

# STRUCTURE OF ZINC SULPHIDE MINERALS

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## ABSTRACT

The topological relations between cubic and hexagonal tetrahedral structures are reviewed, emphasizing the occurrence of regular and random intergrowths of the two extreme types. An approximate method of measuring the ratio of cubic and hexagonal planes in mixed polytypic structures is derived from integrated intensities of the first two  $x$ -ray diffraction spectra. Application of the method to zinc sulphide minerals indicates a small but variable amount of hexagonal packing in sphalerite and a larger and also variable amount of cubic packing in wurtzite. No example of wurtzite with only hexagonal packing ( $2H$  structure) was found.

## INTRODUCTION

The known structures of crystalline zinc sulphide are closely related: all have the same short range order but different long range order, analogous to the structures of silicon carbide. The bonding is dominantly homopolar and interatomic distances are very nearly the sum of the atomic radii (Aminoff, 1923; Evans, 1939, pp. 157–163; Wyckoff, 1951, p. 29). The tetrahedral coordination of both zinc and sulphur necessitates a rather open framework structure (Evans, 1939, pp. 157–163). The zinc atoms (also the sulphur) are related, one to the other, as are the centres of a close-packed lattice (W. L. Bragg, 1937; Ulrich & Zacharaisen, 1925; Fuller, 1929). In recent years it has been determined that the lattice may be other than cubic (three ZnS layers in the unit cell) or hexagonal (two ZnS layers in the unit cell), and that theoretically there are an infinite number of different packing methods, each with the same  $a$  unit cell dimension, but a unique  $c$  dimension and with a lattice which has partly cubic and partly hexagonal packing (Jagodzinski, 1949*a, b, c*, 1954*a, b*; Ramsdell, 1947; Ramsdell & Kohn, 1952; Zhdanov & Minervina, 1947). Five types of zinc sulphide minerals already have been described (Fron del & Palache, 1950), and at least 10 types have been synthesized by vapour reactions (Strock & Brophy, 1955); in the case of silicon carbide, which has a closely analogous structure, at least 19 types are known. The terminology which has become accepted designates the cubic ( $3C$ ) and hexagonal ( $2H$ ) end members of the series as two polymorphs (*beta* and *alpha*, respectively), and the intervening members as polytypes (Thibault, 1944). Since all of the polytypes have hexagonal or trigonal symmetry, they are said to be polytypes of the hexagonal end member. However it seems to be more consistent to consider all of the cubic, hexagonal, and rhombohedral [trigonal] structural varieties related in the above way to be polytypes of the one scheme of coordination. The term polymorph rather than polytype might be preferred by mineralo-

gists, because each polytype may show a unique crystal morphology, but the general usage is such that we expect a significant density and entropy difference between any two polymorphs of a compound, but these are nearly immeasurably small in the case of polytypes. If mineral names were given to each of the various polytypes of a compound such as zinc sulphide, more than the usual confusion would result. However, if the net morphology is isometric, the mineral could be designated as sphalerite (even if it is a cyclic twin of four or eight rhombohedral or hexagonal individuals, occurrences of which have been described by Ramdohr & Websky (1943), and as wurtzite, if the morphology is rhombohedral or hexagonal. Additional information would be given if the number of ZnS layers per cell and the stacking sequences or ratio of cubic to hexagonal ZnS layers were also indicated in a simple way. The former is now given by a number, followed by *H* or *R* to indicate whether the symmetry is hexagonal or rhombohedral, but this scheme does not define the cubic and hexagonal sequences of ZnS layers. These may be given as Ramsdell-Zhdanov symbols which show the zig-zag sequence on the 11.0 plane, or perhaps preferably as a sequence of Jagodzinski symbols (*h* and *k* for hexagonal and cubic planes), but both are too cumbersome for complex and long *c*-period structures. A useful symbol would be one which would give explicitly the ratio of cubic to hexagonal packing. The derivation of this system and a practical method of determining it quantitatively from *x*-ray data, is described below.

In contrast to theoretical crystal structures, the ZnS minerals can be expected to be imperfect in many ways. In addition to substitution of Fe, Mn, Cd, and many other elements for Zn, and of Se, O, and other elements for S, and defect structures, dislocations, strain effects, lineage structure, inclusions, etc., there are many types of variations of the packing pattern possible, from small departures from the general stacking sequence to random stacking or to syntactic intergrowth of two or more types of wurtzite or even of wurtzite and sphalerite (by analogy with the better known SiC polytypes). It will be apparent that the lower limit of determination of structure of the ZnS polytypes would be on atomic dimensions and thus impractical for mineralogical purposes. Probably if the main stacking periods and the ratio of cubic to hexagonal packing were designated for a macroscopic crystal, the structure of the mineral would be adequately described for most mineralogical purposes.

Although a considerable amount is known about cubic-hexagonal polytypic structures, there are no established relations between the conditions during crystallization and the stacking pattern. That temperature is one control follows from the following facts: 1) cubic SiC is the low temperature form (Humphrey *et al.*, 1952) and it is formed, if at all, in

the outer, cooler, part of commercial SiC electric furnace "pigs," in which various hexagonal and trigonal polytypes (6*H*, 15*R*, 4*H*, 21*R*, etc.) are formed (Thibault, 1944, p. 272); 2) Fuller (1929) synthesized 2*H* ZnS at 1100° C. and substantially cubic ZnS has been synthesized at 940° C. (Swanson & Fuyat, 1953); Müller (1952) synthesized several polytypes of ZnS between 870 and 905° C. The composition of the solutions which deposit ZnS in veins has been said to be a control: the greater the acidity, the greater the probability of formation of wurtzite rather than sphalerite (Allen, Crenshaw, & Merwin, 1912, 1914). However, this relation has recently been seriously questioned, if not invalidated altogether (Corey, 1953) and a complete restudy with structural analysis of the ZnS products is desirable. The composition of (Zn, Cd)S has long been known (from synthesis of phosphors) to be a control over the crystalline form which deposits from water solutions: the greater the Cd/Zn ratio, the lower the probability of formation of the cubic form (Schleede, 1935; Randall, 1937). Allen & Crenshaw (1912) showed that the inversion temperature varies nearly linearly with the Fe/Zn ratio, from 1020° for ZnS to 880° when approximately 29 mol. per cent FeS is in solid solution. Manganese has been reported to have a similar effect (Kröger, 1939, 1940). The data in the literature allow the postulate that temperature is one control, but possibly the composition of the fluid phase from which the crystals are formed, and certainly the composition of the crystals, are modifying controls over the polytype structure. Pressure would have a negligible effect because the packing density of all of the polytypes of the same composition is very nearly a constant.

The identification of the simpler pure polytypes may be carried out by analysis of the crystal morphology (Thibault, 1944), and by *x*-ray and other diffraction methods such as Laue (Fron del & Palache, 1950; Mitchell, 1953), rotation (Fron del & Palache, 1950; Ramsdell, 1944, 1945, 1947; Ramsdell & Kohn, 1951*a*, *b*; Ramsdell & Mitchell, 1953; Jagodzinski & Laves, 1948), and also by the powder technique (Thibault, 1944, 1948; Ramsdell, 1947). When there is no regular stacking period or when a number of periods are present in one crystal, quantitative measurements by the above methods are complex. A number of mathematical analyses of the problem have been made (Wilson, 1942; Hendricks & Teller, 1942; Jagodzinski, 1949, 1954; Méring, 1949; Gevers, 1952, 1954; Paterson, 1952). These solutions predict the degree of broadening and/or displacement of certain reflections as a function of degree of defect of either the cubic or hexagonal limiting structure, but the facts are that if the defect is periodic, all reflections are sharp, and also some reflections occur which are not given by either of the limiting structures. What is needed is a simple method such as the relative intensity of a small num-

ber of  $x$ -ray diffractions which will give directly the ratio of cubic to hexagonal packing (and also the dominant stacking period) so that measurements may be made of natural and synthetic minerals. Data of this kind could be combined with temperature and composition data with the possibility that a thermometric relation might be established.

### STRUCTURE

The structure of all of the ZnS polytypes can be referred to common hexagonal axes, whether the symmetry is lower (rhombohedral) or higher (cubic). The conversion from cubic to hexagonal can be made because the fundamental tetrahedral coordination is almost exactly the same in all of the polytypes. In a regular tetrahedron, the trigonal ratio  $c/a = \sqrt{2/3} = 0.81650$ . The average value of three exact determinations of wurtzite by  $x$ -ray diffraction methods (Ulrich & Zacharaisen, 1925; Fuller, 1929; Swanson & Fuyat, 1953) is 0.8185. Dana (1944) gives 0.8179. These data suggest that the tetrahedron in the hexagonal and trigonal polymorphs is very slightly elongated parallel to  $c$ . Some of the tetrahedral distortion may be due to the temperature of synthesis. Pure ZnS crystallized in the presence of NaCl at 1100° C. has a value of 0.8179 (Fuller, 1929), and at 1200° C., 0.8194 (Swanson & Fuyat, 1953). The 3C type is measurably rhombohedral when formed above 850° C. (Buck & Stroock, 1953). The data suggest that the higher the temperature, the more elongated is the structural tetrahedron parallel to the  $c$  axis. Some of the tetrahedral distortion may be due to solid solution and defect structure. Tucker & Senio (1954) found that when hexagonal boron carbide (BC) develops radiation damage from neutron bombardment, the volume increases due to defects, but while  $a$  increases 0.6%,  $c$  decreases 0.8%. Thus radiation damage in ZnS would be expected to flatten the structural tetrahedron. Large atoms such as Cd in Zn positions in general would be more easily polarized and the tetrahedral angles would be less strongly maintained. Other atoms such as Fe and Mn which have a weaker tendency than Zn to form the tetrahedral configuration of O and S, similarly would allow a larger change in the tetrahedral angles. Ulrich & Zacharaisen (1925) give cell dimensions of greenockite (CdS) which give a tetrahedral  $c/a$  ratio of 0.8115, indicating that the structural tetrahedron is flattened parallel to  $c$  when a larger and more easily polarized atom is in the wurtzite structure. However, since the departure from a regular tetrahedron is smaller than would be detected in most  $x$ -ray diffraction studies, it will be ignored in the following discussion.

Another simplification that can be made is to refer all of the hexagonal planes to a hypothetical one-layer ZnS cell. This gives fractional  $l$

values which, when multiplied by the real number of layers in the  $c$ -period, give rational planes when a whole number results. These "unit layer indices" will be used throughout. On this basis, cubic indices ( $HKL$ ) can be converted to hexagonal ( $hk \cdot l$ ) by the transformation matrix  $\frac{1}{2}\frac{1}{2}0/\frac{0}{2}\frac{1}{2}/\frac{1}{3}\frac{1}{3}\frac{1}{3}$ . Using the tetrahedral relation between  $c$  and  $a$ , the usual formula for calculating the spacing of hexagonal planes can be converted to

$$d = a / \sqrt{\frac{8h^2 + 8hk + 8k^2 + 9l^2}{6}}$$

It would be laborious to calculate the relative intensity of  $x$ -ray diffraction from a large number of planes of all of the possible ZnS polytypes, but sufficiently reliable diffraction data can be built up by analogy, as Ramsdell (1947) and Ramsdell & Mitchell (1953) have indicated. For example, if a  $6H$  type gives a fairly strong reflection from  $10.1/6$ , then another polytype with a similar stacking but with a longer  $c$ -period, such as  $51R$ , will give two or more reflections at nearly the same spacing (*i.e.*  $10.2/17$ ,  $01.3/17$ ). This is shown very well in the Laue and rotation  $x$ -ray diffraction patterns of SiC with a very long  $c$  period of 594 layers (Honjo *et al.*, 1950). Also, since the relative reflecting powers of Zn/S are nearly the same as Si/C, the more extensive SiC data can be used without much alteration, especially at small Bragg angles.

Relative intensities of  $10.l$ ,  $20.l$ , *etc.* can readily be estimated when the atomic positions are shown as a right projection on a plane perpendicular to one of the  $a$  directions (Fig. 1). All of the atoms can be shown, and lie at  $0$ ,  $1/3$ ,  $2/3$ , and  $1$  of the projected  $a$  cell dimension. This projection shows very well the zig-zag sequences of Ramsdell and has the advantage of displaying undistorted  $10.l$  and  $01.l$  plane spacings. For example, it can be shown in this way that for regular polytypes more than half cubic, the plane  $10.0$  extinguishes, but  $10.l$  reflections persist, but with diminishing total relative intensity, to the cubic limit, except  $10.1/3$ ,  $10.2/3$ ,  $10.4/3$ ,  $20.1/3$ , *etc.* which become stronger and remain as cubic reflections ( $111$ ,  $200$ ,  $220$ ,  $311$ , *etc.*) at the cubic limit.

The two end members of the cubic-hexagonal polytypes have repeat periods of 3 and 2 layers (Fig. 1). In the Ramsdell notation, the zig-zag sequences are  $\infty$  and  $1\ 1$ , and in other notations  $ABCABC$ ----- and  $ABAB$ -----, or  $3C$  and  $2H$ , or  $k$  and  $h$ , or  $1.0$  and  $0.0$  cubic, respectively. (In cubic packing, any one layer has nearest neighbor layers which are dissimilar, and in hexagonal packing, these are similar.) The simplest regular polytypes have zig-zag sequences of  $2\ 2$ ,  $3\ 3$ ,  $4\ 4$ , -----, or  $4H$ ,  $6H$ ,  $8H$ , -----, or  $hkkk$ -----,  $hkkhkk$ -----,  $hkkkhkkk$ -----, -----, or  $0.50$ ,  $0.67$ ,  $0.75$ ----- cubic, respectively, in which groups of cubic

layers are separated by hexagonal layers at regular intervals. All of these have hexagonal symmetry and an even number of layers of ZnS in the  $c$  period. The intermediate simple polytypes have sequences such as 1 2, 2 3, 3 4----, or 9R, 15R, 21R,----, or  $h h k$ ----,  $h k h k k$ ----,  $h k h k h k k$ ----, or 0.33, 0.60, 0.71---- cubic, respectively. All of these are rhombohedral and have an odd number of layers of ZnS in the  $c$  period. A rare type of hexagonal intermediate polytype has sequences

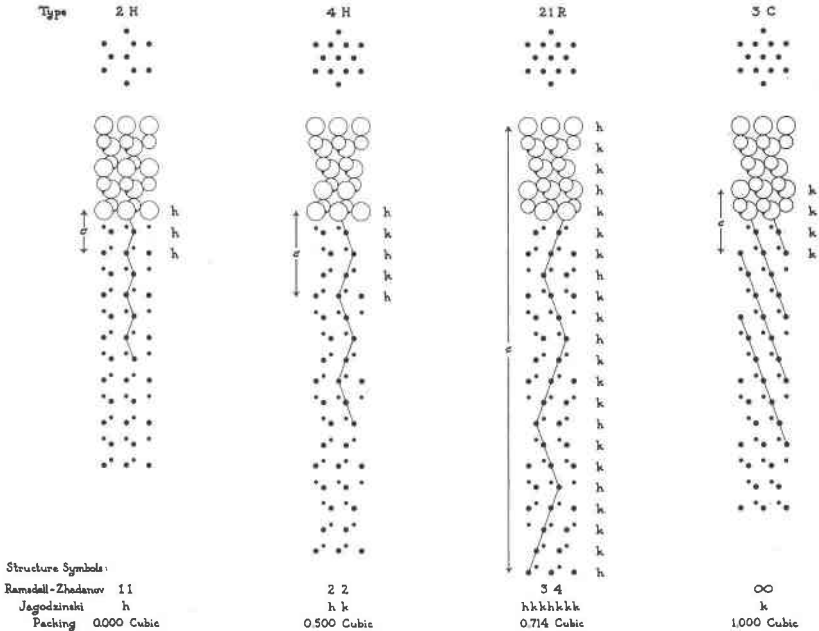


FIG. 1. Schematic representation of the structure of four ZnS polytypes on a plane perpendicular to  $a$ .

such as 2 2 3 3 (10H) (Ramsdell & Kohn, 1951*b*). More complex polytypes are possible and many have been described in the case of SiC, such as 51R, which may be  $3 \times (3 3 3 3 3 2)$  (0.647 cubic) or  $3 \times (2 2 2 2 2 2 3)$  (0.529 cubic) (Ramsdell & Kohn, 1952). In addition, polytypes with imperfect regularity or mixed regularities have been reported (Jagodzinaki, 1949*a, b, c*, 1954; Strock & Brophy, 1955). By extension, it appears possible that crystals of ZnS and SiC could have no regular stacking periods at all. These would not be two-dimensional crystals because they lack a point repetition in the  $c$  direction, since there is a regular layer period. The unit cell, however, would have to be considered to have an infinite extent in the  $c$  direction.

The number of  $x$ -ray diffraction spectra increases with the number of

layers of the  $c$ -period, but when this is very large, or infinite, incomplete resolution gives more or less continuous streaks with greater density near  $10.1/2$ ,  $10.3/2$ ,  $10.5/2$ ,  $20.1/2$ , *etc.*, and other spacings depending on the major  $k$  and  $h$  sequences. Jagodzinski (1949-*c*, 1954) and Strock & Brophy (1955) have suggested that polytypic crystals may have various degrees of regularity of  $c$ -period, so that even if a crystal gives reflections which can be indexed for a  $6H$  type, it may also give streaks and broadened reflections which indicate longer, or infinite  $c$ -periods as well.

Proceeding in the manner indicated above, the spacing of most of the reflecting planes of the simpler polytypes of ZnS were calculated and are shown in Table 1. In this table, no distinction is made between  $10.l$  and  $01.l$ , whereas in the rhombohedral polytypes they are not equivalent. Thibault (1944, pp. 345-346), Ramsdell & Mitchell (1953), and Mitchell (1953) have discussed the extinction conditions of the analogous SiC polytypes.

Considering the hexagonal end member of the ZnS polytypes ( $2H$ ), a calculation of the relative intensity of diffraction by the six 10.0 planes (containing both Zn and S in two planes  $\frac{1}{3}$  or  $\frac{2}{3}$  phase apart) and by the two 00.1 planes (containing Zn in one plane and S in another,  $\frac{1}{4}$  or  $\frac{3}{4}$  phase apart) gave

$$I(10.0)/I(00.1) = 2.04 \pm 0.24.$$

This was arrived at by multiplying together the following factors: structure amplitude factor =  $0.500/0.7365 = 0.679$  for an ideally perfect crystal, but  $(0.679)^2 = 0.46211$  for an ideally imperfect crystal, and 0.606 for approximately  $\frac{2}{3}$  perfection; number of planes factor =  $6/2 = 3$ ; angle factors = 1.12; temperature factor  $\times$  absorption factor = 1. The calculations and assumptions are based on a discussion by Bunn (1945, pp. 195-209). The relative diffracting powers of Zn and S were taken to be 29 and 17 (*i.e.* two valence electrons are shared equally), but the ratio of intensities is not sensitive to small variation of the ratio of diffracting powers. The greatest uncertainty is the relation between intensity and structure amplitude, with 2.28 and 1.55 as the limiting values of the intensity ratio. The choice of value was influenced by the fact that in the case of diamond, also homopolar and structurally analogous, the intensity of diffraction varies as  $F$ , not  $F^2$ . Zinc sulphide, however, is much softer than diamond and probably has a greater amount of mosaic structure. Ulrich & Zacharaisen (1925) calculated the ratio to be  $7.0/4.2 = 1.67$ , and Fuller (1929) calculated it to be  $2.12/1.29 = 1.64$ .

The measured intensity ratios, all on synthetic wurtzite, are 3.3 and 2.0 (Fuller, 1929), 2.1 (Hanawalt *et al.*, 1938), and 1.2 (Swanson & Fuyat, 1953). The average of the four available ratios is 2.1, but since no evidence was presented in any of these determinations that the  $2H$  structure was the only one present, the calculated value (2.04) is preferred.

TABLE 1. ZnS DIFFRACTION SPECTRA

Indices		3.822 ----- = $d$		<i>Polytype Diffractions in Three Degrees of Intensity</i>							
Cubic	Hexag.	$b$		2H	9R	4H	15R	6H	21R	3C	
$hkl$	$hk \cdot l$	$b$	$d(\text{\AA})$	1 1	1 2	2 2	2 3	3 3	3 4		
				.000	.333	.500	.600	.667	.714	1.00	
	10.0	1.155	3.309	—		—					
	10.1/15	1.157	3.302				—				
	10.2/21	1.161	3.293						—		
	10.1/9	1.163	3.287		—						
	10.2/15	1.166	3.279				—				
	10.1/6	1.172	3.261					—			
	10.4/21	1.178	3.244						—		
	10.2/9	1.186	3.223		—						
	10.5/21	1.190	3.210						—		
	10.1/4	1.194	3.202			—					
	10.4/15	1.200	3.187				—				
111	00.1	1.225	3.121	—							
	10.1/3				—						—
	10.8/21			1.245	3.070						
	10.4/9	1.276	2.996		—						
	10.7/15	1.288	2.968				—				
	10.10/21	1.294	2.954						—		
	10.1/2	1.306	2.927	—		—		—			
	10.11/21	1.321	2.894						—		
	10.8/15	1.326	2.882				—				
	10.5/9	1.340	2.853		—						
	10.13/21	1.381	2.768						—		
200	10.2/3	1.414	2.703				—	—	—	—	
	10.11/15	1.462	2.614				—				
	10.3/4	1.475	2.591			—					
	10.1	1.683	2.271	—		—					
	10.11/9	1.890	2.023		—						
	10.25/21	1.905	2.006						—		
	10.5/4	1.916	1.995			—					
	10.19/15	1.934	1.977				—				
220	11.0	2.000	1.911	—							
	10.4/3				—						—
	11.2/7	2.030	1.883						—		
	11.1/3	2.041	1.872		—						
	11.4/7	2.119	1.803						—		
	11.3/5	2.130	1.794				—				
	11.2/3	2.160	1.769		—						
	10.3/2	2.170	1.762	—		—		—			
	11.5/7	2.183	1.751						—		
	11.4/5	2.227	1.717				—				
	11.6/7	2.258	1.693						—		
	20.0	2.309	1.656	—							
	20.1/6	2.319	1.648					—			
	20.4/15	2.332	1.638				—				



TABLE 1. *Continued*

Indices		3.822 ----- = $d$		<i>Polytype Diffractions in Three Degrees of Intensity</i>										
Cubic	Hexag.	$b$		2H	9R	4H	15R	6H	21R	3C				
$hkl$	$hk \cdot l$	$b$	$d(\text{\AA})$	1 1 .000	1 2 .333	2 2 .500	2 3 .600	3 3 .667	3 4 .714	1.00				
311	11.1	2.244	1.631	—	—	—	—	—	—	—				
	10.5/3			2.371	1.612	—	—	—	—	—	—	—		
	20.1/3					2.379	1.606	—	—	—	—	—	—	—
	20.4/9			2.390	1.599			—	—	—	—	—	—	—
	20.7/15							2.400	1.593	—	—	—	—	—
	20.1/2			2.407	1.588	—	—			—	—	—	—	—
	20.8/15					2.433	1.571			—	—	—	—	—
	20.5/9			2.450	1.560			—	—	—	—	—	—	—
	10.7/4					2.612	1.463	—	—	—	—	—	—	—
222	00.2	2.770	1.380					—	—	—	—	—	—	—
	20.2/3			2.828	1.352	—	—	—	—	—	—	—		
	20.1					2.950	1.296	—	—	—	—	—	—	—
	20.5/4	3.055	1.251	—	—			—	—	—	—	—		
400	20.4/3			3.081	1.241			—	—	—	—	—	—	—
	20.3/2	3.117	1.227			—	—	—	—	—	—	—		
	21.0					3.161	1.209	—	—	—	—	—	—	—
331	10.7/3	3.273	1.168	—	—			—	—	—	—	—		
	20.5/3			3.463	1.104			—	—	—	—	—	—	—
	21.1/3	3.565	1.072			—	—	—	—	—	—	—		
	21.1/2					3.674	1.041	—	—	—	—	—	—	—
420	11.2	3.835	0.997	—	—			—	—	—	—	—		
	21.2/3			4.000	0.956			—	—	—	—	—	—	—
	10.5/2	4.182	0.914			—	—	—	—	—	—	—		
422	10.8/3					4.207	0.908	—	—	—	—	—	—	—
	21.4/3	4.324	0.884	—	—			—	—	—	—	—		
	30.0			4.472	0.855			—	—	—	—	—	—	—
	21.3/2	4.550	0.840			—	—	—	—	—	—	—		
	00.3					4.182	0.914	—	—	—	—	—	—	—
333	20.7/3	4.207	0.908	—	—			—	—	—	—	—		
511	21.5/3			4.324	0.884			—	—	—	—	—	—	—
	30.1	4.472	0.855			—	—	—	—	—	—	—		
	20.5/2					4.550	0.840	—	—	—	—	—	—	—
440	20.8/3	4.182	0.914	—	—			—	—	—	—	—		
	22.0			4.207	0.908			—	—	—	—	—	—	—
531	11.3	4.324	0.884			—	—	—	—	—	—	—		
	31.1/2					4.472	0.855	—	—	—	—	—	—	—
	21.5/2	4.550	0.840	—	—			—	—	—	—	—		
620	21.8/3			4.182	0.914			—	—	—	—	—	—	—
	31.3/2	4.207	0.908			—	—	—	—	—	—	—		
	31.3/2					4.324	0.884	—	—	—	—	—	—	—

Two other measurements, by Aminoff (1923), and Ulrich & Zacharaisen (1925) were on polytypes far from the  $2H$  type, or on mixtures of hexagonal and cubic phases (Fuller, 1929).

Noting that in the more cubic polytypes the reflections from the 10.0 planes extinguish but a number of 10.*l* reflections appear between 10.0 and 10.1/3, an approximate calculation showed that the relative value of  $I(10.0+10.(0 \text{ to } \frac{1}{3}))$  shows a linear decrease from 2.04 at the hexagonal limit to zero at the cubic limit. On the other hand  $I(00.1+10.1/3)$  increases nearly linearly from 1 at the hexagonal limit to 4 at the cubic

TABLE 2. ZnS POLYTYPES

Packing		Calculated Ratio of $x$ -ray Intensities
Cubic	Hexagonal	$I(10.0 \text{ to } 10 \cdot \frac{1}{3})/I(00.1+10 \cdot \frac{1}{3})$
0.0	1.0	2.04
0.1	0.9	1.42
0.2	0.8	1.02
0.3	0.7	0.752
0.4	0.6	0.556
0.5	0.5	0.408
0.6	0.4	0.292
0.7	0.3	0.197
0.8	0.2	0.120
0.9	0.1	0.0552
1.0	0.0	0.0000

limit. Assuming both linearities, the calculated values of the ratio  $I(10.0 \text{ to } 10.1/3) / I(00.1+10.1/3)$  are given in Table 2 and are shown in Fig. 2 plotted against the fraction of cubic packing. By means of this curve, and as a first approximation, the ratio of integrated intensities of all the polytype diffractions at a smaller angle than 00.1, added together, to the integrated intensity of the 00.1–10.1/3 diffraction, gives directly the ratio of hexagonal to cubic packing, whether the mixture is on an atomic scale or in syntactic intergrowth or even on a macroscopic scale. However, polytypes with small and regular  $k$ - $h$  periodicities, especially if the  $c$  periods also are small, give many diffractions impossible from a mechanical mixture of the cubic and hexagonal end members, so that indexing of a number of diffraction lines should accompany relative intensity measurements.

Superficial examination of  $x$ -ray diffraction of minerals identified by other means as wurtzite have led, in the past, to erroneous conclusions that the minerals are mixtures of sphalerite and wurtzite or that they

are sphalerite. This is due, obviously, to the fact that the strong spectra of wurtzite polytypes are also those of sphalerite and the weak wurtzite spectra may be too broad to be easily detected. However, since a large amount of work on hexagonal-cubic polytypes has been published since 1920, such cursory treatment should now be considered unsatisfactory.

Edwards & Lipson (1943) used the ratio of intensities of 200 from cubic cobalt and 10.0 from hexagonal cobalt to measure the ratio of abundance

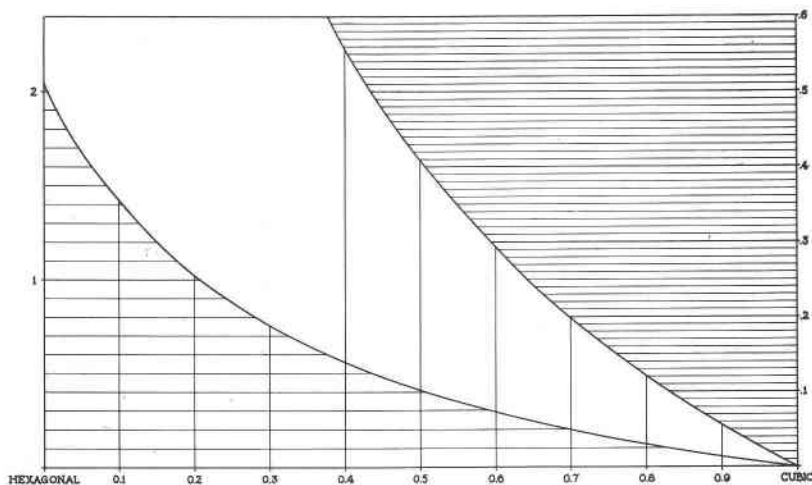


FIG. 2. Graphical representation of Table 2. Calculated ratio of integrated intensities of the low angle diffractions of ZnS polytypes *vs* ratio of cubic to hexagonal packing. The ratio of intensities value (vertical axis) is obtained by dividing 1) the sum of the integrated reflections (resolved or unresolved) from 10.0 to, but not including, 00.1, by 2) the integrated reflection of 00.1 +  $10\frac{1}{2}$ . Hexagonal unit layer indices are used as described in the text.

in a range of transition. This ratio can be used if it is known that only two phases can be present, the  $3C$  and  $2H$  types, but in general this cannot be assumed. For example if the  $4H$  type is the only phase present, the cubic 200 reflection extinguishes (Table 1) although the packing is half cubic. The ratios of several other reflections were considered for measuring the ratio of cubic to hexagonal packing, but the one outlined above has many practical advantages due to the small Bragg angles.

#### THERMODYNAMICS

The small differences in energy of the ZnS polytypes (Allen, Crenshaw & Merwin, 1912, 1914) must be due almost entirely to differences in structural entropy analogous to that in order-disorder systems (Edwards & Lipson, 1943), since the coordination and packing density

are the same. The cubic end member, stable below 1020° C. (Allen, Crenshaw & Merwin, 1914), or 870° C. (Müller, 1952), has a greater degree of order (higher symmetry) than the hexagonal end member. In the analogous SiC system, the heat content of the cubic polytype is only 27.4 cal/gram less than that of the 6*H* polytype (Humphrey *et al.*, 1952). As a first approximation, it can be assumed that the entropy of intermediate polytypes varies linearly between the two end members according to the ratio of cubic to hexagonal packing, both above and below the inversion temperature.

During crystallization of ZnS, most of the growth is on the hexagonal or trigonal planes, and it is not difficult to visualize the sheet mechanism (Verma, 1953) by which one or more layers of ZnS grow with the same relationship to the prior sheet as the nucleus of the sheet had to the prior sheet. This can be seen to be dependent on the probability of the nucleus starting growth of a sheet which is structurally the same as, or different than, the sheet below the surface sheet. This can be said to be a second layer influence which must be weak, being screened by the first layer. The source of the second layer influence may be a partial interaction of S atoms of one plane with Zn of the second (hexagonal) or third (cubic) plane, these distances being 5/4 and 9/4 of the layer spacing. Below the inversion temperature the second layer influence gives a probability between 0.5 and 1.0 that a nucleus of growth will be in a cubic relation to the first and second layers already formed. If growth is by stacks of layers in spirals around screw dislocations (Verma, 1953) the later growth of a crystal is strongly influenced by its early pattern of stacking, but this does not affect the argument (Jagodzinski, 1954*b*). Disregarding compositional effects, the probability would be near 1.0 immediately below the inversion temperature, but would go toward 0.5 (randomness) as the temperature approaches zero, because the ratio of heat of crystallization of the two end types must go toward unity as these values increase with fall of temperature. In other words, the heat evolved during crystallization increases as the temperature falls, but there is less percentage difference between the two end types. From this, it can be derived that the lower the temperature, below the inversion temperature, the weaker is the cubic second layer influence, and the greater is the randomness. Therefore metastable crystallization of hexagonal polytypes in the stable field of the cubic end member would be expected to vary with the temperature, but even at a very low temperature, the most hexagonal type would be 4*H* (0.5 cubic packing). This entire matter deserves a detailed study and theoretical analysis. As an example of the problems remaining, the inversion temperature of ZnS is really a band with the 3*C* structure at one limit, and 2*H* structure at the other limit. The band has a consider-

able temperature extent, because Müller (1952) crystallized several ZnS polytypes at 870–905° C. Perhaps a theoretical treatment would lead to a prediction of the most probable polytype to crystallize, given the crystallization conditions.

#### ZINC SULPHIDE MINERALS

The latest revision of Dana's System (1944) does not mention the ZnS polytypes. Sphalerite is said to be optically isotropic unless strained, and a variety, schalenblende, is said to be a banded intergrowth with wurtzite. The data on wurtzite indicate only the one (2H) type occurs. More recently Frondel & Palache (1950) identified and described crystals of wurtzite, types 4H, 6H, and 15R (in order of abundance), from concretions. They pointed out the absence of exact data on natural wurtzite, and the uncertainty that the 2H type occurs as a mineral.

Jagodzinski & Laves (1948) and Jagodzinski (1949c) discussed *x*-ray rotation diffraction of wurtzite (from the Kirka mine, near Dedeagatsch in Thrace) which was described by Ramdohr & Websky (1943). Heavy streaks connect 10*l* spots of 2H wurtzite and other spots which can be indexed as cubic, even though they used visibly homogeneous single crystals. However, the 10*l* reflections and their relative intensities could be due to a syntactic intergrowth of 4H and 6H wurtzite. The heavy streak between 10.0 and 10.1/3, and the more or less symmetrical broadening of 10.1/2, 10.1, 10.3/2 show that more complex polytypes with long *c*-periods also are present.

The writer examined the ZnS minerals available at the University of Toronto and the pertinent *x*-ray data on file. It was found that optically isotropic sphalerite is rare, but material from ore deposits usually considered to be formed at high temperature approaches this condition. On the other hand, drusy sphalerite from the Tri-State, Illinois, Wisconsin, and similar deposits in sediments is variably anisotropic, optically positive (as is wurtzite) with the uniaxial optic axes perpendicular to octahedral growth planes. Several specimens labelled as wurtzite, from various sources, apparently are no more anisotropic than sphalerite from low temperature deposits. *X*-ray powder diffraction films of two of these specimens showed that they were of mixed polytypes with a substantial amount of hexagonal packing, but neither had the 2H structure, even in part.

Only one *x*-ray powder diffraction film of wurtzite (Llallagua, Bolivia, UT-R595) showed the 10.0 line at least twice as dense as the 00.1+10.1/3 line. This had been measured and indexed for the "Peacock Atlas of *X*-ray Data" by R. M. Thompson. All of the lines were checked against the calculated spacings given in Table 1 and were found

to belong to the  $2H$  type. Thompson calculated the unit cell dimensions to be  $a=3.87$ ,  $c=6.31\text{\AA}$ . These are significantly greater than for ZnS minerals, and a chemical analysis indicated a very high content of iron and manganese. Subsequent investigation showed that this mineral is a manganoan ferroan wurtzite, approximately  $\text{Zn}(\text{Mn},\text{Fe})\text{S}_2$  (this will be reported on later).

It was concluded from this preliminary study of zinc sulphide minerals, and from the data in the literature, that the  $2H$  or wurtzite structure must be uncommon if not absent but that polytypic structures, intermediate between those of the hexagonal and cubic limits, are well represented. Therefore a more extensive study was made of a variety of zinc sulphide minerals to obtain quantitative data.

A suite of zinc sulphide minerals was selected and prepared for  $x$ -ray diffraction study, with the object of representing many localities, origins, compositions and crystal habits. Each specimen was cleaned by suitable means and ground in acetone to about 600 mesh. After drying, the powder was mixed with balsam-xylol solution on a plate glass. A number of control tests were made to determine the optimum powder/balsam ratio, the effect of preferred orientation of cleavage surfaces against the bottom and top of the mixture, and reproducibility of quantitative intensity and angular measurements.

The  $x$ -ray diffraction measurements were made with a Norelco geiger counter scanning apparatus, using  $\text{CuK}\alpha$  radiation. Angles of resolved  $\alpha_1$  peaks were read to  $0.001^\circ$  using a very slow scanning speed. Calibration and control tests indicated that the reproducibility of angle was within  $\pm 0.003^\circ$ . The silicon diffraction angles ( $\alpha_1$ ) taken as calibration standards were  $28.442^\circ$  (111),  $47.302^\circ$  (220),  $56.122^\circ$  (311),  $94.952^\circ$  (333),  $106.708^\circ$  (440). Diffraction angles were converted to spacings using U. S. Bureau of Standards tables of 1950.

Only a few of the diffraction spectra of each preparation were recorded. A traverse was made across the peaks due to 10.0 and 00.1 in order to determine cubic/hexagonal ratio of packing, and also across the peaks due to 11.0 or 22.0 and 00.3 to obtain the  $a$  and  $c$  dimensions. The ratio of integrated intensities was obtained from composite curves 10.0 to 10.1/3 and the single curve due to 00.1+10.1/3. A certain amount of ambiguity in the graphical resolution allows no greater accuracy than about  $\pm 3\%$  in the ratios of integrated intensities.

The results, shown in Table 3, indicate a few relationships that may be significant. No specimen of  $2H$  wurtzite was in the suite, but polytypes with a substantial amount of hexagonal packing were represented, notable specimens from Prizbram (Bohemia), Montserrat (Bolivia) and Moresnet (Belgium). Most of the material has a large proportion

TABLE 3. EXPERIMENTAL RESULTS<sup>1</sup>

Locality	Color, etc.	% Cubic Packing	Lattice Dimensions (Å)		
			Cubic		Hexagonal <sup>2</sup>
			a	a	c
<i>Low(?) temperature zinc sulphide:</i>					
Bautch Mine, Wisconsin	White band	95.8	5.4102	3.8256	(3.1236)
Bautch Mine, Wisconsin	Brown band	92.1	5.4106	3.8259	(3.1238)
Bruce Peninsula, Ontario	Light brown	89.3	5.4106	3.8259	(3.1238)
Clay Centre, Ohio	Very light brown	84.2	5.4097	3.8252	(3.1233)
De Rocher, Wisconsin	Dark brown	84.8	5.4108	3.8260	(3.1238)
El Potosi Mine, Mexico	Black	89.9	5.4232	(3.8348)	3.1311
Gibsonberg, Ohio	Light brown	89.3	5.4095	3.8251	(3.1232)
Mascot, Tennessee	Light yellow	91.1	5.4101	3.8255	(3.1235)
North Hunt Mine, Oklahoma	Very light brown	91.2	5.4108	3.8260	(3.1239)
Ottawa Co., Oklahoma	Very light brown	88.4	5.4122	3.8270	(3.1247)
Picher, Oklahoma (M Bed)	Very light brown	78.4	5.4101	3.8255	(3.1235)
Picher, Oklahoma (J Bed)	Very light orange	88.5	5.4113	3.8264	3.1239
Pine Point, N.W.T., Canada	Light brown crystals	94.8	5.4106	3.8259	(3.1239)
Pine Point, N.W.T., Canada	Brown banded	86.8	5.4105	3.8258	(3.1238)
Pine Point, N.W.T., Canada	Brown fossil filling	91.1	5.4102	3.8256	(3.1236)
<i>Intermediate(?) temperature zinc sulphide:</i>					
Bleisharley Mine, Germany	Brown banded	90.5	5.4106	3.8259	(3.1239)
Butte, Montana	White band	93.0	5.4092	3.8249	(3.1230)
Butte, Montana	Brown band	90.2	5.4106	3.8259	(3.1239)
Darwin Mine, California	Black	89.3	5.4196	(3.8322)	3.1290
Freiberg, Saxony	Light brown band	95.0	5.4132	(3.8270)	3.1247
Freiberg, Saxony	Light brown band	93.8	5.4128	(3.8274)	3.1251
Gaspé, Quebec	Very light yellow	90.0	5.4106	3.8259	(3.1239)
Keno Hill, Yukon	Red	90.3	5.4125	3.8272	(3.1249)
Leadville, Colorado	Light brown	90.2	5.4111	3.8262	(3.1241)
Llallagua, Bolivia	Black	0.0	5.4806	3.8754	3.1638
Llallagua, Bolivia	Very dark brown	24.1	5.4246	3.8358	3.1337
Montserrat, Bolivia	Brown	33.2	5.4113	3.8264	(3.1242)
Moresnet, Belgium	Light brown band	86.0	5.4073	3.8235	(3.1219)
Moresnet, Belgium	Dark brown band	63.0	5.4087	3.8245	(3.1227)
Oswaldo Mine, New Mexico	Brown	92.8	5.4138	3.8281	(3.1256)
Prizbram, Bohemia	Brown acicular	92.3	5.4133	(3.8278)	3.1254
Prizbram, Bohemia	Brown acicular	60.2	5.4138	(3.8281)	3.1256
Santander, Spain	Light yellow	87.3	5.4091	3.8248	(3.1229)
<i>High(?) temperature zinc sulphide:</i>					
Bachelor Lake, Quebec	Light yellow	96.3	5.4111	3.8262	3.1240
Balmat, New York	Brown	99.6	5.4152	3.8291	(3.1265)
Eskaminish, Manitoba	Dark brown	88.8	5.4177	(3.8309)	3.1280
Frontenac Mine, Ontario	Brown	90.6	5.4173	3.8306	(3.1277)
New Calumet Mine, Ontario	Brown	91.3	5.4172	3.8305	(3.1276)
Ogdensburg, New Jersey	Very light yellow	90.0	5.4116	3.8266	3.1240
Parry Sound, Ontario	Brown	92.0	5.4166	3.8301	(3.1273)

<sup>1</sup> The last digit of each number is uncertain.<sup>2</sup> Values in brackets were calculated from  $c/a = \sqrt{2/3}$ .

of cubic packing, but this appears to be less in the specimens from low temperature deposits. In banded brown and white specimens, the brown bands apparently have more hexagonal packing than the white.

The measurements and the data in the literature appear to be compatible with the following hypotheses: 1) the lower the temperature below some temperature which is below the cubic-hexagonal transition, the more nearly equal are the relative amounts of cubic and hexagonal packing in zinc sulphide; 2) manganese and iron in the zinc sulphide phase reduce the temperature of the cubic-hexagonal transition; 3) below but near the cubic-hexagonal transition temperature, there is a range of existence of various polytypes with mixtures of cubic and hexagonal packing. Stated more definitely, it appears that light-colored zinc sulphide from high temperature deposits has mostly cubic packing, but similar material from low temperature deposits has somewhat larger amount of hexagonal packing. Conversely, it appears that very dark-colored zinc sulphide from high temperature deposits has a large amount of hexagonal packing, but similar material from low temperature deposits has mostly cubic packing. However, when light- and dark-colored zinc sulphide are interbanded, the latter has more hexagonal packing than the former.

The relations between the type of packing, composition, temperature and other conditions of crystallization of (Zn, Fe, Mn, Cd)S compounds are now being investigated, with the hope that a new pressure-insensitive geothermometric relation may be derived.

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