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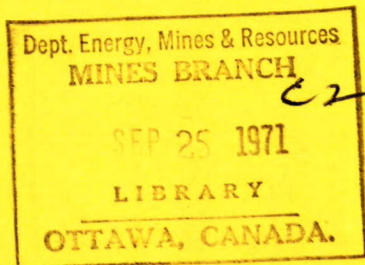
DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

CRYSTAL GROWTH

PART I:

BACKGROUND TO CRYSTAL GROWTH

LEONARD G. RIPLEY

MINERAL SCIENCES DIVISION

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Mines Branch Research Report R 235

CRYSTAL GROWTH.

Part I: Background to Crystal Growth.

by

Leonard G. Ripley*

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ABSTRACT

A programme of crystal growing has been in progress in the Mineral Sciences Division of the Mines Branch, as part of a Sulphide Research Programme, during the past six years. During this time, the growth of crystals of about fifty materials has been attempted in the field of sulphides, arsenides and sulpharsenides of Fe, Co, Ni, Zn and Cu, and with some other compounds, many of them quite successfully, by one or more of the six growth techniques explored.

This report is Part I of an intended five parts, and will deal with the "Background to Crystal Growth" as it applied to the current Sulphide Research Programme.

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Direction des mines

Rapport de recherches R 235

LA CROISSANCE DES CRISTAUX.

PREMIÈRE PARTIE: Données de base sur la croissance des cristaux

par

Leonard G. Ripley*

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RÉSUMÉ

Depuis six ans, la Division des sciences minérales de
la Direction des mines poursuit des travaux sur la croissance
des cristaux dans le cadre d'un programme de recherches sur
les sulfures. Au cours de cette période, les spécialistes ont
pratiqué, souvent avec succès, des essais de culture de
cristaux portant sur environ cinquante composés, notamment
les sulfures, arséniures et sulfarséniures de fer, de cobalt,
de nickel, de zinc, de cuivre et d'autres composés, appliquant
une au moins des six méthodes dont il est question dans la
présent rapport.

Ce texte est le premiér d'une série de cinq rapports et
traite des "données de base sur la croissance des cristaux"
et de leur application au programme de recherches sur les
sulfures.

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des Mines et des Ressources, Ottawa, Canada.

CONTENTS

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LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

When the Sulphide Research Programme of the Mineral Sciences Division was initiated in early 1964 (1), one immediate objective was to grow suitable single crystals of synthetic ZnS, (Zn, Fe)S and $CuFeS_2$ of controlled purity, for the investigation of desired properties by other members of the Division.

The scope of this research programme has been enlarging steadily, and the need for single crystals of a wide variety of sulphides, arsenides and sulpharsenides has so increased that the growth of approximately fifty inorganic compounds has been attempted by one or more of six crystal-growth methods up to the time of writing this report.

The size of the crystals has varied from less than a cubic millimetre to a cubic centimetre. This latter size has been requested as being desirable for physical measurements and for analyses.

Roy and White (2) of Pennsylvania State University have defined crystal-growth studies exclusively as "those designed consciously for the enhancement of the size of crystals over that either previously existing or previously reported, or the understanding of a process of size-enhancement".

Laudise (3) of the Bell Telephone Laboratories has divided crystal growers into two groups,

    (a) those who study how crystals grow, and

    (b) those who grow them.

The latter group study and understand techniques of crystal growth, but he felt that there should be a symbiosis between (a) and (b).

The studies to be reported in this and subsequent reports fall into the second category, inasmuch as the prime objective has been to prepare crystals suitable for the various divisional research projects rather than to study the theory of crystal growth per se with the objective of producing publishable results. Many of the results of this work have been presented informally in

seminars and in periodic progress reports; it is now felt timely to make a more formal collation and publication of the work in a more permanent form, and this is the purpose of the present series of reports.

The presentation of the results obtained from this extensive series of studies can be made in several ways. It is proposed to present the over-all picture of the techniques of crystal growth in the present report as:

Part I: "Background to Crystal Growth", and then to present the results obtained in the various attempts at crystal growth under four headings in subsequent reports in the series:

Part II: The Growth of Zinc Sulphide Crystals.

Part III: The Sulphides of Cobalt, Iron and Nickel.

Part IV: The Arsenides of Cobalt, Iron and Nickel.

Part V: Other Systems.

BRIEF HISTORY OF CRYSTAL GROWING

Crystallization is one of the oldest operations in chemistry and has been used in the production, purification or recovery of solid materials. For many centuries the growing of large crystals has been a pastime of devoted scientists, often for curiosity's sake.

The oldest crystal-growth procedure is growth from a solution. Most salts have solubilities that increase with temperature; a traditional method has been to lower the temperature of a saturated solution to obtain crystals.

There have been several books written on the subject of growing crystals, some of which are: Buckley (1951) (4), Verma (1953) (5), Mullin (1961) (6), Van Hook (1961) (7), Cotton (1962) (8), Gilman (1963) (9), Krüger (1964) (10), Schäfer (1964) (11), Brice (1965) (12).

The crystal-growth community has initiated the publishing of several journals that concern themselves almost exclusively with this subject. These journals are: Journal of Crystal Growth, Materials Research Bulletin, Journal of Materials Science, Kristall und Technik, and Crystal Synthesis

(to be published). In addition, several national and international conferences have been organized, such as at Boston, U.S.A., 1966; at Birmingham, England, 1968; at Washington D.C., U.S.A., 1969; and a projected one at Marseilles, France, 1971. The author attended the Boston and Washington conferences. The proceedings of the Boston and Birmingham conferences have been published (see references 13 and 14).

Many technological industries, particularly in the U.S.A., have initiated crystal-growing programmes to provide single-crystal material for their researches. One such company, visited by the author in 1965, is the General Electric Company at Schenectady, N.Y., where ZnS was being grown by an iodine transport method.

There are very few universities that emphasize crystal growth. Pennsylvania State University, however, does seem to have a good programme in this area. The author visited this university in 1966, learned first-hand about the hydrothermal-growth technique, and had an opportunity to visit their Materials Research Laboratories.

Crystal growth is indeed an inter-disciplinary topic. Schieber (15), in his introductory remarks at the Boston International Conference on Crystal Growth in June 1966, showed the field of crystal growth in a schematic representation. Schieber's model has been modified (see Figure 1) to describe more completely the current research programme. The author's activities have been concerned primarily with matters listed in the central circle and secondly with those in the left-hand circle, while other members of the Mineral Sciences Division of the Mines Branch have been interested in subjects listed in the right-hand circle.

The crystal-growing programme in the Mineral Sciences Division started in 1964. At that time, it was necessary to prepare for this study by amassing suitable furnaces, controllers and related high-temperature apparatus, and also to search the literature in order to "catch up" on a fast-developing field of science that had been expanding for well over a decade.

Sphalerite (ZnS) was chosen by the divisional group as the material with which to launch the Sulphide Research Programme, as the literature

THEORY OF   EXPERIMENTAL   CHARACTERIZATION

NUCLEATION   CRYSTAL   AND USES OF

AND GROWTH   GROWTH   CRYSTALS

GROWTH RATES   GROWTH TECHNIQUES   ANALYSES

EFFECT OF

Vapour   Chemical

Chemical Vapour   Electron-Probe

Hydrothermal   Infrared

Nutrient Temperature   Flux   Neutron-Activation

Melt   Spectrographic

Temperature Gradient   KINETICS   Melt and Anneal   X-ray Diffraction

OF GROWTH   Gel   SEGREGATIONS   X-ray Fluorescence

Variable Temperature Gradient   STOICHIOMETRY D.T.A.

CONDITIONS   USES

Non-Stoichiometry   PURITY

SULPHIDES   Fe Cu   DOPING   Structural Crystallographic

Pressure   ARSENIDES   of   Co Zn   Studies

SULPHARSENIDES   Ni Mn   Electronics

Impurities   Magnetism

Solid-State Physics

Other Properties

MOST SUCCESSFUL CRYSTALS GROWN

ZnS CoS_2 $CoAs_2$

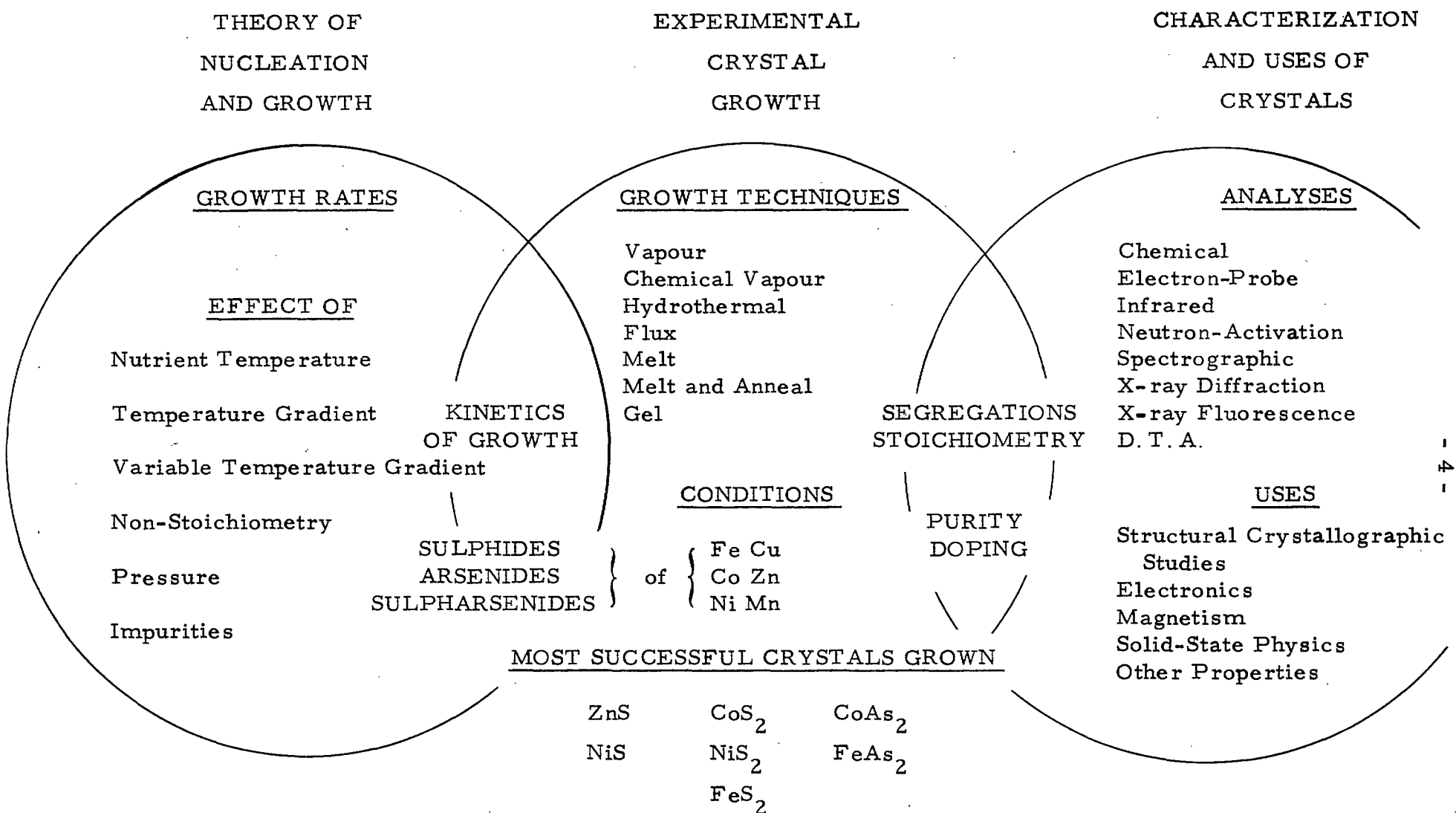NiS NiS_2 $FeAs_2$

FeS_2

Figure 1. Schematic Representation of the Field of Crystal Growth in the Current Research
             Programme.

contained many references to its growth and to its physical properties. This turned out to be a wise choice, for many of the principles and techniques of crystal growth were learned and practiced by the author with this compound as the working substance during the early period.

Since 1967, the Divisional interest has expanded periodically to include an extensive list of sulphides, arsenides and sulpharsenides of Fe, Co, Ni, and Cu. At about this same time, other personnel in the Division became interested in crystal growing; however, this report is concerned only with the crystal-growing activities of the author.

MECHANISM

The process of crystal growth is still referred to as more of an "art" than a "science". The transformation from an "art" to a "science" has been progressing slowly since it became recognized that the key factor lay in the equilibrium of physical properties of the working system (6). Therefore, all crystal growth is based upon an equilibrium that has been shifted so as to cause growth of a single crystal. The equilibrium may be in a solid-solid, liquid-solid, or gas-solid system.

The driving force of crystal growth is based on the concentration gradient of the reactants, and/or the temperature gradient, between the nutrient and growth zones of the system.

Any crystallization operation can be considered to consist of three basic steps:

(1) achievement of supersaturation or supercooling;

(2) formation of crystal nuclei, if a seed is not present; and

(3) growth of the crystal.

There is an optimum temperature of nucleation at which the temperature gradient will cause the right amount of supersaturation in the growth area to produce a nucleus and initiate crystal growth. When a seed crystal of the substance is placed in the system, crystal growth can occur on it. However, a foreign material of the same crystal system may be added to obtain

artificial nucleation, resulting in epitaxial growth. When silica tubing is used as the container, the walls of the tube act as nucleation sites. In order to enhance the dominance of a single crystal growing in a silica tube, the growth zone is formed pointed or contains a constriction, as shown in Figure 2.
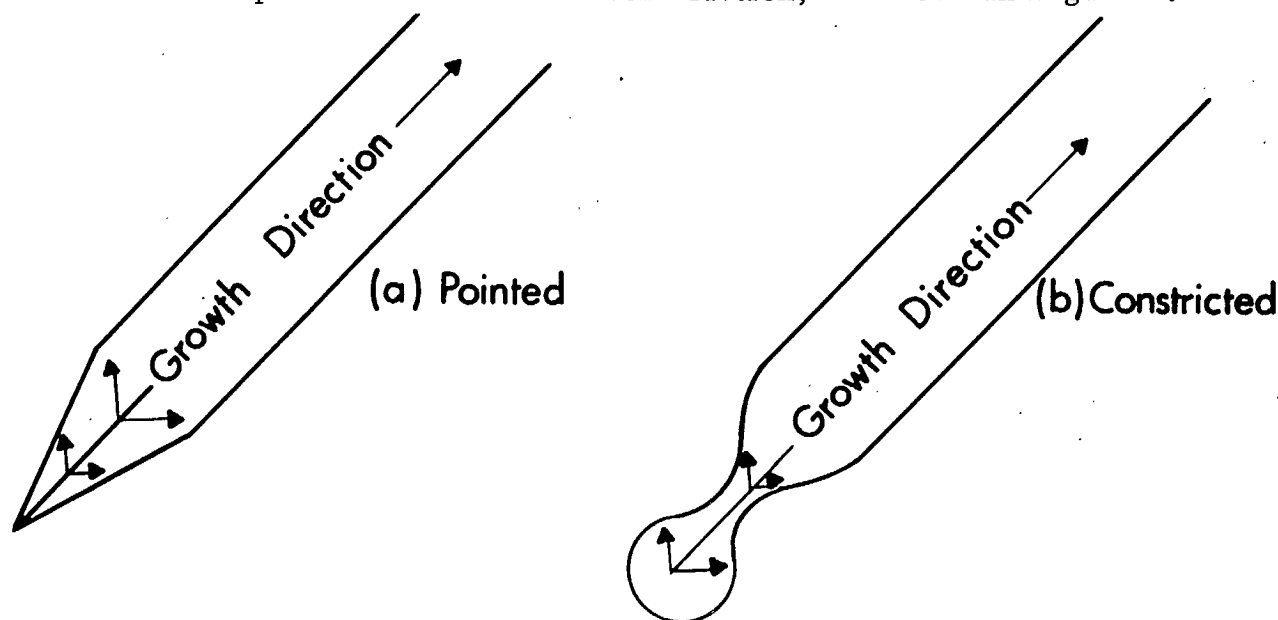
Figure 2. Designs of Silica Tubing for Crystal Growing.

Also, flaming of the tube, prior to the starting of crystal growth, will reduce the number of nucleation sites.

The development of a crystal will, of course, normally proceed in the direction of the most stable form. Sometimes the growth is intermittent and the product will appear more or less in the form of segments of perfect crystals.

Crystal-growth theories have been developed along three main lines (6):

(1) "Surface energy", originated by Gibbs (1878) and by Curie (1885).

(2) "Diffusion", originated by Noyes and Whitney (1897) and by Nernst (1904); and

(3) "Adsorption layer", originated by Volmer (1922).

Today's theories are usually a blend of these three theories*. Growth theories do not include factors limiting the maximum size of a crystal.

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*The author has perused these theories for background knowledge, but, since theory was not one of the goals of the current study, no discussion of them is included in this report.

However, in actual practice, the difficulties of producing good, large, single crystals appear to increase at a compound rate as the size desired increases. There is still a widely held impression that large crystals are necessarily purer than small ones; this, of course, need not be so.

Impurities, either as contaminants or as deliberate additives, can often modify the colour and habit of a crystal and can affect its rate of growth. It should be mentioned that crystals grown from pure solutions are rarely encountered outside the laboratory; consequently, naturally occurring crystals are rarely pure chemical compounds.

The ideal crystal is one with a perfectly regular arrangement of atoms or ions throughout the crystal, whereas real crystals, even when grown synthetically from a pure solution, will deviate from the ideal because of irregularities of growth, such as dislocations, often caused by thermal motion in the growth system. Thus the ideal crystal is a theoretical model, while actual crystals will contain structural irregularities and/or chemical impurities.

EXPERIMENTAL PROCEDURES

a. Chemicals

The majority of the chemicals were of sufficient purity to be used directly. However, some were purified just prior to use.

The oxygen content of some metals was lowered either by a H_2 or a H_2S reduction; the latter reagent gave monosulphides that were used as part of the nutrients. The oxygen content in arsenic and selenium was lowered by subliming the oxide from the metal. Zinc sulphide powders were heated in H_2S to remove oxygen and water and to ensure stoichiometry. Hydrogen chloride gas was frozen with liquid nitrogen, and then, on fractional evaporation, only the middle fraction was used. Several of the salts used in flux growth were dried at 110°C.

A list of the elements and compounds that are most often used is given as Table 1. The manufacturer's quoted purity is given, and mention is made of any additional purification performed.

TABLE 1

The Source and Purity of Some Elements and Compounds Used
for Crystal Growth

Element or Compound	Physical Form	Source	% Purity (Supplier's Data)	Purification Methods Adopted
Al	Turnings		99.999	
As	Powder	Fisher	None given	Sublimation
Bi	Pellets	Cominco	99.999	
Br	Liquid	McArthur Chem.	~99.9**	
Cd	Pellets	Cominco	99.999	
Co	Powder	Fisher	99.2	H_2S
Co	Plate		99.9	
Co	Wire	Koch-Light	99.99	
Cu	Millings	BCS*197d	99.90	
Fe	Millings	BCS*149/1	~99.93**	H_2, H_2S
He	Gas	Matheson	99.995	
HCl	Gas	Matheson	99.0	Fractional evaporation
H_2S	Gas	Matheson	98.5	
I	Solid	Anachemia	~99.9**	
KCl	Powder	Baker	99.7	Dried at 110°C
NH_4Cl	Powder	Mallinckrodt	~99.9**	Dried at 110°C
Ni	Powder	Sherritt-Gordon	~99.5**	H_2S
Ni	Wire	Koch-Light	99.99	
$PbCl_2$	Powder	Matheson Coleman and Bell	99.0	
S	Powder	ASARCO	99.999	
Se	Powder	Fisher	None given	Sublimation
Te	Pellets	Cominco	99.999	
Zn	Rod (millings)	Cominco	99.9999	
ZnS	Powder	Fisher	None given	H_2S
ZnS	Powder	G.E.	~99.5**	H_2S
ZnS	Powder	Koch-Light	99.99	

*B.C.S. = British Chemical Standards.
**Derived by subtracting the quoted impurities from 100%.

The non-availability of rapid, sufficiently accurate chemical analysis procedures has precluded the determination of the purity of many of these elements and, likewise, the analysis of the products from crystal growth. The exception is in the case of ZnS: analytical procedures have been developed in the Mineral Sciences Division for the determination of both Zn and S; several nutrient ZnS samples have been analysed. Work is currently in hand to provide equally good analytical procedures to deal with the Ni-S system.

b. Capsules

Although Reynolds, in a review article in Gilman (9), reported that ZnS crystals can be grown in an open system, in the present studies it has been found that sealed capsules are far superior. For high-temperature experiments (500°-1200°C), silica capsules were made from 13- or 15-mm O.D. tubing. The sealed capsules varied from 13 to 20 cm in length, with an average length of 15 cm. For hydrothermal growths (200-250°C), thick-walled pyrex capsules were employed.

c. Sealing of Capsules

A special all-glass pumping station was prepared that included traps, an aneroid-type manometer, a McLeod vacuum gauge, roughing and fore pumps, an oil diffusion pump, and graded seals for the coupling of silica sample tubes. This system made it possible to evacuate a sample tube, admit any gas up to atmospheric pressure, and then heat the sample tube in a furnace up to 1200°C. The gaseous atmosphere in this system could then be pumped out and either renewed or changed to another gas or mixture of gases, as desired. The system has provision for enclosing a sealed capsule of iodine, which can be opened with a magnetic hammer at the appropriate time and the iodine transferred to the sample capsule by sublimation.

The sample capsule could be sealed at pressures as low as 10^{-5} mm Hg or with HCl, H_2S, or any other gas or mixture of gases in the sample capsule at any selected pressure, between 1 and 760 mm, as determined by the aneroid manometer.

d. Furnaces

Crystal growing is very dependent on temperature and its control. Ideally, the furnace temperature should remain steady.

Fifteen different types and sizes of furnaces have been investigated, as shown in Table 2. Some of these furnaces are fitted with their own controllers, while others have been controlled by various external combinations of Variac, step-transformer, thermoelectronic and Wheelco controllers. The performance of these controllers was improved by placing a 2-ohm resistor across their relay, giving thereby a form of proportional current control instead of the usual on-and-off action.

The tube furnace is one in which the process tube passes through the furnace; this means that both ends of the tube are exposed to room temperature. The box furnaces were modified by bricking up the door, passing one end of the process tube through this bricking into the furnace, and placing this end at the back of the heating zone; this means that only one end of the tube is exposed to room temperature. The main advantage of this latter type of box furnace is that a better temperature control is achieved in the process tube.

e. Temperature Profiles in Furnaces

The temperature profile differs with each furnace and with the same furnace at different heating levels. The differences are caused by uneven heating, the mode of heating, the level of heating, the extent of the insulation, and the presence or absence of baffles. A typical tube-furnace profile is shown in Figure 3.

The temperature profile shown in Figure 3 is typical of the following furnaces described in Table 2: 1, 2, 3, 4, 9, 13 and 15. The short constant-temperature zone of furnaces #3, 4, 13 and 15 made these furnaces unsuitable in the present study. Furnace #9 has a programmer that permits a cooling rate of 0.5 to 6 deg C per hour to be employed.

A typical box-type furnace profile is shown in Figure 4.

TABLE 2

Data on Furnaces and Types of Control Used for Crystal Growth

Furnace	Type	Mode of Heating	Heating Range (°C)	Heating Zone, Length in inches	Constant-Temperature Zone, Length in inches	Controller Type	Additional Power Control
1. Lindberg	Tube	Resistance[a]	Up to 1200°	12	3	Thermo-electronic	Variac
2. Lindberg	Tube	Resistance[a]	Up to 1000°	18	10	Thermo-electronic	Variac
3. Hevi-Duty	Tube	Globar	750-1500°	24	2	Thermo-electronic	Variac
4. Hevi-Duty	Tube	Globar	750-1500°	15	1	Thermo-electronic	Variac
5. Custom-Built*	Box	Globar	750-1500°	10	4	Thermo-electronic	Step-transformer
6. Lindberg	Box	Resistance[a]	Up to 1200°	14	6	Wheelco	None
7. Lindberg	Box	Globar	750-1500°	17	6	Lindberg	Variac
8. Lindberg	3-Zone Tube	Resistance[a]	Up to 1200°	30	12-15	Lindberg	Variac
9. Lindberg	Programmed Tube	Resistance[a]	200-1200°	30	12	Lindberg	None
10. Burrell	Box	Globar	750-1500°	8	4	Thermo-electronic	Step-transformer
11. Hevi-Duty	Box	Resistance[a]	Up to 1000°	8	--	--	Step-transformer
12. Temco	Box	Resistance[a]	Up to 1000°	9	--	Thermo-electronic	Proportional heating
13. Leco 2600	Tube	Globar	750-1500°	18	2	Leco	None
14. Custom-Built*	Tube	Resistance[b]	Up to 1000°	18	1	Wheelco	Variac
15. Custom-Built*	Tube	Resistance[c]	Up to 1700°	12	1	Wheelco	Variac

*Constructed at Mines Branch.

(a) - Nickel-chrome coiled wires.
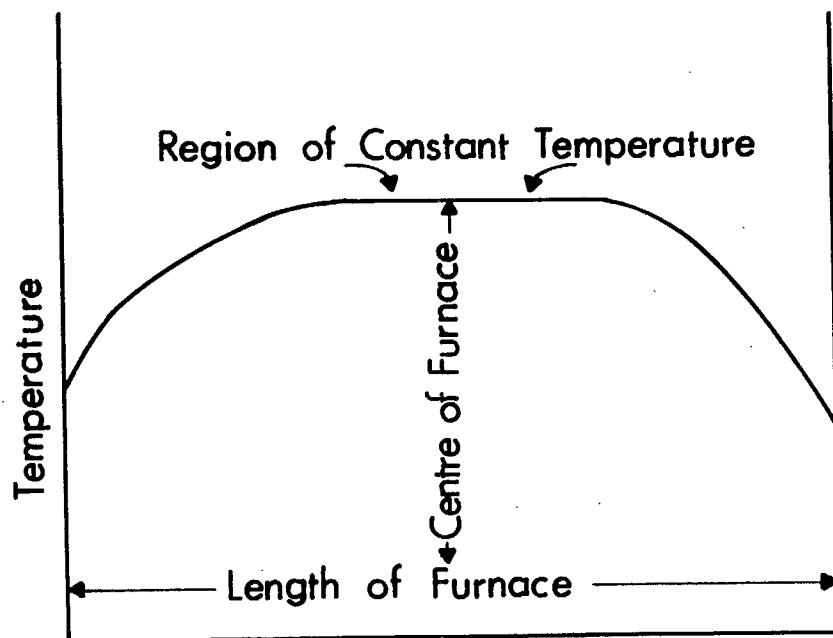
(b) - Kanthal wire.

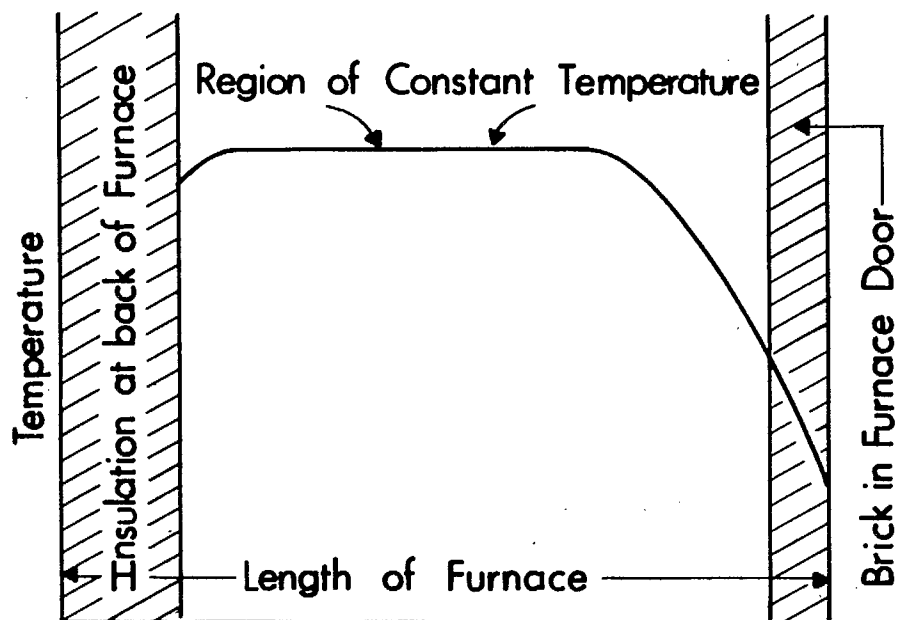Figure 3. Temperature Profile for Typical Tube Furnace.

Figure 4. Temperature Profile for Modified Box-Type Furnace.

The profile shown in Figure 4 is typical of the following furnaces described in Table 2: 5, 6, 7 and 10.

Typical profiles for the 3-zone furnace (#8, Table 2) are achieved by adjusting three controls on the front of the furnace. Each control has 10 settings. Some of the configurations, using identical settings on both the left and right controls with the centre control set at 0, and with the controller set at a fixed temperature, are shown in Figure 5. It is easy to visualize the profile when other symmetrical settings are used.
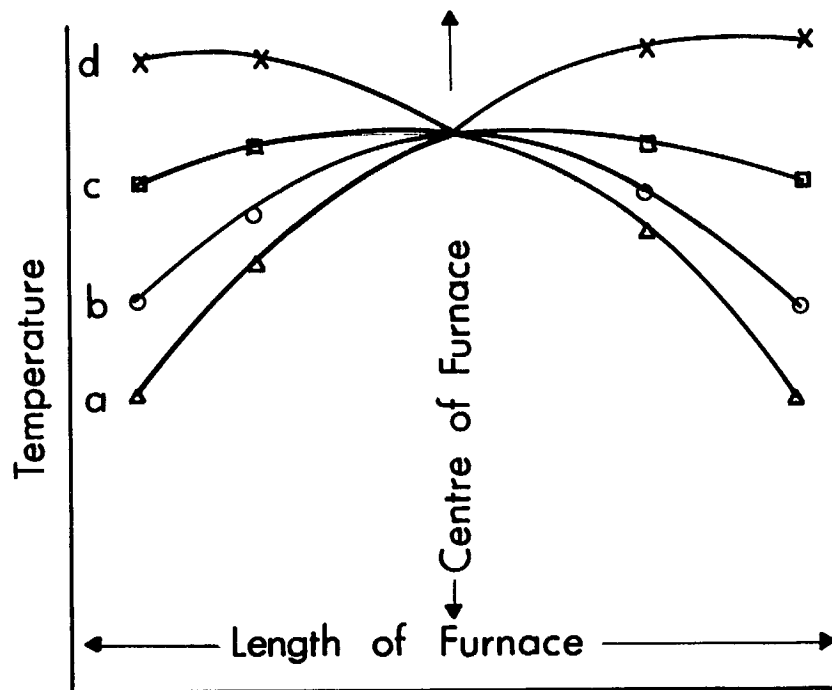

Figure 5. Temperature Profiles for Symmetrical Settings on 3-Zone Furnace.

a = 0, 10, 0

b = 0, 0, 0

c = 5, 0, 5

d = 10, 0, 10

However, if the controls are adjusted with the left-hand control at a higher setting than the right-hand one (that is, in an unsymmetrical manner), even at constant temperature control a new set of temperature profiles, as shown in Figure 6, can be obtained.
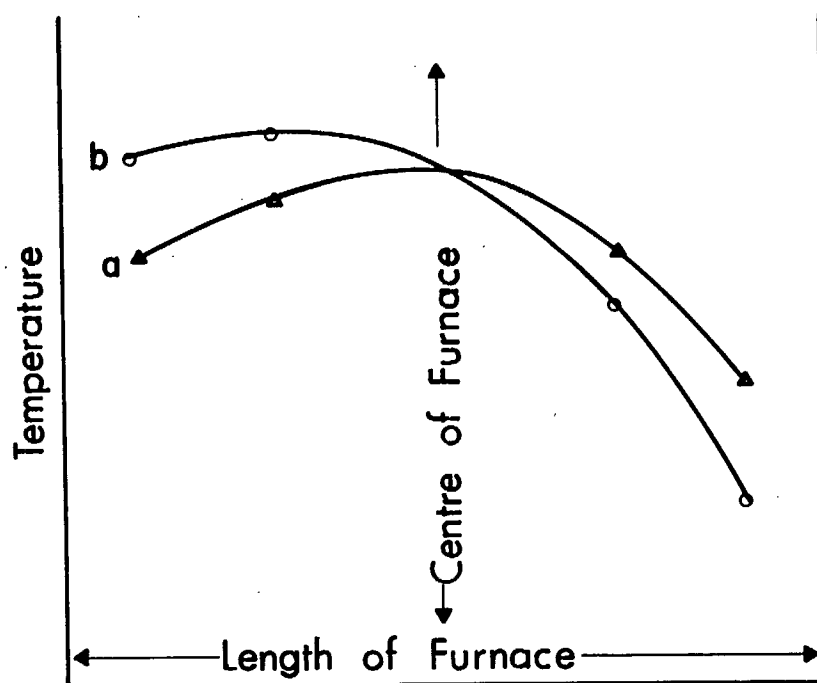
Figure 6. Temperature Profile for Unsymmetrical Settings on 3-Zone Furnace.

$$a = 5, 0, 0$$
$$b = 10, 0, 0$$

The mirror image of these profiles would be obtained if the right-hand control had been increased, instead of the left-hand one as in Figure 6.

The furnace listed as #14 in Table 2 has an unusual spacing of the Kanthal heating-element windings, which resulted in a unusual temperature profile, as shown in Figure 7. Although the constant-temperature zone is only about 25 mm long, this is a very useful furnace for crystal growing.

Figure 7. Temperature Profile of Furnace #14.

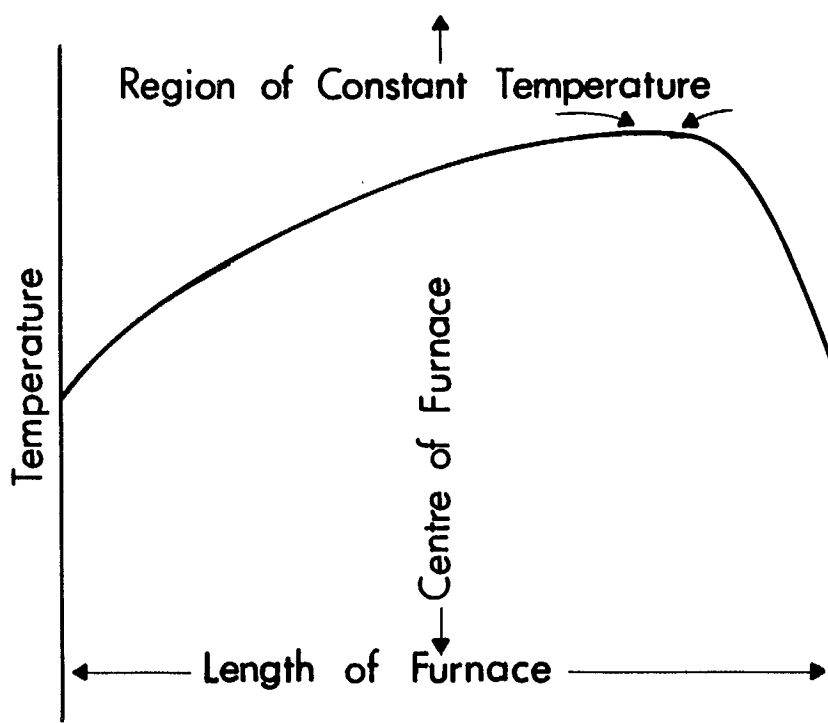The doors of box furnaces #11 and #12 were not bricked in, as described for the other box furnaces. The size and spatial arrangement of the heating elements give rise to unusable temperature profiles. However, these furnaces have been useful in a sample preparation and for some preliminary hydrothermal experiments. A new 2-zone furnace will be constructed in the near future for use in further hydrothermal studies.

f.   Temperature Gradient

The temperature gradient in the furnace is undoubtedly one of the key variables in crystal growth. It has already been stated that "The driving force of crystal growth is based on the concentration gradient of the reactants, and/or the temperature gradient, between the nutrient and growth zones of the system".

A temperature gradient can be obtained and utilized in one of two ways. The first is a static placing of a capsule in the furnace so that a fixed temperature gradient exists. The extent of this gradient, which is dependent on

the positioning in a suitable furnace, would be known from a previously-drawn temperature profile*. If the gradient is too large, polycrystalline growth will result. The second method is a dynamic one, in which a capsule is subjected to an ever-increasing gradient. The speed of movement is an important factor in determining the quality of the crystalline product. The dynamic approach permits the gradient to be increased from zero to a point where adequate supersaturation occurs, resulting in a nucleus being formed. Additional movement increases the rate of growth on this nucleus.

The rate of traverse has been controlled by assembling two similar migration systems. Each system has a Bodine motor, suitable reduction gears, a "Zero-max" transmission, a chain-driven carriage, and either a quartz pushing-tube or a cradle-like pulling tube. The speed of the pushing/ pulling tube is governed by the "Zero-max" transmission; the present assemblages have a range of travel of 1 mm to 40 mm per day. Therefore, guided by the knowledge of the temperature profile, the speed of migration can be varied to achieve the desired temperature gradients for each stage of the growth operation.

The range of temperature gradients, for both the static and the dynamic methods, has been from ~ 5 deg to > 300 deg C; the optimum temperature gradient will vary with the species being grown.

g.   Growth Procedures

Since inorganic sulphides in general have an extremely low solubility in water and in most other solvents, they cannot be grown by the solution method.

One of the earliest methods used for the growth of a sulphide crystal appears to have been that of Lorenz (16) who, in 1841, grew CdS by a vapour-transport method. Since that time, several methods have been developed and modified. The literature contains many references to these various

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*Temperatures were measured on a Leeds and Northrup temperature potentiometer using platinum-13% rhodium vs. platinum thermocouples.

growth techniques, and, although the author has read many of these papers, no attempt will be made to catalogue them comprehensively here. Only a few references will be given in context.

1. Vapour Transport

This procedure is based on the vapour pressure of the compound and is often referred to as a sublimation. In cases in which sublimation occurs at an appreciable rate below 1200°C, a sealed silica tube can be used as shown in Figure 8.
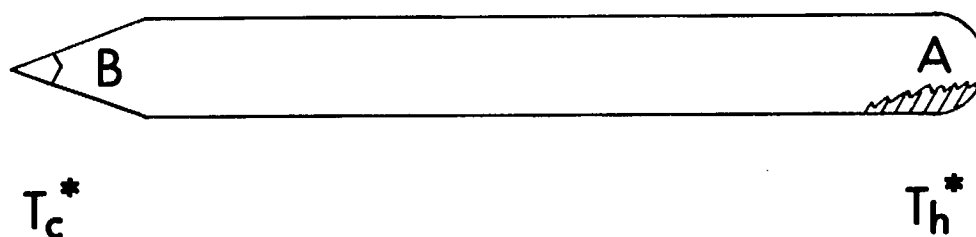

Figure 8. Schematic Arrangement for Vapour Transport.

The temperature gradient causes the nutrient at A to sublime and to condense as a single crystal at B. The pointed growth zone, and a slow migration of the sample tube to give a slow change in the temperature gradient at the growth zone, enhance single-crystal growth. Seeding was found to be not successful in the case of ZnS, even in a vertical furnace.

After a growing period, which can vary from a few days to several weeks, the tube is cooled, cut open with a diamond saw, and the crystal is removed.

A "static method" for growing ZnS was devised by Reynolds and Czyzak (17). A modified method was reported by Greene, Reynolds et al. (18) in which they grew very large single crystals up to 115 g in weight. The exact laboratory conditions for these large crystals were not given.

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*The notations T_h and T_c in this and subsequent figures refer to the hot zone and to the colder zone of the silica capsule, respectively. The difference between T_h and T_c is the temperature gradient.

At temperatures above 1200°C, the silica tube softens and will either collapse or balloon, depending on the inside gas pressure. At such temperatures, a self-sealing tube is required. Indradev (1966) 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 (19). None of the present author's furnaces was suitable for the Indradev tube design; therefore, a modification of the tube was devised (see Figure 9) and worked successfully. The sample tube was coupled to the pumping station, making it possible to maintain an atmosphere of helium at atmospheric pressure during the heating up and at the growth temperature.
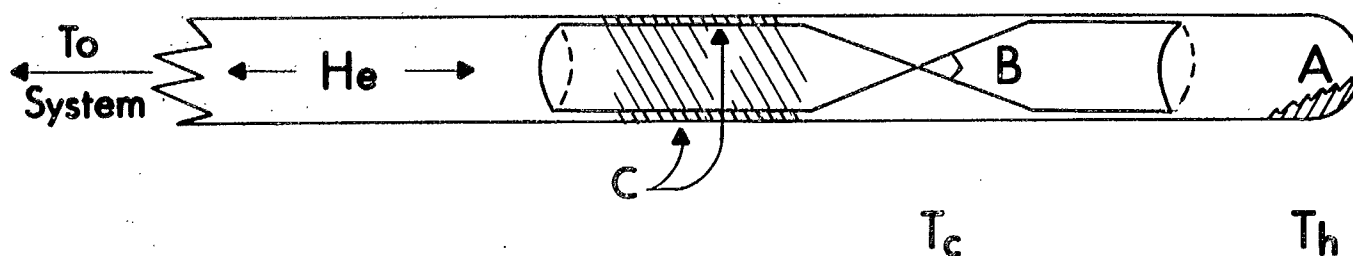
Figure 9. Schematic Arrangement for Self-Sealing Vapour Transport.

Initially, the nutrient A is sublimed to the area C where the growth of crystals will cause the system to self-seal, enclosing He at atmospheric pressure; subsequently, a good single crystal will grow at B. Again, the pointed insert tube at B and a slow migration rate enhance single-crystal growth. Temperatures up to 1400°C have been used successfully, without a tube failure. After a growth period of five days, the silica tube had devitrified internally, causing the tube to fragment on cooling. The crystal was not damaged.

2. Chemical Vapour Transport

As stated by Schäfer (11), "Chemical transport reactions are 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".

Originally, Van Arkel and de Boer (20) used this procedure for the preparation of high-purity refractory metals such as titanium and zirconium ("iodide metals"). Chemical transport reactions have been reviewed extensively by H. Schäfer and published in a book (11). Nitsche (21) described the growth of single crystals of binary and ternary chalcogenides by chemical transport reactions.

F. Jona (22) reported on the kinetics of vapour-solvent growth in the system ZnS:HCl. That author presented an invited paper entitled "Crystal Growth by the Vapour-Solvent Technique" in June 1964 at the 47th Annual Conference of the Chemical Institute of Canada, held at Queen's University, Kingston, Ontario; the present author attended this lecture and had an opportunity to discuss the subject with the speaker.

H. Samelson (23) has described the growth of cubic ZnS single crystals by a chemical transport process. R. J. Bouchard (24) has published the preparation of single crystals of FeS_2, CoS_2 and NiS_2 pyrites by chlorine transport.

In the past decade, this technique has been used successfully for a variety of compounds by many researchers. This procedure is based on a reversible chemical reaction, either

$$RS + 2HCl \rightleftharpoons RCl_2 + H_2S \qquad (Eq. 1)$$

or

$$RS + I_2 \rightleftharpoons RI_2 + S \qquad (Eq. 2)$$
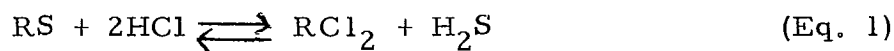
Chlorine and bromine would behave similarly to iodine in these reactions.

The tube design and the overall chemical reaction for this technique are shown in Figure 10.

$$\text{RS} \xrightarrow{\quad \text{HCl} \quad} \text{RS}$$
$$\xleftarrow{\quad \text{RCl}_2 + \text{H}_2\text{S} \quad}$$

T_c $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ T_h
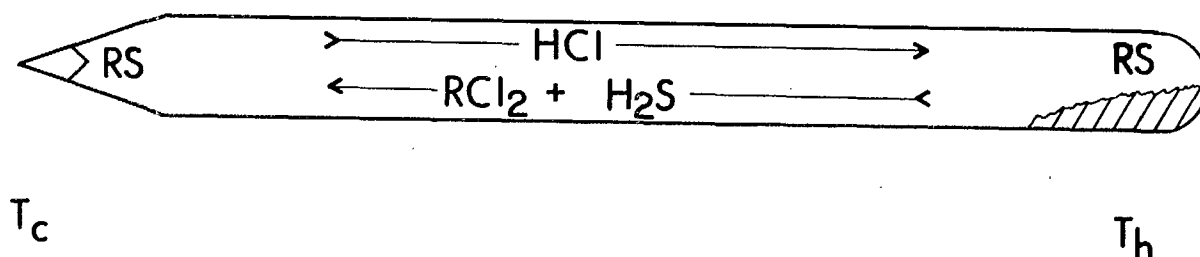
Figure 10. Schematic Arrangement for Chemical Vapour Transport
Reactions.

Again, a pointed growth tube and a slow migration rate enhance single-crystal growth. After a growing period, which may vary from a few days to several weeks, the tube is cooled and cut open with a diamond saw. The transported crystal and the untransported nutrient are leached free of iodine with methanol. If elemental sulphur is present, it is leached out with CS_2. The crystal is then air-dried.

3. Flux Growth

Fluxing involves the changing from a one-component to a two-component system and thereby the lowering of the melting point; alternatively, it can be considered as the dissolution of the nutrient in a molten salt. When the temperature of the fusion mixture is lowered, the dissolved nutrient is deposited as crystals.

It is not known who was the first to apply fluxing in crystal growth. Some pertinent references to its application are: "Phase Equilibrium and Crystal Growth in the System $ZnS-ZnF_2$", by R. C. Linares (25); "Growth of Zinc Sulphide Single Crystals from Flux", by Y. Mita (26), who reported that KCl is most appropriate as a flux for ZnS; "Kristallisation von Disulfiden aus Schmelzlösungen", by K-Th. Wilke, D. Schultze, and K. Töpfer (27) -- this third paper described the growth of metal disulphides with the pyrite structure from a lead chloride flux under an atmosphere of

sulphur vapour in sealed silica capsules; "Growth of Cubic Zinc Sulphide from Molten Lead Chloride", by R. C. Linares (28); and "Synthesis and Growth of ZnS, ZnSe, ZnTe, GaS, Ga_2S_3 and InS Crystals in Ga and In Melts", by M. Hårsy (29).

The majority of fluxes used in crystal growing are low-melting halides. A mixture of two or more salts may form a eutectic that has a melting point lower than that of either of the end members.
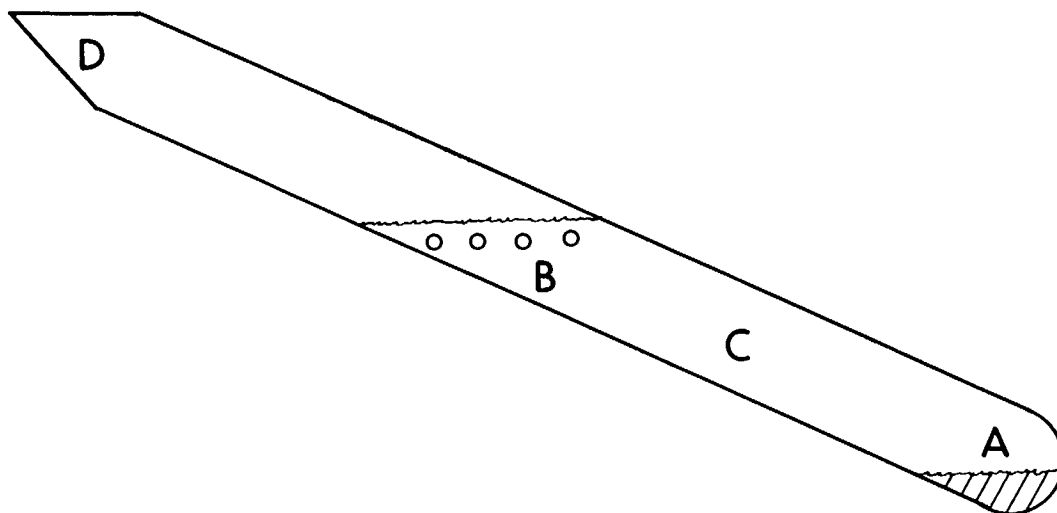
Figure 11. Schematic Arrangement for Flux Growth.

The sealed capsule, as shown in Figure 11, is placed in an oblique position in a furnace; this keeps the molten salt C at the rounded end of the tube. 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 usual procedure is to heat the silica capsule to a temperature 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 is cooled stepwise (1 to 6 deg C per hr) for several hours during the day, followed by a constant-temperature period during the night. This cooling cycle is repeated several times until the melting point of the flux is

reached. After cooling more rapidly to room temperature, the tube is then cut open with a diamond saw. The frozen salt mixture is leached from the crystals with water or acid, the choice depending on the nature of the crystal and the flux involved. Up to the present time, it has been observed that some flux has been entrapped in the crystals. To overcome this problem, a new programmed furnace assembly has been purchased and is currently undergoing initial experiments. The programmer will permit a cooling rate of 0.5 to 6 deg C per hr to be maintained uniformly throughout the growth period. It is hoped thereby to grow flux-free single crystals.

4. Hydrothermal Growth

Hydrothermal crystallization is defined as the use of an aqueous solvent under high temperature and pressure to increase the solubility of the substance to be grown to a level at which single crystals are deposited at the coldest part of the system. Alpha-quartz has been grown by this procedure for over fifty years. However, due to the low solubility of quartz and many sulphides in pure water, even at the extended p-t range experimentally 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 (30); "Hydrothermal Solubility and Growth of Sphalerite", by R.A. Laudise, F.D. Kolb and J.P. DeNeufville (31); and "Crystal Synthesis and Growth in Strong Acid Solutions under Hydrothermal Conditions", by H. Ray and A. Rabenau (32), who described the crystallization of several sulphide compounds from a strong-acid medium in silica capsules, at about 500°C and 3,000 atm.

For low-temperature experiments (100°-225°C), thick-walled pyrex tubing is sufficient. For protection against a possible explosion, that could result from a failure of the sealed tube, an iron-pipe jacket is used to encase the glass tube during the heating stage.

For higher-temperature experiments (225°-500°C), an Inconel metal vessel with 1-in.-thick walls was specially prepared by the Technical Services Division, Mines Branch. The vessel is equipped with a delta seal and a cap that is secured with 6 bolts. A platinum liner has proved useful. The usual furnace temperature is 375°-400°C, with a temperature gradient of 10-20 deg C. The problem with this system, which has hitherto been used for ZnS only, is polynucleation. Seeding and the use of a baffle have not helped.

A new two-zone furnace is to be constructed in which the temperature gradient can be controlled as desired. It is hoped that, with seeding in this system, better crystals will be obtained.

5. Melt Growth

If a substance has a congruent melting point, this physical property can be used to advantage for growing crystals of this material.

One procedure, developed by Bridgman (33), requires a bullet-shaped container that is migrated downward in a vertical furnace, causing the pointed tip to be cooled first. While this movement is maintained, a crystal will develop and seed the balance of the melt. Stockbarger (34) reported on his study of the temperature gradient and the elaborate system for its control, for the growth of KBr and related salts.

A second procedure, developed by Czochralski (35), involving wetting a crystal into a melt of the material and withdrawing it slowly, causing a continuous crystal to be pulled from the liquid bath. This technique is called the Czochralski or crystal-pulling method.

Many of the sulphides encountered in the present study have incongruent melting points and, hence, the above procedures are not suitable.

One way to prevent the loss of volatile components from compounds that dissociate, or from their melts, is the technique of Liquid Encapsulation (36), i.e., the use of an inert liquid (usually B_2O_3) as liquid seal. A high gas pressure must be maintained over the liquid B_2O_3. The present study has

shown that the application of liquid encapsulation at 1 atm of helium pressure, while permitting the melting of α-NiS, failed to prevent disproportionation.

However, a technique that produced good single crystals without the use of B_2O_3 involved a two-step approach. First, nickel monosulphide, contained in a silica capsule, was melted and cooled three times; this gave a uniform melt and some free sulphur. The second step was to anneal this product at 800°C for several days; this resulted in all the sulphur being absorbed, and a single-crystalline product was formed. If the nickel:sulphur ratio was nickel-rich compared with the composition of the stable stoichiometric monosulphide, then a second phase of a nickel-rich sulphide was deposited at the warmer end of the button.

Kozielski (37) described the growth of ZnS single crystals from the melt at 1850°C under an argon pressure of 50 atm. Unfortunately, no suitable high-pressure/high-temperature melting apparatus was available in the present study.

6. Silica-Gel Growth

Crystal growth in gels is suitable for substances that are slightly soluble in water. This growth technique has the advantage of being operated at or near ambient temperatures.

In 1965, Henisch et al. (38) reported on the revival of the use of gels in crystal growth after a dormant period of 35 years. This paper described the growth of metal citrates, tartrates, iodides, but not of sulphides. In 1966, Brenner et al. (39) described the growth of lead sulphide. In 1967, Schwartz et al. (40) reported on the successful growth of α-MnS and on failure with Ca, La, Zn, Cd, Fe, Co, Sn, Ge and Ni sulphides.

The crystals are usually grown in a test tube. The general procedure involves adding a soluble metal salt and an appropriate acid to a nearly saturated solution of sodium silicate and allowing the mixture to gel. An aqueous solution of the desired anion -- in the case of sulphides, either Na_2S or thioacetamide -- is placed on the gel. Crystals grow in the gel

medium; a period of one week or longer is required. After the growth period, the gel medium is easily washed from the crystals.

Many crystal growers often attempt to grow a given crystal by a certain technique, either because the apparatus happens to be available or because it is their favourite technique. While this may be true, it should be pointed out that many crystal species can be grown successfully by several quite different procedures. However, the successful growth of a specific crystal species depends on the use of an appropriate temperature; hence only certain techniques could be applicable. In each case the quality of the crystal is dependent on the procedure.

h. Analyses

The quality of a crystal must be determined by chemical and/or physical analysis. Nine different analytical techniques employed in connection with the present study are shown in Table 3. Infrared analysis of the sulphide materials is currently being investigated within the Mineral Sciences Division; synthetic sulphides are being compared with natural samples.

Although the techniques listed supply valuable information, each has its limitations. In the area of stoichiometry, chemical analysis is invaluable but, unfortunately, neither the author nor the other analysts in the Division have developed these analyses extensively. Up to the present stage in the study, X-ray diffraction analysis has been the technique most often utilized. The electron-probe microanalyser has been the second choice. The remainder of the techniques have been used for the solution of specific problems.

TABLE 3

Data on Chemical and Physical Analyses

Method	Destructive	Sample Size	Advantage in Crystal Study
Chemical	Yes	<200 mg	Very quantitative
Electron-Probe Microanalysis	Yes	As available	Determination of uniformity and composition
Infrared	Yes	<25 mg	Comparison with naturally occurring sulphides
Neutron-Activation	No	5-20 grams*	O_2 and halogen determination
Spectrographic	Yes	<25 mg	Main impurities ascertained
X-ray Diffraction	Yes	<25 mg	Crystal structure
X-ray Fluorescence	No	1-5 grams*	Trace analysis
Precession Camera	No	<10 mg	Perfection of crystallinity
Differential Thermal Analysis	Yes	<500 mg	Detection of rapid phase changes

*Depends on concentration of the sought-after component.

RESULTS AND DISCUSSION

During the past six years, over 700 crystal-growing experiments have been conducted; this total is composed of purifications, preparations, growth procedures, annealings, dopings, and analyses. The scope of the investigation has widened steadily from the original ZnS work to include approximately 50 materials. In some cases, only one or two exploratory runs were made, and in others several runs were performed; but, in the case of ZnS, one-half of the total experimentation was involved.

The scope of the investigation, in terms of success or failure in obtaining good single-crystal material, is shown in Table 4. A successful growth (S) indicates that the growth product was a single crystal of the desired material. A partly successful growth (P) is considered as one in which the growth product was a mixture of the desired crystal with one or more other crystalline compounds. In cases of failure (F), the growth product (if there was one) did not contain the sought-after crystalline material. To complete Table 4, a dash (——) is used to show those techniques that have not been examined for the material concerned.

The two main goals were, firstly, to explore the field of sulphides, arsenides and sulpharsenides of Fe, Co, Ni, Zn and Cu, along with some other isolated compounds, in order to be prepared to supply quickly any of the compounds in which the Divisional scientists working in the Sulphide Research Programme had expressed interest; and, secondly, to grow the crystals as large as possible, preferably in the cubic-centimetre size range. However, not many of the successful growths reported in Table 4 yielded crystals as large as this.

The data concerning the growth procedures and the quality of the crystals produced will be described in the later reports in this series (see).

TABLE 4

Scope of Crystal-Growth Activities

Compound	Mineral Name	Success or Otherwise of Crystal-Growth Technique						
		Direct Combination	Vapour Transport	Chemical Vapour Transport	Hydrothermal	Flux	Melt	Gel
ZnS	Sphalerite	S	S	S	S	S	—	F
ZnS	Wurtzite	S	S	F	F	F	—	—
FeS	Mackinawite	—	—	—	P	—	—	—
FeS	Troilite	—	—	—	P	F	S	—
$Fe_{1-x}S$	Pyrrhotite	S	—	S	S	S	S	F
Fe_3S_4	Greigite	F	—	—	P	—	—	—
Fe_3S_4	Smythite	—	—	—	P	—	—	—
FeS_2	Marcasite	—	—	—	S	—	—	—
FeS_2	Pyrite	S	—	S	P$\rightarrow$S	S	P	—
α-NiS	High-temperature Millerite	S	S	P	—	S	S**	—
NiS	Millerite	—	—	—	S	—	—	—
Ni_7S_6	Godlevskite	F	—	—	—	F	—	—
NiS_2	Vaesite	P	—	S	S	S	—	—
CoS	Jaipurite	P	—	—	—	—	—	—
CoS_2	Cattierite	P	—	S	—	S	—	—
Cu_2S	Chalcocite	S*	—	—	—	—	—	—

*Product was not analysed.

**It was necessary to anneal for several hours at a temperature of 100 deg C below the M. P., after melting, to ensure stoichiometry.

TABLE 4 (Continued)

Compound	Mineral Name	Success or Otherwise of Crystal-Growth Technique						
		Direct Combination	Vapour Transport	Chemical Vapour Transport	Hydrothermal	Flux	Melt	Gel
CuS	Covellite	F	—	F	—	S	—	F
$Cu_{1.8}S$	Digenite	S*	—	F	—	—	—	—
US	———	F	—	—	—	—	—	—
PbS	Galena	S	S	—	—	P	—	S
CdS	Greenockite	S	S	—	—	—	—	F
α-MnS	Albandite	S	—	S	S	S	—	F
MnS_2	Hauerite	F	—	—	P	F	—	—
HgS	Cinnabar	P	P	P	—	—	—	—
HgS	Meta-cinnabar	P	P	P	—	—	—	—
MoS_2	Molybdenite	—	F	S*	—	—	—	—
FeAs	Arseneisen	P	—	F	—	—	—	—
$FeAs_2$	Löllingite	S	—	S	—	—	—	—
CoAs	Modderite	P	—	—	—	—	—	—
Co_2As	———	S	—	—	—	—	—	—
$CoAs_2$	Safflorite	S	—	S	—	—	—	—
$CoAs_3$	Skutterudite	S	—	F	—	—	—	—
NiAs	Niccolite	—	—	—	—	—	S	—
$NiAs_2$	Rammelsbergite	P	—	F	—	—	—	—

*Product was not analysed.

- concluded

TABLE 4 (Concluded)

Compound	Mineral Name	Success or Otherwise of Crystal-Growth Technique						
		Direct Combination	Vapour Transport	Chemical Vapour Transport	Hydrothermal	Flux	Melt	Gel
ZnSe	Stilleite	S*	S*	—	—	—	—	—
ZnTe	—	S*	S*	—	—	—	—	—
Bi_2Te_3	—	S*	S*	—	—	—	—	—
SnS	Herzenbergite	S	—	—	—	—	—	—
$CuFeS_2$	Chalcopyrite	S	—	S	—	S	P	—
Cu_5FeS_4	Bornite	P	—	—	—	P	—	—
$CuFe_2S_3$	Cubanite	F	—	—	—	F	—	—
$Cu_{5.5}FeS_{6.5}$	Idaite	F	—	—	—	—	—	—
$CuFe_{1.37}S_{2.4}$	—	F	—	—	—	—	—	—
FeAsS	Arsenopyrite	F	—	F	—	F	F	—
NiAsS	Gersdorffite	P	—	—	—	—	—	—
CoAsS	Cobaltite	P	—	—	—	—	—	—
$(Ni,Fe)_9S_8$	Pentlandite	P	—	—	—	—	P	—
$(Fe,Ni)S_2$	Bravoite	—	—	—	F	F	F	—
(Co,Ni)As	Langisite	P	—	—	—	—	—	—
(Zn,Fe)S	Sphalerite	P	F	P	—	—	—	—
(Zn,Al)S	Sphalerite	—	F	F	—	—	—	—
$(Co,Fe)As_2$	Safflorite	P	—	—	—	—	—	—
$(Fe,Ni)_{1-x}S$	Pyrrhotite	—	—	—	—	—	S	—

*Product was not analysed.

Several interesting crystals are currently being examined by other members of the Mineral Sciences Division, as at August 1970. These are:

1. ZnS, for single-crystal status;
2. $CoAs_2$ and $FeAs_2$, for crystal structure;
3. FeS_2, CoS_2 and NiS_2, grown by I_2-transport and by $PbCl_2$-flux procedures, for hardness and infrared analysis;
4. α-NiS for thermoelectric power and resistivity.

The feed-back of information that will come from the divisional researchers using these crystals, as described above, and from analytical procedures, will help in perfecting present growth methods.

CONCLUSIONS

The following conclusions are based on our overall experience of crystal growing, to be described in the whole series of reports, and not merely on the work reported in the present document.

1. Considerable progress has been made in the growing of single crystals of sulphides and related materials, but the study is far from complete.

2. It has been found that not all the literature-reported methods work as described. Occasionally, their descriptions of the procedure seem incomplete.

3. The main conclusion reached is that almost any system can be grown if sufficient time is available to find the right method, the right conditions, and the required time for growth. However, when centimetre-sized crystals are desired, the problems of crystal growth are compounded.

ACKNOWLEDGEMENTS

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