kind, but with a  $\rho$  angle of  $75^{\circ} 9\frac{1}{2}'$  for the dominant pyramid  $\{10\bar{1}1\}$ .  $X$ -ray study revealed that these crystals also were based on a hexagonal lattice with the horizontal cell edge identical in length with that of ordinary wurtzite but with the [0001] period doubled. Crystals of this kind, which comprised about three-fifths of the studied material, are designated wurtzite-4H. (3) A very rare kind of crystal of ditrigonal pyramidal symmetry, with a  $\rho$  angle of  $85^{\circ} 53'$  for the dominant trigonal pyramid  $\{10\bar{1}1\}$ .  $X$ -ray study proved the lattice to be rhombohedral, with a horizontal cell edge identical in length with those of wurtzite-2H, 4H and 6H but with a [0001] period  $7\frac{1}{2}$  times that of ordinary wurtzite. This kind of crystal, represented by only four known examples, is designated wurtzite-15R. Two of these crystals proved to be parallel intergrowths of 15R with 4H and 6H.

Wurtzite-4H, 6H and 15R are found to be isotypic with the corresponding polymorphs of silicon carbide, already well known through the work of Ott (1925, 1926), Thibault (1944), Ramsdell (1947) and others. The interfacial angles of crystals of the several wurtzite polymorphs are found to agree to within a few minutes of arc with the interfacial angles of the corresponding silicon carbide polymorphs, although the absolute dimensions of the unit cells of the two groups of substances are of course dif-

ferent. The crystal structures of both the ZnS and SiC polymorphs are based on alternate closest-packed schemes of arrangement of the anions. Both the symmetry and relative dimensions of the various structures have been predicted theoretically by Belov (1939) and Zhdanov (1945) from a consideration of the possible arrangements of equally sized spheres in closest packing. The symmetry of these structures is either hexagonal or rhombohedral with the exception of one special case, the stacking sequence ABC ABC . . . , which is isometric (cubic closest-packing). Ramsdell (1947) has discussed the problem of the nomenclature of the several types of structure, and has recommended a notation comprising a letter, H or R, depending on whether the unit cell is hexagonal or rhombohedral, and a number which states the total number of hexagonally closest-packed individual layers which are stacked within the length of the unit cell. This symbol denotes the type of structure. Within each type, with the exception of the hexagonal four-layer and six-layer types, there are in addition a definite number of possible individual atomic arrangements having the same number of layers but differing in the method of stacking the individual layers. These can be described by the so-called interval sequence or zig-zag sequence of identical atoms as traced vertically in  $\{11\bar{2}0\}$  sections. Types 4H and 6H each have only one stacking sequence; these have the zig-zag notation (22) and (33), respectively, and are represented by known polymorphs in both SiC and ZnS. This system is both nomenclature and classification, and is used for the substances at hand although this represents a departure from the traditional practice of applying given names to minerals.

#### OCCURRENCE AND ASSOCIATION

The wurtzite polymorphs occur in clay-ironstone concretions embedded in black shale of the lower Conemaugh formation of Pennsylvanian age at numerous localities over an area of at least 40 square miles in the general neighborhood of Pittsburgh, Pennsylvania. The original find was made near Shelocta, Indiana County, and eight additional localities were found shortly thereafter. The best of the known localities is in the Baltimore and Ohio Railroad cut at Wittmer, near Etna, Alleghany County. The concretions occur at levels up to twenty feet or more above the Brush Creek limestone of the lower Conemaugh formation. Further collecting activity along the outcrops of this formation will no doubt reveal many additional localities. Recently, the polymorphs have been found in the same geologic horizon near Glouster, Athens County, Ohio, about 125 miles southwest of Pittsburgh. A minor occurrence also has been found in a different horizon at the Wittmer locality, where the concretions have been found immediately above the

Pine Creek limestone which is some 60 to 90 feet over the Brush Creek member. The geology and mineralogy of the occurrences is described in more detail in an accompanying paper by Seaman and Hamilton.

The zinc sulfide polymorphs occur along fractures apparently representing shrinkage cracks in the concretions and generally are solidly embedded in platy white barite. Other associated minerals include calcite, tiny crystals of chalcopyrite and pyrite, and sphalerite both as platy masses and small tetrahedral crystals. The crystals of the polymorphs typically occur as rudely radial aggregates with the acute (antilogous) poles of the individual crystals all pointing inward. All three wurtzite polymorphs occur in immediate association, in fact often side by side or intergrown, and doubtless have crystallized simultaneously. In some instances, the isometric polymorph of zinc sulfide, sphalerite, is also directly associated and in these instances is found to have formed later than the wurtzites. Ordinary wurtzite (2H) was not observed. Both the shale containing the concretions and the Brush Creek limestone are fossiliferous and highly carbonaceous brackish water deposits. The heavy metals present in the concretions are syngenetic with the containing rock. The concretions are believed to have formed on the sea bottom or early in the diagenesis of the sediment. The development of the cracks apparently was a consequence of a process akin to the ageing and syneresis of a colloidal gel, and the concentration and crystallization of the heavy metals as the minerals noted above was a concomitant thereof. The temperatures and pressures existing at this time are presumed to have been close to normal.

#### PHYSICAL AND CHEMICAL PROPERTIES

The three new polymorphs are identical with each other and with ordinary wurtzite in their physical properties. The crystals average about 1 mm. in length and 0.2 mm. across. There is a distinct cleavage on  $\{11\bar{2}0\}$  and traces of a cleavage on  $\{0001\}$ . The color is deep reddish brown to dark brown, and the fine powder is light brown. The luster is brilliant and submetallic on crystal faces and inclines toward resinous on fracture surfaces. The specific gravity of a mixed sample of the 4H and 6H polymorphs weighing 12 mg. was determined on a microbalance as  $4.09 \pm 0.02$ . This value is practically identical with the value 4.087 reported for essentially pure wurtzite. The specific gravities calculated from the measured unit cell dimensions of the several polymorphs on the assumption that the chemical composition is ZnS are given in Table 1. The calculated values vary somewhat between each other due probably to the presence of small and variable amounts of Fe<sup>++</sup> in substitution for Zn with a concomitant variation in cell size.

TABLE 1. X-RAY STRUCTURE CELLS OF CORRESPONDING POLYMORPHS OF ZINC SULFIDE AND SILICON CARBIDE

	Isometric		2H		4H		6H		15R	
	ZnS	SiC	ZnS	SiC	ZnS	SiC	ZnS	SiC	ZnS	SiC
$a_0$	5.400 $kX$	4.349	3.811	3.073	3.806	3.073	3.813	3.073	3.822	3.073
$c_0$	—	—	6.234	10.053	12.44	10.053	18.69	15.079	46.79	37.70
$a_0:c_0$	—	—	1:1.6358	1:3.271	1:3.268	1:3.271	1:4.902	1:4.907	1:12.242	1:12.267
Cell contents	Zn <sub>4</sub> S <sub>4</sub>	Si <sub>4</sub> C <sub>4</sub>	Zn <sub>3</sub> S <sub>2</sub>	Si <sub>4</sub> C <sub>4</sub>	Zn <sub>4</sub> S <sub>4</sub>	Si <sub>4</sub> C <sub>4</sub>	Zn <sub>6</sub> S <sub>6</sub>	Si <sub>6</sub> C <sub>6</sub>	Zn <sub>18</sub> S <sub>18</sub>	Si <sub>18</sub> C <sub>18</sub>
Space group	$F\bar{4}3m$		$C6mc$		$C6mc$		$C6mc$		$S\bar{3}m$	
S.G., meas.	4.084		4.087		4.09					
S.G., calc.	4.090	3.216	4.101	3.217	4.121	3.217	4.099	3.217	4.074	3.217

Sufficient material for a quantitative chemical analysis is not yet available. Qualitative tests show the presence of large amounts of only zinc and sulfur. This fact together with the systematic geometric relations shown to ordinary wurtzite and the identity in physical properties with that substance make it virtually certain that the crystals have the composition  $\text{ZnS}$ . What doubt remains concerns the possible identity with the little-known oxysulfide of zinc, voltzite. The two available analyses of this substance, both very old, indicate the composition  $\text{Zn}_5\text{S}_4\text{O}$ . This formula, which can be interpreted as of an AB-type compound, and the recorded optical and physical properties suggest that voltzite may be isostructural with wurtzite. The measured specific gravity of voltzite is given as 3.66–3.80, which is considerably less than that found for the wurtzite polymorphs. The specific gravity calculated for wurtzite-4H on the basis that one-fifth of the S atoms are substituted for by O, it being assumed that there is no concomitant change in cell dimensions, is 3.43. The possibility also exists that the O substitution is serial, of the nature  $\text{Zn}(\text{S}_{1-x}, \text{O}_x)$  where  $x$  is about 0.2 in the reported analyses of voltzite.

Divalent iron is known to substitute for Zn in natural wurtzite-2H up to at least  $\text{Fe}:\text{Zn}=1:8$ . That  $\text{Fe}''$  is present in the material at hand is suggested by the relatively deep reddish brown color—pure ZnS is colorless—and by the fact that the crystals formed in an environment rich in ferrous iron as evidenced by the occurrence within concretions of siderite,  $\text{FeCO}_3$ . Such a substitution may account for the small but significant variation observed in the cell dimensions and in the specific gravities calculated therefrom on the assumption that the composition is ZnS. These data are summarized in Table 1. This contrasts with the situation in SiC, where it has been shown by Thibault (1944) that the values of  $a_0$  are exactly identical and the values of  $c_0$  exact multiples in the several polymorphs.

#### DESCRIPTION OF THE POLYMORPHS

*Wurtzite-2H and Sphalerite.* Ordinary wurtzite is the prototype of the polymorphs here described and, although it was not identified in our material, its relevant properties may be summarized for purposes of comparison. Both natural and artificial crystals of wurtzite have been repeatedly described from a morphological point of view. Since wurtzite-2H and the 4H and 6H polymorphs belong to the same crystal class and do not differ largely in interfacial angles it might be supposed that crystals of the higher polymorphs have been mistaken in the past for the 2H modification. While several of the early morphological descriptions are not entirely satisfactory, due to the poor quality of the measured crystals, the data indicate that the crystals in all instances were of wurt-

zite-2H. It may be noted, however, that Allen, Crenshaw and Merwin (1912) obtained artificial crystals from the same solution that had very different habits, one long prismatic and another tabular on the base; these may represent different polymorphs but crystallographic data are lacking. The morphological measurements of Friedel (1866) on artificial wurtzite crystals prepared by Sidot (1866) appear to be the best of those available and lead to the ratio  $a:c=1:1.6349$  in the orientation and unit of the structure cell.

The unit cell dimensions  $a_0=3.811 \text{ kX}$ ,  $c_0 6.234$  were obtained by Fuller (1929) by the powder method on wurtzite prepared by heating pure artificial sphalerite with 10% NaCl at  $1100^\circ \text{ C}$ . Comparable but less accurate values have been reported by Aminoff (1923) ( $a_0 3.80$ ,  $c_0 6.23$ ) on natural crystals from Přebram, Bohemia, which probably contained several per cent of Fe and Cd, and by Ulrich and Zachariassen (1925) ( $a_0 3.836$ ,  $c_0 6.277$ ) on material prepared by heating pure artificial sphalerite to  $1100^\circ$ . The specific gravity of wurtzite obtained by heating sphalerite (containing 0.11 per cent Fe) is given as 4.087 at  $25^\circ/4^\circ$  by Allen, Crenshaw and Merwin (1912). A comparable value, 4.0648 at  $25^\circ/4^\circ$ , was obtained by Madelung and Fuchs (1921) on natural material from Přebram. Other values have been reported for natural wurtzite, the highest of these being that of Breithaupt (1863), 4.072, on crystals from Přebram. The Přebram material contains small amounts of both Cd and Fe'' in substitution for Zn. The specific gravity of both wurtzite and sphalerite decreases as the Fe content increases.

The unit cell dimension of the isometric polymorph of ZnS, sphalerite, has been measured repeatedly:

$a_0$ 5.394 kX (Gerlach, 1922)
5.395 (de Jong, 1928)
5.400 (Hartwig, 1926)
5.403 (Braekken, 1934)
5.412 (Chudoba and Mackowsky, 1939)

The best value for the pure or essentially pure compound is probably  $a_0 5.400 \text{ kX}$ , which is close to the average of the reported values. The cell dimensions increase with increasing substitution of Fe for Zn, as shown by Chudoba and Mackowsky (1939) and others. The specific gravity of sphalerite containing 0.11 per cent Fe has been determined as 4.090 at  $25^\circ/4^\circ$  by Allen, Crenshaw and Merwin (1912). Madelung and Fuchs (1921) give 4.0904 and 4.0946 at  $25^\circ/4^\circ$  for unanalyzed natural material from Santander, Spain. On heating, pure sphalerite inverts to wurtzite at about  $1020^\circ \text{ C}$ . The inversion temperature is lowered markedly by the substitution of Fe'' for Zn, and occurs at  $880^\circ$  in material with 17.06 per cent FeO.

*Wurtzite-4H*. When examined under moderate magnification the extreme dissymmetry of crystals of this kind is remarkable (Fig. 1). At one end is a hexagonal pyramid of high inclination which tapers to a sharp point; at the other end is the basal pedion alone, or together with a flat pyramid. On most crystals a prism truncation in zone with the pyramids

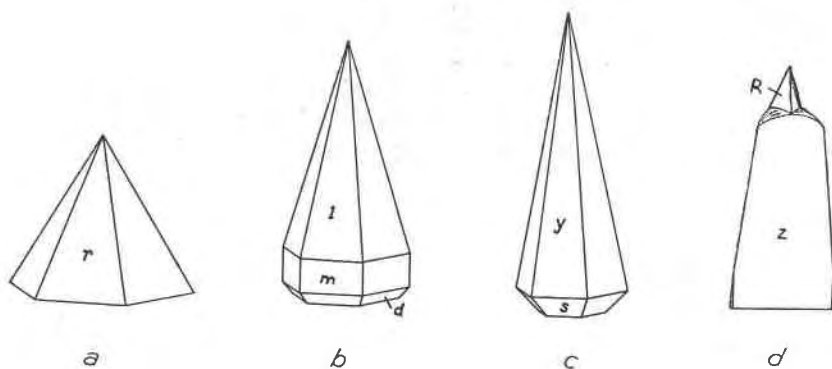


FIG. 1. Typical habit of (a) wurtzite-2H, (b) wurtzite-4H, (c) wurtzite-6H, and (d) wurtzite-15R. Forms: (a)  $r\{10\bar{1}1\}$ ,  $\bar{c}\{0001\}$ ; (b)  $l\{10\bar{1}1\}$ ,  $\bar{d}\{10\bar{1}3\}$ ,  $m\{10\bar{1}0\}$ ,  $\bar{c}\{0001\}$ ; (c)  $y\{10\bar{1}1\}$ ,  $\bar{s}\{10\bar{1}3\}$ ,  $\bar{c}\{0001\}$ ; (d)  $z\{10\bar{1}1\}$ ,  $R\{01\bar{1}3\}$ .

may be seen on the basal edges. The measured two-circle goniometric angles and an angle table derived in the unit and orientation of the structure cell are given in Table 2. Crystals in which the principal axis is polar are conventionally drawn with that end of the axis uppermost which acquires a positive electric charge on cooling or compression—the so-called antilogous pole. The small size of the present crystals precluded such tests and the crystals are here drawn with the steep termination uppermost, this being generally found to be the antilogous pole.

TABLE 2. ANGLE TABLE FOR WURTZITE-4H  
Hexagonal—P; dihexagonal pyramidal— $6mm$   
 $a:c=1:3.268$ ;  $p_0:r_0=3.774:1$

Lower	Upper	Measured $\rho$ angles*	$\phi$	Calculated angles		
				$\rho$	M	$A_2$
$\bar{c}$	0001	—	—	0°00'	90°00'	90°00'
	$m$ 10 $\bar{1}0$	90°00'	30°00'	90 00	60 00	90 00
	$\bar{d}$ 10 $\bar{1}3$	51 53	30 00	51 31	66 57½	90 00
	$l$ 10 $\bar{1}1$	74 59	30 00	75 09½	61 06	90 00

\*  $\{10\bar{1}1\}$  average of 28 faces of medium to good quality on 7 crystals.

$\{10\bar{1}3\}$  average of 4 narrow faces of poor quality on one crystal.



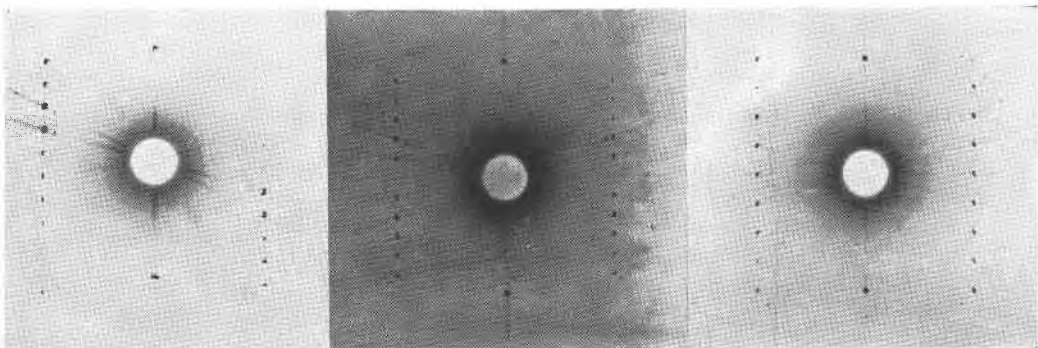


FIG. 2. Precession photographs taken in unfiltered copper radiation around the  $a$ -axis of wurtzite-4H (right), wurtzite-6H (center) and wurtzite-15R (left). The spots on the vertical central lattice lines of the photographs are (0004), (0006) and (000.15), respectively.

X-ray Weissenberg photographs were taken of the 0-levels about both horizontal axes and of the 0-level and 1-level about [0001]. These photographs established the lattice as hexagonal and the centrosymmetrical point group as  $6/mmm$ . The morphology identifies the crystal class as dihexagonal pyramidal,  $6mm$ . The systematic extinctions observed were  $(hh\bar{2}hl)$  present only when  $l=2n$ , corresponding to the space group  $C6mc$ . The unit cell dimensions calculated from high order reflections on the 0-layer photographs are given in Table 1.

The most informative single-crystal photographs of this and of the other polymorphs of ZnS and also of SiC are afforded by the precession method as developed by Buerger (1944). Photographs taken by this method about a horizontal axis reveal the lattice type, whether hexagonal or rhombohedral, and the order number of the first reflection of  $(000l)$  to appear identifies the layer period in the nomenclature of Ramsdell (1947). Reproductions of precession photographs taken around an  $a$ -axis of the 4H, 6H and 15R polymorphs of ZnS are shown in Fig. 2. The separate identity of crystals of the several polymorphs also can be done conveniently by direct comparison of Laue photographs. Drawings of such photographs taken along [0001] in tungsten radiation are shown in Fig. 3. Laue photographs taken in this orientation of the SiC polymorphs have already been published by others, and Weissenberg photographs of the same substances have been reproduced by Thibault (1944) and by Ramsdell (1947).

The present polymorph is shown by its symmetry and dimensional relationships to be of the type designated as 4H, and it is isotypic with the polymorph of SiC originally designated as Type 3 and later termed 4H. While the absolute dimensions of the ZnS and SiC structures are differ-

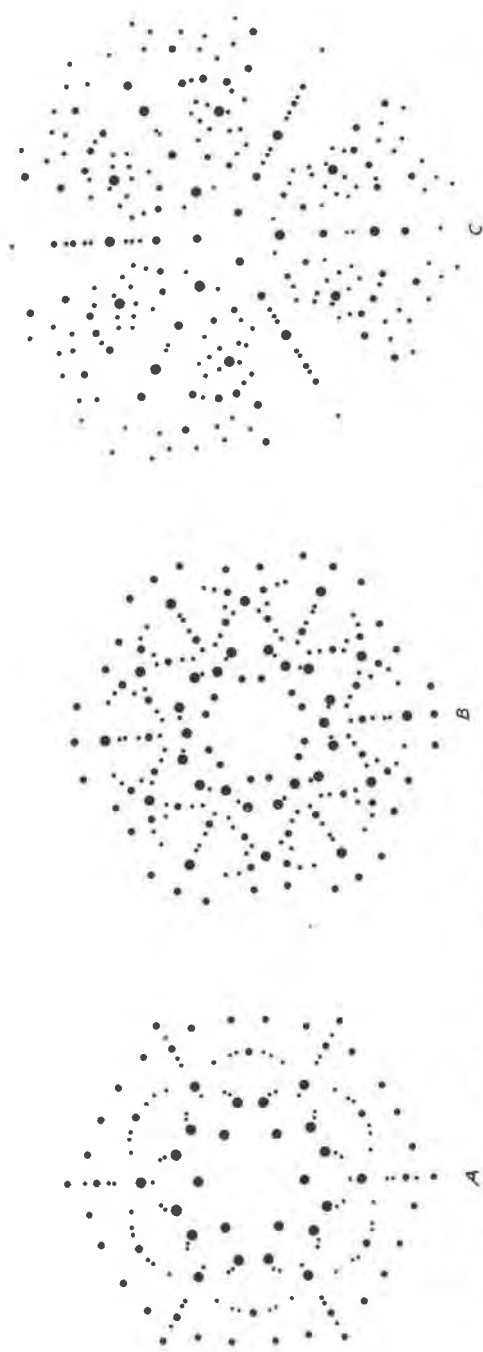


FIG. 3. Drawings of x-ray Laue photographs (W radiation at 45 KV and 10 ma) of wurtzite-4H (left), and wurtzite-6H (center) and wurtzite-15R (right). Taken along [0001].

ent, due to the difference in the size of the atoms involved, the ratios of the cell edges are practically identical and the measured interfacial angles differ by only a few minutes or so of arc. This is true not only of the 4H but also of the 6H and 15R polymorphs of ZnS and SiC. A 2H polymorph has not yet been discovered in SiC.

*Wurtzite-6H.* The crystal habit of this polymorph on casual examination appears to be identical with that of wurtzite-4H, with a steep upper hexagonal pyramid, a negative pedion and a flat negative pyramid. Narrow faces of additional negative pyramids are present on some crystals. Goniometric measurement, however, reveals that the dominant pyramid  $\{10\bar{1}1\}$  is steeper by about  $5^\circ$  than in wurtzite-4H. A typical crystal habit is shown in Fig. 1. The morphological development identifies the crystal class as dihexagonal pyramidal— $6mm$ . The measured two-circle goniometer angles and an angle table derived in the orientation and unit of the structure cell is given in Table 3.

TABLE 3. ANGLE TABLE FOR WURTZITE-6H  
Hexagonal—P; dihexagonal pyramidal— $6mm$   
 $a:c=1:4.902$ ;  $p_0:r_0=5.660:1$

Lower	Upper	Measured $\rho$ angles*	Calculated angles			
			$\phi$	$\rho$	M	$A_2$
$\bar{c}$	0001	—	—	$0^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$
$\bar{o}$	$10\bar{1}6$	$44^\circ 17'$	$30^\circ 00'$	43 20	69 56	90 00
$\bar{n}$	$10\bar{1}5$	47 21	30 00	$48\ 32\frac{1}{2}$	$67\ 59\frac{1}{2}$	90 00
$\bar{s}$	$10\bar{1}3$	62 40	30 00	$62\ 04\frac{1}{2}$	63 47	90 00
$y$	$10\bar{1}1$	79 57	30 00	79 59	$60\ 30\frac{1}{2}$	90 00

\*  $\{10\bar{1}1\}$  average of 78 faces of medium to good quality on 13 crystals.

$\{10\bar{1}3\}$  from one face of poor quality.

$\{10\bar{1}5\}$  average of 10 faces of poor quality on 3 crystals.

$\{10\bar{1}6\}$  average of 7 faces of very poor quality on 2 crystals.

X-ray Weissenberg photographs were taken about both horizontal axes and about the  $[0001]$  axis. These established the lattice as hexagonal and the space group as  $C6mc$ , identical with that of wurtzite-4H and 2H. The lengths of the cell edges are given in Table 1.

*Wurtzite-15R.* Four hemimorphic crystals were found in the course of the study that differed from those of the two hexagonal polymorphs in possessing a marked trigonal habit without trace of the usual hexagonal pyramids. These crystals showed a steep trigonal pyramid above and a broad basal pinacoid below, the lower corners being truncated by minute faces of a negative trigonal pyramid. The upper trigonal pyramid in all

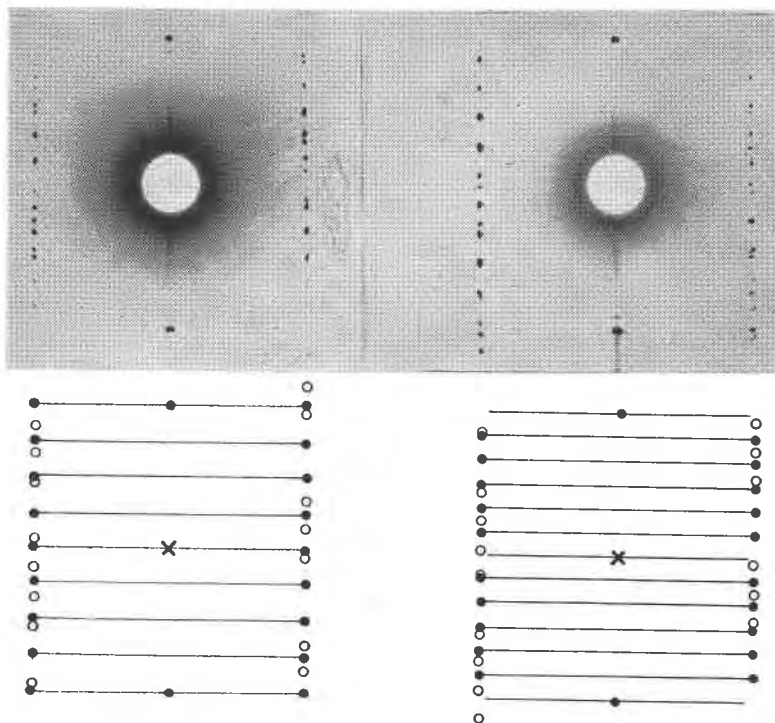


FIG. 4. X-ray precession photographs taken about an  $a$ -axis showing parallel intergrowths of wurtzite-4H and 15R (left) and wurtzite-6H and 15R (right). The  $x$ -ray beam impinged on the boundary between the intergrown parts in each case. Open circles show spots belonging to 15R, solid circles to spots belonging to 4H or 6H.

TABLE 4. ANGLE TABLE FOR WURTZITE-15R  
Hexagonal—R; ditrigonal pyramidal— $3m$   
 $a:c=1:12.242$ ;  $\alpha=13^{\circ}56'$ ;  $p_0:r_0=14.136:1$ ;  $\lambda=119^{\circ}30\frac{1}{2}'$

Lower	Upper	hkl	Measured $\rho$ angle*	Calculated angles			
				$\phi$	$\rho=C$	$A_1$	$A_2$
$\bar{c}$		0001 111	—	—	0°00'	90°00'	90°00'
	$s$	1.1.2.18 765	53°52'	0°00'	53 40 $\frac{1}{2}$	45 45	45 45
$\bar{M}$		1.0.1.13 544	47 42	30 00	47 24	50 24	90 00
	$g$	10 $\bar{1}$ 4 211	74 15	30 00	74 12	33 33 $\frac{1}{2}$	90 00
	$z$	10 $\bar{1}$ 1 100	85 53	30 00	85 57	30 15	90 00
$\bar{h}$		0.1.1.11 443	52 20	-30 00	52 06 $\frac{1}{2}$	90 00	46 53
	$R$	01 $\bar{1}$ 3 441	78 03 $\frac{1}{2}$	-30 00	78 01	90 00	32 06

\* {10 $\bar{1}$ 1} average of 6 faces of good quality.  
 {10 $\bar{1}$ 4}, {1.0.1.13} and {0.1.1.11} all from one face only.  
 {01 $\bar{1}$ 3} average of 3 faces of fair quality.  
 {1.1.2.18} average of 3 faces of very poor quality.

four cases showed a peculiar termination consisting of a deep shelf-like indentation on the vertically trending edges rising from which was a tiny spire-like projection itself bounded by very steep positive and negative trigonal pyramids. The appearance of these crystals is shown in Fig. 1. All four crystals were identical morphologically, although all of the observed forms were not present on each individual. An angle table for the observed forms in the orientation and unit of the structure cell is given in Table 4.

A complete Weissenberg  $x$ -ray study was made of one crystal, the negative or butt end of the crystal being placed in the  $x$ -ray beam. The photographs established the lattice as rhombohedral and the centrosymmetry as  $3m$ . These results were confirmed by both Laue and precession photographs. The crystal class is fixed as ditrigonal pyramidal,  $3m$ , by the morphological development. The space group is  $R3m$  as fixed by the observed characteristic reflections:  $(hh\bar{2}hl)$  present when  $l=3n$ ,  $(hh\bar{0}l)$  present when  $2h-l=3n$ , and  $(hk\bar{l}l)$  present when  $h-k-l=3n$ . The dimensions of the unit cell are given in Table 1. This polymorph is identified by its symmetry and dimensional relations as 15R and is isotypic with the so-called Type 1, or 15R, polymorph of SiC.

It was considered that the spire-like projection at the upper termination of the crystals might represent a different polymorph, intergrown in parallel position perhaps as a core through the main individual. Weissenberg photographs obtained by exposing only the spire in the  $x$ -ray beam, however, proved them to be identical with the main body of the crystal. Two of the crystals showed small inserted areas bounded by surface sutures, quite distinct from the spires, which proved on investigation to be different polymorphs intergrown in parallel position; these are described in the following section.

#### PARALLEL INTERGROWTHS BETWEEN DIFFERENT POLYMORPHS

Two crystals of wurtzite-15R were observed to have small intergrown parts irregularly bounded by surface sutures. Precession photographs were taken so that the  $x$ -ray beam impinged directly on the boundary of the intergrowth. One crystal gave a photograph consisting principally of the pattern of 15R on which was superimposed a system of spots corresponding to an  $a$ -axis precession photograph of a crystal of 6H, as shown in Fig. 4. This crystal thus is a parallel intergrowth of wurtzite-15R and 6H. The other crystal when examined similarly (Fig. 4) proved to be a parallel intergrowth of wurtzite-15R and 4H. Parallel intergrowths between different polymorphs are relatively common with SiC and have been described by Thibault (1944) and Baumhauer (1915). In SiC the surfaces of juncture are planar and parallel to  $\{0001\}$  while in

wurtzite the boundaries are irregular and trend roughly vertically. In the latter instances, at least, it must be presumed that the different polymorphs grew simultaneously.

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