PHASE TRANSFORMATION IN ZINC SULPHIDE[1]

V. G. HILL[2]
University of Toronto, Toronto, Canada

ABSTRACT

The study of phase transformation in the zinc sulphide system shows that the $3C{:}2H$ equilibrium at 1020° C.±5° C. is metastable. At 1010° C.±10° C. the $4H$ polytype is the stable phase, and, from the determination of the variation of cubic-hexagonal packing relationship with temperature, it is suggested that the polytypes all have a stability range between that of the $2H$ and $3C$ polymorphs. On this basis, the $3C{:}2H$ transition is seen to be of the diffuse first-order type. The reaction trend in the development of a polytype near the $2H{:}3C$ equilibrium temperature is

$$3C \rightarrow 3C{:}2H \text{ (intergrowth)} \rightarrow \text{polytypes}$$
$$\text{or } 2H \rightarrow 2H{:}3C \text{ (intergrowth)} \rightarrow \text{polytypes}$$

If the reaction temperature is far removed from the $2H{:}3H$ metastable equilibrium temperature, then this transformation from $2H$ to $3C$ or *vice versa* first occurs and thereafter the polytype develops from the intergrowth and/or polymorph first formed. It is suggested that the nucleation and growth of the various phases is a probability function dependent on starting material, temperature and reaction time.

INTRODUCTION

Prior to 1950 zinc sulphide was known to exist in only two polymorphic forms, sphalerite and wurtzite, with cubic and hexagonal morphology respectively. Subsequently Frondel & Palache (1950) described three other naturally occurring polymorphs whose structures were different from the prototype structures of wurtzite and sphalerite, but they had hexagonal or rhombohedral symmetry. Later Strock & Brophy (1955), reported the synthesis of similar polymorphs, and also a new polymorph with a three layer rhombohedral structure. The question of the relationship of various polymorphic structures has been discussed by several authors from a structural standpoint, and so it is interesting to consider the energy relationships between these structures and their relative stability.

These minerals were studied by Bragg (1937, pp. 32–66) who deduced their structures, and discussed their structural relationship. Frondel & Palache (1950), Patterson (1952), Smith (1955), Strock (1955), and Strock & Brophy (1955) discussed the structures of the polymorphs and polytypes and correlated these with the silicon carbide structures as

---

[1] Extracted from thesis presented in partial fulfilment of the Ph.D. degree, University of Toronto.

[2] Present address, Geological Survey Department, Kumasi, Ghana.

deduced by Ramsdell (1944, 1945, 1947, 1951*a*, *b*, 1952, 1953), and Thibault (1954).

This investigation was undertaken specifically to obtain answers to the following problems:

(*a*) The character of inversion (ideal first order, etc.) that occurs between the hexagonal and cubic polymorphs of zinc sulphide.

(*b*) The stability relationships of the polytypes to the cubic and hexagonal polymorphs.

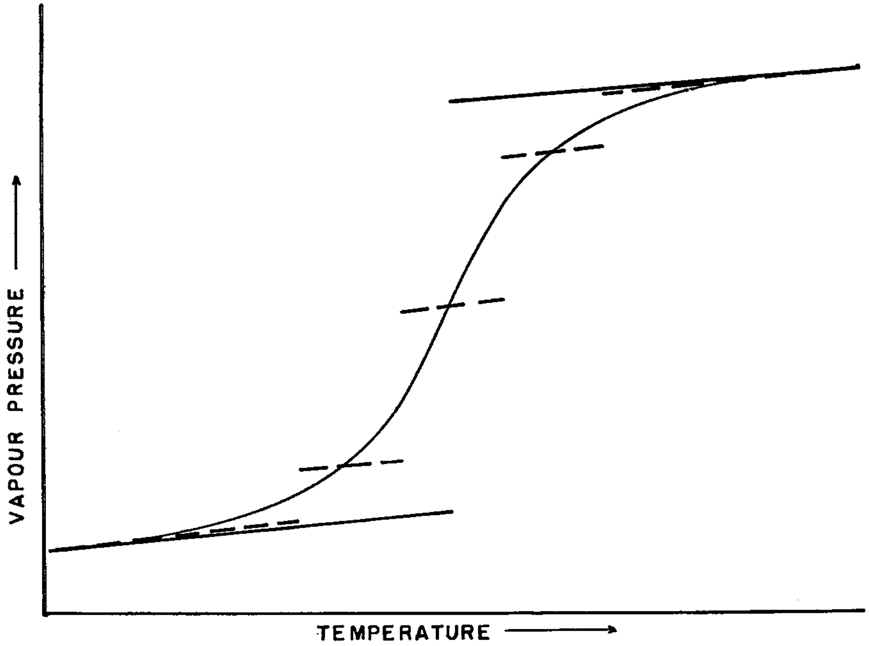

FIG. 1. Possible equilibrium transformation curves in zinc sulphide: (A) Heavy lines show the transformation as being ideal first order; (B) Dashed lines show the transformation as a series of discrete ideal first order transformations; (C) Light line shows the transformation as diffused first order, proceeding over an infinite series of steps.

The importance of this is that the polytypes all have stacking sequences intermediate between that of the $3C$ and $2H$ modifications, and a determination of many of the properties of the crystalline phases may show either of the following (Fig. 1):

(*a*) A sharp break or discontinuity during the inversion of the cubic to hexagonal polymorph, indicating an ideal first order transition and with the polytypes having no stability region between the $3C$, $2H$ fields.

(*b*) A stepwise inversion with at least some of the polytypes having stable fields between those of the 2*H* and 3*C* polymorphs.

(*c*) A gradual stable transition between 3*C* and 2*H* with all the polytypes having a stability field between the two polymorphs.

The ratio of cubic to hexagonal packing was selected as the parameter likely to give most information. The method developed by Smith (1955) was used as an approximate measure of this. There are certain dangers inherent in this technique because it does not distinguish between mixtures of the two forms on a gross scale from "mixtures" on the atomic scale. However, implemented with optical methods and *x*-ray rotation photographs when necessary, this ambiguity would be minimized if not removed.

EXPERIMENTAL METHODS AND EQUIPMENT

Furnaces

The furnaces used in these experiments are standard Kanthal-A wound vertical muffles, about 15 in. high and 1½ in. bore. Temperatures were read by a Bristol indicating pyrometer in routine runs and a Leeds and Northrop portable potentiometer was used in the critical runs. Chromel-alumel thermocouples were used for temperatures up to 1100°C and above that a Pt-Pt 10% Rh thermocouple was used. The temperature was controlled to a precision of ±5°C but more precise values were obtained in shorter runs.

X-ray Work

Virtually all of the samples were examined by a Norelco High Angle Geiger Counter *X*-ray Diffractometer, using CuK_α radiation. The phases present were usually determined by scanning the region between 26° to 31° (2θ), but other portions of the spectrum were examined when necessary. Various scanning speeds and time constants, etc., were used, depending on results desired.

Samples for the spectrometer were prepared by grinding the specimens under ether. The pulverised sample was then air dried and mixed with a solution of Canada balsam in xylol on a microscope slide, baked at 110°C, and polished flat when cold. The effect of the grinding technique is discussed by Smith & Hill (1956).

The next question is the measurement of the necessary parameters. It is agreed in the literature (Klug & Alexander, 1955, pp. 270–317, 410–416) that the most accurate method of measurement of intensities is by counting the rate of emission of gamma photons at the angle of peak intensity. However, where a set of the reflections being measured can be broad, asymmetric or not completely resolved, this method cannot be conveniently applied. It was, therefore, necessary to resort to integration of the reflection or reflections under specific areas of the curve as recorded by the spectrometer.

Since there is no difference in chemical composition between the structures under consideration, the linear relationship for the phases as shown by Klug & Alexander (1955, p. 414) for quartz-cristobalite was assumed to hold for this system and the requirements for minimizing the errors in measurements of this kind were taken into account. Because of the complexity of some of the stacking sequences, it was decided to separate the three types of reflections and plot them as numerical entities. Several broad assumptions are made in this decision. The neglecting of the effect of variations caused by the time constants in the recording circuit and the effect due to impurities in the wave length used (α_2 and β) will undoubtedly affect the accuracy of the result, but since the entire series was done under similar conditions these variables are constant and their effect is small compared with the parameters being measured.

The possibility of the presence of an infinite number of polytypes each giving its own characteristic diffraction spectra, would make the problem of the analysis of the resulting pattern exceedingly complex. Fortunately, only a few polytypes were encountered in appreciable amounts in each run under the conditions of the experiments because the composite diffraction patterns were dominated by only a few structures. The unresolved complex diffraction lines caused an apparent rise in the background, but there were always definite specular reflections. These unresolved reflections were lumped together and treated separately. Because the (10.0) line was absent from many structures and replaced by lines which were often unresolved, it was necessary to treat the unresolved reflections as related to it in order to obtain a continuous function.

Briefly, what was done was to assume that the specular reflections (10.0) and (111) (00.1) as recorded are symmetrical curves. This was found by actual measurement under the conditions of the experiment to be approximately true, especially for the (111) (00.1) reflection (Fig. 2). Very often the (10.0) was found to be asymmetric and this was to be expected by *a priori* considerations of the various structures involved. This curve was always made symmetrical and the portion left over summed with the reflections occurring between (10.0) and (111) (00.1). The integrated areas of the three sets of reflections were recorded as *H* for the (10.0), *C* for the (111) (00.1), and *M* for the reflections between these. A planimeter was used to measure the areas indicated under the curve (Fig. 2). It should be stated that *H*, *C*, and *M* must not be confused or associated with hexagonal or cubic symmetry, although they are functions of cubic and hexagonal closest packing. This was really a

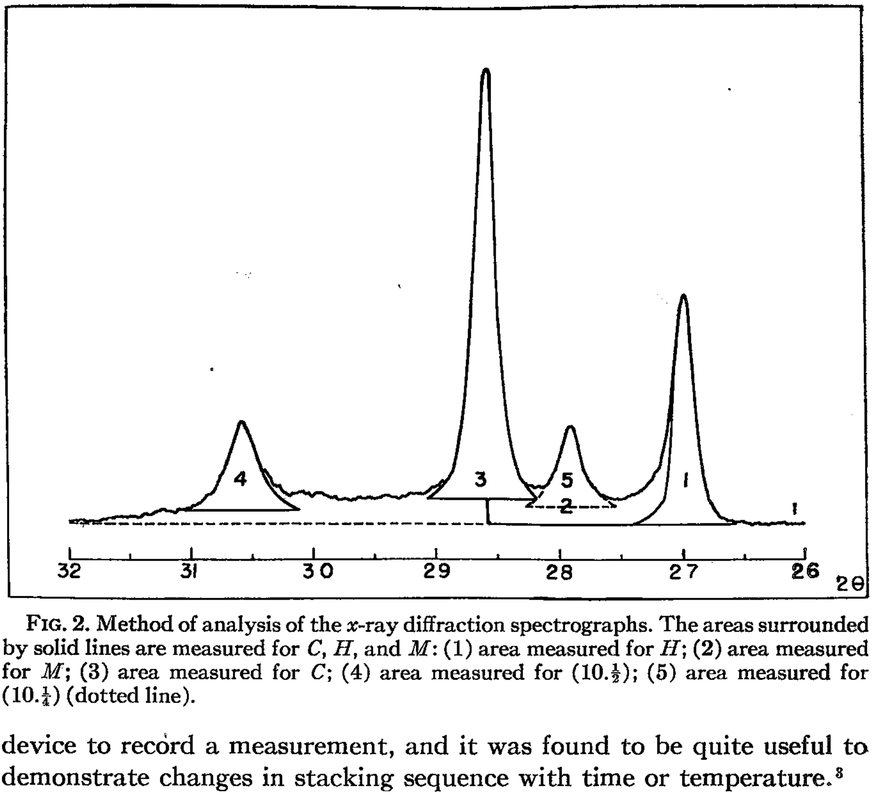

FIG. 2. Method of analysis of the *x*-ray diffraction spectrographs. The areas surrounded by solid lines are measured for *C*, *H*, and *M*: (1) area measured for *H*; (2) area measured for *M*; (3) area measured for *C*; (4) area measured for (10.½); (5) area measured for (10.¼) (dotted line).

device to record a measurement, and it was found to be quite useful to demonstrate changes in stacking sequence with time or temperature.[3]

An analysis of variance was done on the results and it showed:

TABLE 1. ERRORS IN MEASUREMENT OF REFLECTIONS (Davies, 1954a)

Error	*C*	*H*	Average
σ_s^2	1.80	1.32	1.56
σ_r^2	2.04	5.15	3.60
σ_m^2	2.45	2.94	2.70

σ_s^2 = variance between two samples heated simultaneously.

σ_r^2 = variance between two sets of repeats.

σ_m^2 = variance between two sets of measurements (including *x*-ray spectrometer error) on the same sample.

[3] The relative intensities of *x*-ray diffraction lines as determined by the diffractometer can be affected by the following factors:

1. Factors causing line broadening: (*a*) Small grain size; (*b*) Mosaic structures; (*c*) Strain.
2. Dilution effects: (*a*) Differential absorption of primary and secondary *x*-rays; (*b*) Sampling errors due to grain size and shape effects.
3. Cement. 4. Impurities. 5. Temperature. 6. Instrumental effects.

Since the values of C and H are approximately of the same order of magnitude, the errors for C and H can be regarded as estimates of the same value so that their values can be averaged.

If one run is done and one measurement made, the total variance will be $\sigma^2 = 7.86$. Therefore $\sigma = 2.80$ and $2\sigma = 5.6$. The measurement of C and H (as normally done in these experiments) can be regarded as having a $2\sigma = 5.6$.

Powder photographs were also taken with a Philips camera. These were very useful in determining a- and c-values and also in examining all the lines in the spectrum of an unknown phase. Professor E. W. Nuffield also took a number of rotation photographs to help in deciding the stacking sequence of some of the products obtained. These single crystal determinations also serve as direct evidence of the scale on which the hybridization of structures occur.

Microscope

All samples were examined with the petrographic microscope. The information obtained was invaluable in interpreting the x-ray data. For example, it is sometimes a simple matter to differentiate by optical means between a gross mixture of cubic and hexagonal polymorphs or an intergrowth of these, from a stacking disorder and polytypes.

EXPERIMENTAL WORK

Starting Materials

1. *Colloidal Zinc Sulphide*: This was prepared by precipitating ZnS with alkaline sodium sulphide from a slightly alkaline zinc sulphate solution. The gel, with a slight excess of sulphide ion in the solution was allowed to digest on a water bath for about twenty-four hours, then washed by decantation with 0.1% ammonium chloride solution, and finally filtered through a sintered glass funnel. The precipitate was then sucked dry before a final drying under vacuum on a water bath. The x-ray diffraction pattern showed very broad reflections, probably due to the small crystallite size, corresponding to the cubic structure, but there was a slight increase in the "background" starting from about $2\theta = 26°$. (Fig. 3A).

2. *Zinc Sulphide* (*pure*), *Baker and Adamson*:[4] This material gave an x-ray pattern that looked like a mechanical mixture of $3C$ and $2H$. However, its thermal reaction was quite different from that of the mechanical mixture, and so it is believed that this also has a 3 2 sequence although the exact polytype was not determined (Fig. 3B).

---

[4] The results of a qualitative spectrographic analysis of this material (made by Mr. Wylie Taylor, through the courtesy of Mr. D. A. Moddle of the Ontario Department of Mines are (approximate):
Mn—0.001% Fe —0.1% Co—0.05% Al —0.01% Mg—0.01% Si —1%
Cd—0.01% Cu —0.01% Ni—0.00% Pb —0.005% B —0.1% Ca—1%

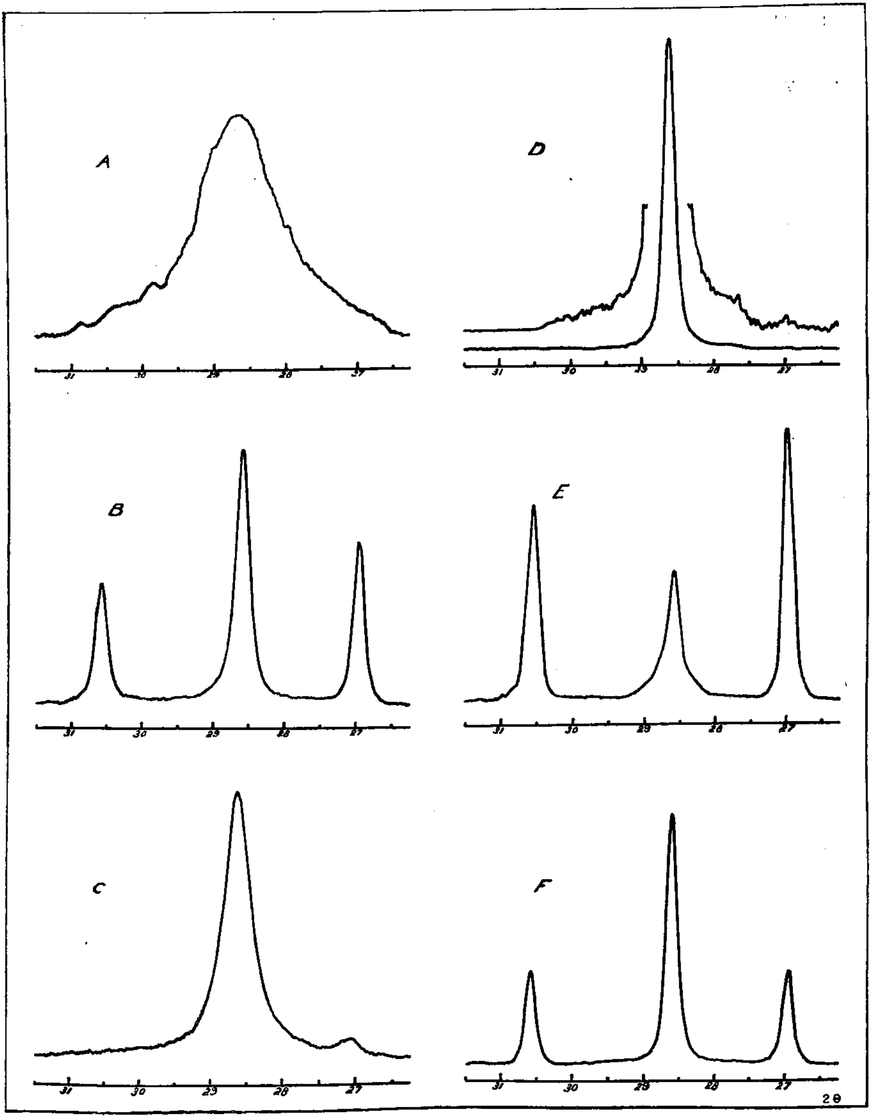

FIG. 3. X-ray diffraction spectrographs of starting materials: (A) Fine-grained zinc sulphide (scale factor 8); (B) B and A zinc sulphide (scale factor 8); (C) RCA zinc sulphide (scale factor 6.4); (D) $3C$ zinc sulphide (scale factor 1) (scale factor 8); (E) $2H$ zinc sulphide (scale factor 3.2); (F) (1:1) $3C$:$2H$ mixture (scale factor 6.4).

3. *Zinc Sulphide "spectrographic grade"* (IM576, RCA 1732): This was supplied by the R.C.A. Research Laboratory; it gave what is essentially a cubic pattern with a few weak extra lines (Figs. 3, 4). This material behaved very much like the $2H$ and B & A

zinc sulphide. On the basis of its reaction rate and the x-ray pattern, it is believed that this material has essentially a 3 2 sequence (Fig. 3C).

4. *Zinc Sulphide—3C*: This was synthesized by heating B & A zinc sulphide with 10% sodium chloride at 800° C. for three to five days. The product was freed from fines and salt by washing by decantation. The x-ray diffraction pattern (Fig. 3D) show that these crystals have some hexagonal packing.

5. *Zinc Sulphide—2H*: This was prepared by heating B & A zinc sulphide with about 10% sodium chloride above 1080° C. for two to ten hours. The resulting product was washed free of fine-grained material and sodium chloride before use. The x-ray diffraction pattern (Fig. 3E) showed that the product was never pure *2H* but really a polytype with a structure nearly similar to *2H*.

6. *Zinc Sulphide* (1:1) *2H:3C Mixture*: A mechanical mixture of *2H* and *3C* was prepared by weighing out equal amounts of the *2H* and *3C* zinc sulphide prepared as described above. This was done in batches of 5 to 10 g. and thoroughly homogenized (Fig. 3F).

7. *Zinc Sulphides Polytypes*: The product from some runs or a mixture of these products were used as starting materials in other runs to test changes that occur with varying temperatures when different starting materials were used (Fig. 2).

TABLE 2. RELATIVE INTENSITY MEASUREMENTS ON *2H* ZnS

Number	Relative intensity by integrating areas								Relative intensity from peak heights			
	C	*H*	*M*	$\frac{H+M}{C}$	10.0	00.1	10.½	$\frac{10.0}{00.1}$	10.0	00.1	10.½	$\frac{10.0}{00.1}$
					FINE-GRAINED CRYSTALS							
H–301	27.6	72.4	0.0	2.62	10.0	3.8	9.3	2.62	10.0	3.9	8.9	2.53
	32.4	67.6	0.0	2.07	10.0	4.8	10.3	2.07	10.0	4.8	8.6	2.45
	31.1	68.9	0.0	2.22	10.0	4.8	9.0	2.22	10.0	4.5	8.9	2.22
	36.4	63.6	0.0	1.75	10.0	5.7	9.4	1.75	10.0	6.0	9.0	1.68
	35.8	64.2	0.0	1.79	10.0	5.6	10.0	1.78	10.0	6.9	9.2	1.49
	33.4	66.6	0.0	1.95	10.0	5.0	—	1.95	10.0	5.4	—	1.84
	26.6	73.4	0.0	2.76	10.0	3.6	—	2.76	10.0	3.3	—	3.17
Total	223.3	476.7	0.0	15.16	—	33.3	48.0	15.15	—	34.7	44.6	15.38
Mean $(\bar{X}_1)$	31.9	68.1	0.0	2.17	10.0	4.8	9.6	2.16	10.0	5.0	8.9	2.20
s^2	14.20	14.20	—	0.161	—	0.66	0.28	0.157	—	1.58	0.02	0.366
s	3.77	3.77	—	0.40_2	—	0.25_7	0.5_3	0.39_6	—	1.26	0.14	0.191
$2s$	7.5	7.5	—	0.80	00	0.51	1.1	0.79	—	2.5	0.28	0.38
					PULVERIZED CRYSTALS							
H–301G	30.2	64.0	5.8	2.31	10.0	4.7	7.5	2.11	10.0	5.1	6.3	1.97
	29.0	64.3	6.7	2.41	10.0	4.5	7.5	2.22	10.0	5.1	6.0	1.98
	29.6	63.9	6.5	2.38	10.0	4.7	7.3	2.16	10.0	5.2	5.6	1.92
	29.5	62.3	8.2	2.40	10.0	4.7	7.4	2.12	10.0	5.4	5.9	1.86
	29.9	62.5	7.6	2.34	10.0	4.8	7.4	2.09	10.0	5.3	5.7	1.87
Total	148.2	317.0	34.8	11.84	—	23.4	37.1	10.70	—	26.1	25.9	9.60
Mean $(\bar{X}_2)$	29.6	63.4	7.0	2.37	10.0	4.7	7.4	2.14	10.0	5.2	5.9	1.92
s^2	0.20	0.86	1.0	0.0018	—	0.02	0.01	0.0032	—	0.02	0.075	0.0030
s	0.45	0.93	1.0	0.042	—	0.14	0.1	0.056	—	0.14	0.27	0.055
$2s$	0.90	1.86	2.0	0.084	—	0.28	0.2	0.11	—	0.28	0.54	0.11
$\bar{X}_1$-$\bar{X}_2$	2.3	4.7	−7.0	−0.20	—	0.1	2.2	0.02	—	−0.2	3.0	0.28

Determination of the Cubic-hexagonal Packing

To be able to relate the measured relative values to those of 2*H*, 3*C*, or, in fact any polytype, it is necessary to quantitatively determine the effect of the preparation technique before any conclusion based on the quantitative aspect, can be drawn from the measurements. To determine this effect, a sample of 2*H* ZnS was synthesized by heating B & A zinc sulphide at 1275°C for 10 minutes in a sodium chloride flux, and replicate measurements were made of the relative intensity of the (10.0), (00.1) and (10.$\frac{1}{2}$) lines on the crushed and uncrushed samples. The values obtained and their standard deviations are shown in Table 2.

It is apparent from the table that there is only a minor difference between measurement of relative intensities from peak heights and that by integration of areas under these peaks. This difference on the (10.0) and (00.1) lines is of the same order of magnitude as that introduced by crushing. The measurement by integration of areas under the curves is the most reproduceable value, and this is even more so when the sample is crushed, so it will be used, in spite of the fact that it is not identical with that obtained by measuring peak heights.

If we use the measured ratio $(H+M)/C$ for the crushed 2*H* to set up the regression curve for the relative intensity measurements to be used in determining the proportion of cubic hexagonal packing in mixtures of these crystals, then the values will be as shown in Table 3.

TABLE 3. CALCULATED INTENSITY RATIOS FOR 3*C*-2*H* MIXTURES*

Packing		Calculated ratio of *x*-ray intensities
Cubic	Hexagonal	$\frac{I(10.0 \text{ to } 10.1/3}{I(00.1 \quad 10.1/3}$
0.00	1.00	2.37
0.10	0.90	1.64
0.20	0.80	1.19
0.30	0.70	0.873
0.40	0.60	0.646
0.50	0.50	0.474
0.60	0.40	0.339
0.70	0.30	0.230
0.80	0.20	0.140
0.90	0.10	0.0648
1.00	0.00	0.0000

*Modified from Smith, 1955, p. 667.

The 3C-2H Equilibrium

The first problem was a restudy of the 3*C*-2*H* equilibrium. For this, a mechanical mixture (on the discrete particle level) was prepared by weighing out equal amounts of 3*C* and 2*H* zinc sulphide and thoroughly mixing them.[5] These were held at the desired temperatures for varying lengths of time, air quenched, then the sodium chloride was washed out and the dried product examined under the microscope. A portion was also examined by the *x*-ray diffraction spectrometer and *C*, *H*, and *M* measured from the tracings. The results of these runs are given in Table 4.

By observing the anisotropism of the crystals under crossed Nicols, it was seen that below 960°C the 2*H* zinc sulphide dissolved and the 3*C* grows. Between 960°C and 1025°C discrete 2*H* and 3*C* crystals dissolved and the product was an intergrowth of cubic and hexagonal zinc sulphide in the same crystal. The rate of solution of the 2*H* polymorph is greater than the 3*C* polymorph. In many cases the crystals were seen to have discrete blocks of cubic and hexagonal material. Four wurtzite crystals growing out from the faces of a sphalerite tetrahedron were also seen. The size of the sandwiched cubic and hexagonal blocks in the crystals decreased with time until they appeared homogeneous. Examination under high magnification, however, showed that the crystal faces were striated parallel to the base and that there was a difference in the birefringence and refractive index between the areas on opposite sides of these striations. This could be caused, at least in part, by different thicknesses of the crystals (if they are the "pagoda" types) and by plates not strictly in orientation. (See crystal drawings by Strock & Brophy, 1955). Single crystal photographs showed several structure types were present, thus proving that these crystals were of composite types along the *c*-axis. In many crystals, careful examination showed that the corners where the prism faces met were not smooth straight lines, but appeared to be almost the near limiting cases of oscillating pyramid faces. Above 1025°C, the cubic crystals dissolved and the hexagonal crystals first grew. The prism faces of the hexagonal crystals showed marked striations when the heating was continued even for as long as thirty hours. Heating the charge for long times at temperatures between 960°C and 1300°C often produced a new phase, which we may conclude is more stable than either 3*C* or 2*H*. The first step in the crystallization at the new stage was that the faces of pre-existing crystals become very irregular and showed "pagoda" etched lines.

From the above experiments we can conclude the following:

(*a*) The transition temperature between the 3*C* and 2*H* polymorphs is 1020°C±10°C, and it is a metastable equilibrium point since the product of the transformation changes with time.

---

[5] It will be later shown that these are really near 3*C* and 2*H* polytypes.

TABLE 4. THE 3*C*:2*H* TRANSITION*

Number	°C	Hours	*C*	*H*	*M*
H-201-202	—	0	69.9	24.1	6.0
206	900	1	83.5	9.0	7.5
207	902	2	88.8	4.9	6.3
208	901	4	95.5	0.7	3.8
209	901	8	95.0	—	5.0
205	900	16½	93.8	—	6.2
H-220	—	0	67.3	23.1	9.6
221	952	1	83.5	10.7	5.8
222	951	2	82.5	7.8	9.7
223	953	4	91.7	1.1	7.2
224	952	7½	93.7	0.2	6.1
225	950	15	94.5	—	5.5
226	949	34	94.3	—	5.7
H-201-202	—	0	69.9	24.1	6.0
210	995	½	71.7	19.4	8.9
211	995	1	73.3	18.9	7.8
212	995	2	74.3	16.1	9.7
213	995	4	80.5	10.1	9.4
214	996	8	83.4	4.0	12.6
215	995	16	83.8	5.2	11.0
H-220	—	0	67.3	23.1	9.6
229	1007	½	70.4	21.0	8.6
230	1006	1	66.7	21.5	11.8
231	1008	2	67.3	23.0	9.7
232	1006	4	71.4	18.4	10.2
H-220	—	0	67.3	23.1	9.6
239	1028	½	72.0	15.5	11.6
240	1025	1	67.7	19.9	12.4
242	1026	4	71.0	16.8	12.2
244	1027	16	61.2	23.5	15.5
H-220	—	0	67.3	23.1	9.6
245	1055	½	51.4	30.8	17.8
246	1050	1	70.5	16.6	12.9
247	1047	2	47.6	32.2	20.2
248	1045	4	54.1	27.5	18.4
249	1051	9½	44.5	32.5	23.0
250	1050	16	42.0	35.3	21.7
*	—	0	67.3	20.8	12.3
*	1065	¼	41.5	44.2	14.3
*	1065	½	37.1	49.1	13.8
*	1065	1	36.0	47.6	16.4
*	1065	2	34.8	47.6	17.6
*	1065	4	34.1	45.6	20.3
*	1065	8	32.8	40.3	26.9
H-220	—	0	67.3	23.1	9.6
261	1082	1	49.4	35.9	14.7
262	1081	2	31.8	47.6	20.6
263	1082	4	35.2	46.4	18.4
264	1082	10	39.4	41.7	18.9

*These are average values of results obtained.

(*b*) In the temperature range 960°C–1020°C, an intergrowth of 3*C* and 2*H* crystals is more stable than either of these polymorphs or a mechanical mixture of them.

The Stability Fields of the Polytypes

When it was realized that above 960°C both 3*C* and 2*H* polymorphs tended to transform to polytypes, an attempt was made to identify these polytypes and to determine their stability fields. The first approach was to use different starting materials and heat them simultaneously at the same temperature for the same length of time and then examine the products. In many of these runs the same product was not obtained from all the starting materials. The results are summarized in Table 5.

TABLE 5. THE STABILITY OF THE POLYTYPES

				Charge			Product		
No.	°C	Hours	Source	*C*	*H*	*M*	*C*	*H*	*M*
H–175	920	42	2*H*[a]	23.2	63.6	3.2	93.4	0.05	6.6
176	920	42	3*C*[b]	95.0	—	5.0	94.3	—	5.7
H–167	968	23	F.G.[c]	—	—	—	92.5	1.2	6.3
168	968	23	2*H*[a]	30.1	68.7	1.2	47.2	40.5	12.3
169	968	23	3*C*[b]	95.4	—	4.6	94.7	—	5.3
306	962	216	d	—	—	—	90.0	—	10.0
H–235	1005	23	B & A[e]	60.5	31.2	8.3	47.7	37.8	14.5
236	1005	23	3*C*[e]	94.5	—	5.5	72.8	20.0	7.2
237	1005	23	3*C*	94.5	—	5.5	85.6	4.5	9.9
228	1005	8	B & A	60.5	31.2	8.3	42.2	49.7	8.1
232	1006	4	1:1[f]	67.3	23.1	9.6	71.4	18.4	10.2
233	1008	8	B & A	60.5	31.2	8.3	37.8	53.1	9.1
234	1008	16	B & A	60.5	31.2	8.3	44.6	46.5	8.9
300	1005	114	1:1[f]	67.3	23.1	9.6	47.9	23.5	28.6
301	1005	114	2*H*	30.3	55.5	14.2	37.8	34.5	27.7
302	1005	114	B & A	60.5	31.2	9.6	44.1	36.8	19.1
H–256	1014	40	RCA	87.1	—	12.9	37.8	32.6	29.6
257	1014	40	B & A	60.5	31.2	8.3	45.3	32.0	22.7
258	1014	40	3*C*	94.5	—	5.5	84.8	1.7	13.5
259	1014	40	2*H*	30.3	55.5	14.2	45.5	33.7	20.8
260	1014	40	1:1[c]	67.3	23.1	9.6	75.3	7.9	16.8

[a] These are really near 2*H* phases.
[b] These are really near 3*C* phases
[c] Fine-grained ZnS used.
[d] A mixture of H–260, H–303 and 3*C* used.
[e] H–215 seeds added.
[f] (1:1) 3*C*:2*H* mechanical mixture.

The next step was to establish the trend in the structural changes that occur in time when a particular starting material was heated at one temperature. To do this twenty-four samples from (1:1) 3*C*: 2*H* mechanical mixture were taken from the homogenized starting material and sealed in dried evacuated glass tubes in the usual manner. Two of these at a time were randomly selected from the lot and heated together at 1065°C for either $\frac{1}{4}$, $\frac{1}{2}$, 1, 4, or 8 hours; the heating times were not selected in any particular order. Each was done in duplicate. The products from the various runs, after removal of the sodium chloride, were examined with the *x*-ray spectrometer, scanning all the reflections from (10.0) to (00.1). From the tracings, *C*, *H*, and *M* were measured, and an analysis of variance was done on the results. The results of this test are given in Tables 6 and 7.

TABLE 6. REACTION TREND AT 1065°C USING (1: 1) 3*C*:2*H* MIXTURE

Hours	*C*	*H*	*M*
0	67.3	20.8	12.3
1/4	41.5	44.2	14.3
1/2	37.1	49.1	13.8
1	36.0	47.6	16.4
2	34.8	47.6	17.6
4	34.1	45.6	20.3
8	32.8	40.3	26.9

The existence of a definite time trend in the reaction can be seen from from the data. This suggests that at this temperature there is a polytype that is more stable than either the 2*H* or 3*C* polymorphs, and that the reaction was proceeding along a path that would eventually lead to the synthesis of this particular polytype.

TABLE 7. ANALYSES OF VARIANCE IN MEASUREMENTS OF *C*- AND *H*-PARAMETERS*

Source of variation	Degrees of freedom	Sum of squares	Mean square	Variance†	Sum of square	Mean square	Variance
Between times	5	373.3	74.7	17.4	402.3	80.4	18.4
Within times	42	222.5	5.1	5.0_6	290.9	6.9	6.9
Repeats	6	91.2	15.2	2.0_4	157.2	26.2	5.1^5
Samples	12	72.6	6.0	1.8_0	67.1	5.6	1.3_2
Measurements	24	58.7	2.4	2.4_5	70.6	2.9	2.9_4
Totals	47	595.8	12.6		693.2	14.7	

Error	*C*	*H*	Average
σ_s^2 (Samples)	1.80	1.32	1.56
σ_r^2 (Repeats)	2.04	5.15	3.60
σ_m^2 (Measurements)	2.45	2.94	2.70

*Davies(1954a).

†The variance is that due only to the source of variation indicated.

Heating various types of zinc sulphide at different temperatures for varying lengths of time should indicate the structure or packing sequence that is most stable at any particular temperature. The results obtained from all the runs made were dependent on starting material, time, temperature and perhaps other variables, suggesting that equilibrium was not attained. During long heatings in the low temperature range 970°–1015°C, *x*-ray reflections typical of the *4H* polymorph were obtained. In some cases, the intensity of the reflections decreased with time and complex reflections resulted. Others (H-300) showed that the intensity of the reflections increased with long heating. However, the novel *4H* reflections were only prominent when (1:1) cubic to hexagonal mixtures and cubic zinc sulphide were used as starting materials. When the starting material was *2H*, RCA, or B & A zinc sulphide and heating times were increased to 114 hours, a change in the intensities of the (10.0) and (00.1) reflections was seen. There were also unresolved reflections between these two, and resulted in a rise of the background.

Figure 4 shows this quite clearly, and the faint suggestion of a $(10.\frac{1}{4})$ peak in H-301 and H-302 supports the hypothesis that the reactions in these various starting materials were proceeding in a direction that would eventually lead to the same end product for them all.

Single crystals from the runs at 1014°±5°C were examined by E. W. Nuffield, using single crystal methods. A crystal from the batch which

Table 8. Results of Single Crystal Work

H–260*		H–306		H–259	
Spacing	Intensity	Spacing	Intensity	Spacing	Intensity
12.21	m	12.2	w	12.44	s(1)
9.33	s	9.3	s	9.15	s
6.24	ms	6.1	w	6.28	s(1)
4.68	ms	4.68	m	4.66	w
4.18	vw	4.1	vw	4.26	w(1)
3.13	s	3.13	s	3.09	multiple
—	—	—	—	2.69	vvw
2.50	m	—	—	2.50	vvw(1)
2.33	s	2.33	s	2.35	s
2.08	ms	2.08	vw	2.09	s
1.87	ms	1.87	s	1.88	s

s—strong; m—medium; w—weak; v—very; (1)—small spot. *Platy hexagonal crystal used.

Sample	°C	Hours	Charge	Product
H–306	962	216	H–260	*3C*, minor *4H*, other polytypes
H–259	1014	40	*2H*	*3C*, *2H*, *4H*, other polytypes
H–260	1014	40	1:1	*3C*, *4H*, *6H*, other polytypes

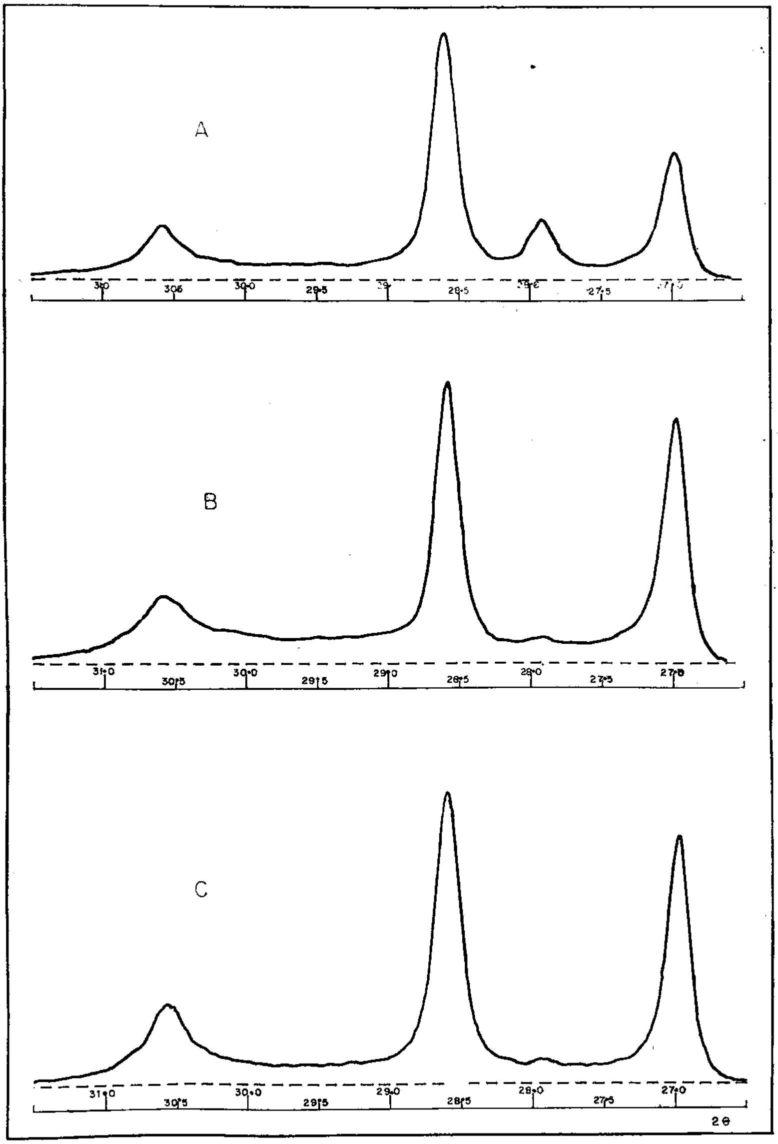

FIG. 4. *X*-ray diffraction spectrographs of products from runs with different starting materials at 1005°C for 114 hours: (A) H-300, (1:1) 3*C*:2*H* starting material (scale factor 8); (B) H-301, 2*H* zinc sulphide starting material (scale factor 4.8); (C) H-302, B and A zinc sulphide starting material (scale factor 4.8). Note suggestion of $(10.\frac{1}{4})$ reflection in B and C.

had 2*H* ZnS as a starting material (H-259) was found to contain substantial amounts of 2*H* and 3*C*, with minor amounts of 4*H* intergrown (see table 8). The product from H-260 which had (1:1) 2*H*-3*C* mechanical mixture as the starting material contained crystals which had an elongated hexagonal habit, and another set of crystals which appeared to be hexagonal plates. The former crystals were more abundant than the latter. Single crystal work on one of the crystals with the elongated hexagonal morphology proved it to be 6*H*, while another crystal with the platy hexagonal morphology proved to be predominantly 4*H* but contained 3*C*. The logical conclusion is that at 1014°C both 6*H* and 4*H* crystals are more stable than a mechanical mixture of 3*C* and 2*H*, but we cannot decide at present which of the two is more stable. Another run, (H-300) at 1005°C, with (1:1) 3*C*: 2*H* mechanical mixture as the starting material contained predominantly 4*H* crystals, as determined by powder work.

In H-306, with a mechanical mixture of 3*C*, H-260 and H-303 as the starting material, the product after heating for 216 hours at 962°C appeared to be isotropic with only slight anisotropism. The *x*-ray spectrometer tracing and powder pattern looked predominantly cubic. The rotation photograph of a single crystal from this batch is almost identical with that of the platy crystal from H-260, but it shows less streakiness. The film showed the presence of 3*C* and 4*H* phases. There were also weak streaky spots which could be interpreted as due to the presence of other less well-defined structures.

Because in the temperature range 960°–1015°C 4*H* and 6*H* crystals grew from a melt containing 2*H* and 3*C* crystals, the conclusion is that in this range they are more stable than either 2*H* or 3*C*.

Equilibrium Diagram

In order to be able to draw an equilibrium diagram, it is necessary to identify unequivocally the phases present. In this system, no pure single phase has been found as is normally the case in a one-component system, except on a phase boundary. We should point out that although we have no concrete evidence to support this hypothesis, there is the possibility that in reality the system is two component, in that small amounts of chlorine from the sodium chloride flux used, and/or oxygen from the silica tubes used enter the zinc sulphide structures and the polytypes occur in the two phase region of this complex system. This possibility seems somewhat remote, especially as the amount of these ions involved would be quite small but we cannot say that this process is improbable, and in fact investigations to check this possibility are currently being undertaken and will be reported later. However, in the meantime, it is necessary to devise a method of determining the cubic-hexagonal packing in the products from the various runs. As previously stated, the method suggested by Smith (1955) works for a mechanical mixture of $3C$ and $2H$ ZnS. When there is evidence that the product contains a regular polytype (H-300 is predominantly $4H$ and so has a packing of approximately 50% cubic), the function $(H+M)/C$ does not fit on the $2H:3C$ curve. The reason for this is that the measured intensities of the reflections are not simply related to the hexagonal-cubic packing in a polytype.

When it was realized that the intensities of the lines studied were such that in the $4H$ structure $(10.0+10.\frac{1}{4})/00.1$ was not equal to the value obtained by mixing $2H$ and $3C$, it seemed evident that the mixing curve for $2H:3C$ was only one of a family of curves, in which case it is necessary to know the polytypes present before the packing can be determined by the spectrometer. The next step was to measure the intensity of $(10.\frac{1}{4})$ for H-300 and calculate the corresponding intensities of (10.0) and (00.1) in the mixture due to $4H$. These calculated values were then subtracted from the measured intensities of the appropriate

TABLE 9. DATA FOR NEAR EQUILIBRIUM CONDITIONS

Sample No.	°C	Flux	Charge	Hours	Product		
					C	*H*	*M*
H-272	800	NaCl	B & A	48	95.5	—	4.5
2	824	(Li, K, Na)Cl	F.G.	72	96.2	—	3.8
201	845	NaCl	B & A	44	94.5	—	5.5
7	863	NaCl	F.G.	72	93.6	—	6.4
205	900	NaCl	B & A	16	93.8	—	6.2
3	907	NaCl	F.G.	47	93.2	—	6.8
175	920	NaCl	$2H$	42	93.4	—	6.6
176	920	NaCl	$3C$	42	94.3	—	5.7
226	949	NaCl	(1:1)	34	94.3	—	5.7
306	962	NaCl	H-260, 303, $3C$	216	90.0	—	10.0
227	965	NaCl	B & A	16	91.8	1.8	7.8
167	968	NaCl	F.G.	23	92.5	1.2	6.3
315	980	NaCl	(1:1)	264	86.7	2.0	11.3
238	990	NaCl	B & A	72	88.4	1.6	10.0
215	995	NaCl	(1:1)	16	83.8	5.2	11.0
300	1005	NaCl	(1:1)	114	47.9	23.5	28.6
301	1005	NaCl	$2H$	114	37.8	34.5	27.7
302	1005	NaCl	B & A	114	44.1	36.8	19.1
260	1014	NaCl	(1:1)	40	75.3	7.9	16.8
244	1027	NaCl	(1:1)	16	61.2	23.7	15.5
307	1045	NaCl	$2H$	74	31.9	53.8	14.3
303	1047	NaCl	(1:1)	38	38.5	42.2	19.3
250	1050	NaCl	(1:1)	16	32.0	36.0	21.7
264	1082	NaCl	(1:1)	10	39.4	41.7	18.9
266	1097	NaCl	(1:1)	8	37.6	38.4	22.4
304	1183	NaCl	(1:1)	20	36.4	46.6	17.0
305	1275	NaCl	B & A	21	34.4	52.0	13.6

TABLE 10. TEMPERATURE-PACKING RELATIONSHIP

No.	°C	$\frac{H+M}{C}$	% Cubic packing	Remarks
H–272	800	0.0471	92	Rise in background at $2\theta = 27.5°$
2	824	0.0390	94	Suggestion of peak at $d = 2.30$ Å background rises from $2\theta = 27.5°$
201	845	0.0582	91	Slight rise in background from $2\theta = 27.5°$
7	863	0.0984	85	Background starts rising from $2\theta = 27.5°$
205[a]	900	0.0660	90	Suggestion of faint peak at $d = 3.28$ Å background starts rising from $2\theta = 26.5°$
3	907	0.0730	88	Background starts rising from $2\theta = 26.5°$
175	920	0.0706	88	Suggestion of very faint reflection at $d = 3.2$ Å; background continues rising from this point
176	920	0.0604	90	Suggestion of very faint reflection at $d = 3.2$ Å; background continues rising from this point.
226	949	0.0604	90	Suggestion of very faint reflection at $d = 3.2$ Å; background continues rising from this point
306[a]	962	0.111	84	Background starts rising from $2\theta = 26.75$; suggestion of peaks at $d = 3.3$, 3.29, 3.18 Å, (10.½) peak not seen
227	965	0.105	83	(10.0) peak very faint, and suggestion of (10.½) peak; (10.½) reflection very very faint
167	968	0.0811	87	Very faint 3.3 Å reflection, thin background, continues rising
315[a]	980	0.153	78	Very weak peak at $d = 3.30$ Å and faint peak at $d = 3.20$ Å
238	990	0.131	81	(10.½) and (10.0) weak, suggestion of (10.¼)
215	995	0.181	75	Weak (10.0), (10¼), and (10.½) reflections
300[b]	1005	1.09	(23)*	(10.¼) peak distinct. (10.0) peak asymmetric
301[b]	1005	1.65	(10)*	(10.0), (00.1), (10.½) peaks asymmetric, background high between, suggestion of (10.¼) peak
302[b]	1005	1.27	(18)	(10.0) asymmetric, (10.½) very broad and background between high, suggestion of (10.¼) peak
260	1014	0.328	61	(10.0) and (10.¼) peaks weak, background not very high
244	1027	0.634	41	(10.½) peak weak and asymmetric, (10.0) peak asymmetric, background high
307	1045	2.13	(3)*	(10.0) and (10.½) peaks asymmetric, background between high
303[c]	1047	1.60	11	(10.0), (000.1) peaks asymmetric, (10.½) broad, background between high, and suggestion of specular reflections
250	1050	1.37	16	(10.½) peak weak and asymmetric, suggestion of peak at $d = 3.07$ Å, (10.0) peak asymmetric, background high
264	1082	1.54	12	(10.0) peak asymmetric, suggestion of peak at $d = 2.95$ Å, (10.½) peak weak
266	1197	1.62	10	(10.0) peak asymmetric, (10.½) peak weak and broad background between high
304[c]	1183	1.75	8	(10.0), (00.1), (10.½) peaks asymmetric, background high
305[c]	1275	1.91	5	(10.0), (10.½) peaks asymmetric, background between high

*Values in brackets are uncertain, due to high background.

[a]See Figs. 5, 6. [b]See Fig. 4. [c]See Fig. 5.

reflections. When this was done, it was found that $(H+M)/C$ for the remainder is 0.51, which supports the idea that the measured intensities

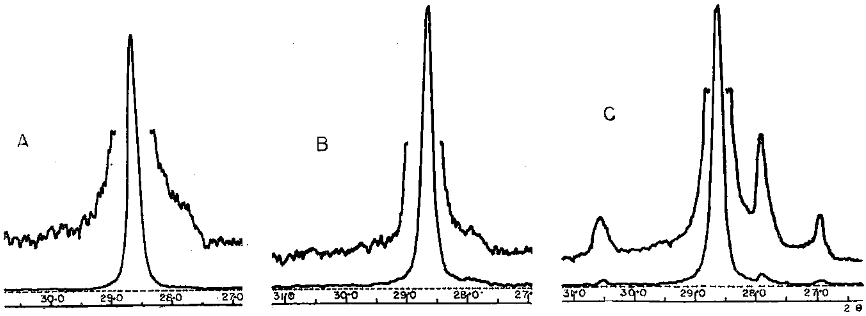

FIG. 5. X-ray diffraction spectrographs of products from runs at different temperatures with (1:1) $3C{:}2H$ mixture as starting material: (A) H-205–900°C (scale factor 1 and 16); (B) H-306–962°C (scale factor 1.2 and 4.8); (C) H-315–980°C (scale factor 2 and 16).

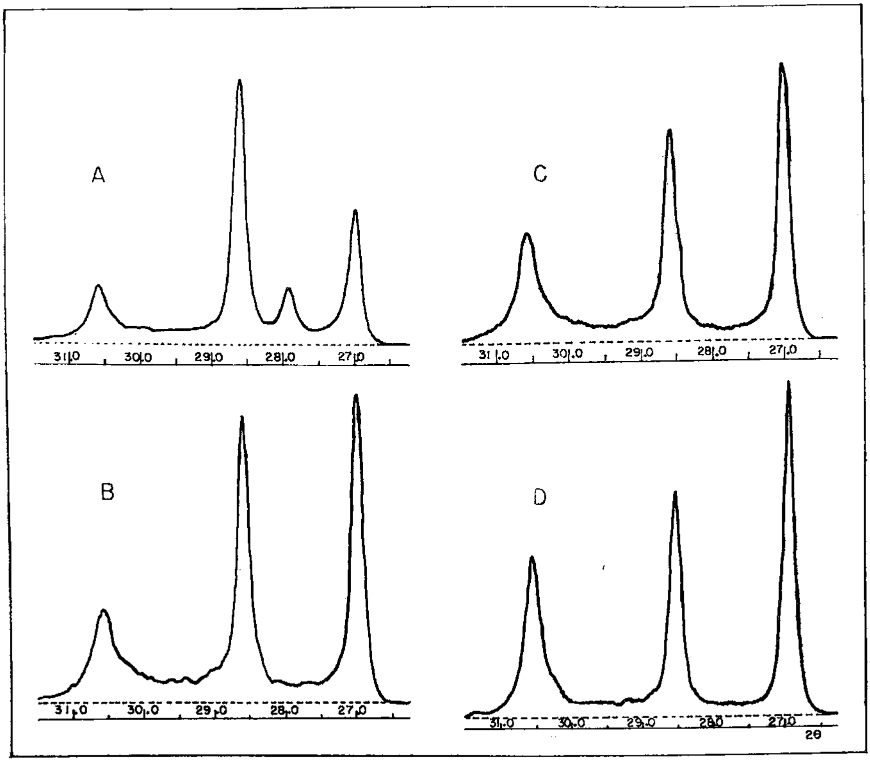

FIG. 6. X-ray diffraction spectrographs of products from runs at different temperatures with (1:1) $3C{:}2H$ mixture as starting material: (A) H-300–1005°C (scale factor 6.4); (B) H-303–1047°C (scale factor 3.2); (C) H-304–1173°C (scale factor 4); (D) H-305–1275°C (scale factor 4).

are higher than those calculated on the basis of simple mixing. In this case the M value is a very important contributor to the total intensities of the reflections measured. This is not the case in a mechanical mixture, so the logical deduction is that if M is large then the $2H:3C$ curve cannot be used to determine packing in the polytype.

An examination of Table 5 shows that the products from various runs at the same temperature, but different reaction times, become more similar with increased reaction time. In none of these runs was there

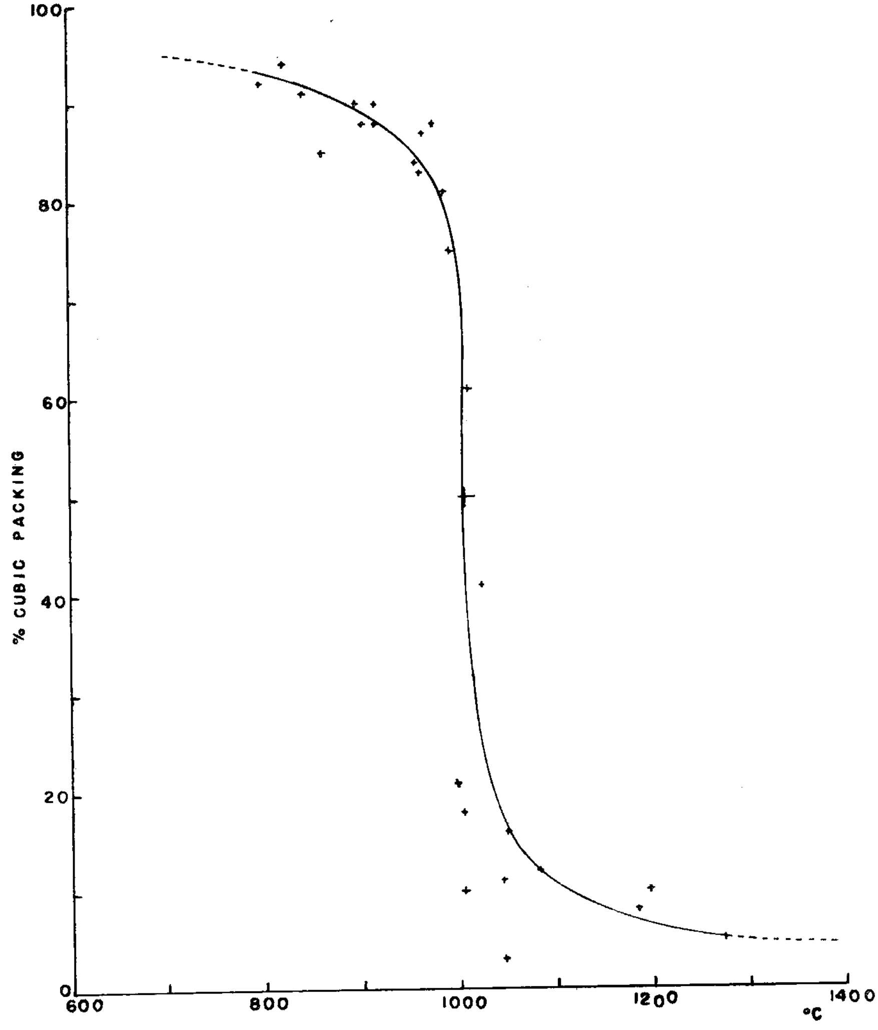

FIG. 7. Equilibrium temperature-packing diagram for the system ZnS.

any evidence that stable equilibrium was reached. However, increased reaction time brought a closer approach to stable equilibrium. Where different starting materials give essentially the same product, then stable equilibrium should lie somewhere between these. In order to determine the equilibrium structure at any particular temperature, the products from various starting materials after reaction for long periods of time are compared and the average value taken as the best approximation. The results of some of these runs are given in Tables 10 and 11.

The derivation of the equilibrium diagram (Fig. 7) is based on the use of the *2H*: *3C* curve when *M* value is low. However, when this value is high, the packing is approximated from the single crystal work.

DISCUSSION OF RESULTS

Equilibrium

In all of these experiments it was found that the properties of the system were functions of temperature and time (pressure, composition, etc., being constant or approximately so). This is definite proof that we are mainly dealing with a series of metastable equilibria, because the properties of a one-component system in stable equilibrium are single valued functions of temperature, if pressure, etc., are constant. In fact, it is only in about two runs, and these at high temperatures, that there is any evidence that the product was not largely influenced by the starting material. The constant similarity of the results when *2H*, B & A, and RCA zinc sulphide were used as the starting materials, and their difference from *3C* and (1:1) *3C*: *2H* mechanical mixtures show that the influence of the starting materials is important in these experiments.

The quantitative aspects of the results are rather unsatisfactory, owing to the fact that it was only for mechanical mixtures of two polymorphs that a method of determining the packing was found. No satisfactory means of determining the packing in complex mixtures of zinc sulphide polytypes was available. However, when only mechanical mixtures of *2H* and *3C* are considered (the degree of mixing being microscopic or submicroscopic but without formation of significant amounts of any true polytype), the temperature-packing curve is approximately an ogive. The equilibrium temperature-packing curve should be similar to that obtained from the study of the sandwiched *2H*: *3C* structures. The equilibrium curve can then be uniquely located by plotting the stability temperature of the *4H* polytype (50% hexagonal packing) at 1010°±10°C, if the general shape is known.

The various equilibria can be qualitatively represented by plotting the energy (vapour pressure) of the various polytypes against temperature (see figure 8). This plot represents the various metastable transformations

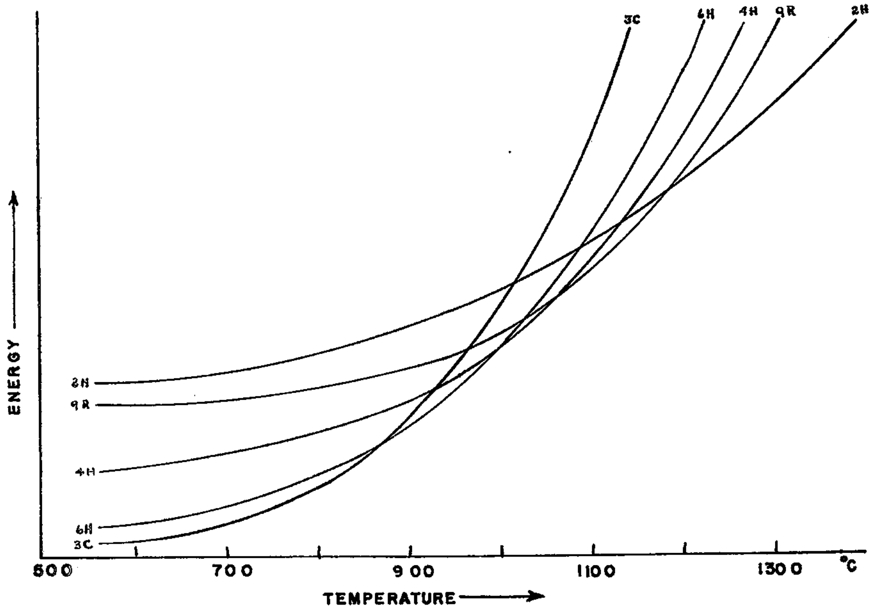

FIG. 8. Diagrammatic illustration of the variation of energy with temperature for the polymorphs and some polytypes in the system ZnS. If an infinite number of polytypes are present, then it is seen that each polytype will be stable at a point temperature only, and these points of stability will generate the equilibrium curve. Some of the many possible metastable equilibrium points are also shown.

deduced and explains the apparent reversals in reaction trends which occurred during heating. For example, the experimental results show that if a mechanical mixture of $2H$ and $3C$ crystals is heated at a temperature above the equilibrium temperature, the $2H$ content at first increases and then decreases with increased reaction time. This apparent reversal of direction of the reaction supports the hypothesis that the reaction goes through a series of metastable equilibria before stable equilibrium is finally reached. When the reaction occurs below the transition temperature, $2H$ rapidly inverts to $3C$, and it is only after long heating that the stable polytype will crystallize. Furthermore, there are indications that simple polytypes may crystallize metastably, but they are resorbed as the reaction proceeds in the direction of the stable polytype.

Since some polytypes have a random stacking sequence (Jagodzinski, 1949 *a*, *b*, *c*, 1954; Strock & Brophy, 1955), one cannot help wondering why ordered structures like $2H$ and $3C$ should go to random structures. Various explanations have been advanced for the occurrence of the polytypes (Mitchell & Corey, 1954; Strock, 1955; Strock & Brophy, 1955), but, in view of the fact that in this study the reaction was found to occur under conditions permitting equilibrium, it is concluded that the free energy of the stable polytype in the temperature range investigated is less than that of mixtures of polymorphs with identical cubic-hexagonal packing. The departure from a linear relationship in the heat content or free energy of the hybrid structures is the driving force of the reaction, and may be due to an interaction between the two types of packing occurring in the same crystal.

As stated earlier there is the possibility that during the course of reaction the system changes from a true one component to a two or even a polycomponent system. This could be due to a disproportionation of the sulphur between the solid, liquid and vapour phases, so that we can have the solid phase having a composition $ZnS_{(1-x)}$ and the vapour phase $ZnS_{(1+x)}$ or *vice versa* where x can be of the order of parts per million. This change in composition could explain some of the observations, but it seems insufficient to explain all, and we have no evidence such as there is in FeS to support this. The possibility of oxygen and/or chlorine replacing sulphur in the lattice cannot be overlooked, but here again we have no concrete evidence of this.

The important deduction is that the phase transformation of zinc sulphide is of the diffused first order type, because it shows no discontinuity of the parameter measured but only an inflection. Diffused first order transformations are known in the liquid and gaseous states. The change of water from a liquid to a gas under super-critical conditions is an example of this. The transition of cubic to hexagonal cobalt during cold working approximates the type of transformation found in zinc sulphide (Wells, 1950, p. 679), but there is no previous evidence of such transformations occurring in the solid state under equilibrium conditions. This implies that the generality is the diffused first order type of transition rather than the so-called normal first order transition. In fact, if this assumption is made, then there is no necessity to regard transitions like the α-β transition in quartz as anomalous, for such transitions can be regarded as a special case of the diffused first order. Previous results obtained in studying transitions may in reality have reflected inability to detect the diffuseness of the change. The spread of the transition over a range of temperatures can be regarded as the hybridization range of the structures involved. In the ideal normal first order transition, this range is zero.

The Effect of Trace Substitutions

The suggestion has been made that the various polytypes and crystal intergrowth phases observed are due to the substitution of minor amounts of elements like oxygen, chlorine and metallic ions in the structure. It is further claimed that the effect of these may be the initiation of dislocations on the growing faces, and in fact it does seem that this could be a logical and conventional explanation of the observed "reversal" of packing with time discussed earlier. The differences in packing of phases formed by rapid growth from the vapour phase as contrasted with growth in the solid and fluid phases seems to be contrary to this. Again, if the observed region of growth of polytypes were in fact a true two phase region in a complex system of the type ZnS-SiO_2 or ZnS-NaCl then the progressive series of two phases to intergrowth to polytype mentioned earlier would be difficult to explain. The introduction of Fe and Mn in the structure produces the same trend and so the conclusion is that trace amounts of these will have the same effect as larger quantities.

There is also the possibility that there is a disproportionation of the Zn and S between the solid and vapour phases. We can visualize the possibility of a reaction trend of the type:

$$\begin{tikzcd}
\text{ZnS } (3C) \arrow[rr, leftrightharpoons] \arrow[dr, leftrightharpoons] & & \text{ZnS } (2H) \arrow[dl, leftrightharpoons] \\
& Zn_{1-x}S &
\end{tikzcd}$$

Polytype

However this does not fit the observed trend and does not explain the observed decrease in size of the intergrowths as does the sequence:

$$\underset{\text{discrete crystals}}{2H+3C} \longrightarrow \underset{\text{intergrowth}}{2H.3C} \longrightarrow \text{Polytype.}$$

That this explanation is insufficient to account for all the observations seems quite reasonable, but it does merit more detailed study, and this work is currently being done and we hope to report on it more fully in the future.

ACKNOWLEDGMENTS

The writer wishes to express his thanks to Prof. F. G. Smith for suggesting the problem, supervising the work and materially assisting in several phases of the investigation. He obtained all the diffractometer tracings used in this work.

The x-ray diffraction spectrographs were made with an apparatus in the Department of Metallurgical Engineering of the University of Toronto, with the kind permission of Prof. L. M. Pidgeon. Prof. E. W. Nuffield did the single crystal work and advised on several phases of the investigation.

Dr. D. B. DeLury of the Ontario Research Foundation helped in the design of the experiments conducted to determine the variance in the measurements made. Only a few of these experiments are quoted in this paper. Prof. B. A. Griffith gave valuable advice on the statistical side of the investigation. The R.C.A. Research Laboratories kindly donated to us the spectrographic grade zinc sulphide used in some of the runs.

REFERENCES

ALLEN, E. T., CRENSHAW, J. L., & MERWIN, H. E. (1912): The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions, *Amer. Journ. Sci.* (4), **34**, 341–396.

——— (1914): Effect of temperature and acidity in the formation of marcasite (FeS_2) and wurtzite (ZnS); a contribution to the genesis of unstable forms, *Amer. Jour. Sci.* (4), **38**, 393–431.

BRAGG, W. L. (1937): *Atomic Structure of Minerals.* Cornell Univ. Press.

BUERGER, M. J. (1948): The role of temperature in mineralogy. *Am. Mineral.*, **33**, 101–121.

——— (1951): Crystallographic aspects of transformation. *Phase Transformation in Solids.* John Wiley & Sons, Inc.

COREY, A. S. (1953): Note on sphalerite and wurtzite. *Am. Mineral.*, **38**, 141–143.

DAVIES, O. L. (1954): *Statistical Methods in Research and Production.* Oliver & Boyd.

——— (1954a): *The Design and Analysis of Industrial Experiments.* Oliver & Boyd.

FRONDEL, C., & PALACHE, C. (1950): Three new polymorphs of zinc sulphide *Am. Mineral.*, **35**, 29–42.

JAGODZINSKI, H. (1949 *a*, *b*, *c*): Eindimensionale Fehlordnung in Kristallen und ihr Einfluss auf die Rontgeninterferenzen. 1. 11. 111, *Acta Cryst.*, **2**, 201–207, 208–214, 298–304.

——— (1954*a*): Der Symmetrieeinfluss auf den allgemeinen Lösungsansatz eindimensionaler Fehlordnungsprobleme, *Acta Cryst.*, **7**, 17–25.

——— (1954*b*): Polytypism in SiC crystals, *Acta Cryst.*, **7**, 300.

KLUG, H. P., & ALEXANDER (1955): *X-ray diffraction procedures*, John Wiley and Sons, Inc.

MITCHELL, R. S. & COREY, A. S. (1954): The coalescence of hexagonal and cubic polymorphs in tetrahedral structures as illustrated by some wurtzite-sphalerite groups. *Am. Mineral.*, **39**, 773–782.

MULLER, H. (1952): Die eindimensionale Unwandlung Zinkblende-Wurtzit und die dabei auftretendon Anomalien. *Neues Jahrb. Min.*, **84**, 43–76.

PATERSON, M. S. (1952): *X*-ray diffraction by face-centred cubic crystals with deformation faults. *Journ. Appl. Phys.*, **23**, 805–811.

RAMDOHR, P., & VON WEBSKY, C. (1943): Wurtzitkristalle und Zwillinge. *Neues Jahrb Min.*, Mon. A, 1943, 65–71.

RAMSDELL, L. S. (1944): The crystal structure of alpha-SiC, type IV, *Am. Mineral.*, **29**, 431–442.

——— (1945): The crystal structure of alpha-SiC, type VI, *Am. Mineral.*, **30**, 519–525.

——— (1947): Studies on silicon carbide, *Am. Mineral.*, **32**, 64–82.

——— & KOHN, J. A. (1951*a*): Three new polymorphs of silicon carbide, 8*H*, 75*R*, and 84*R*, *Acta Cryst.*, **4**, 75.

——— (1951*b*): Disagreement between crystal symmetry and *x*-ray diffraction data as shown by a new type of silicon carbide, 10*H*, *Acta Cryst.*, **4**, 111–113.

——— (1952): Developments in silicon carbide research, *Acta Cryst.*, **5**, 215–224.

——— & MITCHELL, R. S. (1953): A new hexagonal polymorph of silicon carbide, 19*H*, *Am. Mineral.*, **38**, 56–59.

SMITH, F. G. (1955): Structure of zinc sulphide minerals. *Am. Mineral.*, **40**, 658–675.

——— & HILL, V. G. (1956): On the reported transformation of wurtzite to sphalerite by grinding, *Acta Cryst.*, **9**, 821–822.

STROCK, L. W. (1955): Atomic arrangements in close-packed structures, *Sylvania Tech.*, 8–71–75.

——— & BROPHY, V. A. (1955): Synthetic zinc sulphide polytype crystals, *Am. Mineral.*, **40**, 94–106.

THIBAULT, N. W. (1954): Morphological and structural crystallography and optical properties of silicon carbide, *Am. Mineral.*, **29**, 249–278.

WELLS, A. F. (1950): *Structural Inorganic Chemistry*, Oxford.