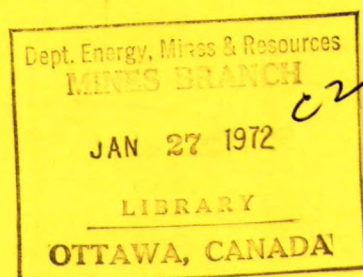**CANADA**

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

CRYSTAL GROWTH   PART II:

THE GROWTH OF ZINC SULPHIDE CRYSTALS

LEONARD G. RIPLEY

MINERAL SCIENCES DIVISION

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<u>ERRATA SHEET FOR RESEARCH REPORT R 236</u>

Page 89 - Figure Captions for Figures 19 and 20.

<u>Figure 19.</u> Photograph of the $PbCl_2$ Flux Growth (Run #374,
see Table 51).

<u>Figure 20.</u> Photograph of the Hydrothermal Growth (Run #402,
see Table 52).

Mines Branch Research Report R236

CRYSTAL GROWTH

PART II:
THE GROWTH OF ZINC SULPHIDE CRYSTALS

by

Leonard G. Ripley*

ABSTRACT

This report is an in-depth study of problems encountered in the growth of synthetic single crystals of zinc sulphide. The four growth procedures explored were: Chemical Vapour Transport, Vapour Transport (Sublimation), Flux Growth, and Hydrothermal Growth. The prime goal of growing centimetre-sized crystals of sphalerite was achieved by both the chemical vapour transport method, using either HCl or I_2 as the carrier, and by the vapour transport method. A few millimetre-sized single crystals of wurtzite have been obtained by the vapour transport method.

The report includes sections dealing with the purification of zinc sulphide powders, the doping of zinc sulphide crystals with either Al or Fe, various analyses of powder and crystalline samples, and also some characterizations of the single crystals.

The yellow-green colouration in some synthetic ZnS crystals has been found to be caused by departure of the Zn:S ratio from the required 1:1 stoichiometry.

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Direction des Mines
Rapport de recherches R236

LA CROISSANCE DES CRISTAUX

DEUXIÈME PARTIE:

LA CROISSANCE DES CRISTAUX DE SULFURE DE ZINC

par

Leonard G. Ripley*

RÉSUMÉ

Ce rapport est une étude approfondie des problèmes éprouvés dans la croissance des monocristaux synthétiques de sulfure de zinc. Les quatre méthodes de croissance explorées ont été: transport chimique en phase vapeur; transport en phase vapeur (sublimation); croissance par la méthode des fondants; et croissance hydrothermique. Le but principal de faire croître des cristaux de sphalérite de dimensions "centimètres" a été réalisé à la fois par la méthode de transport chimique en phase vapeur, utilisant soit le chlorure d'hydrogène soit l'iode comme porteur, et par la méthode de transport en phase vapeur. Quelques monocristaux de wurtzite de dimensions "millimètres" ont été obtenus par la méthode de transport en phase vapeur.

Le rapport comprend des sections traitant de la purification des pourdres de sulfure de zinc, le dopage des cristaux de sulfure de zinc soit avec l'aluminium soit avec le fer, des analyses variées des poudres et des cristaux, et aussi quelques caractérisations des monocristaux.

On a trouvé que la coloration jaune-verte dans quelques cristaux synthétiques de sulfure de zinc a été causée par la déviation de la proportion Zn:S de la stoechiométrie exigée de 1:1.

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Contribution de recherches sur les sulfures No. 42.

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INTRODUCTION

In Part I of this series of Research Reports entitled "Background to Crystal Growth" (1), it was stated that, during the past six years, the crystal growth of fifty materials had been attempted in the field of sulphides, arsenides, and sulpharsenides of Co, Cu, Fe, Ni, and Zn, and also some other compounds, many of them quite successfully, by one or more of the six different growth techniques explored. This present report is Part II of a five-part series, and will deal with the growth of zinc sulphide crystals.

When this programme was initiated in early 1964 (2), one of the main objectives was to grow single crystals of synthetic ZnS and (Zn, Fe)S of controlled purity and suitable size for use in the investigation of desired properties by various scientists in the Mineral Sciences Division, Mines Branch. Two main requirements were specified. The first was that the crystals should be at least a cubic centimetre in size, in order that these single crystals could be cut for specific electrical or optical experiments; and, secondly, that the crystal must be entirely in the cubic form, i.e., sphalerite, and not contain any of the hexagonal form, wurtzite. Zinc sulphide is known to exhibit the special one-dimensional polymorphism called polytypism. The polytypes differ only in the stacking sequence. The sphalerite structure can be considered as two inter-penetrating face-centered cubic lattices, with the characteristic stacking sequence ...ABCABC... for the close-packed layers. The wurtzite structure can be considered as two inter-penetrating hexagonal sequences ...ABAB... for the close-packed layers. Faults in the stacking sequences are common; these faults, if ordered, give rise to polytypes that can develop regions of the "wurtzite" structure in an otherwise "sphalerite" crystal and vice versa.

The above-stated terms of reference have been successfully accomplished. Many crystals have been supplied to various divisional researchers who have submitted internal reports, the essentials of which have

included herein in context, dealing with the chemical and physical analysis of these crystals.

Existing growth procedures have been modified to suit the equipment available in the Mineral Sciences Division. But, in order to achieve this goal, many details of technique that required study cropped up from time to time, whereby the quality of the crystals was improved and the chemistry of zinc sulphide became better understood.

Since the growth of large single crystals of ZnS was the prime goal, many interesting areas of study related to this compound were touched upon; however, if they were not advantageous to the achievement of this goal, they were not pursued in any great detail. It is with this explanation that some incomplete aspects are recorded herein; however, it is hoped that, with additional research, some of these topics can be reported upon in greater detail at a later date.

This report gives a detailed account of several aspects of the zinc sulphide crystal-growth problem; namely:

> Sources
> Purification
> Stability
> Growth Procedures and Results
> Doping
> Analysis at all stages
> Characterization of the crystalline* product.

SOURCES OF ZINC SULPHIDE

The starting material for ZnS growth reactions, to be described later in this report, was obtained in various ways:

1. Zinc Sulphide Obtained Synthetically (by any of the following reactions).

(a) $Zn + S \rightarrow ZnS$

(b) $Zn + H_2S \rightarrow ZnS + H_2\uparrow$

(c) $ZnCl_2 + H_2S \rightarrow ZnS + 2HCl\uparrow$

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*The adjective "crystalline" is used throughout this report to denote a macro-crystalline growth product, as opposed to a micro-crystalline material.

(d) $Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$

$+ H_2S$

$\downarrow$

$ZnS + 2HCl \uparrow$

(e) $ZnO + H_2S \rightarrow ZnS + H_2O \uparrow$
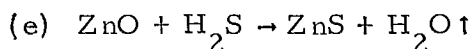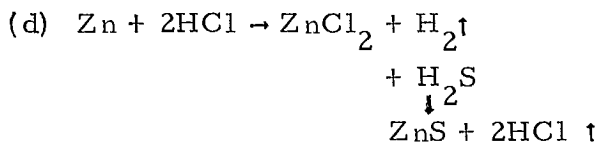
The most satisfactory of the five methods was (a). In this case, high-purity zinc and sulphur were combined in sealed silica tubes and annealed at 790°C for six days.

Reaction (e) has been used successfully for the removal of oxygen (as ZnO) in the purification of ZnS powders.

2. Zinc Sulphide Obtained Commercially

(a) Fisher Scientific purified ZnS, Cat. No. Z-72. This powder became available very early in the project, but, because of a green colouration in the powder, which was imparted to the growing crystals, it was not used extensively. The colouration was originally assumed to be due to the presence of copper, but subsequent analysis showed it to be due to the presence of cobalt.

(b) General Electric Luminescent-Grade ZnS, Cat. No. 118-8-1. This material became available about a year after the start of the Sulphide Programme. This product is claimed to be spectrographically pure; however, it contains some water and a small amount of sulphate ion; these latter impurities created some purification problems.

(c) Koch-Light Laboratories Ltd., Electronic-Grade ZnS, purity 99.99%, Cat. No. 8845h. This material was obtained only recently, and has proved to be the purest of the three commercially-available zinc sulphides.

ANALYSIS

Although the manufacturers' purity claims were available for some of the starting materials, it was considered desirable to analyse the individual batches of these chemicals in our own laboratories. In addition, many of the intermediate (purified) materials and also the final crystalline materials were analysed. These analyses were performed in the laboratories of the

Mineral Sciences Division, Mines Branch, as shown in Table 1. The analyses have played a vital role in this study and are reported in context.

TABLE 1

Methods of Analysis of Zinc Sulphide and Analysts of the
Mineral Sciences Division Involved

Method of Analysis	Analyst
Atomic-Absorption Spectrophotometric	Mr. J. C. Hole
Chemical*	Miss E. Mark and the present author
Electron-Microprobe	Dr. D. C. Harris and Mr. D. R. Owens
Electrical Resistance Measurements	Dr. G. Springer (Postdoctorate Fellow)
Infra-red Spectra	Dr. A. H. Gillieson and Mr. D. M. Farrell
Neutron-Activation	Mr. C. McMahon
Stereoscopic Microscope	Dr. E. H. Nickel
Semi-quantitative Spectrochemical	Mr. D. P. Palombo
Precession Camera	Mr. J. F. Rowland
D. T. A. and T. G. A. Thermograms	Mr. R. H. Lake
X-ray Diffraction	Mr. E. J. Murray
X-ray Fluorescence	Mr. J. L. Dalton

*Miss E. Mark (3) and the present author worked independently, using
different methods of analysis.

The various analyses performed have been recorded, as received, and appear in various tables of this report. An examination of these various results will show that, in a few cases, the values reported are different from those obtained by another method; others deviate from the anticipated value. These variations may be due to several causes; however, the exact reasons have not been ascertained.

The zinc concentration of many sulphide samples was determined by oxidizing them in air at 900°C for at least 1 hour. The resulting ZnO was weighed and the equivalent concentration of zinc calculated. This method

appears to be very reliable. In the few cases where sulphur values are given, the method used was to collect the oxides of sulphur, evolved in the air-oxidation of zinc sulphides, in a (sodium hydroxide + potassium permanganate) solution. The resulting sulphate ions were precipitated with $BaCl_2$, then filtered and dried as $BaSO_4$. This sulphur value appears to be slightly low; the reason is that a small amount of sulphur is volatilized from the sulphide as black elemental sulphur, which escapes to the exit end of the combustion system and is not oxidized.

In studying the purification steps, many gravimetric analyses were undertaken; in all cases, the sample was placed in a small Vitreosil boat and heated in a combustion system consisting of a quartz process tube and a 12-in.-long, hinged furnace.

PURITY OF REAGENTS

The purity of the above chemicals was of considerable significance in this investigation. The elemental zinc and sulphur were of sufficient purity to be used directly; however, two of the three commercial ZnS powders were heated in H_2S to remove oxygen and water and to ensure exact 1:1 stoichiometry.

1. Zinc

Zinc metal was obtained from the Consolidated Mining and Smelting Company of Canada Ltd., in the form of a zone-refined rod; this was milled prior to each experiment. This metal was labelled "Cominco 69 Grade Zinc" and had a reported purity of 99.9998%, obtained by difference. The data on this zinc are shown in Table 2.

2. Sulphur

Special high-purity sulphur was obtained from American Smelting and Refining Company (ASARCO). This sulphur was labelled 99.999+%, Lot 5-64-1. The analyses are shown in Table 3.

3. Synthesized Zinc Sulphide (made at the Mines Branch)

As mentioned earlier, a supply of ZnS was obtained by the reaction of stoichiometric proportions of zinc and sulphur. The analyses of this product are shown in Table 4. The theoretical values for ZnS are Zn = 67.094% and

S = 32.906%. The zinc values indicate a fairly good and uniform product, but the sulphur values, by comparison, appear to be slightly low.

4. Fisher Scientific ZnS

In the case of the commercial ZnS powder obtained from Fisher Scientific, the manufacturer did not provide any analysis. In Tables 5a and 5b, the analyses performed in the Mines Branch Laboratories on this product are shown. The cobalt content of the sample is credited with imparting a greenish colouration to the powder. This impurity precluded the wide usage of this material in crystal growing.

5. General Electric ZnS

The second supply of commercially-available ZnS was obtained from the General Electric Chemical Products plant in Cleveland, Ohio, U.S.A. The comparison of the manufacturer's analyses with those of the Mines Branch Laboratories is shown in Tables 6a and 6b. The analyses show that this product is of "spectrographic" purity with respect to trace impurities. However, water and sulphate ions are present and their sum represents approximately 4.0% of the sample. These impurities must be removed prior to its use for crystal growth. The details of this purification will be described later in this report.

6. Koch-Light ZnS

The third source of supply of commercially-available ZnS was Koch-Light Laboratories Ltd. in England. The manufacturer described this product as being 99.99% pure. The analyses obtained in the Mines Branch laboratories are shown in Tables 7a and 7b. The analyses show this product to be the purest of the three commercial products.

TABLE 2

Analyses of High-Purity Cominco 69 Grade Zinc Metal (in PPM)

Source of Analysis	Sb	Cd	Ca	Cu	Fe	Pb	Mg	Si	Ag	O_2
Cominco	0.1	0.3	0.1	0.1	0.5	0.2	0.1	0.1	0.1	-
Mineral Sciences Division	N.D.*	-	N.D.*	N.D.*	N.D.*	N.D.*	40*	80*	N.D.*	30** 140***

*Internal Report MS-AC-68-649. Semi-quantitative Spectrographic Analysis; in addition to the above values, the following elements were reported as being not detectable: Ba, Mn, Mo, W, Sn, Cr, Nb, Ta, Bi, Al, V, In, Zr, Na, Ti, Ni, Co, Sr.
**Internal Report MS-AC-68-641. Neutron-Activation Analysis, on tear-drop Zn 69.
***Internal Report MS-AC-68-641. Neutron-Activation Analysis, on milled cuttings of Zn 69.

TABLE 3

Analyses of Special High-Purity "ASARCO" Sulphur (in PPM)

Source of Analysis	Na	Cl	Mg	Cu	O_2
ASARCO*	1	< 1	N.D.	–	–
Mineral Sciences Division	N.D.**	–	80**	400**	55***

*In addition to the above elements, the following elements were reported as being
not detectable by spectrographic means: Sb, Tl, Mn, Pb, Sn, Si, Cr, Fe, Ni,
Bi, Al, Ca, In, Cd, Zn, Ag.
**Internal Report MS-AC-68-649. Semi-quantitative Spectrographic Analysis:
in addition to the above, the following elements were reported as being
not detectable: Ba, Mn, Mo, Sb, W, Pb, Sn, Cr, Nb, Ta, Fe, Bi, Al, V,
Ca, In, Zn, Ti, Ni, Co, Sr.
***Internal Report Report MS-AC-68-642. Neutron-Activation Analysis.
Note: 400 ppm Cu (= 0.04%Cu) is a somewhat high figure in view of the 99.999+%
purity of this sulphur, claimed by the manufacturer.

TABLE 4

Analyses of ZnS Prepared from High-Purity Zinc and Sulphur

Analyst	Sample	Zinc		Sulphur		Sum of	Calculated
		On Fines	On Lump	On Fines	On Lump	Zn + S	Formula
Miss E. Mark*	1	–	–	34.107%	–	–	$ZnS_{1.055}$***
	2	–	67.006 ±0.125%	–	32.757 ±0.030%	99.764%	$ZnS_{0.996}$
L.G. Ripley**	3	67.057%	–	–	–	–	$ZnS_{1.002}$***
	4	–	67.074%	–	–	–	$ZnS_{1.001}$***

*Internal Report - MS-AC-69-698. Chemical analysis.

**Results obtained by oxidation of ZnS in air at 900°C for 1 hour, and calculation of zinc content from the ZnO produced.

***These formulae were calculated on the basis that the balance of the sample was totally the other element.

TABLE 5a

Micro-Analyses of Fisher Scientific ZnS Powder (in PPM)

Analytical Method	Si	Mg	Fe	Al	Ca	Cu	Co	Ni	Cd	Mn
Semi-quantitative Spectrographic*	287	1640	153	1810	220	3	637	-	-	31
Atomic-Absorption Spectrophotometry**	-	-	20	-	-	5	330	10	5	-
Colorimetric***	-	-	37	-	-	-	-	-	-	-

*Report SL 65-046.
**Report MS-AC-66-830.
***Private communication from Miss E. Mark, Analytical Chemistry Section, Mineral Sciences Division.

TABLE 5b

Other Analyses of Fisher Scientific ZnS Powder

Analyst	Zinc	H_2O (L.O.H.)***	Calculated Formula	Acid-Insoluble
Miss E. Mark*	-	0.16% (Evolved up to 135°C)	-	0.16%**
L.G. Ripley	67.00%	0.11% (Evolved up to 225°C)	$ZnS_{0.999}$	-

*Private Communication.
**Report 69-192; X-ray diffraction analysis indicated that this material was $MgAl_2O_4$, spinel.
***L.O.H. = Loss on heating.

TABLE 6a

Micro-Analyses of General Electric ZnS Powder (In PPM)

Source of Analysis	Cu	Fe	Ni	Pb	Mg	Si	Mn	Al	Ca	Co	Ag	Cd
General Electric*	0.2	1	0.3	3	Trace	Trace	N.D.	N.D.	Trace	N.D.	N.D.	Trace
Mineral Sciences Division**	5	N.D.	N.D.	N.D.	41	140	N.D.	N.D.	N.D.	N.D.	N.D.	-

*In addition to the above elements, the following elements were not detectable by spectrographic means; As, Sb, Bi, B, Cr, Co, In, Hg, Mo, P, Sr, Sn, Ti, V, and W; also, the alkali metals are very low in concentration.
**Report SL 65-046, Semi-quantitative Spectrographic Analysis.

TABLE 6b

Other Analyses of General Electric ZnS Powder

Source of Analysis	Zinc	Sulphur	Zn+S	Calculated Formula	Acid-Insoluble	$SO_4^=$	Cl^-	H_2O
General Electric	-	-	-	-	-	< 0.5%	< 0.015%	-
Miss E. Mark*	(20)64.062%***	(10)32.072%***	96.135%	$ZnS_{1.026}$	0.40%**	1.1%	-	-
L.G. Ripley	64.51%	32.15	96.66%	$ZnS_{1.015}$	-	-	-	3.60%

*Report MS-AC-70-120.
**Reports 70-113; 70-114; X-ray diffraction analysis indicated the presence of free sulphur and of an undetermined organic compound.
***The circled numbers indicate the number of determinations made.
Note. The dash indicates no analysis obtained.

TABLE 7a

Micro-Analyses of Koch-Light ZnS Powder (in PPM)

Analytical Method	Si	Mn	Mg	Fe	Al	Ca	Cu	Co	Ag	Pb
Semi-quantitative Emission Spectrographic*	40	N.D.	70	600	80	N.D.	200	N.D.	10	700
Atomic-Absorption Spectrophotometry**	–	10	–	10	–	–	10	–	10	<10

*Report MS-AC-69-53.
**Report MS-AC-69-523.
Note: The reason for the variation between the results given by the two procedures has not been ascertained.

TABLE 7b

Other Analyses of Koch-Light ZnS Powder

Analyst	Zinc	Sulphur	Zn+S	Acid-Insoluble	L.O.H. (H_2O)	Calculated Formula
Miss E. Mark*	67.35%	32.67%	100.02%	0.04%	None (up to 135°C)	$ZnS_{0.989}$
L.G. Ripley	67.287%	–	–	–	0.023% (up to 400°C)	$ZnS_{0.991}$

*Report MS-AC-69-686.

ASSESSMENT OF PURIFICATION TECHNIQUES

The impurities in any zinc sulphide powder are dependent on its mode of preparation. It is possible for spectrographically-pure zinc sulphide to contain several contaminants: occluded gases, water, carbonaceous material, oxygen (either as an oxide or as a sulphate), and excess sulphur or zinc over the requirement for exact 1:1 stoichiometry.

The purification of zinc sulphide powder was found to be a four-step procedure:

(a) pumping - to remove occluded gases and water;

(b) low-temperature oxidation - to remove carbonaceous material;

(c) hydrogen sulphide treatment - to remove oxygen (from either an oxide or a sulphate) and also to ensure 1:1 stoichiometry of the zinc and sulphur;

(d) a second pumping - to remove residual gases produced in steps (b) and (c).

In order to determine the nature of the reactions occurring, several of the possible contaminants were studied individually.

1. Zinc Sulphate

Since zinc sulphate is a possible contaminant (see Table 6b), several experiments were performed to determine its behaviour during the anticipated purification steps. A commercial grade of $ZnSO_4.7H_2O$ was used.

(a) Pumping while Heating of $ZnSO_4.7H_2O$

The rate of water removal while pumping is shown in Table 8. The + sign indicates the additional time at the temperature shown in the left-hand column; the % loss is the cumulative total observed up to that stage in the experiment.

It is evident that the water of hydration in $ZnSO_4$ is released extremely slowly under the conditions used in this work.

(b) Heating of $ZnSO_4.7H_2O$ in Various Gases

The results obtained when this compound was heated in three different gases are shown in Table 9.

TABLE 8

Removal of Water from $ZnSO_4 \cdot 7H_2O$ by Pumping and Heating

Temp. (°C)	Heating Time (hr)	Cumulative Heating Time (hr)	Cumulative Loss (%)	End Product*
R.T.	1.0	1.0	10.32	
R.T.	+1.0	2.0	17.35	
R.T.	+2.0	4.0	18.92	$\sim ZnSO_4 \cdot 3 \cdot 5H_2O$
R.T.	+2.0	6.0	22.54	$\sim ZnSO_4 \cdot 3 \cdot 0H_2O$
R.T.	+1.0	7.0	24.85	$\sim ZnSO_4 \cdot 2 \cdot 65H_2O$
R.T.	+1.0	8.0	25.10	
R.T.	+1.0	9.0	25.35	
R.T.	+1.5	10.5	25.76	$\sim ZnSO_4 \cdot 2 \cdot 5H_2O$
R.T.	+1.5	12.0	26.16	$\sim ZnSO_4 \cdot 2 \cdot 44H_2O$
R.T.	+1.0	13.0	29.47	
R.T.	+1.0	14.0	29.68	
150	+1.5	15.5	37.28	$\sim ZnSO_4 \cdot 0 \cdot 728H_2O$
200	+1.0	16.5	39.41	
250	+1.0	17.5	42.89	$ZnSO_4$

*Calculated from the weight losses.

From the value of ZnO obtained by the air treatment, the calculated formula for the starting material was $ZnSO_4 \cdot 6 \cdot 55H_2O$. The above results indicated that the water of hydration can be removed at 550°C with a stream of N_2, also that the sulphate radical is converted to sulphide in a stream of hydrogen sulphide at temperatures as low as 550°C but not at 500°C.

2. Zinc Oxide

A synthetic sample of ZnO, prepared by oxidation of ZnS, was treated with H_2S; the results are shown in Table 10.

TABLE 9

The Heating of $ZnSO_4 \cdot 7H_2O$ in Various Gases

Gas	Temp (°C)	Time (hr)	Loss (%)	End Product*
N_2	250	2.0	29.13	$ZnSO_4 \cdot 0.5H_2O$
N_2	550	1.0	43.12	$\sim ZnSO_4$
H_2S	500	1.0	41.85	$\sim ZnSO_4$
	550	1.0	64.39	$\sim ZnS$
	980	1.0	64.78	$\sim ZnS$
Air	1000	1.0	70.86	ZnO

*Calculated from the weight losses.

TABLE 10

Effect of Heating ZnO in a Stream of H_2S

Temp (°C)	Heating Time (hr)	Cumulative Heating Time (hr)	Converted to ZnS (%)
550	1.0	1.0	97.15
550	+1.0	2.0	98.50
525	+2.0	4.0	99.35
750	+1.0	5.0	100.00

This reaction appeared to be rapid and all the oxygen would be completely removed at about 750°C.

3. Carbonaceous Material

It is well known that carbonaceous material should be completely oxidized at about 500°C in a stream of air. To determine the effect of air on ZnS, a synthetic sample of ZnS, prepared by H_2S treatment of General Electric ZnS, was heated in air; the results are shown in Table 11.

TABLE 11

Effect of Heating ZnS in a Stream of Air

Temp (°C)	Heating Time (hr)	Cumulative Heating Time (hr)	Converted to ZnS (%)
500	1.25	1.25	0.0
620	+1.0	2.25	10.31
725	+1.0	3.25	95.41
980	+1.0	4.25	99.85
1020	+0.5	4.75	99.84

It appears that no ZnS is oxidized at 500°C; therefore, carbonaceous material should be preferentially oxidized. However, at higher temperatures, the sulphide is oxidized quantitatively to the oxide.

PURIFICATION OF ZINC SULPHIDE POWDERS

It is evident that purification of ZnS is dependent on two main procedures. The first one is the sweeping with various gases over heated ZnS samples to remove various impurities; the second involves pumping, while the sample is being heated, to remove volatiles.

These two procedures will be discussed separately for the three commercial ZnS powders.

1. Purification of ZnS Powders by Gas Sweeping

In this procedure, the ZnS powder samples were placed in a Vitreosil boat that was heated in the combustion system shown in Figure 1.
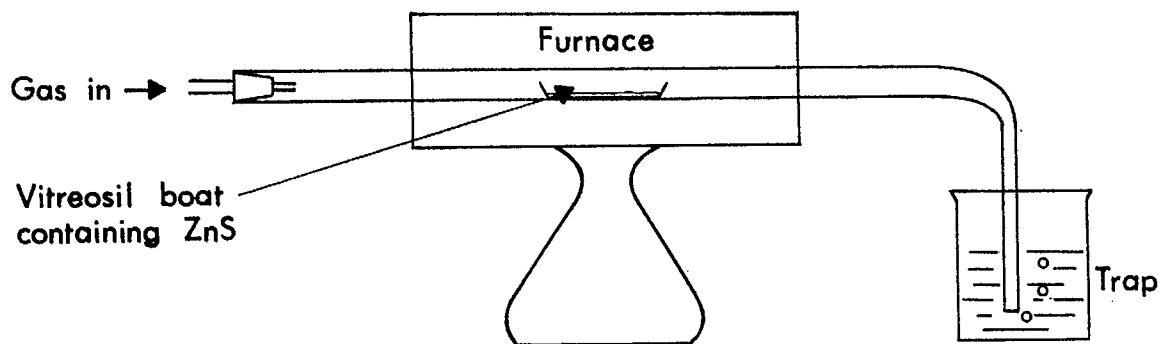
Figure 1. Combustion System for Gas-Purification of ZnS.

(a) General Electric Powder

Of the three commercial ZnS powders, the General Electric product has been used the most extensively. Therefore, the bulk of the purification results to be presented here involved this product. It was recognized from the beginning that water was present in this sample. A direct experiment, involving the pumping of a sample at 700°C and trapping the exit material, indicated the volatiles to be 3.60% water, 0.26% solids, and 0.43% gases. These values serve as a guide in assessing the following gas-treatment experiments.

Six different gases were used; viz., air, argon, helium, hydrogen, sulphide, nitrogen and sulphur. In the last-mentioned case, sulphur was mixed with the ZnS powder and heated in a stream of helium.

The results obtained when a sample was heated in a stream of air are shown in Table 12.

TABLE 12

Effect of Heating G. E. ZnS Sample in Air

Gas	Temp (°C)	Time (hr)	Loss %
Air	460	2.0	2.29
Air	520	1.0	2.16
Air	1020	2.0	19.74

In the case in which the sample was heated in air at 1020°C, the product is undoubtedly zinc oxide. From this value, the total zinc content in G. E. ZnS was calculated to be 64.48%, corresponding to a ZnS content of 96.10%. Therefore, the sum of the foreign substances must be 3.90%.

The results obtained when a sample was heated in a stream of helium are shown in Table 13. The visual appearance of the powder after cooling to room temperature is also given. The white residue is assumed to be "pure" ZnS.

TABLE 13

Successive Heating of a G. E. ZnS Sample in Helium Gas

Temp (°C)	Heating Time (hr)	Cumulative Heating Time (hr)	Cumulative Loss (%)	Residue Colour
300	1.0	1.0	1.72	Olive
350	+3.0	4.0	2.24	Dark olive
500	+1.0	5.0	3.42	Black
560	+2.5	7.5	3.78	Sl. black
540	+1.0	8.5	3.81	Sl. black
660	+1.0	9.5	4.08	Tr. of black
650	+1.0	10.5	4.16	White
800	+1.0	11.5	4.32	"
830	+1.0	12.5	4.41	"
850	+2.5	15.0	4.60	"
1010	+1.0	16.0	7.85	"
1010	+1.5	17.5	9.40	"
1010	+2.0	19.5	11.01	"
1010	+2.0	21.5	13.32	"
1010	+2.0	23.5	15.49	"

In Table 14, two other samples of G.E. ZnS were heated for different lengths of time in helium gas.

TABLE 14

Effect of Heating G.E. ZnS Samples for Various Lengths of Time in Helium

Temp (°C)	Time (hr)	Loss (%)	Residue Colour
650	13	4.75	White
650	72	6.05	White

It is apparent, from Tables 13 and 14, that two side reactions are occurring; namely, a black discolouration which formed and later disappeared and, secondly, a weight loss increasing with increasing temperature. A plausible explanation of the black discolouration seemed to be that it was a form of elemental sulphur; this is supported by the following references:Mellor (4) quoted G. Magnus as stating that black sulphur is really a metallic, allotropic form that could be obtained when sulphur is heated repeatedly to 300°C and cooled abruptly; also, the Kirk-Othmer "Encyclopedia of Chemical Technology" reports that there are allotropes of S_1 to S_n (where n is very large, but unidentified, probably $n \sim 10^6$); these allotropes are dependent on thermal history, time and impurities(5). However, further experimentation showed this explanation to be unsatisfactory.

The effect of heating a sample of G.E. ZnS in an atmosphere of hydrogen sulphide is shown in Table 15. As in Table 13, the sample was subjected to successive heatings and weighings. Although there is a similarity in the colour of the residue, the overall weight-loss at the higher temperatures is much less than when helium was used.

TABLE 15

Heating G.E. ZnS in Hydrogen Sulphide Gas

Temp (°C)	Heating Time (hr)	Cumulative Heating Time (hr)	Cumulative Loss (%)	Residue Colour
550	1.5	1.5	3.77	Black
750	+1.0	2.5	3.81	Yellow
1000	+1.0	3.5	3.89	Nearly White
1000	+1.5	5.0	4.05	White
1000	+1.5	6.5	4.18	White

For comparison, Table 16 shows the results obtained when six other portions of G.E. ZnS were heated in hydrogen sulphide. These samples show that, at temperatures of 1200°C, the weight losses are increasing with time and that the colour of the residue has changed from white to grey or to yellow.

TABLE 16

Six Additional G.E. ZnS Samples Heated in Hydrogen Sulphide Gas

Temp (°C)	Time (hr)	Loss (%)	Residue Colour
480	1.0	3.66	Black
1000	4.0	4.15	White
1025	4.0	3.95	Sl. black
1200	3.0	5.50	Black
1200	3.5	8.77 }	Yellow patches
1200	+1.0	9.47 }	Yellow patches
1200	4.0	6.90	Grey

The third gas used was nitrogen. In Table 17, the results obtained on three samples are shown. One sample was subjected to a series of heatings and weighings, similar to those reported in Tables 13 and 15. The other two were individual samples for which the results are similar to those obtained previously with either helium or hydrogen sulphide treatment.

TABLE 17

Effect of Heating Three G.E. ZnS Samples in Nitrogen

Temp (°C)	Heating Time (hr)	Cumulative Heating Time (hr)	Cumulative Loss (%)	Residue Colour
225	1.0	1.0	1.84	
640	+3.0	4.0	3.97	
700	+4.0	8.0	4.13	White
830	+1.0	9.0	4.44	
900	+1.0	10.0	4.61	
600	1.0	-	3.73	Black
600	4.0	-	3.79	Black

Only two experiments were performed using other gases: argon and sulphur. Therefore, they are shown together in Table 18. The sulphur was mixed with the ZnS powder in a 1:1 wt ratio and then heated in a helium stream. Again, the black colouration was obtained.

TABLE 18

Effect of Heating G.E. ZnS Samples in Other Gases

Gas	Temp (°C)	Time (hr)	Loss (%)	Residue Colour
Argon	600	1.5	3.71	Black
Sulphur and helium	550	5.0	3.85	Grey

Several experiments were performed to determine if the black
colouration in the residues could be removed easily. The air treatment not

TABLE 19

Attempts to Remove the Black Film from Residues

Gas	Temp (°C)	Time (hr)	Loss Prior to Expt.	Change in Wt.
Air	425	5.0	3.85	+0.61
H_2	500	1.0	3.86	-0.095
H_2S	950	1.0	3.50	-0.29

only did not remove the black colouration, but it caused a slight gain in weight.
The H_2 caused very little change in the black colouration. The H_2S helped to
clear most of black colouration, but the results indicated that more than one
hour at 950°C would be required.

In additional experiments, it has been observed that a black film,
which was deposited on the wall of a quartz tube, had these properties:

(i) it sublimed slowly at 700°-800°C;

(ii) it sublimed into yellow, white, and black forms;

(iii) it was insoluble in CS_2.

Also, it was observed that another black deposit, containing wurtzite (ZnS),
that was obtained in a purification experiment, was extremely resistant to
air-oxidation at 900°C. Therefore, it is assumed that the yellow or black
colourations are due to some interaction of excess sulphur or zinc with
ZnS to form non-stoichiometric material.

An alternative method of analysis of G.E. ZnS was by Differential Thermal Analysis (D.T.A.), and by Thermogravimetric Analysis (T.G.A.); these analyses were performed by R.H. Lake, Physical Chemistry Group. The D.T.A. of ZnS in an air atmosphere indicated reactions as shown in Table 20.

TABLE 20

D.T.A. of an Air-Oxidation of G.E. ZnS

Temp (°C)	Type of Reaction
90	Endothermic
319	Endothermic
381	Exothermic
600-700	Exothermic (several)
798	Endothermic

The T.G.A., showed only one main reaction, an oxidation, at 600-700°C, with the suggestion of a small reaction, a slight loss of weight at 960°C and the recovery of this loss at 1010°C.

The T.G.A. in an argon atmosphere showed a steady weight-loss from 100°C to a maximum loss at 650°C and then a steady slight gain to 900°C.

The conclusions drawn from all the above experiments on G.E. ZnS powders, are that at least four reactions were occurring;

(i) evolution of water (and occluded gases?) when the sample was heated in any of the atmospheres listed;

(ii) interaction of oxide and sulphate with hydrogen sulphide;

(iii) formation of the various colourations, which occur while heating in several gaseous atmospheres, but disappear only in some cases; and

(iv) sublimation of ZnS at high temperatures, even in an atmosphere of hydrogen sulphide.

(b) Fisher ZnS Powder

Only a few experiments were attempted for the purification of this commercial sample. Fisher ZnS was heated in the presence of four gases; the results are shown in Table 21.

TABLE 21

Effect of Heating Fisher ZnS in Various Gases

Gas	Temp (°C)	Time (hr)	Loss (%)	Residue Colour
Air	950	1.25	16.59	White
Argon	390	1.50	0.165	
N_2	225	4.0	0.11	White
	460	1.5	0.11	White
He	825	2.0	0.39	

Calculations, based on the heating in air at 950°C, which should yield a product consisting of ZnO, indicated that the total zinc content of Fisher ZnS was 67.00%, corresponding to a ZnS content of 99.87%. The sum of this latter value and the loss when the sample was heated in nitrogen indicated that 0.13% represents the maximum value for occluded gases and/or moisture.

(c) Koch-Light ZnS Powder

Four K-L samples were heated in the presence of various gases; the results are shown in Table 22. In the case of the last sample, it was heated first in H_2S and later in air.

TABLE 22

Effect of Heating K-L ZnS in Various Gases

Gas	Temp (°C)	Time (hr)	Change in wt (%)	Residue Colour
Air	1000	2.0	-16.24	White
Argon	400	3.0	-0.023	
H_2S	740	2.0	+0.080	Sl. yellow
H_2S	800	2.0	+0.092	Yellow
Air	1000	1.5	-16.36	White

Calculations based on the heatings in air at 1000° are shown in Table 23.

TABLE 23

Calculation of the Composition of Koch-Light ZnS

Sample	Total Zn (%)	Calculated ZnS (%)	Calculated Formula
1	67.29	100.29	$ZnS_{0.990}$
4	67.19	100.14	$ZnS_{0.995}$

Two observations were made from the results in Tables 22 and 23.
The first is that, when the sample was heated in argon, the moisture and/or
occluded-gas content appeared to be 0.023%. The second is that there was a
gain in sample weight when hydrogen sulphide gas was used. If this is assumed
to be a sulphur gain, then a recalculation of the composition of product would
yield a formula of $ZnS_{0.9988}$, which is very nearly stoichiometric.

2. Purification of ZnS Powders by Pumping of Heated Samples

The general procedure was to place ZnS powder at the bottom of
a quartz tube 30 cm long and 15 mm in diameter. This tube was joined to the
pumping station either by fusion to a graded-seal connection or with rubber
tubing. The position of tube in the furnace is shown in Figure 2.
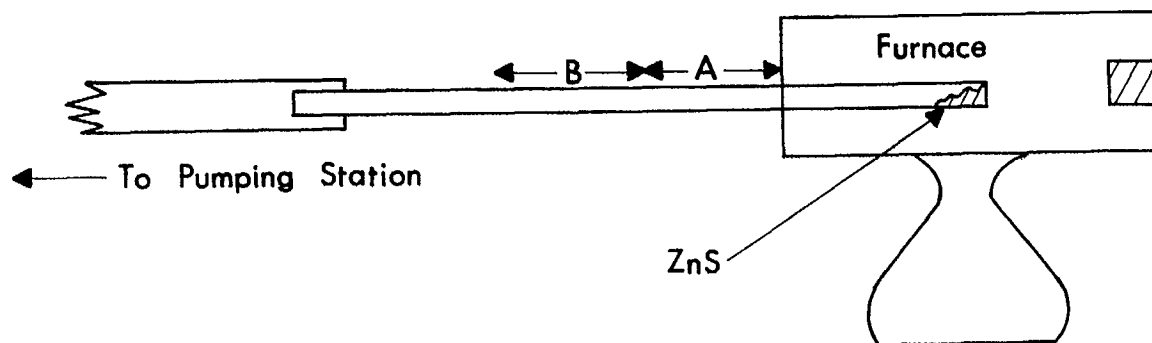
Figure 2. Apparatus for the Purification of ZnS Powder.
Zone A = 0 to 2 in. outside furnace. Zone B = over 2 in. outside furnace.

A suitable pumping station was constructed (1), making it possible to pump a sample, admit any gas up to atmospheric pressure, and then to heat the sample tube in a furnace up to 1200°C. The gaseous atmosphere in this system could then be removed by pumping, and renewed or changed to another gas or mixture of gases, as desired.

During the heating procedures, multi-coloured (black, white, and yellow) sublimates formed outside the furnace area, i.e., at Zones A and B (See Figure 2). The extent of these zones seemed to vary with heating rates and time.

Recently, a systematic approach has been followed in analysing the sublimates. The zones A and B were cut apart from each other and from the process tube; each section was oxidized separately in a combustion system (see Figure 1) to give ZnO. After weighing the (tube + ZnO), the deposit was dissolved in dilute acid and the tube dried and weighed. Then, from the three weights, i.e., the (tube + sublimate), the (tube + ZnO), and the tube, the zinc content could be obtained; and, by assuming the balance of the sample to be sulphur, the composition of the sublimate could be calculated.

The composition of the unsublimed residue was determined by removing some of this material and placing it in a Vitreosil boat; the oxidation, leaching of ZnO, and calculations were similar to those described above.

The Zn:S ratio obtained from these experiments will be expressed as ZnS_x or as $ZnS_{1 \pm x}$ for convenience, in this report. These formulae give only the gross Zn:S ratio and in no way imply that the material is single-phased.

(a) Fisher and Koch-Light ZnS Powders

One sample of Fisher ZnS and three samples of Koch-Light ZnS were pumped, while being heated. The sublimates, as well as the unsublimed residues, were analysed. The results are shown in Table 24.

The interpretation of the results in Table 24 can be summed up in three conclusions:

TABLE 24

Pumping/Heating of ZnS Samples

Sample	Zone A*			Zone B**			Sample Product	
	Colour	Formula	%	Colour	Formula	%	Formula	%
Fisher (Powder)[a]	Black	$ZnS_{0.88}$	0.4	Yellow	$ZnS_{1.581}$	0.7	$ZnS_{1.004}$	99
K-L (Powder)[b]	Black	***		Yellow	***		$ZnS_{0.991}$	99.8
K-L (Powder)[c]	Yellow	$ZnS_{1.015}$	2	Black	$ZnS_{0.913}$	1	$ZnS_{0.989}$	97
K-L (Powder)[d]	White	Not Analysed		Yellow and Black	Not Analysed		All sublimed	

*0-2 in. outside of furnace, $\approx 500°C$

**Over 2 in. outside of furnace, $< 500°C$

***Insufficient sample.

	Weight (g)	Temp. (°C)	Press. (mm)	Time (min.)
(a)	2.463	800°	1×10^{-3}	90
(b)	3.074	600°	1×10^{-3}	360
(c)	2.754	850°-900°	1×10^{-2}	60
(d)	2.022	1000°-1020°	2×10^{-3}	150

(i) sublimation of ZnS in a low-pressure system starts at about 800°C and is very rapid at 1000+°C;

(ii) the unsublimed residues are essentially stoichiometric ZnS; and

(iii) the sublimates have variable compositions.

When the furnace temperature was 750°–800°C the sublimate that formed near the edge of the furnace at a temperature of $\approx$500°C was nearly black to silvery-coloured and was found to be zinc-rich, i.e., ZnS_{1-x}, where x reached 0.12. While, further away from the furnace, a white to deep-yellow deposit formed that was found to be sulphur-rich, i.e., ZnS_{1+x}, where x reached 0.58. The explanation appears to be that an ideal sublimation of ZnS is based on the following reversible equation:

$$ZnS \rightleftarrows Zn^\circ\uparrow + S^\circ\uparrow \qquad \text{(Eq. 1)}$$

but, when the experimental system has a long exit tube (as is the case here) with a temperature gradient that extends down to room temperature, the Zn° and S° are able to migrate toward the cooler regions of the tube until some portions of them recombine and condense on the walls of the tube, while other portions condense individually at preferential-temperature sites and then recombine with the vapours of the other element. The net result is the formation of deposits along the walls of the exit tube containing zinc and sulphur in variable proportions.

Now, when the furnace temperature is increased during the experiment, the deposits appear to migrate, thereby causing the colours, as well as the compositions, to change. This condition is really a progressive sublimation. In effect, the individual elements, in seeking their preferential-temperature sites, find them in a zone further from the furnace than at the lower furnace temperatures. The result is that Zone A (see Figure 2) is changed from ZnS_{1-x} to a slightly sulphur-rich ZnS_{1+x}, and Zone B is changed from ZnS_{1+x} to a gradation of ZnS_{1-x}, next to Zone A, to nearly stoichiometric ZnS further away, and to ZnS_{1+x} still further away from Zone A.

(b) General Electric ZnS Powders

The pumping of the sample, both at room temperature and at 230°C, shows that a weight loss is still occurring after 10 hours, as shown in Table 25. The tube containing the residual sample was weighed, successively, after a period of time at each temperature (indicated as +hr) and the total cumulative weight-loss was calculated.

TABLE 25

Effect of Pumping and Heating G. E. ZnS Powder

Temp	Heating Time (hr)	Cumulative Heating Time (hr)	Cumulative Loss (%)
R.T.	0.50	0.50	0.35
R.T.	+0.67	1.17	0.48
R.T.	+3.0	4.17	0.73
R.T.	+1.0	5.17	0.73
210	+1.0	6.17	1.72
210	+1.0	7.17	2.11
210	+0.5	7.67	2.21
230	+3.0	10.67	2.29

These results indicate that the removal of water and occluded gases by pumping at the above temperatures is very slow. It was also noted that a blackish substance was being entrapped on the quartz-wool plug.

In other purification experiments, it has been observed that, when a ZnS sample was heated too rapidly to approximately 500°C, the sample-product (residue) also became coloured with black and yellow zones that were extremely slow in disappearing, even at 1000°C.

When a G. E. ZnS powder sample was heated in the presence of H_2S at 1000°C for 3.5 hr and then pumped at 500°C for 2 hr, the compositions of the products were as shown in Table 26.

TABLE 26

Products Resulting from a G.E. ZnS Purification in H_2S

Zone A	Quartz-wool plug*	Sample Product
$ZnS_{78.98}$**	$ZnS_{1.018}$	$ZnS_{0.998_3}$

*This quartz-wool plug was placed adjacent to the ZnS material to prevent dusting during the pumping cycles.
**This formula is used only to give the Zn:S ratio; there is no implication that the material is single-phased.

Three conclusions can be drawn from these results:

(i) the material in Zone A is predominantly (96%) elemental sulphur which originated from the decomposition of H_2S; the balance is ZnS. This implies that ZnS is subliming slowly at 1000°C in the presence of H_2S;

(ii) the ZnS material adjacent to the quartz-wool plug is slightly sulphur-rich; and

(iii) the sample-product is essentially stoichiometric.

The consequence is that, if the purified product and the wool plug were used in a growth procedure, the ZnS would be unintentionally grown in a slightly sulphur-rich environment. Therefore, the wool plug should be replaced with a new one before sealing the tube for crystal growth experiments.

3. General Purification Procedure

The most acceptable purification procedure appears to be as follows.

The sample should be pumped at room temperature and, later, at a temperature slowly increasing to 400°C to remove the bulk of the occluded gases and water.

If carbonaceous material is present, it can be removed by igniting the sample in air at about 500°C. However, if any carbonaceous compound had been present in the ZnS powders of this report, it must have been volatilized in the initial pumping-heating step.

The next step should be to heat the above product in H_2S at temperatures of 400° to 1000°C and to hold it at the upper temperature for several hours; all the oxygen, whether as oxide or in a sulphate, is thus removed and any free zinc would be sulphided.

The final step should be to pump this latter product, while heating it at 500°C, for several hours. This step should remove all the H_2S and the excess sulphur, leaving a white, stoichiometric zinc sulphide.

The above procedure was used to purify over 50 portions of General Electric zinc sulphide for crystal growing experiments.

THE ZINC-SULPHUR SYSTEM

Although ZnS has been studied for more than 100 years, the only points known on the Zn-S phase diagram are:

(i) the mp and bp of zinc, which are 419.4°C and 907°C, respectively;

(ii) the mp and bp of sulphur, which are 112.8°C and 444.6°C, respectively; and

(iii) the mp of ZnS, which is 1850°C under an argon pressure of 150 atm.

Hansen (6) suggested that the Zn-S phase diagram was similar to that of Zn-Se; if this were so, then it would be as shown in Figure 3. However, the present author has used broken lines to imply the possibility of areas of non-stoichiometry ($ZnS_{1\pm x}$), as described elsewhere in this report. The exact locations of the broken lines have not been determined.

The application of the areas of non-stoichiometry to crystal growth was demonstrated when Rubenstein (7) used the liquidus solubilities of ZnS in zinc, in the range of 1000°-1300°C, to grow transparent, colourless, single crystals of 1-cm cross-section.

The transition temperature of the phase change of sphalerite to wurtzite is given as 1020°C (8). The transition has, however, been recorded as occurring at varying temperatures. Scott (9) found, in hydrothermal studies, the transition occurred as low as 600°C. Banks (10)concluded that
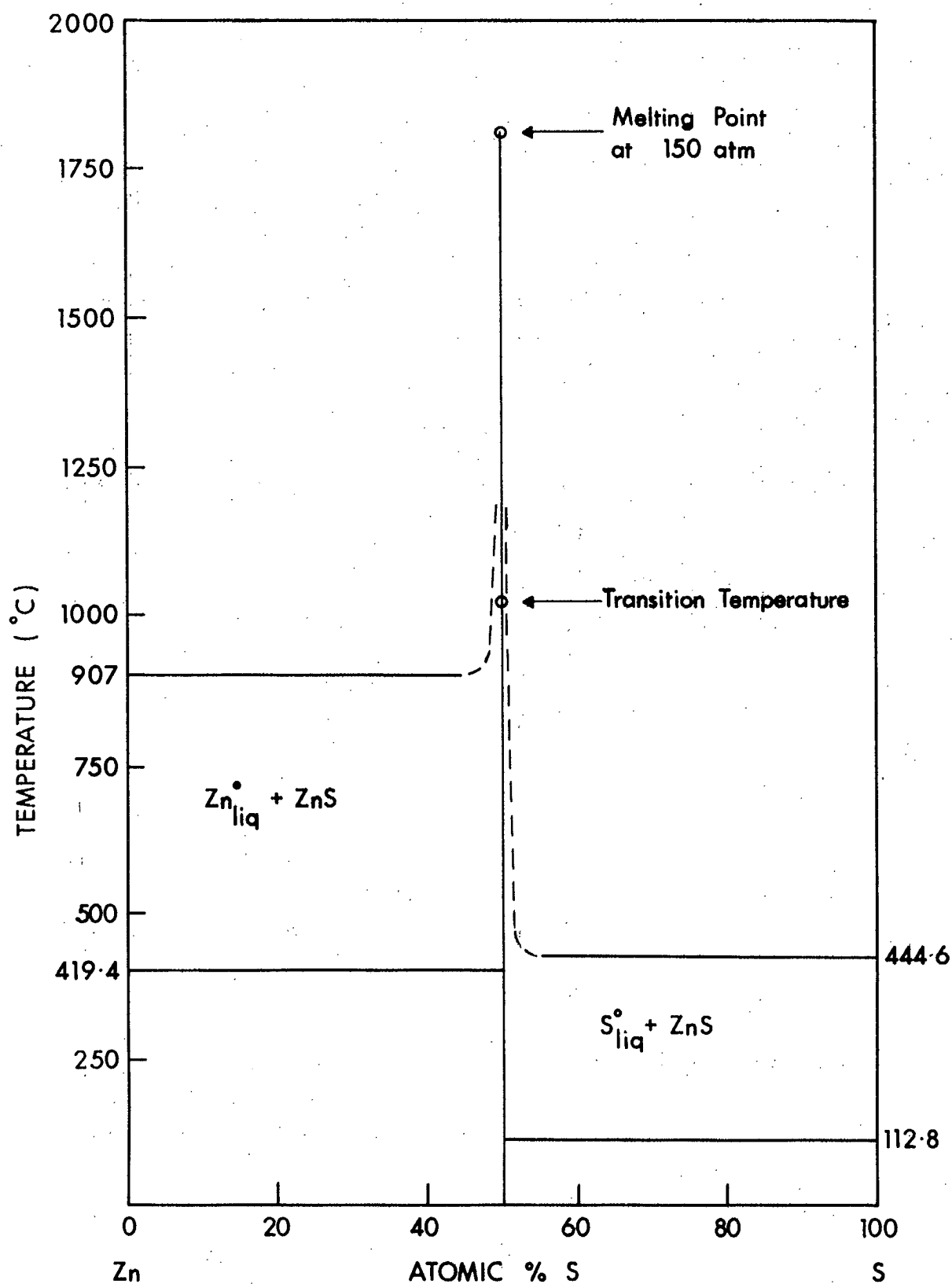
Figure 3. A Partial Zinc-Sulphur System.

the values for the transition temperature were a reflection of the kinetics of the formation of wurtzite from the vapour phase rather than a representation of any true thermodynamic equilibrium. Supplementary experiments, based on zinc analysis, showed no significant differences in transition temperature between the sphalerite powder, heated in vacuum, with excess zinc or with excess sulphur. However, it was also noted that a small amount of excess sulphur was incorporated into the crystal when experiments were performed at 1 to 2 atm sulphur pressure.

The phases of ZnS, that were found in the starting materials, are described for the following five cases:

1. Phase of Commercial Zinc Sulphide Material

The commercial ZnS powders show the following phase(s) present:

Fisher Scientific ZnS	=	sphalerite
G.E. ZnS	=	sphalerite with a trace of wurtzite
Koch-Light ZnS	=	wurtzite

2. Preparation of Sphalerite Material

The preparation of ZnS obtained by heating Zn and S in a sealed tube at 800°-870°C for several days always gave sphaleritic material.

3. Conversion of Sphalerite to Wurtzite

Originally it was assumed that one of the main differences between wurtzite and sphalerite was that wurtzite was zinc-rich and that sphalerite was sulphur-rich. Duplicate experiments were performed in which sphaleritic powder was heated in a stream of helium containing zinc vapour from 200°C to 1060°C, over a period of 8 hours, and held at 1050° to 1060°C for 1 to 2 hours. In both cases, there was some sample loss from the boat, and the product was predominantly sphalerite with a minor amount of wurtzite. An alternative approach was to prepare two synthetic compounds $ZnS_{0.995}$ and $ZnS_{0.990}$. The former material was identified as being sphalerite with a trace of wurtzite while the latter was entirely sphalerite.

Sphalerite was converted to wurtzite when the sample was heated at between 1050° and 1200°C in a stream of either helium or hydrogen sulphide. The apparatus used was the same as in Figure 1.

The conversion of seven samples is shown in Table 27. The colour of the wurtzite product varied from "antique" white to yellow-brown.

The product from Experiment #380E was oxidized in the same manner as described on page 4. A calculated formula of $ZnS_{0.9978}$ was obtained. These results and others to be given later in this report indicate that there is no essential difference in the zinc to sulphur ratio of wurtzite and sphalerite.

4. Conversion of Wurtzite to Sphalerite

No experiments were undertaken to study the conversion of wurtzite powder to sphalerite. However, two attempts were made to convert crystalline material. In the first case, crystalline zinc sulphide showing a high degree of birefringence, i.e., wurtzite, was sealed in an evacuated quartz tube and heated at 910°C for 112 hours. A black film was deposited on the inside of the tube; this was later shown to be a form of sulphur. Optical studies showed that the crystalline material still had the same degree of birefringence.

In the second case, a different crystalline zinc sulphide which had a high degree of birefringence, i.e., wurtzite, was sealed in a quartz capsule with 1 atm. H_2S (at R.T.) and heated at 950°C for 85 hours. A white film, which was assumed to be sulphur, was deposited on the inside of the tube. Again, optical studies showed that the crystalline material still had the same degree of birefringence.

These results indicate the rate of conversion of crystalline zinc sulphide from the wurtzite form to the sphalerite form, if it occurs at all, is extremely slow.

5. Use of Wurtzite Powder

The main purpose in preparing wurtzite was to have nutrient material of this phase for use in crystal growing; the results of these experiments will be shown in tables involving various growth techniques.

However, some of the powders were used for various other analyses:

TABLE 27

The Conversion of Sphalerite to Wurtzite

Expt. No	Gas	Time (hr)	Temp (°C)	Loss in Heating (%)	Phase of Product Major	Minor	Colour of Product
288A	He	2.0	950-1000	-	Sphalerite	Wurtzite	White
288B	He	+1.5	1050	-	Wurtzite	Tr Sphalerite	White + some yellow colonies
367	He	2.5	1150	15.24	Sphalerite	Wurtzite	Yellowish
378	H_2S	4.0	1200	25.5	Wurtzite	-	Yellow + yellow grey
380B	H_2S	12.0	900	-	Sphalerite	-	Yellow
380E	H_2S	4.0	1200	-	Wurtzite	Sphalerite	Yellow brown
386A	H_2S	1.0	1200	-	Wurtzite	-	White + black areas
386B	H_2S	+2.0	1200	8.18	Wurtzite	Amorphous(S^o?)	"Antique" white
391	H_2S	3.5	1200	-	-	-	White + yellow patches
	H_2S	+1.0	1200	9.46	Wurtzite	Sphalerite	White + yellow patches
397	H_2S	2.5	1200	6.90	Wurtzite	-	White + grey + yellow

(a) semi-quantitative spectrographic analysis showed the level of impurities of two wurtzite products to be as given in Table 28;

(b) differential thermal analysis showed a similarity between the oxidation of sphalerite and that of wurtzite; and

(c) infra-red analysis showed the spectra of sphalerite and of wurtzite to be quite different.

CRYSTAL GROWTH

It has been known for many years that zinc sulphide (as well as other sulphide) crystals have several interesting properties. Naturally-occurring crystals usually contain sufficiently high levels of impurities that many of the true properties of the pure compound are masked. Therefore, synthetic single crystals of usable size and quality are desirable for the investigation of these properties.

Crystals can be grown in many ways, and the size and quality of crystals obtained by a method depends on many factors. Indradev stated in 1966 that zinc sulphide crystals had been grown for over a decade by various workers but centimetre-sized crystals of good quality were still rare (11).

Zinc sulphide can be grown in the following ways: hydrothermally (12) (13), by chemical vapour transport (14)(15)(16), by vapour transport (sublimation) (11)(17)(18), from fluxes (19)(20)(21)(22), and from the melt (23).

The present investigation was concerned originally mainly with the growth of centimetre-sized sphalerite single crystals. This programme was developed by studying the literature and then by utilizing this information to modify existing furnaces and other apparatus for crystal growing.

1. Chemical Vapour Transport (C.V.T.)

Of all the growth techniques for ZnS that have been reported, those involving a chemical vapour transport showed the greatest potential of satisfying the terms of reference of the current programme i.e., centimetre-sized single crystals of sphalerite. Therefore, the majority of the experiments to be reported were of this type.

TABLE 28

Semi-Quantitative Spectrographic Analyses of Synthetic
Wurtzite (% by Weight)

Expt. No	Si	Al	Mn	Mg	Fe	Ca	Cu	Ni	Ti	Zn	
380E	0.2	0.07	0.04	0.05	0.1	0.15	0.08	0.07	0.04	Pc	*
391	0.1	0.004	0.003	0.02	0.08	N.D.	0.08	N.D.	N.D.	Pc	**

Other elements reported as not detectable: Ba, Sb, Mo, Pb, Cr, Bi, V, Ag, Co, Zr, Sn.

*Internal Report MS-AC-68-87.
**Internal Report MS-AC-68-91.

Schäfer (24) describes chemical transport reactions as "those in which a solid or liquid substance A reacts with a gas to form exclusively vapour-phase reaction-products which, in turn, undergo the reverse reaction at a different place in the system, resulting in the re-formation of A".

In the past decade, this technique has been used successfully by many researchers, including Nitsche (14), Samelson (16), and Jona (15), in the growth of ZnS.

The two reactions used most often are:

$$ZnS + I_2 \rightleftarrows ZnI_2 + S^o \qquad \text{(Eq. 2)}$$

$$ZnS + 2HCl \rightleftarrows ZnCl_2 + H_2S \qquad \text{(Eq. 3)}$$
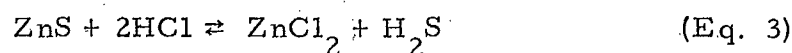
The very nature of these reactions requires that the experiment be carried out in sealed tubes. Silica is the preferred material. The schematic arrangement for this type of crystal growth is shown in Figure 4.
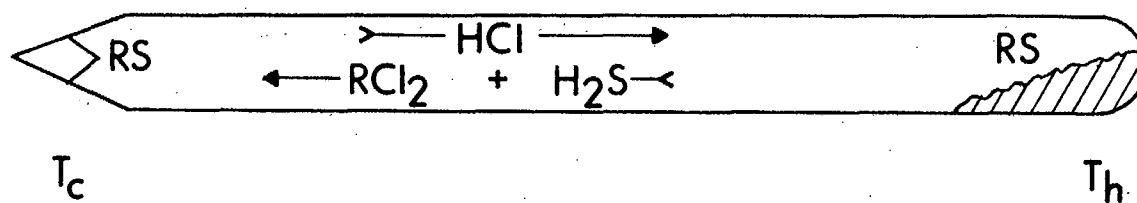
Figure 4. Schematic Arrangement for Chemical Vapour Transport.

The mechanics of this growth procedure are based on the reversible chemical reactions given in Eq. 2 and 3. In the hot zone of the tube (T_h) the equation is proceeding from left to right, while, in the cold zone (T_c) the opposite is occurring, i.e., the re-forming of ZnS in such a way that a crystal is formed in cold zone. The rate of the reaction is known to be proportional to the temperature difference. The iodine and hydrogen chloride act as carriers or transporting agents.

The dimensions of the silica tubes used in this work were 13 mm I. D. and 15 to 20 cm long. The starting material, which had been purified as described previously, is placed at the rounded end of the reaction tube and will be referred to as the nutrient in this report. The tube is sealed so as to create a pointed end which will become the growth zone; the reason for this design is to enhance single-crystal growth through restriction of the number of possible nucleation sites.

Three attempts at seeding the reaction, i.e., placing a small piece of crystalline ZnS at or near the pointed tip of the growth zone, failed because it was (almost) impossible to place this seed at the coldest point of the growth zone with the result that the seed was transported along with the nutrient material.

The difference in temperature between the pointed end and the nutrient zone is called the temperature gradient. This latter term will be used throughout this report.

In all cases, the reaction tubes were placed in a suitable furnace at a selected position to give the desired nutrient temperature and temperature gradient. If these conditions are not changed throughout the growth period, this technique is referred to as a "static" growth.

(a) Variables in C. V. T. Crystal Growth

In order to study and have cognizance of the variables of this technique, many growth runs were made; some of the results are shown in Figure 5. In some cases, the runs were single while others were in multiplicate.

Although the results shown in the graph are rather limited, the effects of some of the key variables on the rate of growth have been observed. The effects were as follows:

(i) Nutrient Temperature and Temperature Gradient

The growth rate, as was to be expected, had a definite relationship to both the nutrient temperature and to temperature gradient. In Figure 6, shows that the growth rate increases linearly with increasing nutrient temperature and that the slope of the growth rate/ nutrient temperature plot increases with increasing temperature gradient.
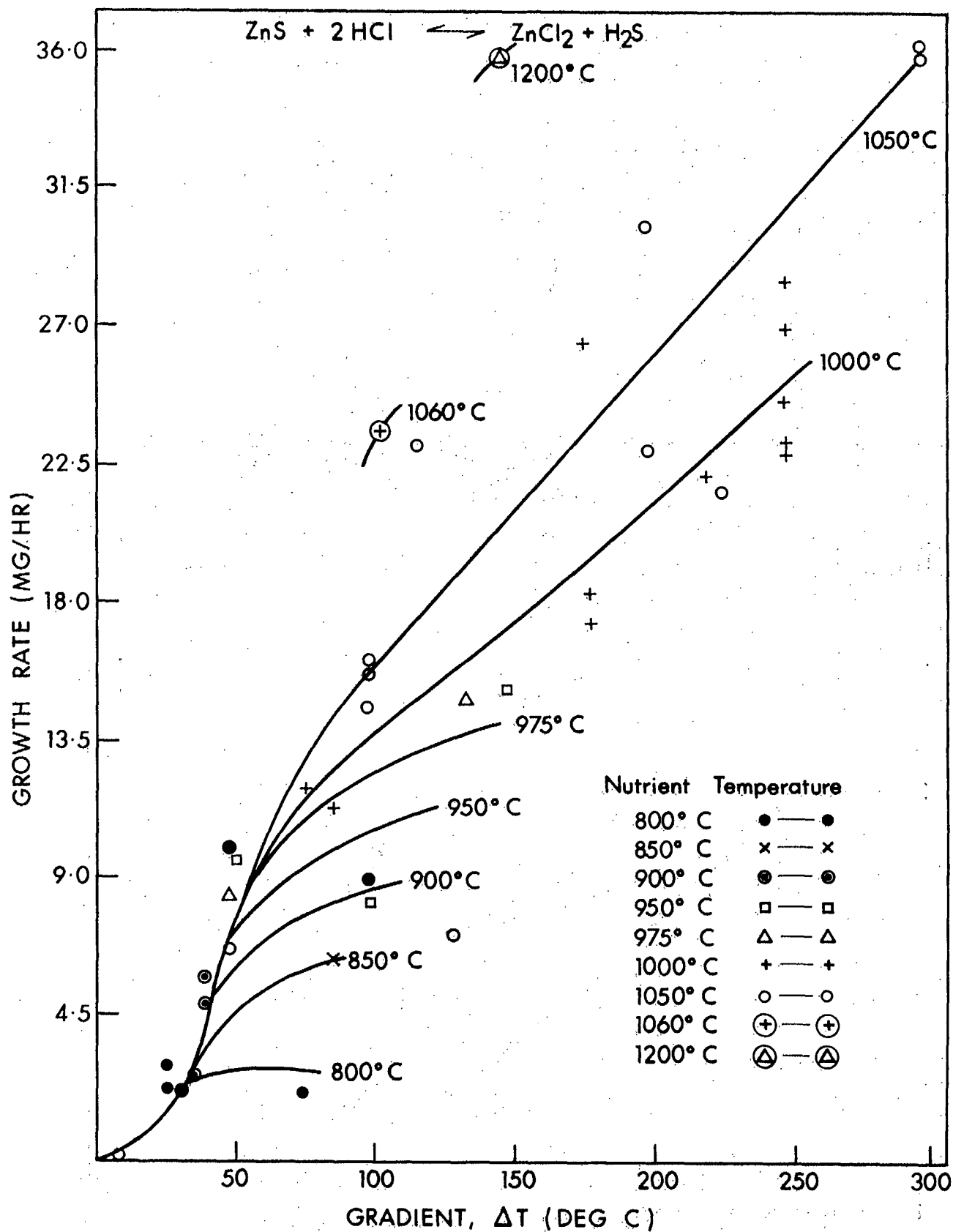
Figure 5. Static Growth Rate of Zinc Sulphide.
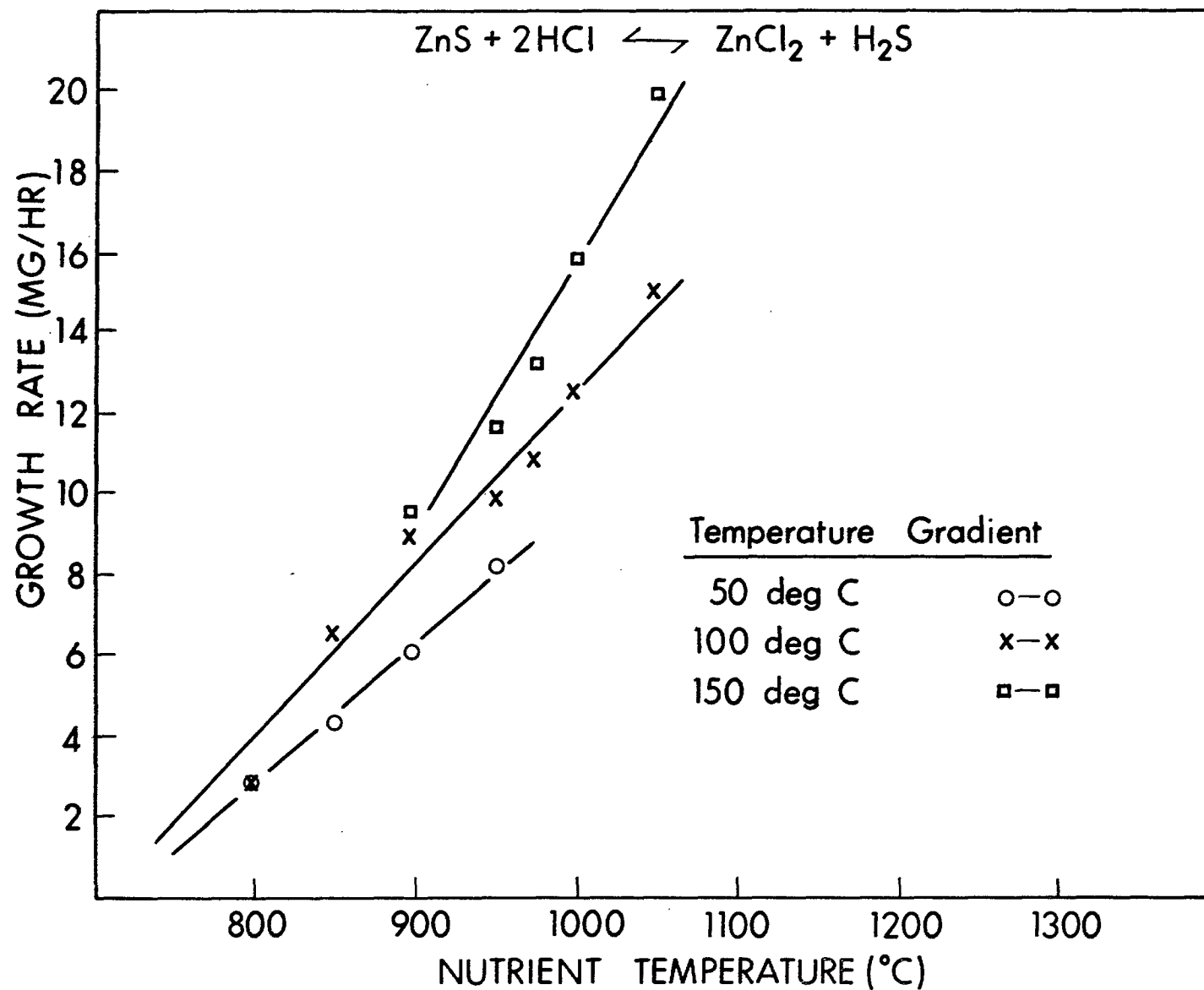
Figure 6. Effect of Nutrient Temperature.

(ii) <u>Time</u>

When some of the above results were plotted against time, as shown in Figure 7, it was observed that growth varies directly with time for each temperature gradient when the nutrient temperature is held constant.

(iii) <u>Hydrogen Chloride Concentration</u>

In the experiments shown in Figure 5, the usual hydrogen chloride concentration was controlled by sealing in the tubes such a quantity of gas that would give 0.5 atm pressure at room temperature. The exceptions were three of the five points shown at 1000°C nutrient temperature and at a temperature gradient of 250°C. When these five points are replotted, as shown in Figure 8, it can be seen that the growth rate passes through a maximum at an initial hydrogen chloride gas pressure of 0.75 atm. This is similar to Jona's (15) findings.

(iv) <u>Effect of Excess Sulphur</u>

Three special experiments were performed under identical conditions except for the quantity of excess sulphur. The furnace was in a vertical position with the growth zone below the nutrient zone. Figure 9 shows that the presence of excess sulphur caused a drastic decrease in growth rate.

(v) <u>Effect of Gas Mixtures</u>

Three special experiments were performed to determine the effect of three different gas mixtures, viz., $(HCl + H_2S)$,$(HCl + Argon)$, and $(HCl + helium)$ as shown in Figure 10. Although the HCl gas was not present at the same concentration in all these experiments, it was in the range described in section (iii). The addition of H_2S to the system caused a decrease in growth rate. However, when argon or helium was added, the growth rate became almost nil. Additional experiments would be necessary before any conclusions could be drawn as to the significance of these observations.

(vi) <u>Diameter of the Reaction Tube</u>

The effect of the inside diameter of the reaction tube was determined by preparing two tubes; one of 13-mm and the other of 11-mm ID. The

$$ZnS + 2HCl \longleftrightarrow ZnCl_2 + H_2S$$
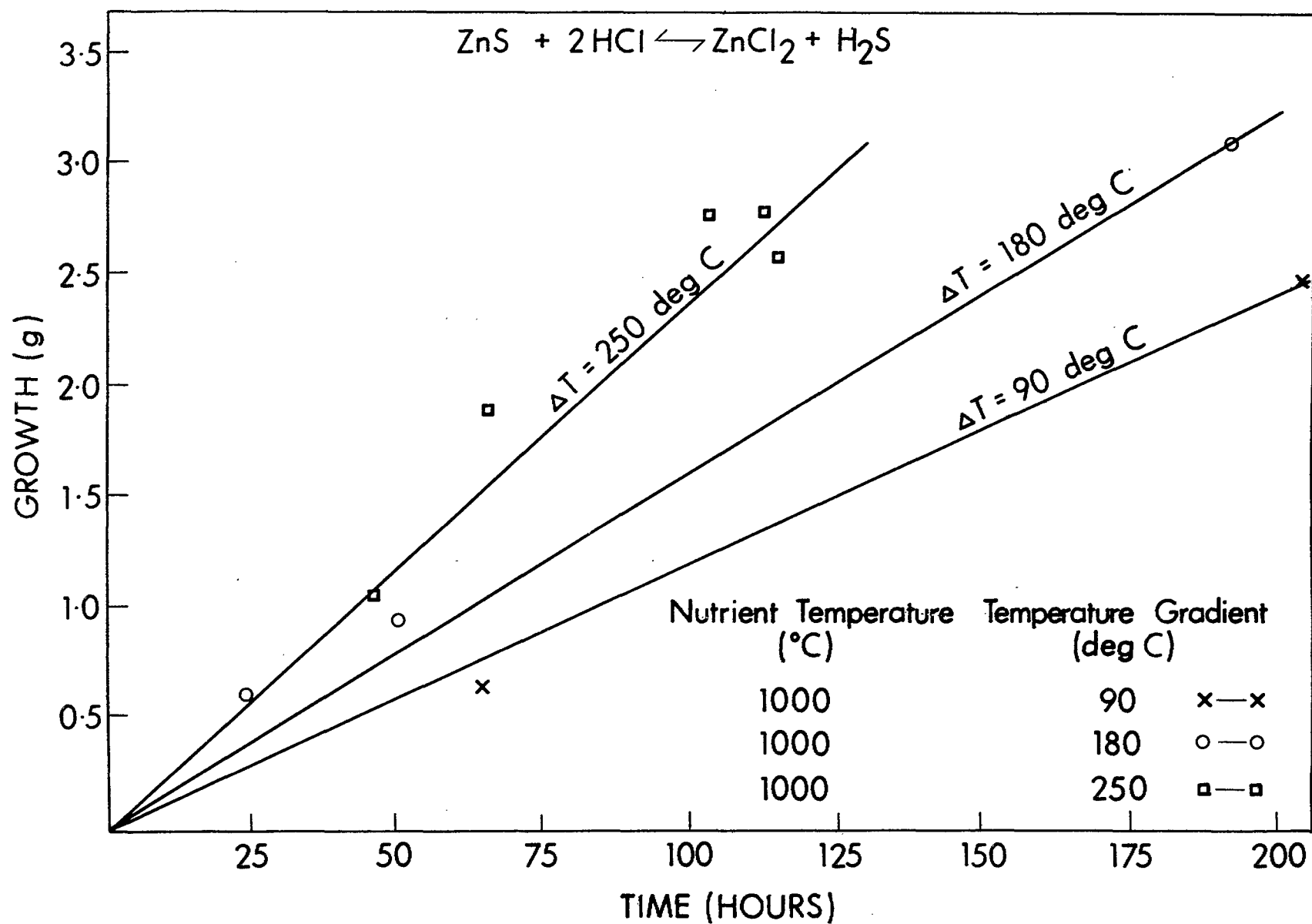
Figure 7. Effect of Time on Total Growth of ZnS.
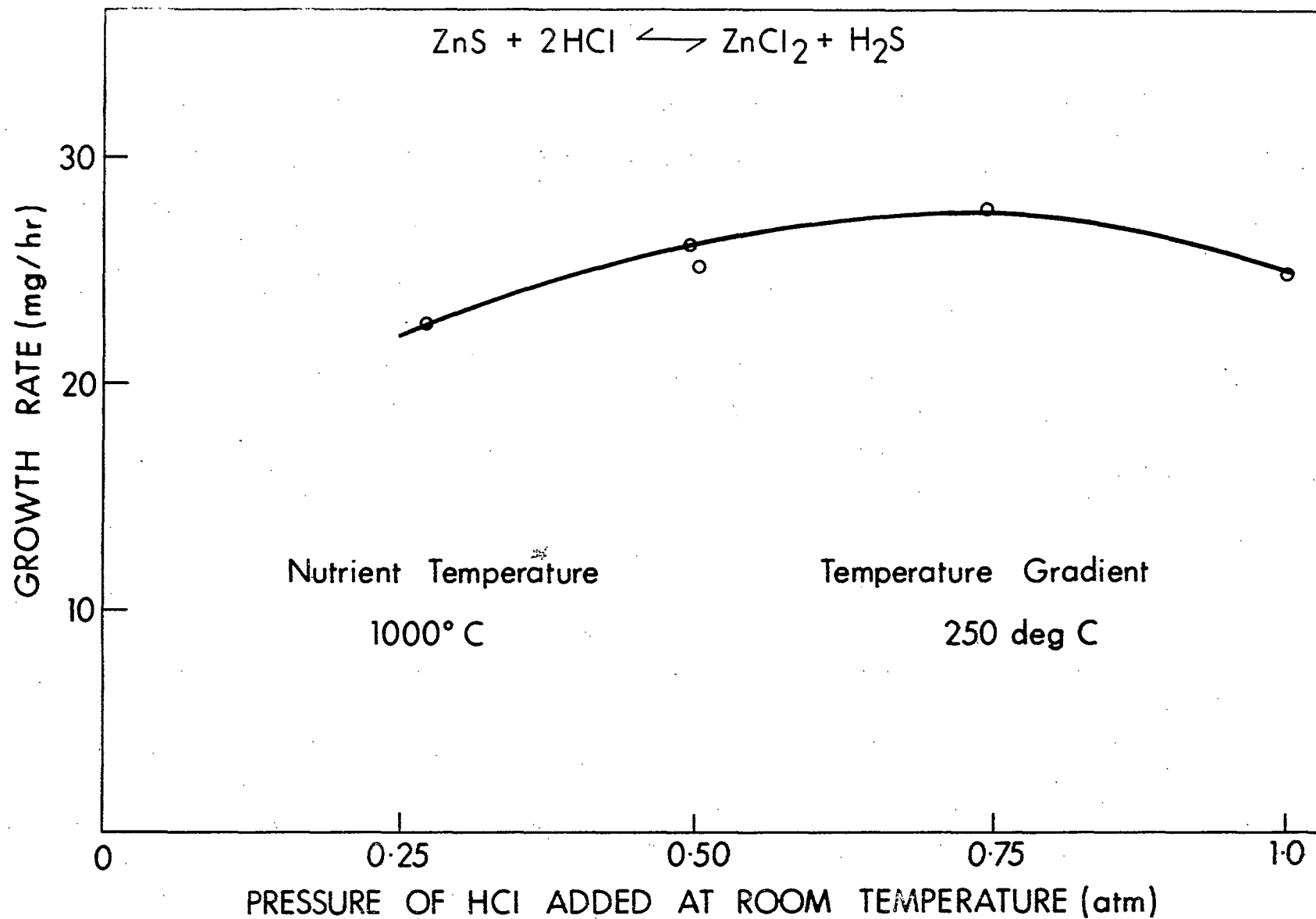
Figure 8. Effect of Hydrogen Chloride Concentration.
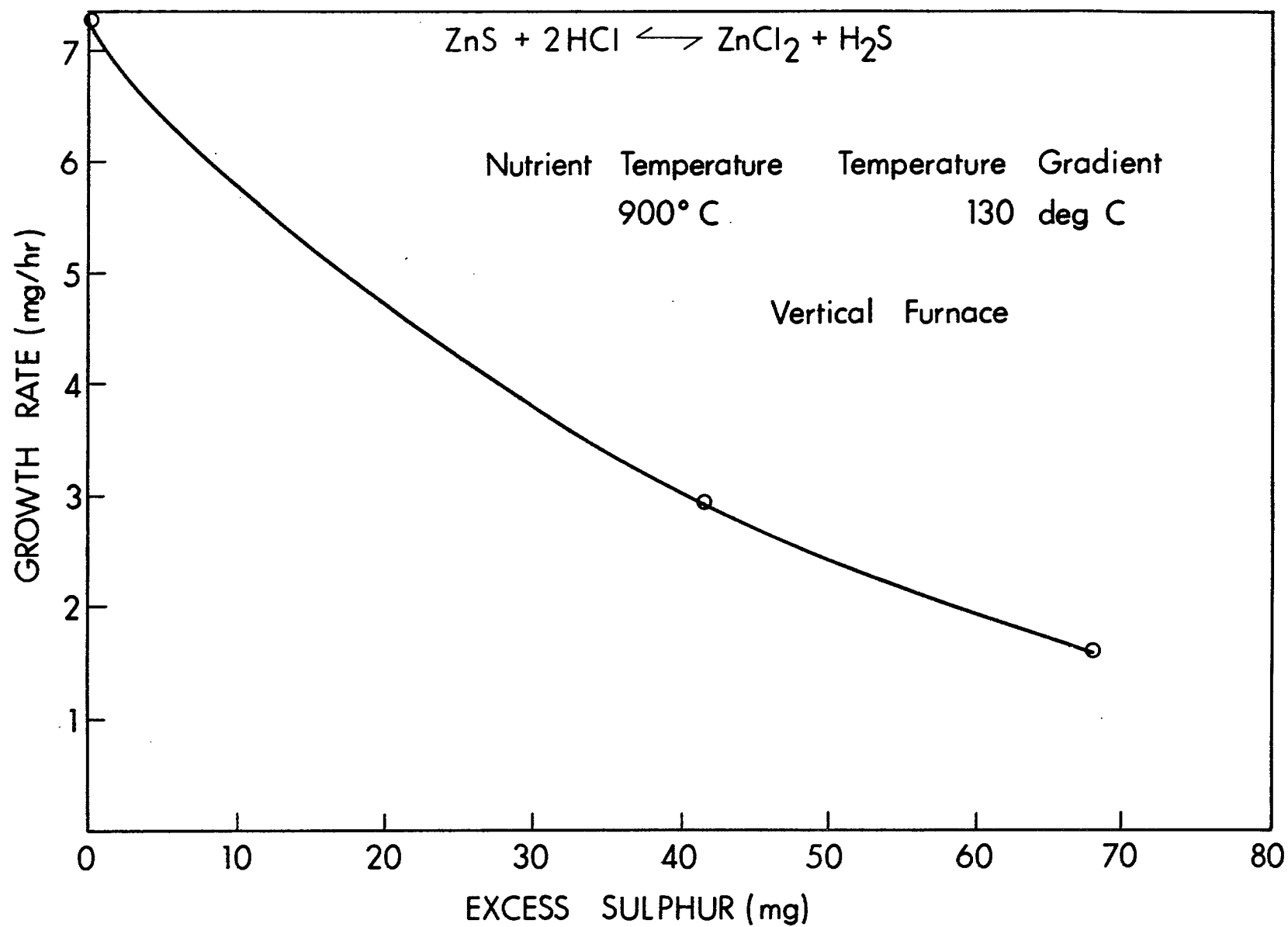
Figure 9. Effect on Excess Sulphur on ZnS Growth.

$$ZnS + 2HCl \longleftrightarrow ZnCl_2 + H_2S$$

Foreign Gas	Nutrient Temperature	Temperature Gradient	
H_2S	950° C	100 deg C	o——o
Argon	950° C	200 deg C	△——△
Helium	950° C	100 deg C	□——□
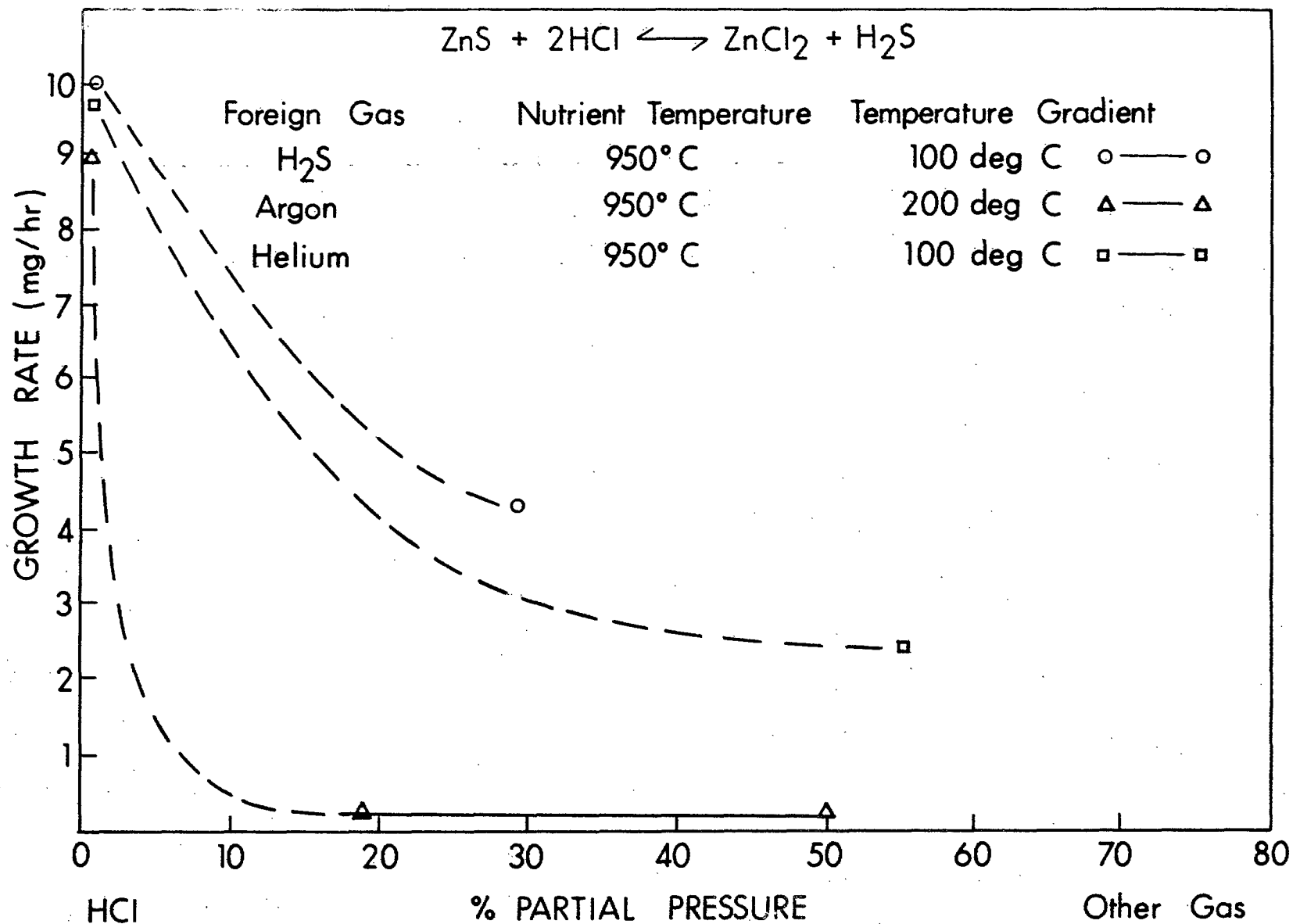
Figure 10. Effect of Gas Mixtures.

other variables: HCl conc., nutrient temperature, temperature gradient and tube length, were comparable. The results showed that the rate of growth is directly proportional to the inside diameter. The above relationship showed better agreement than the comparison with the cross section (Nitsche (14)). Again, more experimental information would be required before a firm conclusion could be drawn.

(vii) Length of the Tube

The effect of the length of the tube was not determined because all of the tubes were of the same general length viz., 15 to 20 cm. However, an experiment was conducted in which the tube used was 30 cm long and, when placed in a furnace, the temperature profile varied from 1050°C to >300°C, see Figure 11.
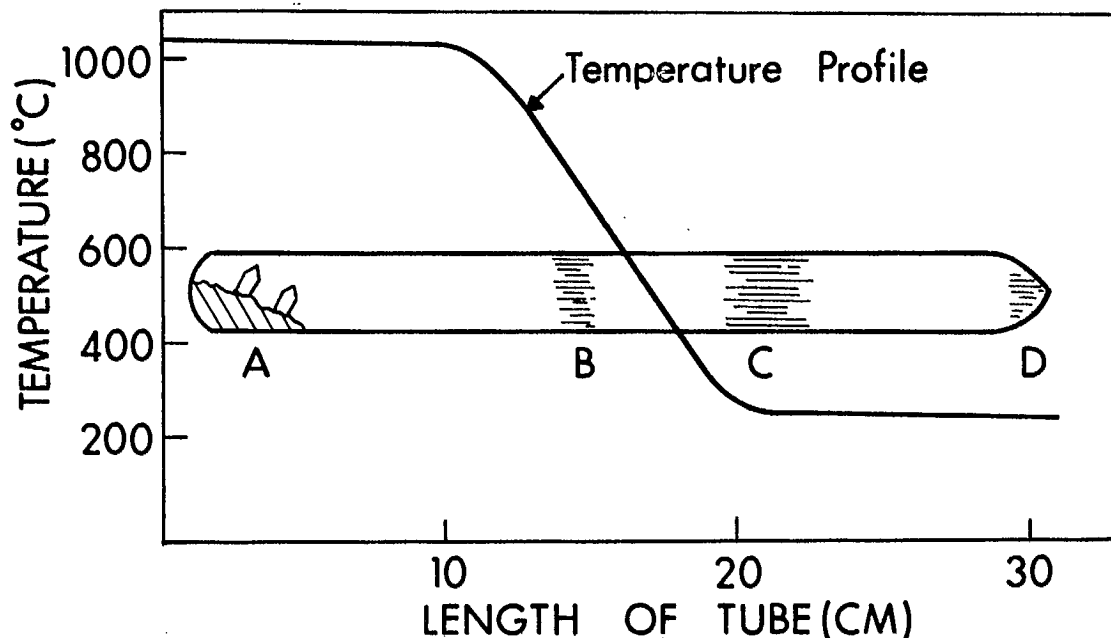
Figure 11. Effect of a Long Tube Subjected to a Large Temperature Gradient.

The interpretation of the results is as follows:

Because of the low temperatures at the right-hand end of the tube, the products of the reversible equation, namely, $ZnCl_2$ and some S^o (due to the thermal decomposition of H_2S at the nutrient temperature), were frozen out at C and D, respectively, thereby stopping the chemical vapour reaction. However, a little ZnS had apparently grown at B, either by chemical vapour transport at the start of the experiment or by vapour transport later. Also,

it was noted that the nutrient ZnS had undergone some crystallization in situ by vapour transport.

The main conclusion is that the entire tube, including the growth zone, should be above the boiling point of all the <u>reactants</u> - in the case of ZnS formation, above 732°C, the boiling point of $ZnCl_2$ - so that none of the species involved in the chemical vapour transport will condense and terminate the growth reaction.

(viii) <u>Quartz Wool Plugs</u>

These plugs were loosely-packed quartz wool and were placed next to the nutrient ZnS. Their purpose was to prevent dusting of the sample during the purification step and/or in the growth step. In the latter step, particles of ZnS sticking to the tube in the growth zone would act as unwanted additional nucleation sites.

The present study concurs with Jona's (15) finding in that these plugs do not appear to affect the transport rate.

The results presented in paragraphs (v) and (viii) indicate that the transport process was by diffusion and not by convection.

(b) <u>Quality of the Initial C.V.T. Crystals</u>

The form of the crystals obtained by "static" growth was usually found to be polycrystalline growth. The pointed shape of the reaction tube helped to reduce this polycrystalline growth but, apparently, a second technique (1) was required to eliminate it. This alternative approach was to move or "migrate" the tube slowly and mechanically through the furnace during the growth period. In this way the temperature gradient can be started at any desired level and then increased at any predetermined rate through the growth cycle.

Fifteen ZnS crystalline products, obtained early in the programme, were prepared under varying conditions, as shown in Table 29. Some of these products were prepared by a combination of the "migration" technique, which should produce one single crystal followed by the "static" method in an attempt to induce extra growth on this single crystal. In one case, an attempt was made at annealing a "static"-grown crystal to remove some of its imperfections.

To assess the quality of these products, they were submitted to Dr. E. H. Nickel, formerly Head, Mineralogy Group, Mineral Sciences Division for examination of their optical characteristics (25). In general, nearly all of the submitted samples showed low to high birefringence, i.e., a low to high concentration of wurtzite. It was also noted that a certain amount of strain, due to crystal imperfections that showed up as undulatory extinction, was present in most of the crystals. The colour, which varied from colourless to yellow or to green, was recorded.

TABLE 29

Conditions for ZnS Growth

Sample No.	HCl Pressure (atm*)	Procedure	Nutrient Temp (°C)	Temp Gradient (deg C)	Time (hr)
96	0.58	Static	1050	200	103
97	0.58	Static	1060	110	112
105	0.53	Migration	990	0→270**	114
		Static	990	270	89
110	0.60	Static	1040	100	136
115	0.57	Migration	1000	0→25**	72
		Static	1000	25	336
120	0.58	Migration	1010	0→210**	72
		Static	1010	210	125
124	0.25	Static	1195	150	64
125	0.25	Static	1190	390	64
127	1.0	Static	1050	220	112
128	0.51	Static	1050	300	133
		Annealed	910	0	94
131	0.57	Static	900	40***	588
137	0.05	Static	1050	300	384
141	0.035	Static	950	100	936
145	0.093	Static	950	100	432
146	0.17	Migration	950	0→125**	72
		Static	950	125	408

*At room temperature.
**The arrow means that the temperature gradient was increased slowly from zero to the other value quoted.
***The rate of crystal growth was 4.87 mg/hr.

The best products were #131, followed by #115; both were colourless with low birefringence and low undulatory extinction and contained single crystals of 3 mm and 5 mm respectively. These two samples were grown at the lowest temperature gradients and, of the two, #131 was grown at a lower nutrient temperature.

In contrast, the products from experiments #110, #120, #124, #125, and #128, which were highest in wurtzite content, were grown at higher nutrient temperatures and with much higher temperature gradients, while the products #127, #137, #141, #145, and #146, which were the more highly coloured, were grown at lower nutrient temperatures, but also had a wide range of temperature gradients and HCl concentrations.

The conclusions from these experiments are that (i) the best crystal was grown at the lowest nutrient temperature and lowest temperature gradient and that (ii), no direct cause could be pinpointed that had produced the colourations.

(c) Expansion of the C.V.T. Programme

(i) Other Carriers

In the initial part of this programme, only HCl was used as the carrier. Later in the programme, I_2 was substituted for HCl in many experiments and, more recently, a trial run using only Br_2 was tried. No runs were made with mixtures of carriers.

Bromine was not acceptable as a carrier because it was found to be difficult to handle and to seal in the reaction tube. Also, the rate of growth with bromine was much smaller compared with either HCl or I_2 under the same conditions.

Iodine was found to be as easy to handle and to seal in the reaction tube as hydrogen chloride. Usually 100 mg of iodine were used. The rate of growth, at a nutrient temperature of 1000 °C and a temperature gradient of 100 deg C, was found to be 12.7 and 13.3 mg/hr for hydrogen chloride and iodine, respectively. Although no direct comparative experiments were conducted at nutrient temperatures of 800 °C, indirect evidence supports the fact that the growth rate, at this temperature, is similar for either HCl or I_2 reactions.

Table 30 gives a break-down of the total use of the carriers
and also a comparison of "static" and "migration" systems.

TABLE 30

Types of Chemical Vapour Transport of ZnS Growth Reactions

Carrier	Number of Experiments	
	Static	Migration
HCl	85	28
I_2	13	20
Br_2	1	0

(ii) Source of ZnS for Total C. V. T. Programme

The source of the ZnS for the above 147 C. V. T. growth reactions
is shown in Table 31.

TABLE 31

Source of ZnS for the C. V. T. Reactions

	% of Total Expts.	Expts.
Fisher Scientific	10. 2	15
General Electric	38. 1	56
Koch-Light	5. 4	8
Synthetic (Zn + S)	45. 6	67
Naturally-occurring mineral	0. 7	1

(iii) Low Temperature Gradients

Low temperature gradients of 5 to 30 deg C caused one or more
crystals to grow part-way along the tube, (2 to 4 cm from the tip
of the growth zone). These crystals were well formed. The rate of growth
was estimated to be 0. 15 mg/ hr. However, after the temperature gradient
was increased to 37 deg C, all of these crystals as well as some additional

nutrient material were transported to the tip of the growth zone. The growth rate had increased tenfold to 1.4 mg/hr. Therefore, it is clear that, in any similar "migration" growth from 0 to 37 deg C or more, these two sequential growth conditions would have occurred. Unfortunately, none of these low-temperature-gradient crystals have been isolated for analysis or observation.

(iv) Colour of the Crystals

It was observed that the colour of the crystalline products varied. Usually, when growth had occurred at higher temperatures, there has been more colour than in those products grown at or near 800°C, as shown in Table 32. In these five samples, the temperature gradients were low, and, in four of them, a nutrient temperature of 800°C was used.

TABLE 32

Comparison of Some I_2-Transported ZnS Samples

Expt. No.	Carrier	Nutrient Temp. (°C)	Temp. Grad. (deg C)	Time (days)	Growth Rate (mg/hr)	Colour
290 a, b	I_2	800	0→62 62	17 8	} 4.8 Av.	Colourless with entrapped I_2
309 b	I_2	800	0→30	16	2.24	Colourless
419 b	I_2	800	5→30	16	2.8	Sl. yellow
728 c	I_2	800	5→37	10	1.4	V. Sl. yellow
377 d	I_2	1125	5→35	13	1.4	Deep brownish yellow

a. In this experiment, the early growth period was during a "migration" and the later stages were at a "static" condition.
b. The quality of samples #290, #309, and #419 was very acceptable.
c. Sample #728 was polycrystalline.
d. The single crystal in #377 was the best-formed of this group, having good angles and faces.

It is generally accepted that ZnS crystals should be colourless. Alternatively, the presence of the colour has been attributed to the presence of impurities such as Fe, Cu, O, Cl, and I_2. Therefore, some experiments were performed and some analysis were made in an attempt to pin-point the cause of the colour.

(v) Analysis of the C.V.T. Crystals

One approach adopted was to submit some samples for semi-quantitative spectrographic analysis; the results are shown in Table 33. The level of impurities varied from sample to sample but, unless the small amounts of Fe and/or Cu have a large tinctorial factor, it is not likely that the source of colour in these ZnS crystalline products is due to any of the elements listed in Table 33.

The second approach adopted was to analyse for oxygen and the halogens. These analyses were attempted by a neutron-activation procedure. The results, as shown in Table 34, suggest that the oxygen level is indeed very low. Unfortunately, low concentrations of chlorine and iodine are very difficult to analyse by this procedure. Therefore, under the conditions used in this neutron-activation analysis, the conclusion was that Cl and I were not detectable.

Samelson (16) reported that chlorine impurities in his ZnS samples varied from 90 to 600 ppm; a background level of chlorine in crystals grown in a non-chlorine atmosphere was stated to be 90 ppm. Also, the amount of chlorine in his crystals did not appear to be dependent on the growth temperature.

Therefore, it is assumed that this level of chlorine or iodine is very unlikely to be the cause of the colouration in ZnS.

The third approach was an attempt to transport ZnO with HCl or I_2. In the case of HCl, a transport was tried at 900°C; after about 2 days the tube exploded. The equation for the transport reaction would be:

$$ZnO + 2HCl \rightleftharpoons H_2O + ZnCl_2 \qquad \text{(Eq. 4)}$$
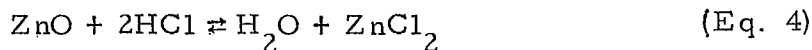
Apparently, the cause of the explosion was the reaction of the water with silica tube.

When I_2 was used, the equation would be:

$$ZnO + I_2 \rightleftharpoons ZnI_2 + [O] \qquad \text{(Eq. 5)}$$
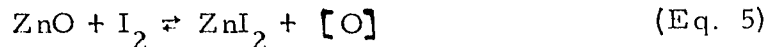
TABLE 33

Semi-Quantitative Spectrographic Analysis of C.V.T.-Grown ZnS
(% by Weight)

Expt. No	Carrier	Si	Al	Mn	Mg	Fe	Cu	Sn	Ca	Ti	Ni	Zn	Pb	Notes	Remarks
47	HCl	0.03	0.07	0.09	0.08	0.04	N.D.	-	-	-	-	Pc	-	*	1st Growth
145	HCl	0.06	0.1	0.1	0.2	0.1	0.04	N.D.	0.2	0.03	0.035	Pc	N.D.	**	1st Growth
146	HCl	0.03	0.2	0.003	0.04	0.05	0.04	N.D.	N.D.	0.02	0.03	Pc	N.D.	**	1st Growth
327	I_2	0.1	0.06	0.008	0.1	0.1	0.06	N.D.	0.1	0.03	N.D.	Pc	N.D.	**	1st Growth
373*****	I_2	0.5	0.4	0.07	0.36	0.7	0.2	N.D.	N.D.	0.16	0.2	Pc	N.D.	**	2nd Growth[a] ex-143
373*****	I_2	0.2	0.02	0.02	0.08	0.06	0.1	N.D.	N.D.	0.07	0.2	Pc	N.D.	****	
377	I_2	0.05	0.09	0.009	0.05	0.08	0.06	N.D.	N.D.	0.02	N.D.	Pc	0.06	***	2nd Growth[a] ex-327

Other elements reported as not detectable: Ba, Sb, Mo, Sn, Cr, Bi, V, Ag, Co.

    *Internal Report MS-AC-65-96.

    **Internal Report MS-AC-68-87.

    ***Internal Report MS-AC-68-90.

    ****Internal Report MS-AC-68-82.

    *****Analysis on different portions of the sample.

Pc = Principal constituent.

a = Re-growth was made in a new tube and under new conditions.

54

TABLE 34

Neutron-Activation Analysis of C. V. T.-Grown ZnS

Expt. No	Carrier	Remarks	O_2	Cl_2	I_2	
137	HCl	-	<100 ppm	-	-	*
117	HCl	Probably High Cl^-	-	N. D.	-	**
308	None	Blank	-	-	-	**
315	HCl	Probably Low Cl^-	-	N. D.	-	**
327	I_2	-	-	-	N. D.	**

*Report PR 66-15. N. D. = Not detectable.

**Private communication from C. McMahon, Mineral Sciences Division.

No growth was observed after 96 hr, even with the nutrient temperature at 1100°C and with a temperature gradient of 100 deg C.

Therefore, it appears safe to assume, if some zinc oxide were present in the nutrient material, and if I_2 were used, that little or no oxygen would be transported to the zinc sulphide crystal. However if HCl were used, small amounts of oxygen might be transported.

A fourth approach was to determine the total zinc in the crystalline product by oxidization procedure (see page 4) and then to calculate the formula. The results, as shown in Table 35, indicate that the colourless materials were essentially stoichiometric ZnS. However, the compositions of the coloured crystals indicated deviations from stoichiometry. The depth of colour and whether the crystal was greenish or yellowish seemed to have no direct relationship to the magnitude of the deviation from stoichiometry.

Table 36, which is really an extension of Table 35, shows the comparison of the calculated formulae of the nutrient material, the transported crystal, and the untransported residue.

These results indicate that the I_2 in #728 and #739 played a double role: firstly, as the usual carrier (see Eq. 2), and secondly, as a complexer of most of the excess zinc. In effect, this would mean that the crystal growth in #728 and #739 had proceeded in a ZnI_2-rich atmosphere and, at the conclusion of the run, the ZnI_2 must have been leached out with the remaining I_2.

The most important conclusion is that neither the transported material nor the residue were stoichiometric ZnS. The extension of this fact, based on Tables 35 and 36, suggests that the composition of the crystal-growth products are changing throughout the growing period.

Therefore, this changing composition of the growth products could very probably be the cause of the crystal imperfections and the wurtzite intergrowths and, **finally after** the stoichiometry has changed appreciably, the cause of the colour formations.

TABLE 35

Calculated Formula of Various C. V. T. -Grown ZnS vs. Colour

Expt. No	Carrier	Nutrient Temp. (°C)	Temp. Gradient (deg C)	Early Growth Colour	Early Growth Formula	Later Growth Colour	Later Growth Formula	Average Growth Colour	Average Growth Formula
141	HCl	950	100	Colourless	$ZnS_{1.000_9}$	Sl. greenish	$ZnS_{0.9960}$	-	-
144	HCl	950	150	-	-	-	-	Deep Yellow	$ZnS_{1.001_9}$
165	HCl	905	130	-	-	-	-	Sl. Yellow	$ZnS_{0.996_4}$
213	HCl	940	165	Colourless	$ZnS_{0.999_4}$	Yellowish	$ZnS_{1.001_4}$	-	-
728	I_2	800	5→37	-	-	-	-	Sl. Yellow	$ZnS_{0.998_3}$
739	I_2	1000	100	-	-	-	-	Dark Brownish-Yellow	$ZnS_{1.002_5}$
739 duplicate	I_2	1000	100	-	-	-	-	Dark Brownish-Yellow	$ZnS_{1.002_0}$

TABLE 36

Calculated Formula of Transported and Untransported Products Obtained by C.V.T. of ZnS

Expt. No	Carrier	Nutrient Temp. (°C)	Temp. Gradient (deg C)	Time (days)	Formula of Nutrient Material	Formula of Transported Product (Average)	Formula of Untransported Product (Average)
213	HCl	940	165	17	Not determined*	$ZnS_{1.000_4}$	$ZnS_{1.003_1}$
693	I_2	1100	8→55	4	$ZnS_{0.998}$	$ZnS_{0.996_8}$	$ZnS_{1.001_3}$
728	I_2	800	5→37	11	$ZnS_{0.990_5}$	$ZnS_{0.998_3}$	$ZnS_{0.997_2}$
739	I_2	1000	100	2	$ZnS_{0.990_5}$	$ZnS_{1.002_2}$	$ZnS_{0.999_4}$

*Related work would indicate $ZnS_{0.998+}$.

(d) Attempts to Remove Colour from C.V.T.-Grown ZnS

Three different approaches were used in attempts to remove the colour from ZnS crystals.

(i) Re-Growth

Previously, it has been stated that low nutrient temperatures and low temperature gradients usually produced colourless crystals. Therefore, two coloured crystals were re-grown under the "presumed ideal" conditions shown in Table 37. In both cases, the intensity of the colour may have changed but it certainly was not removed. Various analyses were made on Sample #373. The electron-probe analysis showed that neither Cl or I_2 was detectable, that the Zn to S ratio was constant, and that there was the possibility of twinning. Meantime, an X-ray fluorescence analysis had indicated a faint trace of iodine on one plane of the crystal. The semi-quantitative spectrographic analyses, reported in Table 33, (see #327 and #377) indicated no increases in Si, Al, Mg, Fe, Cu, Ti, and Ni contents over those in the product from only one transport reaction.

The reason for the failure to remove the colour from the re-transported material is assumed to be that the stoichiometry was not shifted close enough to ZnS to give a colourless crystal.

(ii) Improvement in Stoichiometry

Since it has been shown, in Table 35, that the colour is probably caused by a deviation from stoichiometry, two experiments were undertaken with coloured ZnS crystals. In one case, the ZnS was re-grown with I_2 in presence of added sulphur and, in the other case, the ZnS was re-grown with I_2 in presence of added zinc. In both cases, the re-grown ZnS was still as coloured as the nutrients had been. A possible explanation might be that, due to the large excess of sulphur or zinc added over that required to give stoichiometry, the composition may have been changed from ZnS_{1-x} to ZnS_{1+x}, or vice versa, a condition which would again result in a coloured crystal.

TABLE 37

Re-Growth of Coloured ZnS Crystals

Expt. No	Previous Carrier	Re-growth Carrier	Nutrient Temp. (°C)	Temp. Gradient (deg C)	Time (days)	Colour
373	HCl	I_2	800	$0 \rightarrow 36$	14	Unchanged
607	I_2	I_2	775	20	7	Unchanged

TABLE 38

Pumping/Heating of ZnS (Coloured) Crystal #618

Sample	Weight (g)	Temp. (°C)	Press (mm)	Time (min)	Zone A* Colour	Formula	%	Zone B** Colour	Formula	%	Residue Colour	Formula	%
I_2-grown crystal	0.6282	850-1000	4×10^{-3}	60	White	$ZnS_{1.024}$	5	Yellow	$ZnS_{1.025}$	86	Blackish	$ZnS_{1.008}$	9

* Within 2 in. from outside of furnace ($\approx 500°C$).
**Over 2 in. from outside of furnace ($< 500°C$).

(iii) <u>Pumping/Heating of the Coloured ZnS Crystals</u>

An I_2-grown coloured crystal was pumped while being heated in a manner similar to that described under "Purification of ZnS powders by Pumping of Heated Samples" on page 25. In Table 38, the results show that, although white and yellow sublimates which represented 91% of the coloured ZnS sample were obtained, the residue was still highly coloured.

Therefore, it appears that, although the pumping/heating treatment has removed sulphur-rich sublimates, the residue is still sufficiently sulphur-rich to be highly coloured. It is evident that, because over 90% of the sample was sublimed without achieving a colourless residue, this procedure is unsatisfactory for the desired purpose.

A summary of the chemical vapour transport method indicates that the best crystals are grown at nutrient temperatures of about 800°C with a temperature gradient of less than 50 deg C and preferably obtained by a "migration" procedure. Usually, the crystals are colourless but if colour has been obtained in the crystals, it appears that it cannot be removed by any subsequent chemical vapour transport treatment. Because non-stoichiometry is the root cause of the discolouration, the main conclusion is that nutrient materials must have been $ZnS_{1 \pm x}$. Therefore, to enhance the probability of obtaining colourless crystals, the nutrient material should be purified (treated) to lower the value "x" to the lowest possible level.

(e) <u>Phase Changes Occurring in C.V.T. Growth of ZnS</u>

In Table 39, the growth of two samples of sphalerite and two samples of wurtzite at 800°C and 1100°C are shown. In all cases, the crystalline product was sphalerite, even at 1100°C, where wurtzite would have been expected if the 1020°C transition temperature were meaningful.

(f) <u>Epitaxial Growth</u>

Two special experiments were undertaken to deposit ZnS onto a halite crystalline substrate, as shown in Table 40.

TABLE 39

Phase Changes Occurring in Chemical Vapour Transport Growth of ZnS

Expt. No	Carrier	Nutrient Temp. (°C)	Temp. Gradient (deg C)	Phase of Nutrient	Phase of Transported Product		Phase of Untransported Product	
					Major	Minor	Major	Minor
327	I_2	800	9→23	Sphalerite	Sphalerite	**	Sphalerite	**
377	I_2	1100	5→35	Sphalerite	Sphalerite***	–	Sphalerite	Tr. Wurtzite
386	I_2	800	0→80	Wurtzite	Sphalerite	**	All Transported	
409	I_2	1100	0→30	Wurtzite	Sphalerite	**	Sphalerite	**

**Not detectable.

***Stereoscopic microscope examination indicated the presence of sphalerite with an extremely low birefringence.

TABLE 40

Epitaxial Growth on Halite Substrate

Expt. No	Carrier	Nutrient Temperature (°C)	Temperature Gradient (deg C)
134	HCl	825	85
481	HCl	750	2→8

In #134, the halite had melted somewhat during the growth run. This condition was corrected in #481; here, the transported ZnS formed as a rounded, opaque, whitish deposit on the halite; meanwhile, some ZnS was transported to the extremities of the tube as small yellowish crystals. No follow-up experiments have been conducted.

(g) Doping

It will be recalled that the cobalt impurity in Fisher Scientific ZnS was transported to give a greenish product. Unfortunately, this cobalt was an unwanted dopant.

A limited number of growth runs has been made with the objective of deliberate doping of zinc sulphide with Al or Fe.

(i) Aluminum

Two attempts were made to dope with aluminum, but the rate of growth was nil in one case (#188) and very low in the other (#619), as shown in Table 41. In the former case, the reason for the absence of transported material is assumed to be that the aluminum combined with all the available chlorine, and, due to an unfavourable thermodynamic equilibrium shown in the Eq. 6, of which the right-hand side is highly favoured, the chemical vapour transport of ZnS was blocked by the removal of the HCl.

$$Al_2S_3 + 6HCl \rightleftharpoons 2AlCl_3 + 3H_2S \qquad (Eq. 6)$$
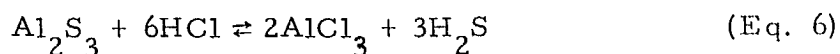
TABLE 41

Attempts to Dope ZnS in a C.V.T. Growth Reaction

Expt. No	Sample	Carrier	Nutrient Temp. (°C)	Temp. Gradient (deg C)	Growth Product
188	$ZnS + 1\% \ Al_2S_3$	HCl	1050	180	Practically no growth
619	$ZnS + 0.67\% \ Al_2S_3$	I_2	950	50	Sl. yellow - sphalerite [a]
173	Natural-occurring 6% Fe (ZnS)	HCl	960	35	All transported; jet black; polycrystalline
177	Natural-occurring 6% Fe (ZnS)	HCl	960	15→100	All transported (as above)
180	$ZnS + 10\% \ FeS$	HCl	960	125	All transported - no single crystals [b]
186	Natural-occurring 6% Fe (ZnS)	HCl	965	20	All transported (black)
291	$ZnS + 1\% \ FeS$	I_2	800	0→86	Good transport, segregated
484	$ZnS + 1.8\% \ FeS_{1.1}$	I_2	800	7→30	Brownish crystal sphalerite [c]
658	$ZnS + 11.7\% \ FeS$	I_2	792	63	Practically no growth
659	$ZnS + 10.2\% \ FeS_{1.084}$	I_2	794	65	Considerable growth

(a) Rate of Growth = 0.54 mg/hr.
(b) Rate of growth appears to be similar to iron-free ZnS growths = 14.0 mg/hr.
(c) Rate of Growth = 0.97 mg/hr.

However, in #619, an excess of iodine over the amount that might be combined with the aluminum to form AlI_3, was used and some transport took place. An examination of this product by the electron-probe micro-analyser showed the zinc to sulphur ratio to be constant and no aluminum or iodine was detectable in the crystal.

(ii) Iron

Eight experiments involving (Fe, Zn) S-type of samples were conducted, as shown in Table 41. Although several conclusions can be drawn from these results, much more experimentation should be undertaken in order to fully understand the growth mechanism in this situation.

The first observation is that the rate of growth is markedly affected by the concentration and ratio of iron to sulphur in the nutrient material. Experiments involving only FeS_x nutrients have shown that $FeS_{1.00}$ is not transported with iodine under the usual temperature range, but that $FeS_{1.08}$ is transported. Unfortunately, this behaviour has not been sufficiently explored yet, but further information on it will be reported in Part III of this series of reports, "The Sulphides of Cobalt, Iron and Nickel". Therefore, the results shown in Table 41 indicated the possibility of a reaction occurring in which the $FeS_{1.0}$ is combining irreversibly with the small amount of free sulphur produced by Eq. 2 and 3 (see page 38) until the iron to sulphur ratio reaches a level at which the reaction is reversible at the temperature of the experiment. (A guess would be in the range of $FeS_{1.08}$.) On examining Table 41, it is evident that, in #658, this reversible level was not reached and that no growth of a transported product resulted. In other cases, where a low concentration of $FeS_{1.10}$ (#484) and a high concentration of $FeS_{1.084}$ (#659) were present, respectively, there was a transported product.

The second observation was in connection with (#291); the initial crystal growth was colourless and this intermediate growth become yellowish until the last growth was dark brown. This product was cut and a part was

analysed at a series of 24 locations 300 microns apart from the darkest to the lightest edge. The results of the electron-microprobe analysis showed a rapid decrease of iron content from 2.08% to 1.02%, and then a gradual decrease to 0.20%. There was a corresponding change in sulphur and zinc values, as shown in Table 42. This means that the early growth was predominantly ZnS and, as the experiment progressed, the quantity of FeS_x being transported increased at an increasing rate. Part of the product was sent to the Georgia Institute of Technology, Atlanta, Georgia, in November 1969, for a study of textural features related to growth history; to date, no report of their findings has been received.

The third observation was that, in samples #173, #177, #180, and #186, the products were polycrystalline and black.

The fourth observation was that the transported product of sample #484 was sphalerite.

2. Vapour Transport (V.T.) by Sublimation

Sublimation of ZnS was encountered, as mentioned earlier in this report, during the purification of ZnS powders. In order to determine the rate of sublimation, ZnS powder was placed in a Vitreosil boat and heated in a stream of helium. The loss of ZnS at various temperatures is shown in Figure 12 which indicates that sublimation starts at about 800°C and is increasing rapidly in rate at 1050°C.

The application of the phenomenon of sublimation to the process of crystal growing is dependent on containing the reaction in a controlled-atmosphere system. The type of system used is controlled by the fact that silica tubing softens in the vicinity of 1200°C. Therefore, two different systems were developed, one for temperatures under 1200°C and the other for higher temperatures.

(a) Sublimation at 1200°C and below

In the cases where sublimation is occurring at temperatures below 1200°C, a closed silica tube can be used, as shown in Figure 13.

TABLE 42

Results of Microprobe Analysis of the Sphalerite No. 291
(% by weight)

| Iron	Sulphur	Zinc	Totals
2.08	33.39	65.69	101.16
1.51	33.38	66.41	101.30
1.18	33.71	66.81	101.70
1.02	33.70	66.72	101.44
0.94	33.50	67.36	101.80
0.78	32.89	67.23	100.90
0.73	33.08	67.70	101.51
0.73	32.99	67.67	101.39
0.87	31.97	67.47	100.31
0.81	33.28	67.92	102.01
0.62	32.49	68.25	101.36
0.65	33.56	67.56	101.77
0.67	33.00	67.76	101.43
0.72	32.52	67.45	100.69
0.53	32.50	67.69	100.72
0.41	31.76	68.05	100.22
0.48	31.88	67.54	99.90
0.51	32.72	67.61	100.84
0.39	32.26	67.98	100.63
0.34	32.17	67.77	100.28
0.25	33.16	67.58	100.99
0.21	32.75	68.00	100.96
0.17	32.52	68.16	100.85
0.20	31.92	67.77	99.89
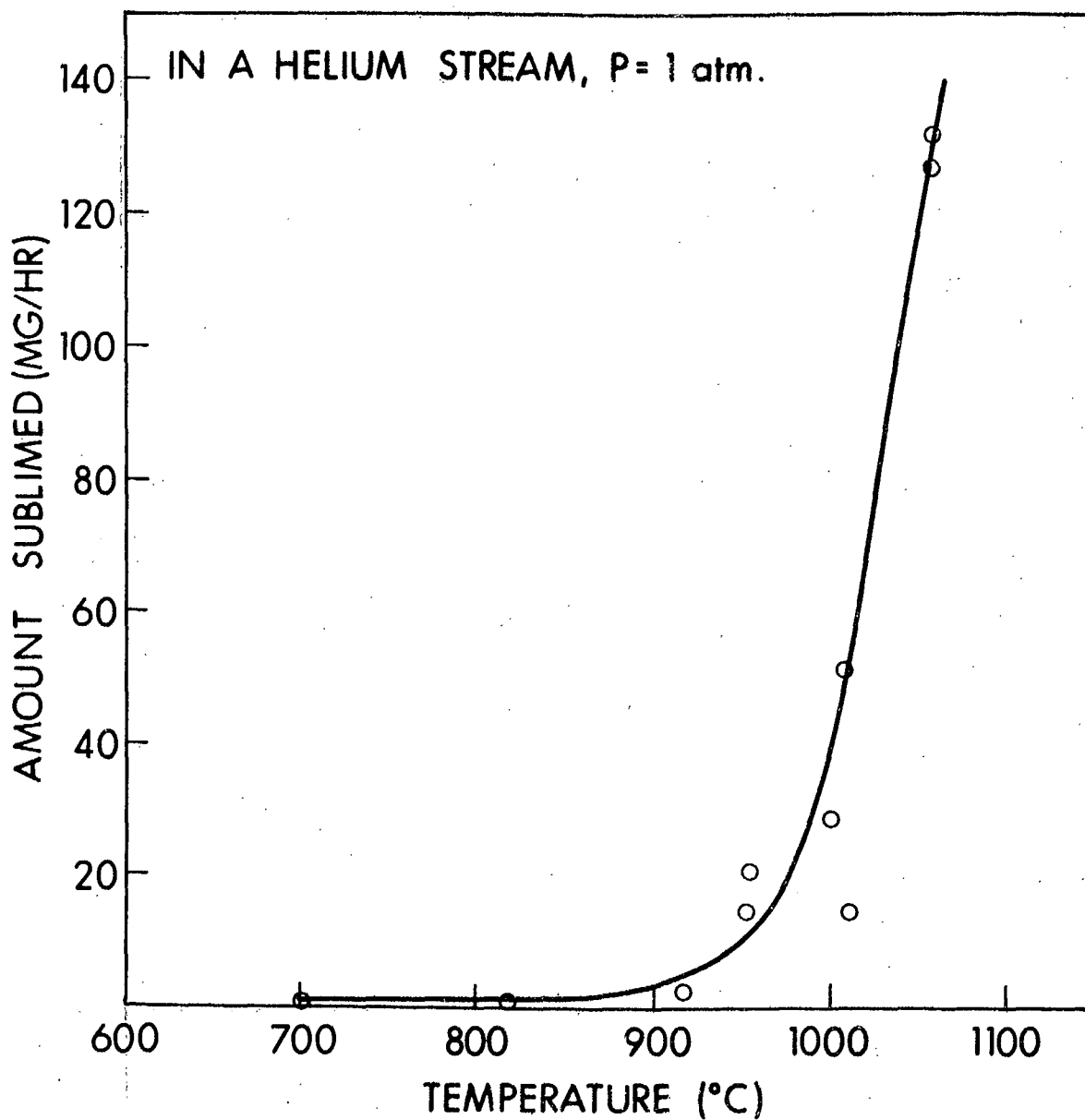
Figure 12. Sublimation of Zinc Sulphide.
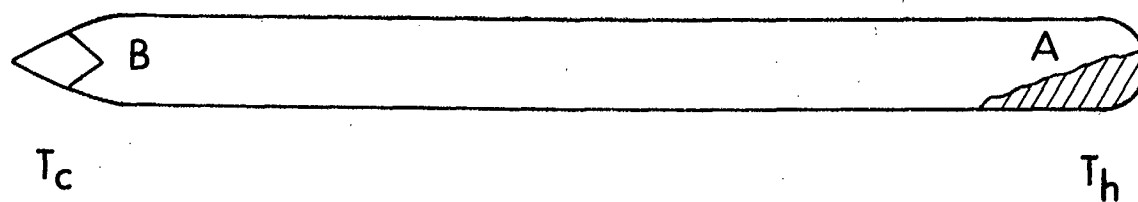
Figure 13. Schematic Tube for Vapour Growth.

The first fourteen experiments, using this approach to growing ZnS crystals, were largely exploratory in nature but proved that very little transport (sublimation) occurred at temperatures at 1150°C or lower. The rate of growth did not increase when large temperature gradients were used. In all cases, the crystalline products were of poor quality.

When the temperature was increased to 1200°C, the evacuated silica capsules collapsed after about two days. To counteract the collapsing of the tube, a sufficient amount of a gas, e.g., argon, helium, hydrogen sulphide, or nitrogen was sealed in the tube, to give an internal pressure of one atmosphere at 1200°C. However, it was observed that helium and hydrogen (produced by the decomposition of hydrogen sulphide) diffused slowly through the walls of the silica capsule, causing the tube partly to collapse. The presence of argon, nitrogen, or sulphur prevented tube collapse but tended to impede the sublimation.

The results of ten experiments are shown in Tables 43 and 44 which indicate two aspects of crystal growth, (a) the rate of growth and (b) the phase of the various products, respectively.

Five main conclusions can be drawn from these experiments:

(i) in all cases, small crystals were obtained;

(ii) the rates of growth are dependent on the nature of the gas;

(iii) the difference in the growth rate between #408 and #746 implies that a 25-deg C increase in nutrient temperature caused a 15-fold increase in the rate of sublimation;

(iv) the phases of nutrient, transported, and untransported materials show no set pattern; and

(v) in general, the products were colourless or had a slight yellow colouration. In one case (#471) where excess sulphur was present, the crystal was colourless; in another case (#511), the nutrient was a yellowish crystal and gave a sublimed product of some colourless and some slightly yellow crystals.

TABLE 43

Experimental Conditions and Results of Some Vapour Transport Growth Reactions of ZnS

Expt. No	Atmosphere	Temp. Nutrient (°C)	Temp. Gradient (deg C)	Time (hr)	Rate of Growth (mg/hr)
384	He	1200	10→20 Mig	24	Not weighed
385	He	1200	5→18 Mig	66	4.0
387	H_2S	1200	5→45 Mig	113	0.36
393	He	1200	7→16 Mig	48	13.7
394	H_2S	1200	3→17 Mig	108	0.36
403	Argon	1200	7→26 Mig	100	1.27
408	Vacuum	1200	5→11 Mig	42	4.55
471	S^o	1200	10→22 Mig	88	0.11
511	N_2	1200	5→28 Mig	156	1.12
746	Vacuum	1175	25 Static	117	0.31

Mig = "migration" technique.

TABLE 44

Phase Changes Occurring in Vapour Transport Growth Reactions of ZnS

Expt. No	Phase of Nutrient	Phase of Transported Product		Phase of Untransported Residue	
		Major	Minor	Major	Minor
384	*	Wurtzite	**	*	*
385	*	Sphalerite	Tr. Wurtzite	*	*
387	Sphalerite	Wurtzite	Sphalerite	Sphalerite	**
393	Wurtzite	Sphalerite	**	*	*
394	Wurtzite	Sphalerite	**	*	*
403	*	Sphalerite	Tr. Wurtzite	*	*
408	*	Sphalerite	**	Sphalerite	Wurtzite
471	Sphalerite	Sphalerite	Wurtzite	Sphalerite	Wurtzite
511	Sphalerite	Wurtzite	**	Wurtzite	**
746	Wurtzite	Sphalerite	Wurtzite	Wurtzite	**

*Indicates that these materials were not submitted for X-ray diffraction analysis.
**Not detectable.

(b) Sublimation at 1200°C and above

Indradev studied the parameters of growth from the vapour phase of ZnS crystals; he was able to grow large crystals by using a self-sealing method (11).

The present author's furnace was not suitable for the Indradev tube design; therefore, a modification (Figure 4), was devised that was successful.
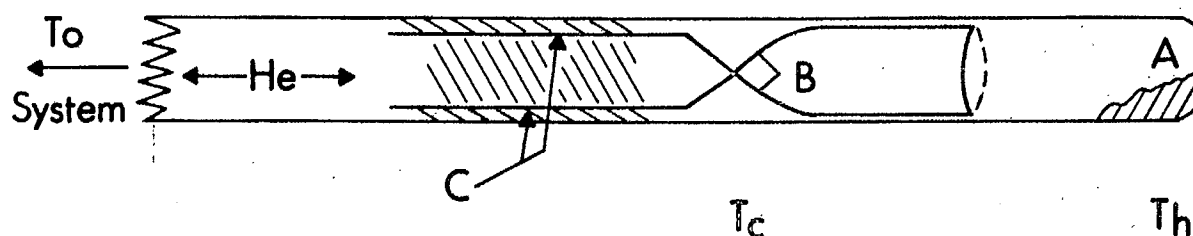
Figure 14. Schematic Arrangement for Self-Sealing Vapour Transport.

This tube is coupled to the pumping station and, after a suitable out-gassing procedure, helium is admitted to give a constant pressure of one atmosphere by means of an overflow bubbling tower. This arrangement permitted the heating of the tube to temperatures much higher than 1200°C while still maintaining atmospheric pressure inside. Since all experiments were conducted in helium; hence it is not possible to predict the effect of using another gas, e.g., argon, hydrogen sulphide or nitrogen.

At the growth temperature, nutrient A is sublimed to area C, where initial crystal-growth will seal the system with a helium atmosphere equal to atmospheric pressure; then a good single crystal will grow at B. A slow migration of the tube enhances single-crystal growth.

After a period of two to five days, the silica tube had devitrified internally, causing the tube to fragment on cooling; however, the crystal was undamaged. The general condition of the tube, after growth, is shown in Figure 15.

Figure 15. Schematic Condition After Crystal Growth.

The main difference between Figures 14 and 15 is the presence of deposits at D and F. These deposits are composed of several zones of white and yellow, which are sepa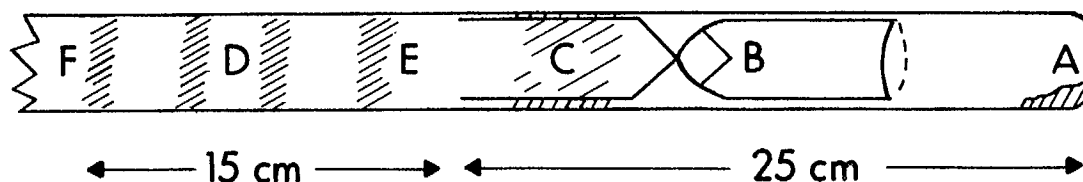rated by clear spaces. The intensity of the yellow varies from one zone to another. In several cases, these deposits had formed after the vapours had passed through quartz wool at E. In two cases, a greyish zone formed at F. The zones F to D, were deposited at a temperature of 1000° to 1200°C, respectively. The yellow bands were originally thought to be sulphur-rich impurities.

The growth conditions and rates of growth for nine experiments are listed in Table 45. The crystal at B was always colorless, and the reported rate of transport was based on this crystal only. The amount of transported material that was lost in zones C, D, and F varied from 0.04 to 1.0 g, with the average being 0.33 g. This variation is due to the tolerance in sizes of the inserts and the outside tube.

The best-looking single crystal was #307, but #308 and the 1200°C runs (#381, #383 and #392) gave polycrystalline products.

The phase relationships shown in Table 46 involve the same samples that are listed in Table 45. It appears that the transported and untransported products are always sphalerite, sometimes with a trace of wurtzite. Table 46 exhibits a sharp contrast to Table 44 which showed no set pattern of phase occurrence.

The true identity of the white and yellow zones at D of #346 was found by X-ray diffraction analysis (see Table 46) to be ZnS (both sphalerite

TABLE 45

Experimental Conditions and Results of Some Vapour Transport Growth Reactions of ZnS

Expt. No	Source	Nutrient Temp. (°C)	Temp. Gradient (deg C)	Time (hr)	Rate of Growth (mg/hr)
237	GE ZnS	1322	37 static	20	39.3
284	Zn + S	1350	0→90 Mig	75	32.1
289	Zn + S	1375	12→38 Mig	100	17.3
307	Zn + S	1335	9→27 Mig	132	10.0
308	Zn + S	1350	21→42 Mig	137	25.6
346	Zn + S	1335	7→15 Mig	36	14.3
381	Zn + S	1200	10→37 Mig	108	1.5
383	Zn + S[a]	1200	10→37 Mig	88	3.5
392	GE ZnS	1200	8→35 Mig	72	0.63

Mig = "migration" technique.

(a) This material was the untransported residue of #377, an I_2 transport at 1100°C; it was greenish in colour.

TABLE 46

Phase Changes Occurring in Vapour Transport Growth Reactions of ZnS

Expt. No	Phase of Nutrient		Phase of Transported		Phase of Intermediate		Phase of Untransported	
	Major	Minor	Major	Minor	Major	Minor	Major	Minor
237	*	*	*	*	*	*	*	*
284	*	*	*	*	*	*	*	*
289	Sphalerite	**	*	*	*	*	*	*
307	*	*	Sphalerite	**	*	*	*	*
308	*	*	Sphalerite	**	*	*	*	*
346	Sphalerite	Wurtzite	Sphalerite	Tr. Wurtzite	See ① below	–	Sphalerite	Wurtzite
381	Sphalerite	Wurtzite	Sphalerite	Tr. Wurtzite	*	*	Sphalerite	Wurtzite
383	Sphalerite	Tr. Wurtzite	Sphalerite	Tr. Wurtzite	See ② below	–	Sphalerite	Wurtzite
392	Wurtzite	Sphalerite	Sphalerite	Wurtzite	*	*	Sphalerite	Wurtzite

*Indicates these materials were not submitted for X-ray diffraction analysis.

**Not detectable.

① Two products that were analysed separately.
   (i) White product = Major sphalerite + low minor wurtzite + Tr. amorphous.
   (ii) Yellow product = Major unidentified + minor sphalerite + Tr. amorphous.

② Yellow section of tube was cut and the product was re-grown in closed tube (#384); this re-growth product was wurtzite.

and wurtzite) and an amorphous material, which was probably sulphur. A second experiment involved the cutting of zone D from the tube assembly of #383 (after growth), and sealing the tubing and its deposit in another silica capsule and subjecting it to a vapour transport at 1200°C. The product was colourless crystals of wurtzite. A similar experiment involved cutting zone D from #401 (see Table 50, page 80), and sealing this section of tube and its yellow deposit with iodine in another silica tube, and transporting at 800°C. The product was very deep yellow and X-ray diffraction analysis indicated it to be sphalerite. Therefore, these coloured deposits are similar in colour and range of ZnS composition to the sublimates obtained during the purification of ZnS powders (see page 25).

Transported sample #308 was analysed for zinc content by the oxidation method (see page 26); a value of Zn = 67.128% was obtained, corresponding to a calculated formula of $ZnS_{0.998}$. A second portion of #308 was pumped while being heated (see page 25), and the yellow sublimate and the residue were analysed (see Table 47). These results agree with those of previous samples reported in Tables 24 and 38 and support the conclusions on page 26.

Four vapour-transported ZnS products were submitted for spectrographic analysis (see Table 48); a comparison with Table 33 indicates that there was no additional contamination from the silica tube at this higher temperature.

A survey of the results obtained by the vapour transport method shows that the crystals are colourless to slightly yellow when grown at 1200°C and always colourless when grown at temperatures above 1200°C. The probable explanation appears to be that, at 1200°C, the zone of $ZnS_{1\pm x}$ must be very narrow (see Figure 3) and, at temperatures above 1200°C, the composition of the crystals must be essentially ZnS. Conversely, any excess sulphur or zinc, which would cause non-stoichiometry of the nutrient, must either sublime to zone D (see Figure 15) or, if still present in the growth atmosphere, be unable to enter the crystal because $ZnS_{1\pm x}$ (where $x \neq 0$) is unstable at these temperatures and only ZnS can grow.

TABLE 47

Pumping/Heating of ZnS (Colourless) Crystal #308

Sample	Weight (g)	Temp. (°C)	Press (mm)	Time (min)	Zone A*			Zone B**			Residue		
					Colour	Formula	%	Colour	Formula	%	Colour	Formula	%
V.T. grown crystal	0.7128	850-900	3×10^{-3}	300	White	Insufficient sample	≈5	Yellow	$ZnS_{1.010}$	54	White	$ZnS_{0.998}$	41

*0-2 in. outside of furnace ≈500°C.
**Over 2 in. outside of furnace <500°C.

TABLE 48

Semi-Quantitative Spectrographic Analysis of V.T.-Grown ZnS
(% by Weight)

Expt. No	Si	Al	Mn	Mg	Fe	Ca	Cu	Sn	Zn	
14	0.06	0.1	0.01	0.1	0.08	0.009	0.2	–	Pc	*
60	N.D.	0.001	0.005	N.D.	0.02	–	N.D.	0.02	Pc	**
284	0.03	0.04	N.D.	0.02	0.02	N.D.	0.03	N.D.	Pc	***
383	0.9	0.2	0.05	0.25	0.2	0.3	0.06	N.D.	Pc	***

Other elements reported as not detectable: Ba, Sb, Mo, Pb, Cr, Bi, V, Ag, Co, Ti, Ni, Zn, Co.
*Internal Report MS-AC-64-108.
**Internal Report MS-AC-65-96.
***Internal Report MS-AC-68-87.

(c) Sublimation of Naturally-Occurring and Doped ZnS at Temperatures above 1200°C

The following three naturally-occurring ZnS samples were used, as received, as nutrients in the method described in Section (b) above.

(i) Sphalerite from Santander, Spain; this material is mostly colourless with occasional red or black spots dispersed in it.

(ii) Sphalerite from Timmins, Ont., coded M-22550; this material contains $\approx 6\%$ Fe, and is very black.

(iii) Sphalerite from Fisher Scientific; this product is assumed to be naturally-occurring due to the impurities that it contains (see Table 5a).

In addition, three synthetic mixtures of zinc sulphide, containing either 1% Fe or 0.6% Al as dopants, were used as nutrients in the method described in Section (b) above. The growth conditions of both of these groups are shown in Table 49. The rates of growth appear to be similar to those obtained with the undoped materials (see Table 45); the main difference is that the transported products have a slight yellow colouration.

The phase changes occurring during the growth reactions are shown in Table 50. The general pattern is that the transported and untransported products are predominantly sphalerite, occasionally associated with a minor amount of wurtzite.

Only two of the transported products (see Table 49) were analysed. Sample #439 was scanned by the electron microprobe*; this revealed no evidence of the presence of Co, Cu, Fe, or Al. Electrical measurements on #650 showed a very low conductivity, implying that little or no doping with aluminum had occurred.

The deeply-coloured untransported products suggest that neither iron nor cobalt was transported. X-ray diffraction analyses (see Table 50) indicated the presence of Co_3O_4 and of Al_2SiO_5 in #439 and #650, respectively.

An interesting fact concerning the intermediate product, (see zone D, Figure 17), is that, in one case, #401, it was predominantly sphalerite, whereas, in another case #650, it was wurtzite only.

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*Report EP 68-30

TABLE 49

Experimental Conditions and Results of Naturally-Occurring or Doped ZnS

Expt. No	Source of ZnS	Nutrient Temp. (°C)	Temp. Gradient (deg C)	Time (hr)	Rate of Growth (mg/hr)	Colour of Transported ZnS	Colour of Residue
389	Santander	1200	10→19	72	1.86	Sl. yellowish	Blackish
398	Syn. + 1% Fe	1200	7→16	138	1.10	Colourless	Blackish
400	Syn. + 1% Fe	1200	7→15	42	12.3	Colourless	Blackish
401	Nat. + 6% Fe	1350	7→17	42	1.7	Yellow + black crystals	Blackish
439	Fisher Scientific	1335	7→22	133	17.1	Sl. yellowish	Blue, green, black
650	Syn. + 0.6% Al	1385	7→22	100	21.5	Sl. yellowish	White

Nat. = Naturally-occurring mineral.
Syn. = Synthetic material.

TABLE 50

Phase Changes Occurring in Vapour Transport of Naturally-Occurring or Doped ZnS

Expt. No	Phase of Nutrient		Phase of Transport		Phase of Intermediate		Phase of Untransported	
	Major	Minor	Major	Minor	Major	Minor	Major	Minor
389	Sphalerite	**	Sphalerite	Wurtzite	*	*	Sphalerite	Wurtzite
398	Sphalerite	Sl. Wurtzite	Sphalerite	Sl. Wurtzite	*	*	*	*
400	*	*	Sphalerite Wurtzite	-	*	*	*	*
401	Sphalerite	**	*	*	Sphalerite	Wurtzite	*	*
439	Sphalerite	Wurtzite	Sphalerite	**	*	*	Sphalerite	Wurtzite***
650	Wurtzite	**	Sphalerite	**	Wurtzite	**	****	-

*Indicates these materials were not submitted for X-ray diffraction analysis.

**Not detectable.

***Co_3O_4 was also detected.

****Al_2SiO_5 and SiO_2 were detected.

The above evidence thus indicates that Co, Fe and Al are not transported and, hence, the vapour-transport growth procedure appears to be unsatisfactory for providing Co-, Fe- or Al-doped ZnS crystals.

3. Flux Growth

A third procedure used for growing ZnS crystals is by fluxing. The mechanism of growth is based on the dissolving of a nutrient in a flux salt and heating to a temperature well above the melting point of the flux, but below its boiling point, and then lowering the temperature of the fusion mixture slowly, thereby causing the dissolved nutrient to be deposited as crystals.

Some pertinent references to flux growth are: "Phase Equilibrium and Crystal Growth in System $ZnS-ZnF_2$" published by R. C. Linares (19) and a report by Y. Mita (20) that KCl is most appropriate as a flux for growth of ZnS. "Growth of Cubic Zinc Sulphide from Molten Lead Chloride" by R. C. Linares (21) and also, "Synthesis and Growth of ZnS, ZnSe, ZnTe, GaS, Ga_2S_3 and InS Crystals in Ga and in Metals" by M. Hársy (22).

The usual procedure adopted is to seal the nutrient, A, in a silica tube with 10 to 20 times as much flux, C.

The sealed capsule is placed in an oblique position in a furnace; this arrangement keeps the molten salt, C, in the rounded end of the tube, as shown in Figure 16. If the crystals are grown in an atmosphere of excess sulphur, the pressure in the tube (and over the molten salt) is controlled by the temperature at D, the coldest part of the tube. The crystals grow at B.
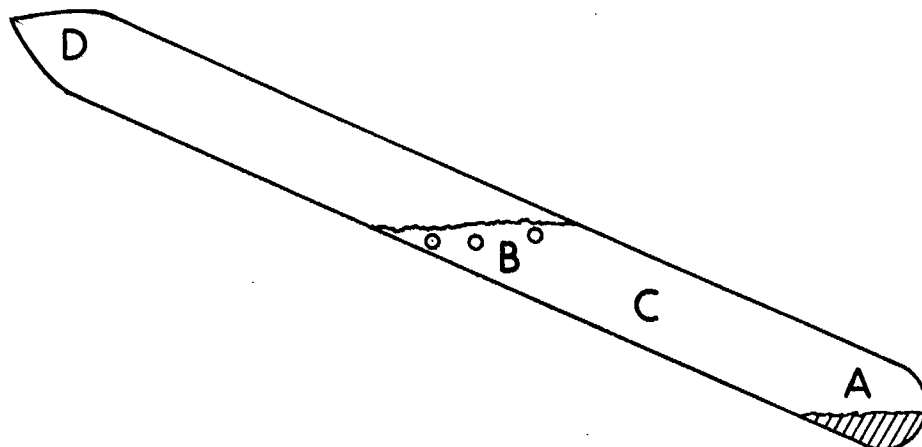

Figure 16. Schematic Arrangement for Flux Growth.

Eight exploratory experiments were attempted in the area of flux growth. Two different growth techniques were tried.

(i) Static growth; i.e., using a fixed nutrient temperature and a fixed temperature gradient. The growth occurs by a continuous migration of ions from the nutrient zone to the growth zone, caused by a difference in concentration gradient due to the temperature gradient.

(ii) Cooling process; i.e., using a decreasing nutrient temperature with a constant temperature gradient. This technique relies on the solution of a sufficient amount of nutrient material in the flux at the peak temperature of the experiment. Then, on cooling, crystals are formed in the flux medium at a place removed from the nutrient zone, due to the temperature gradient. The experimental conditions are listed in Table 51.

Three of the five fluxes, viz., KI, Zn, and $ZnCl_2$ were unsuitable. The KI-flux experiment ended with the silica tube exploding; no crystals of ZnS could be found in the debris. The solubility of ZnS in molten Zn or $ZnCl_2$ appears to be extremely low, resulting in no crystal growth of the ZnS.

One of the other two fluxes used, KCl, was reasonably successful. This flux gave smallish ZnS crystals, and, because Fisher Scientific ZnS was used, they were greenish. In the second experiment, #196, an unsuccessful attempt at seeding was made; the product was still polycrystalline. The rate of growth was similar for #195 and for #196 (0.55 mg/hr), even though the temperature gradient was much higher for #196.

Lead chloride proved to be a successful flux; but, unfortunately, some of the flux or PbS was entrapped in the ZnS crystals (see Eq. 7) from the possible side-reaction.

$$ZnS + PbCl_2 \rightleftharpoons ZnCl_2 + PbS \qquad \text{(Eq. 7)}$$
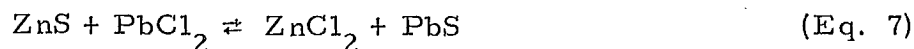
Hydrochloric acid will remove any $PbCl_2$ or PbS on the surface of the crystal, but some black-coloured particles (possibly PbS) remained in the interior of the crystals. X-ray fluorescence analysis indicated the presence

TABLE 51

The Growth of ZnS by the Flux Method

Expt. No	Flux	Method	Nutrient Temp. ($°C$)	Temp. Gradient (deg C)	Time (days)	Degree of Success
195	KCl	Static	850	15	4	Some
196	KCl	Static	865	80	4	Some
197	Zn	Static	834	15	4	None
306	$PbCl_2$	Static	730	≈ 15	4	Some
349	KI	Cooling	900	≈ 15	4	None
374	$PbCl_2$	Cooling	800	≈ 15	9	Very good
690	$PbCl_2$	Static	570	≈ 15	7	Good
741	$ZnCl_2$	Cooling	675	≈ 15	3	None

of Pb in the cleaned ZnS crystals, but X-ray diffraction analysis did not detect any lead compound.

The growth procedure in the successful run#374 was as follows: the silica capsule, containing the ZnS and the $PbCl_2$ flux, was heated to about 250 deg C above the melting point of the flux and, after holding the temperature constant for several hours to ensure maximum solubility, the tube was cooled stepwise at 5 deg C/hr by manual control for several hours during the day, followed by a constant-temperature period during the night. This cooling cycle was repeated several times until the melting point of the flux was reached. The system was then rapidly cooled to room temperature and the tube was cut open with a diamond saw. The frozen salt mixture was leached from the crystals with water and finally with dilute hydrochloric acid.

It is hoped that the inclusion problem will be overcome by the use of a programmed furnace assembly that has recently been purchased and is currently undergoing initial trials. The programmer will permit a cooling rate of 0.5 to 6 deg C/hr to be maintained uniformly throughout the growth period.

The X-ray diffraction patterns of #374 and #690 indicate that the products were exclusively sphalerite.

4. Hydrothermal Growth

The fourth procedure employed for growing ZnS crystals was by the hydrothermal technique.

Hydrothermal crystallization is defined as the use of an aqueous solvent under high temperature and pressure to increase the solubility of a substance to a point at which single crystals are deposited at the coldest part of the system. α-Quartz has been successfully grown by this procedure for over fifty years. However, due to the low solubility of quartz and of many sulphides in pure water even at the extended p-t range available, mineralizers must be added to increase the solubility, through the formation of soluble complexes. Some useful mineralizers are: NaOH, KOH, and NH_4Cl.

Some useful references are: "Hydrothermal Synthesis of Zinc Oxide and Zinc Sulphide" by R. A. Laudise and A. A. Ballman (12), and "Hydrothermal Solubility and Growth of Sphalerite" by R. A. Laudise, F. D. Kolb and J. P. DeNeufville (13).

Early experiments in the present study, using NaOH solutions contained in thick-walled Pyrex tubing at 200°C, failed because the glass tube was attacked, causing it to explode*.

In the next series of experiments, the NaOH solution was contained in a stainless-steel bomb that had 1-in.-thick walls. The furnace temperature was 400°C. Three of these bombs failed due to "stress corrosion" that allowed the solution to escape along the grain boundaries of the metal.

A new bomb, made of Inconel metal, with 1-in.-thick walls and equipped with a Delta seal and a cap secured with six bolts, was especially prepared by the Technical Services Division, Mines Branch; they had also prepared the three stainless-steel bombs mentioned above. A platinum liner has proved to be useful.

The reaction vessel was filled to between 70 and 75% of its available volume. This fill would give an estimated pressure of 6400 psi at 400°C (26). The pressure increases rapidly with increasing temperature under these conditions.

A one-zone furnace was used to provide a nutrient temperature of 370 to 400°C and an estimated temperature gradient of 10 to 20 deg C. The variation in the rate of growth (see Table 52) suggests that the temperature gradients were not reproducible. It is hoped that a two-zone furnace will permit a better control of the temperature gradient and thereby improve the quality of the crystal.

Thirteen experiments were performed using the Inconel bomb. Some of the results are shown in Table 52. The main problem with this system was polynucleation, which causes many small crystals to grow rather than a large single crystal. Seeding and the use of a baffle did not help towards producing fewer and, conversely, larger crystals.

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*For protection against these explosions, an iron-pipe jacket was used to encase the glass tube during the heating stage.

TABLE 52

Conditions for Hydrothermal Growth of ZnS

Expt. No	Source of ZnS	Strength of NaOH Soln.	Temp. (°C)	Time (days)	Colour of Crystals	Rate of Growth (mg/hr)	Analysis
157	Fisher	2M	325	4	-	Nil	
160	Fisher	6M	400	4	Grey + yellow	-	
170	Fisher	6M	400	$4\frac{1}{2}$	Yellowish	4.6	
182	Fisher	6M	400	10	Greenish	-	
187	Fisher	6M	400	30	Pale green	-	$Zn = 67.01\%; = ZnS_{1.003}$
295	Fisher	6M	375	15	Greenish	All transported	Crystal = Sphalerite
163	G.E.	6M	370	5	Yellowish	All transported	
166	G.E.	6M	400	$4\frac{1}{2}$	Yellowish	3.15	
172	G.E.	6M	400	10	Yellowish	10.58	
167	G.E.	6M	370	$4\frac{1}{2}$	Dark grey	5.6	
399	G.E.	6M	375	7	Yellowish	All transported	Crystal = Sphalerite; $Zn = 66.38 \pm .25$ ③*; $ZnS_{1.032} \pm 0.012$ ③*.
402	Zn + S	6M	375	7	Some colourless Some Yellowish	All transported	Crystal = Sphalerite

*Circled figures indicate the number of determinations.

The colour of the crystals varied; some of the causes of variation are:

(i)   when the platinum liner was not used, the crystals were greyish due perhaps to an attack on the Inconel vessel that resulted in some contamination;

(ii)   in general, the Fisher Scientific ZnS gave a greenish product, and the G.E. ZnS gave a yellowish product; and

(iii)   the chemical analysis shows the green product of #187 to be $ZnS_{1.003}$ while the yellow product of #399 was $ZnS_{1.032\pm0.012}$ (from three analyses); these results agree with the colours and compositions found in previous studies.

The phase of the starting material in #399 was wurtzite and, in #402, it was sphalerite. The growth product of these two samples and that of #295 was exclusively sphalerite.

5.   Melt Growth

The growth of ZnS single crystals from the melt at 1850°C under argon pressure of 50 atm has been described by M. Kozielski (23).

These crystals were grown by a Bridgman technique and required slightly over 2 hours to complete the melt and growth steps.

Unfortunately, no apparatus suitable for this temperature and pressure was available for use in the present study.

SIZE OF THE CRYSTALS

Photographs of representative crystals of each of the four growth procedures used are shown in Figures 17, 18, 19, and 20. Each division of the scale at the bottom of these photographs represents 1 mm. The growth details can be found in the Tables indicated in the captions. The quality of these crystals has been described earlier.
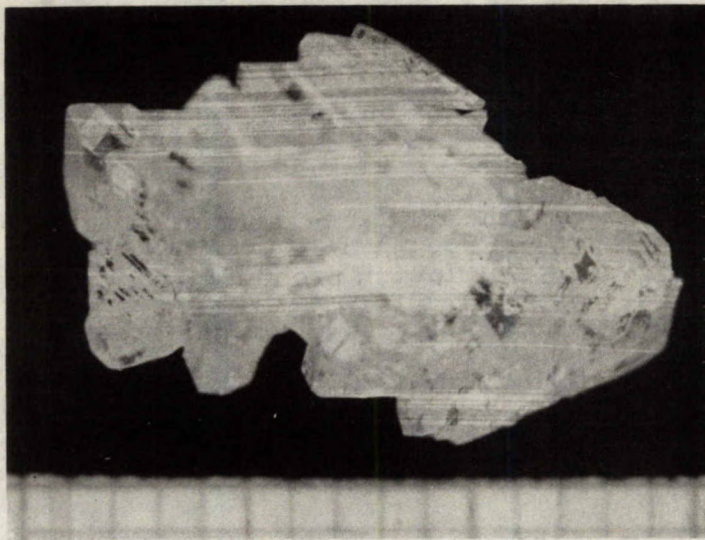
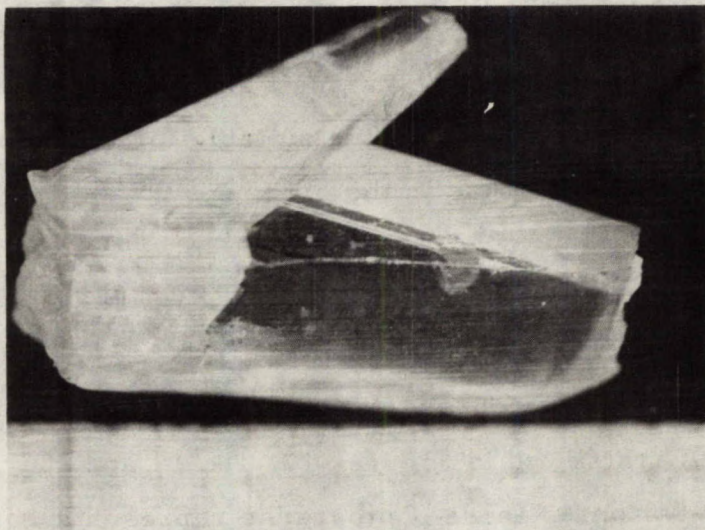Figure 17. Photograph of the Iodine Vapour Growth (Run #419, see Table 32).

Figure 18. Photograph of the Vapour Transport Growth (Run #307, see Table 45).
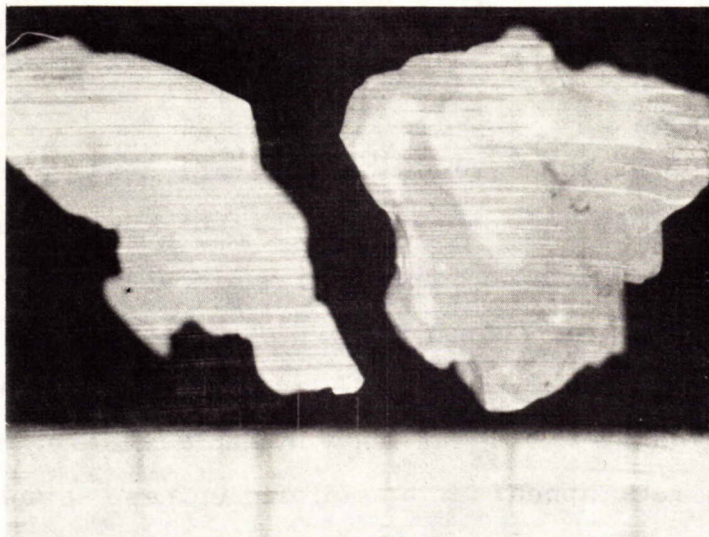
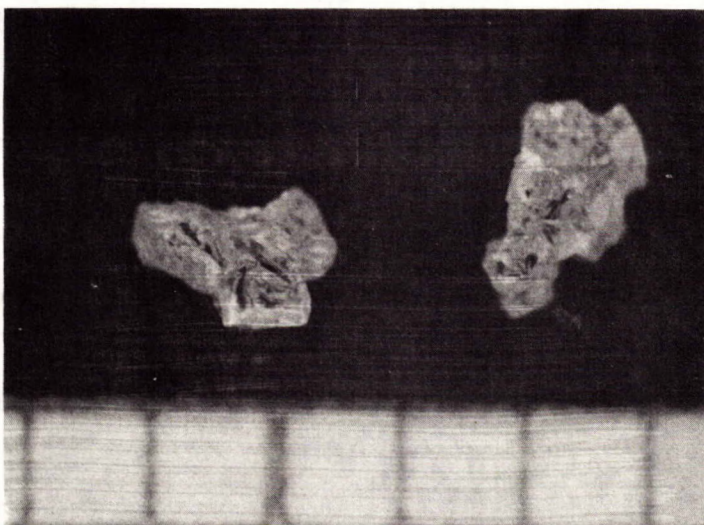Figure 19. Photograph of the PbCl$_2$ Flux Growth (Run #419, 374
see Table 32). 51

Figure 20. Photograph of the Hydrothermal Growth (Run #307, 402
see Table 45). 52

CHARACTERISTICS OF SOME SYNTHETIC ZINC SULPHIDE

In addition to the results of several types of analyses previously described herein, a brief account of four related studies involving several of the synthetic zinc sulphide crystals will now be given.

(1) Electron-Microprobe Analysis

Electron-microprobe analysis has been very informative. Two aspects of the results that do not show in Table 53 are, firstly, that the zinc to sulphur ratio appears to be uniform in these samples and, secondly, no chlorine or iodine was detectable. The presence of other impurities (in #439, #483, and #484) has been discussed earlier in this report.

(2) Infra-Red Spectra Recordings

Approximately ten samples have been submitted for infra-red spectral analysis. These samples were representative of the variety of synthetic zinc sulphide crystals grown, i.e., from only sphalerite or wurtzite to sphalerites containing minor amounts of wurtzite, and from colourless to deeply-coloured specimens.

Tracings of the spectra have been received, but no formal report has yet been released.

(3) X-ray Precession Camera Studies

This procedure gives a measure of the degree of perfection within the crystal structure.

The five following samples (see Table 54) have been submitted for such examination.

TABLE 53

Electron-Microprobe · Analysis of Various ZnS Samples

Expt. No	Source of ZnS	Growth Procedure	Impurities Found	Report No.
141	Zn + S	HCl at 950°C	None	EP-68-53
413	Zn + S	I_2 at 800°C	None	EP 68-19
439	Fisher Scientific	V.T. at 1335°C	Mg and Si	EP 68-30
483	Fisher Scientific	I_2 at 800°C	Co in crown of crystal as high as 0.7%, but fell off to 0 within 100 microns.	EP 69-06
484	Zn + S + Fe (1%)	I_2 at 800°C	Some Fe in varying amounts.	EP 69-20
619	Zn + S + Al (0.67%)	I_2 at 950°C	None	EP 69-111

TABLE 54

Description of Samples Sent for Precession Camera Studies

Expt. No	Method of Growth	X.R.D. Single-Crystal Sample Number
307	V.T., self-sealing at 1335°C	131
308	V.T., self-sealing at 1350°C	123
309	C.V.T., I_2 at 800°C	114
377	C.V.T., I_2 at 1100°C	133
419	C.V.T., I_2 at 800°C	--

The examination of the last of these samples, #419, had not been completed at the time of the writing of this report.

One of the samples, #309, was a good single crystal with no indication of twinning.

Samples #307 and #308 showed twinning; the former had possible traces of wurtzite and polytypes present, and the latter was composed of at least three twinned portions in different orientations.

Sample #377 was bounded by flat, shiny, top and bottom surfaces with rough tapered edges. The sample is sphalerite twinned equally in two orientations; also, there is a possibility that small amounts of wurtzite and ZnS polytypes could be present.

These studies confirm that good single crystals of sphalerite can be grown at 800°C using the iodine transport method.

(4) D.T.A. Thermograms

The results of the D.T.A. thermogram of an air-oxidation of G.E. ZnS powder were listed in Table 20 (see page 23).

In addition, several intermediate products resulting from purification procedures, as well as essentially-pure sphalerite and wurtzite have been examined.

Tracings of the thermograms have been received, but no formal report has yet been released.

SUMMARY

During the course of the present investigation, much progress has been achieved in understanding the problem of the growth of large crystals of zinc sulphide. However, time has not permitted the solving of some related problems, e. g. , doping and epitaxial growth.

It has been shown that zinc sulphide crystals can be grown by several techniques; it has been found that the best method to grow large, single, colourless crystals of sphalerite is by the iodine vapour transport technique at 800 °C of purified, stoichiometric ZnS.

At higher temperatures, the zinc sulphide crystals grown by the chemical vapour transport usually contain some green-yellow colour that appears to be caused by non-stoichiometry in the crystal. Although much has been learned about this colour problem, it was found that re-growth by chemical vapour transport, under several different conditions, failed to remove the colour.

REFERENCES

1. L. G. Ripley, "Crystal Growth. Part I: Background to Crystal Growth", Mines Branch Research Report R 235, March 1971.

2. A. T. Prince et al., "A Proposal for a Sulphide Research Programme in the Mineral Sciences Division of the Mines Branch", Mineral Sciences Division Internal Report, MS-64-43 (1964).

3. E. Mark, "An Investigation of the Determination of Zinc in Zinc Sulphide", Mineral Sciences Division Internal Report MS-69-75 (1969).

4. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. X, 33. (Quotes G. Magnus and F. Knapp, Journ. prakt. Chem., 38, 48 (1888)). Published by Longmans, Green and Co., London (1930).

5. A. Standen, Executive editor, "Kirk-Othmer Encyclopedia of Chemical Technology", 2nd Ed., Vol. 19, 339, published by Interscience Publishers, a division of John Wiley and Sons Ltd., New York (1969).

6. M. Hansen and K. Anderko, "Constitution of Binary Alloys", 2nd Ed., p. 1171, published by McGraw-Hill Book Co. Inc., New York (1958).

7. M. Rubenstein, "A Portion of the Zn-S Liquidus Phase Diagram", paper given at the I. C. C. C. Conference on Crystal Growth, August 13, 1969, at Gaithersburg, Maryland, U. S. A.

8. R. C. Weast, Editor-in-chief, "Handbook of Chemistry and Physics", 48th Ed., p. B-241, published by The Chemical Rubber Co., Cleveland, U. S. A. (1967).

9. S. D. Scott, "Stoichiometry and Phase Changes in Zinc Sulphide", Ph. D. Thesis, The Pennsylvania State University, Diss. Abstr., B 29, [10], 3852 B (1969).

10. E. R. J. Banks, "A Study of the Transformation of Sphalerite to Wurtzite in Atmospheres of Zinc and Sulphur", Ph. D. Thesis, University of Denver, Diss. Abstr., B 28, [3], 823 B, (1967).

11. Indradev, "Parameters of Growth from the Vapour Phase of ZnS Crystals", Mat. Res. Bull., 1, 173, (1966).

12. R.A. Laudise and A.A. Ballman, "Hydrothermal Synthesis of Zinc Oxide and Zinc Sulphide", Journ. Phys. Chem., 64, 688, (1960).

13. R.A. Laudise, E.D. Kolb and J.P. DeNeufville, "Hydrothermal Solubility and Growth of Sphalerite", Am. Mineralogist, 50, 382, (1965).

14. R. Nitsche, "The Growth of Single Crystals of Binary and Ternary Chalcogenides by Chemical Transport Reactions", Journ. Phys. Chem. Solids, 17, 163, (1960).

15. F. Jona, "Kinetics of Vapour-Solvent Growth in the System ZnS: HCl", Journ. Phys. Chem. Solids, 23, 1719, (1962).

16. H. Samelson, "Growth of Cubic ZnS Single Crystals by a Chemical Transport Process", Journ. Appl. Phys., 33, 1779, (1962).

17. D.C. Reynolds and S.J. Czyzak, "Single Synthetic Zinc Sulphide Crystals", Phys. Rev., 79, 543, (1950).

18. L.C. Greene, D.C. Reynolds, S.J. Czyzak and W.M. Baker, "Method for Growing Large CdS and ZnS Single Crystals", Journ. Chem. Phys., 29, 1375, (1958).

19. R.C. Linares, "Phase Equilibrium and Crystal Growth in the System ZnS-ZnF$_2$", Metallurgy of Advanced Electronic Materials, 19, 329, (1962).

20. Y. Mita, "Growth of Zinc Sulphide Single Crystals from Flux", Journ. Phys. Soc. Japan, 17, 784, (1962).

21. R.C. Linares, "Growth of Cubic Zinc Sulphide from Molten Lead Chloride", Trans. Met. Soc. AIME, 242, 441, (1968).

22. M. Hàrsy, "Synthesis and Growth of ZnS, ZnSe, ZnTe, GaS, Ga$_2$Se$_3$ and InS Crystals in Ga and In Melts", Mat. Res. Bull., 3, 483, (1968).

23. M. Kozielski, "Growth of ZnS Single Crystals from the Melt at 1850°C under Argon Pressure of 50 atm.", Journ. Crystal Growth, 1, 293, (1967).

24. H. Schäfer, "Chemical Transport Reactions", published by Academic Press, New York, London (1964).

25. E.H. Nickel, "Microscopic Characteristics of some Synthetic ZnS Crystals, Part I", Mineral Sciences Division Internal Report MS-66-38 (1966).

26. L.G. Ripley, "Visit to Pennsylvania State University, Aug. 1 to 5, 1966", Mineral Sciences Division Internal Report MS-66-63 (1966).

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