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CRYSTAL GROWTH PART IV: THE ARSENIDES AND SULPHARSENIDES OF COBALT, IRON, AND NICKEL

LEONARD G. RIPLEY

MINERAL SCIENCES DIVISION

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CRYSTAL GROWTH

PART IV:

THE ARSENIDES AND SULPHARSENIDES OF COBALT, IRON, AND NICKEL

by

Leonard G. Ripley*

ABSTRACT

This report deals with an applied research project to explore the preparation and the growing of single crystals of sixteen arsenides and sulpharsenides of cobalt, iron, and nickel. A significant start has been made in the understanding of the growth problems presented by this group of compounds, but much more research needs to be done.

The prime growth procedure was the chemical vapour transport using iodine as the carrier. Good single crystals of safflorite ($CoAs_2$), loellingite ($FeAs_2$), skutterudite ($CoAs_{3-x}$), and cobaltite ($CoAsS$) were obtained by this procedure; the first two listed were in the millimetre size range. Three other growth procedures were tried: (1) the modified "melt-and-anneal" method, which was partially successful in the preparation of langisite ($Co_{0.8}Ni_{0.2}As$); (2) the vapour transport method; and (3) the flux growth method. The last two methods were not successful in the cases to which they were applied.

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Direction des mines
Rapport de recherches R 238

LA CROISSANCE DES CRISTAUX
IV^e PARTIE:
LES ARSÉNIURES ET LES SULFARSÉNIURES DE COBALT, DE FER ET DE NICKEL

par

Leonard G. Ripley*

RÉSUMÉ

Dans ce rapport l'auteur traite d'un projet de recherche appliqué sur l'étude de la préparation et de la croissance des monocristaux de seize arséniures et sulfarséniures de cobalt, de fer et de nickel. L'auteur a fait un commencement significatif pour bien comprendre les problèmes de croissance présentés par ce groupe de composés mais il y a encore beaucoup plus de recherches qui doivent être faites.

Le premier procédé de croissance était le transport chimique en phase vapeur utilisant l'iode comme porteur. L'auteur a obtenu de bons monocristaux de safflorite($CoAs_2$), de loellingite ($FeAs_2$), de skuttérudite ($CoAs_{3-x}$) et de cobaltine (CoAsS) par ce procédé; les deux premiers monocristaux étaient dans la série de dimensions en millimètre. Il a essayé trois autres procédés de croissance: (1) la méthode modifiée de "fondre-et-recuire" qui était en partie une réussite dans la préparation de langisite ($Co_{0.8}Ni_{0.2}As$); (2) la méthode de transport en phase vapeur; et (3) la croissance par la méthode des fondants. Les deux dernières méthodes n'étaient pas une réussite dans les cas auxquels elles étaient appliquées.

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Contribution de recherches sur les sulfures No. 56.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

Page

INTRODUCTION

The work of the present author in the crystal-growth aspects of the Mineral Sciences Division Sulphide Research Programme is being described in an intended five-part series of Research Reports.

Part I (R 235), entitled "Background to Crystal Growth" (1), includes a review of the experimental techniques available and the various growth procedures actually used in this programme.

Part II (R 236), a comprehensive report on the growth of zinc sulphide crystals, is entitled "The Growth of Zinc Sulphide Crystals" (2).

Part III (R 237), dealt with the second main class of compounds studied and is entitled "The Sulphides of Cobalt, Iron, and Nickel" (3).

This present report is Part IV, and deals with "The Arsenides and Sulpharsenides of Cobalt, Iron, and Nickel". This subject relates to the third class of compounds undertaken in the crystal-growing programme. It is well known that the naturally-occurring arsenides and sulpharsenides are frequently solid solutions of complex composition containing all three metals, cobalt, iron, and nickel. Therefore, the main purpose of the present study was to prepare and/or grow single crystals of the end members.

This group of compounds has attracted some attention in the Mineral Sciences Division in their identification and characterization, and in the study of their chemical, mineralogical, and physical properties. The need for single crystals of several of these arsenides and sulpharsenides arose from the desire of some members of the Mineral Sciences Division to study some of their physical properties; however, some of these members are no longer with the Division and the need for these crystals has waned. Because the present study has reached the point where some significant results have been obtained on the preparation and on the growth of several arsenides and sulpharsenides, the present report is compiled at this time.

Nevertheless, much more work needs to be done on this family of compounds.

CLASSIFICATION AND NOMENCLATURE

The classification and nomenclature of naturally-occurring arsenic-rich arsenides of cobalt, iron, and nickel have long been a mineralogical problem. One such classification was published by Holmes (9) who quoted the 7th Edition of Dana's "The System of Mineralogy" (5) as his source; this classification is shown in Table 1. A review of this Table indicates that, although there are only two main structures, the cubic and the orthorhombic, there are two areas that cause some difficulty in classification:

(1) The naturally-occurring minerals usually contain at least two of the three metals Co, Fe, and Ni in varying proportions.

(2) The total metal:arsenic ratio in the isometric series is variable from $1 : \sim 2$ to $1 : \sim 3$.

A detailed study of many naturally-occurring minerals in the above composition range was made by Holmes (9, 22) who found that the lattice constants of the isometric arsenides are related to the ratio between the three metals, varying directly with increasing nickel, iron, or nickel-iron contents. Variations in the metal:arsenic ratio, however, do not appear to influence the lattice constants appreciably. The lattice constants range from 8.187 to 8.31 Å. These isometric arsenides are usually zoned and are inhomogeneous, containing both isometric and some non-isometric constituents. He also found that the orthorhombic diarsenides exhibit both discontinuous and limited isomorphism between the cobalt, iron, and nickel compounds. The nickel-rich arsenides are separated from the iron-rich arsenides by a broad wedge of isometric arsenides.

Holmes (22) recommended that the name "skutterudite" be used for the entire group of isometric arsenides of cobalt, iron, and nickel because the cobalt triarsenide is the most firmly established of all the

TABLE 1

Classification and Nomenclature of the Higher Arsenides of Cobalt, Iron, and Nickel

Series	Structure	Mineral Name	Formula
Skutterudite	Isometric (a)	Skutterudite	$(Co,Ni)As_{3-x}$
		Nickel-skutterudite	$(Ni,Co)As_{3-x}$
		Ferrian-skutterudite	$(Fe,Ni,Co)As_{3-x}$
	Isometric (b)	Smaltite	$(Co,Ni)As_{3-x}$
		Chloanthite	$(Ni,Co)As_{3-x}$
		Chathamite	$(Fe,Ni,Co)As_{3-x}$
		Arsenoferrite ?	$FeAs_2$
Diarsenides	Orthorhombic	Rammelsbergite	$NiAs_2$
		Pararammelsbergite	$NiAs_2$
		Loellingite	$FeAs_2$
		Safflorite	$CoAs_2$ with considerable iron (4-16%)

Note: (a) In this series x = 0.0 to 0.5.

(b) In this series x = 0.5 to 1.0.

Note: This Table was taken from Holmes (9) who quoted the 7th Edition of Dana's System (5) as his source.

isometric arsenides of these metals. He also recommended that the use of the names smaltite, chloanthite, chathamite, and arsenoferrite be discontinued. Also, it would be preferable to apply an appropriate prefix, e.g., nickel-skutterudite to the high-nickel variety.

In the case of the orthorhombic arsenides, Holmes recommended that the term "rammelsbergite" be retained for the commoner high-nickel member and pararammelsbergite for the rarer nickel-rich form. It was also recommended that the term "loellingite" be used for all the iron-rich diarsenides, containing more than 85 per cent iron; however, an iron-rich arsenide, containing less than 85 per cent iron but containing either cobalt dominant over nickel or nickel dominant over cobalt, may be termed cobaltian or nickelian loellingite, respectively. Holmes stated that the term "safflorite" has been accepted for the cobalt end-member of this series. His studies with naturally-occurring and with synthetic material gave no evidence for the orthorhombic structure. However, he suggested that the term safflorite be used for the monoclinic diarsenide of cobalt and iron in which the ratio of the two metals was approximately unity.

Petruk (23) quoted Darmon and Winterberger (24) as saying that safflorite can have either a monoclinic or an orthorhombic structure; the monoclinic structure appears to be stable over a narrow compositional range near $CoAs_2$.

Radcliffe and Berry (20) used the name safflorite for natural $(Co,Fe,Ni)As_2$ having compositions between 3 and 100 mole per cent $CoAs_2$, with nickel ranging between zero, in low-cobalt minerals, and about 30 per cent in low-iron minerals. Also, they described safflorite as belonging to two crystal systems : orthorhombic, between 97 and about 20 mole per cent iron, and monoclinic in the low-iron compositions. The exact range of the monoclinic safflorite was not established.

Although the nomenclature of the monoarsenides appears to be better understood, there are some points that should be mentioned. The commonest monoarsenide is niccolite (NiAs). The terms modderite (CoAs) and arseneisen (FeAs) are acceptable but are rarely used in the literature.

Langisite ($Co_{0.8}Ni_{0.2}As$) was first described by Petruk, Harris, and Stewart (16) in 1969, and is the end member of the solid-solution series NiAs-$Co_{0.8}Ni_{0.2}As$, which was reported by Heyding and Calvert (7). The compound Co_2As appears to be devoid of a mineral name.

The three sulpharsenides mentioned in this report, viz., cobaltite (CoAsS), arsenopyrite (FeAsS), and gersdorffite (NiAsS), have mineral names that have long been accepted.

The nomenclature of the sixteen arsenide and sulpharsenide species included within the scope of the present study is based on the foregoing remarks, and is listed in Table 2, along with the corresponding ideal formula and the crystal system for each of the sixteen compounds.

STABILITY OF COBALT, IRON, AND NICKEL ARSENIDES AND SULPHARSENIDES

(a) Two-Component Arsenide Systems

A survey of the literature reveals that temperature-composition equilibrium studies of the cobalt-arsenic system are far fewer in number than those of either the iron-arsenic or the nickel-arsenic systems.

An incomplete phase diagram for cobalt-arsenic has been given by Hansen and Anderko(4) and is shown in Figure 1. Subsequently, Heyding and Calvert (7), who prepared alloys of cobalt containing up to 60 per cent by weight of arsenic, found that only two compounds exist at room temperature, viz., Co_2As and CoAs, and that these compounds undergo crystallographic transformations at between 400 and 500°C and between 944 and 960°C, respectively. A third compound, probably Co_3As_2, is formed at temperatures above 940°C. In view of these results, the phase diagram as shown in Figure 1, will need to be revised.

$CoAs_2$ has been prepared by Heyding and Calvert (10) and has been found to be unaltered by any heat treatment below 900°C; also it was unchanged in the presence of CoAs or $CoAs_3$.

TABLE 2

Nomenclature of the Compounds Included in the Present Report

Formula	Mineral Name	Crystal System
α-Co_2As	---	Pseudohexagonal
β-Co_2As	---	Hexagonal
α-CoAs	Modderite	Hexagonal
β-CoAs	Modderite	Orthorhombic
$CoAs_2$	Safflorite	Monoclinic
$(Co_{0.5}Fe_{0.5})As_2$	Safflorite	Monoclinic
$CoAs_3$	Cobaltian Skutterudite	Cubic
FeAs	Arseneisen	Orthorhombic
$FeAs_2$	Loellingite	Orthorhombic
NiAs	Niccolite	Hexagonal
α-$NiAs_2$	Pararammelsbergite	Orthorhombic
β-$NiAs_2$	Rammelsbergite	Orthorhombic
$Co_{0.8}Ni_{0.2}As$	Langisite	Hexagonal
CoAsS	Cobaltite	Cubic
FeAsS	Arsenopyrite	Orthorhombic
NiAsS	Gersdorffite	Cubic

Note: The α- and β-forms refer to the low- and high-temperature polymorphs, respectively.

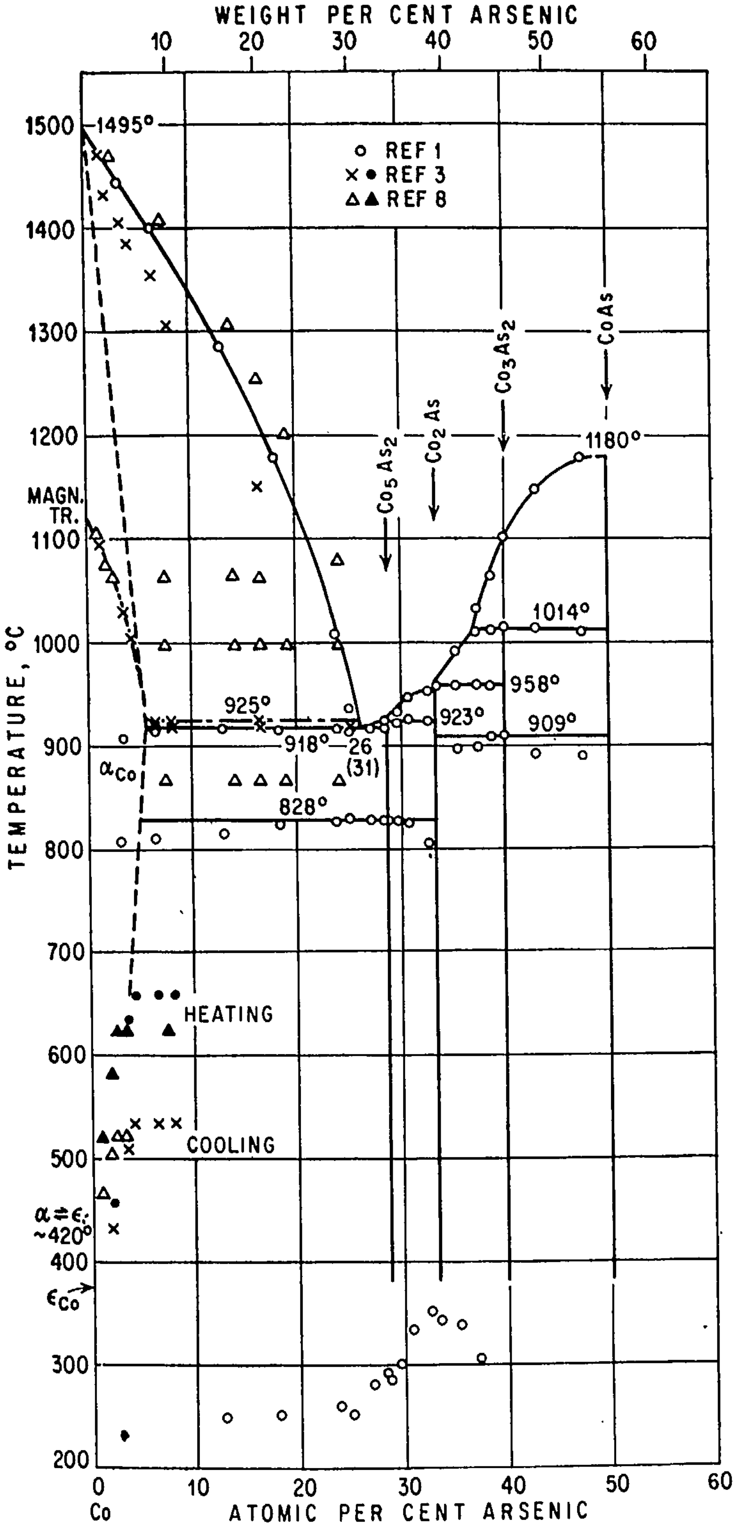

Figure 1. - Partial Cobalt-Arsenic System According to Hansen and Anderko (4).

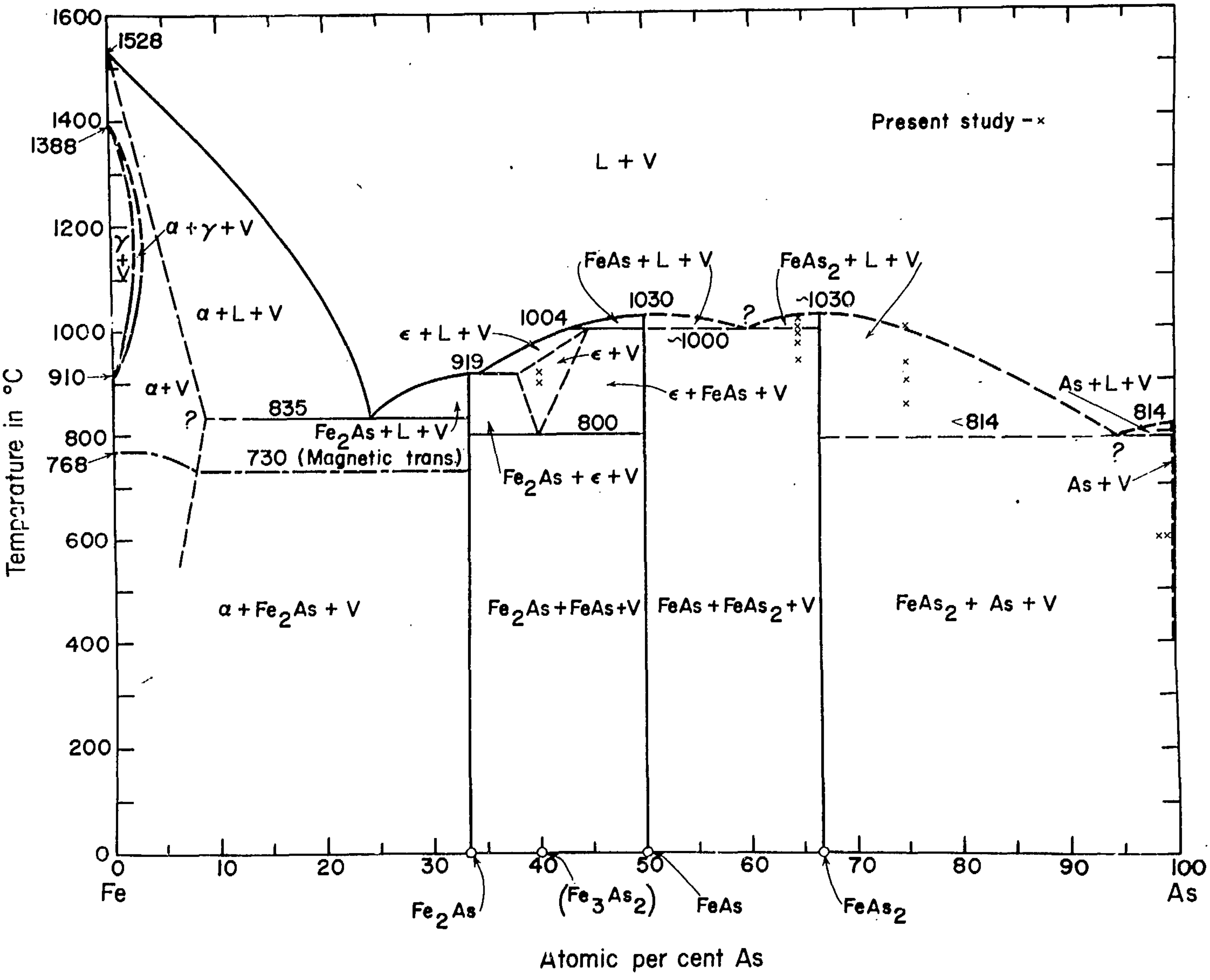

Figure 2. - Phase Relations in the Fe-As System According to Clark (25), Published by Kullerud (26).

Synthetic skutterudite has been prepared by Roseboom (12), who was able to obtain a maximum composition of $CoAs_{2.96}$ at a temperature of 800°C.

The present author believes that a complete phase diagram for the cobalt-arsenic system has not yet been published.

The phase relations in the iron-arsenic system have been studied by Clark (25) and published in Kullerud's review paper (26). This system is shown in Figure 2. Heyding and Calvert (10) found that the decomposition pressures of the higher arsenides of iron and nickel are appreciable, and that the quantities of arsenic which separated on quenching from 700°C were prohibitive.

A detailed study of the nickel-arsenic system has been made by Yund (8). It is from Yund's study that the phase diagram shown in Figure 3 was taken. Four of the phases, viz., maucherite, niccolite, rammelsbergite, and pararammelsbergite are shown by the following abbreviations: ma, nc, rm, and prm, respectively. This figure shows that the inversion of pararammelsbergite to rammelsbergite occurs at 590°C. The dashed lines represent earlier work or relations that are not accurately determined.

(b) Multiple-Component Arsenide Systems

(i) Isometric structures

Roseboom (11) prepared many of the synthetic diarsenides and triarsenides in the Co-Fe-Ni-As system and determined the cell edges and compositional ranges of these compounds. The extent of Co-, Fe-, and Ni-substitution in synthetic skutterudite solid solution at 800°C is shown as the shaded area in Figure 4. He also reported that all the analysed naturally-occurring skutterudites fell either within or close to the shaded area.

(ii) Orthorhombic structures

The approximate extent of Co-, Fe-, and Ni-substitution in naturally-occurring diarsenides is shown as the shaded area in Figure 5.

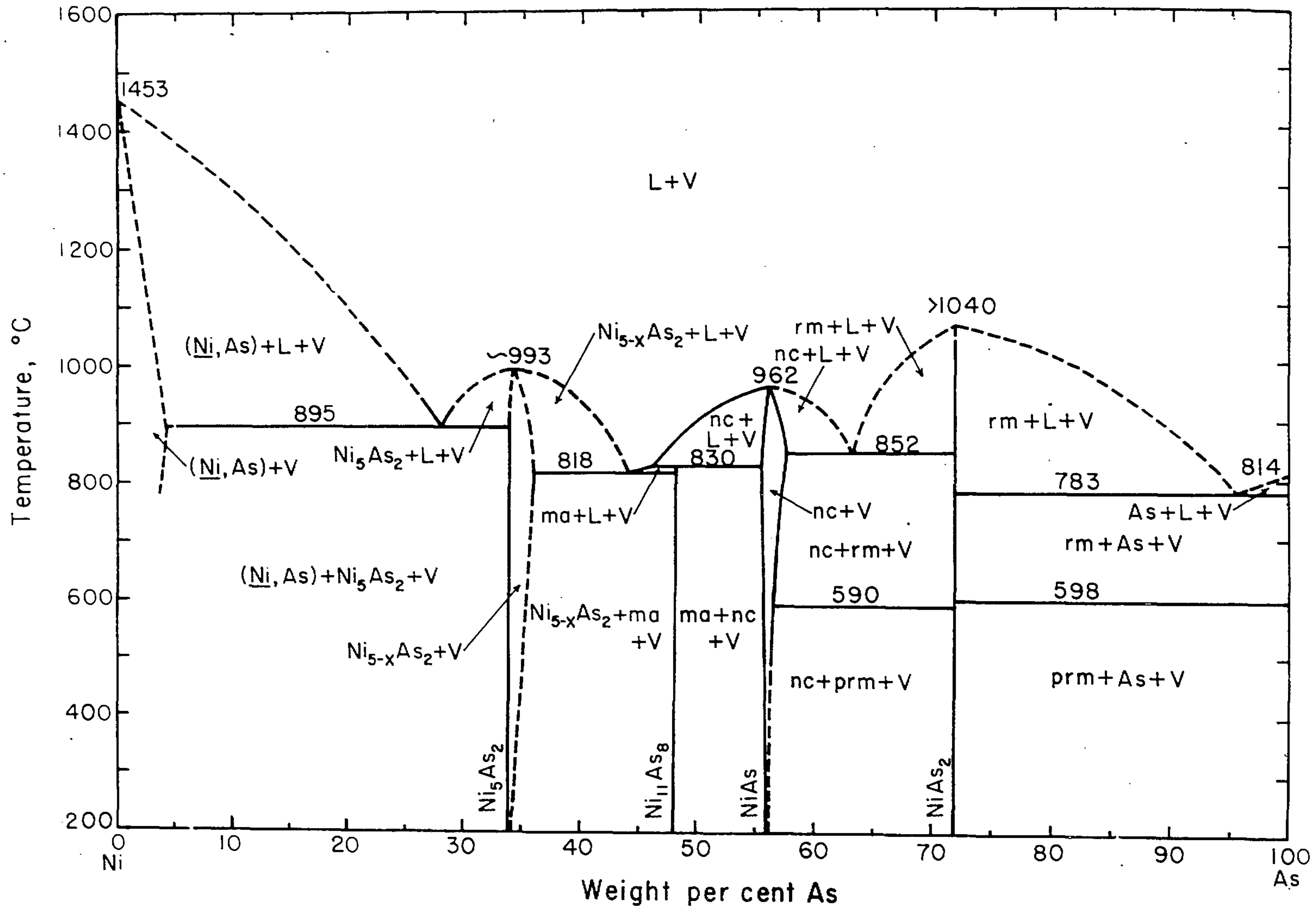

Figure 3. - Phase Diagram of the Condensed Ni-As System According to Yund(8).

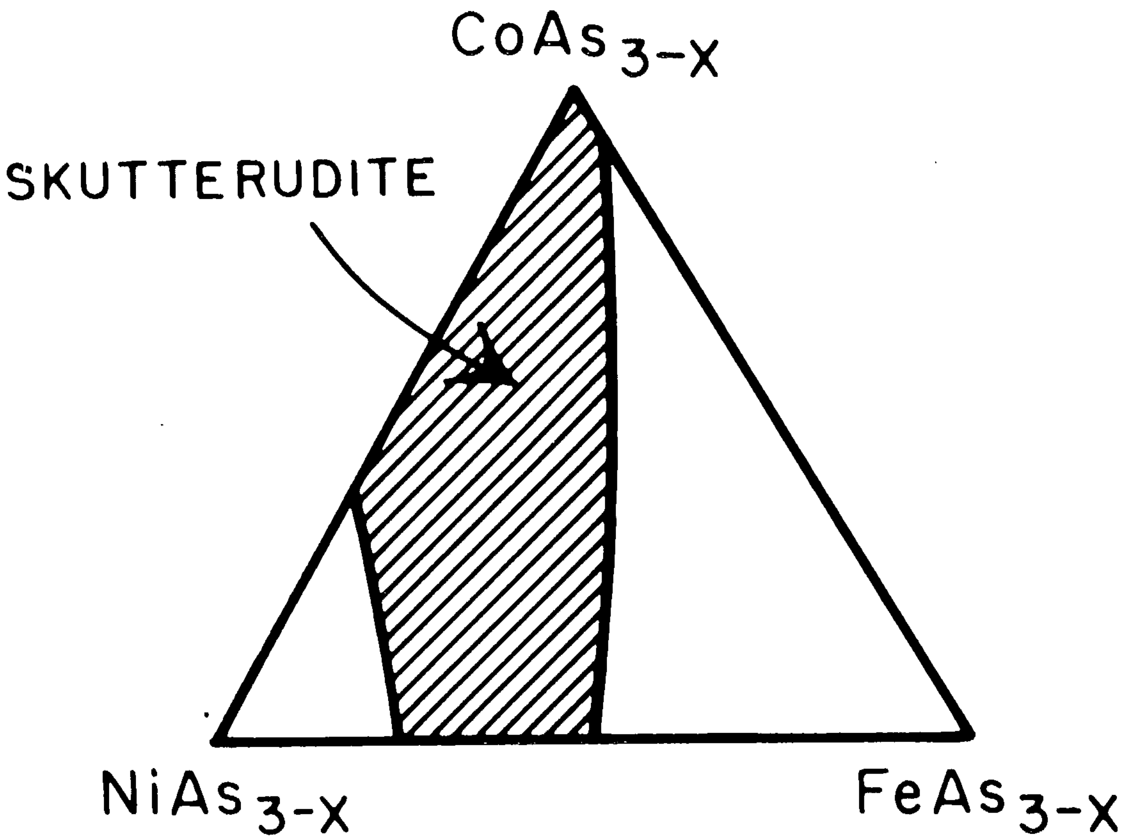

Figure 4. - The Extent of Co-, Fe- and Ni- Substitution in Skutterudite According to Roseboom (11).

At 800°C, the solid solution extends over the entire triangle, except for the area within the dashed line. This diagram is taken from the work of Roseboom (11).

Radcliffe and Berry (20) have made an extensive study of the safflorite-loellingite solid-solution series. They analysed synthetic and naturally-occurring $(Co,Fe,Ni)As_2$ materials in this compositional range. They found that there is a complete solid solution between $CoAs_2$ and $FeAs_2$, limited solution of $CoAs_2$ in $NiAs_2$, and no solid solution between $FeAs_2$ and $NiAs_2$.

As a result of the above study, the X-ray diffraction patterns of safflorites have been divided into five types. The compositions of these safflorites, which have been assigned the appellation safflorites I-V, are shown in Figure 6.

(c) Sulpharsenide Systems

(i) Cobaltite, CoAsS

The author believes that no complete phase diagram for the cobalt-arsenic-sulphur system has yet been published.

Peacock and Henry (18) report that the eleven naturally-occurring cobaltites which they examined contained iron in a proportion of 1.62 to 14.30 per cent, but that the majority had 1.62 to 5.30 per cent iron.

Kraus, Hunt, and Ramsdell (27) indicate, by analyses for cobalt, arsenic, and sulphur listed in their report, that the composition of cobaltite is CoAsS but they state that cobaltite may contain up to 12 per cent iron and up to 3 per cent nickel.

Giese and Kerr (19) studied the heat treatment of cobaltite and found that, when it was heated to 850°C, a disordered structure was obtained due to partial substitution of the sulphur and arsenic for one another. However, when the disordered material was heated at 450°C, a completely ordered structure was obtained. They also observed that, when orthorhombic cobaltite was heated to 850°C and quenched, the isotropic form was obtained.

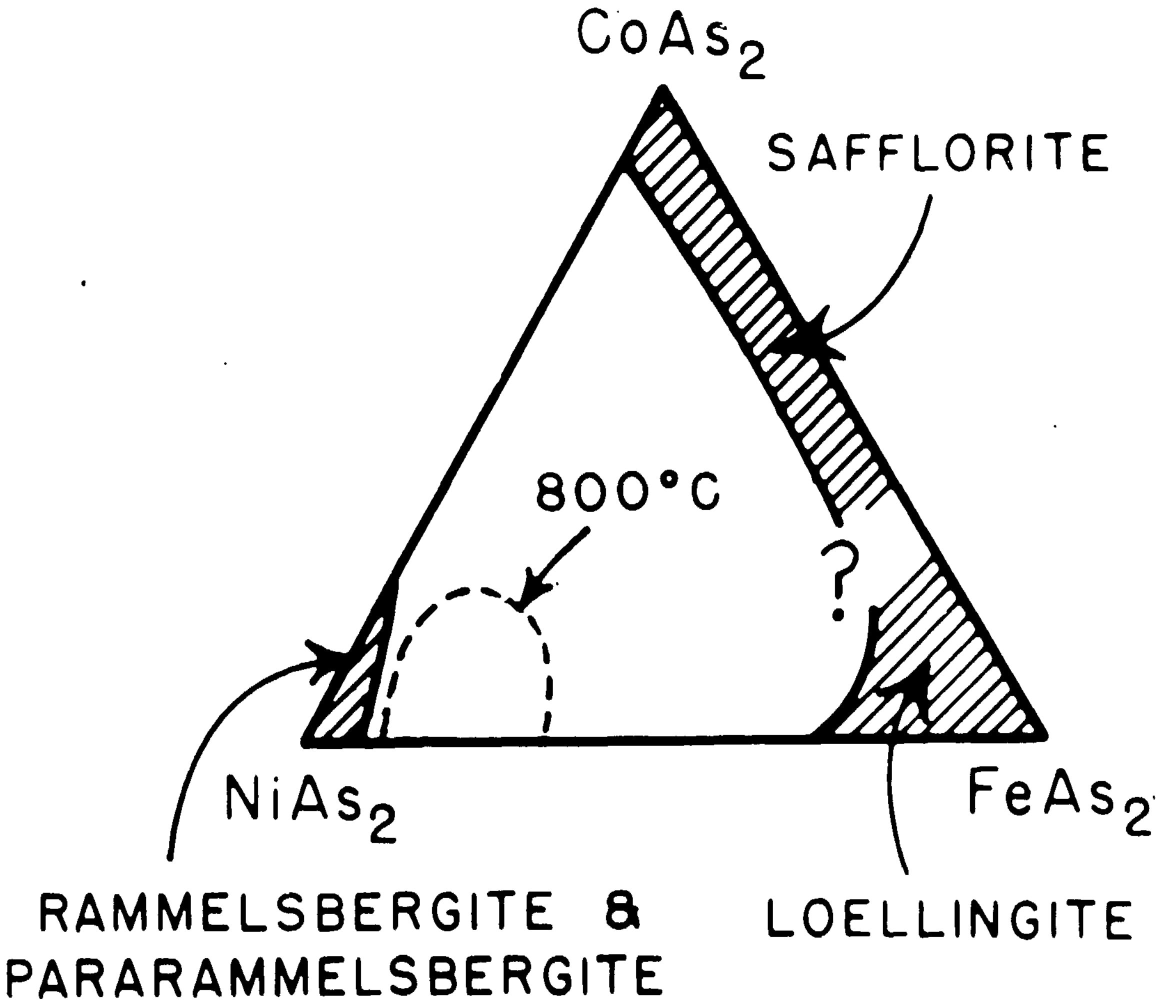

Figure 5. - The Approximate Extent of Co-, Fe-, and Ni- Substitution in Naturally-Occurring Diarsenides (Shown by shading) According to Roseboom (11).

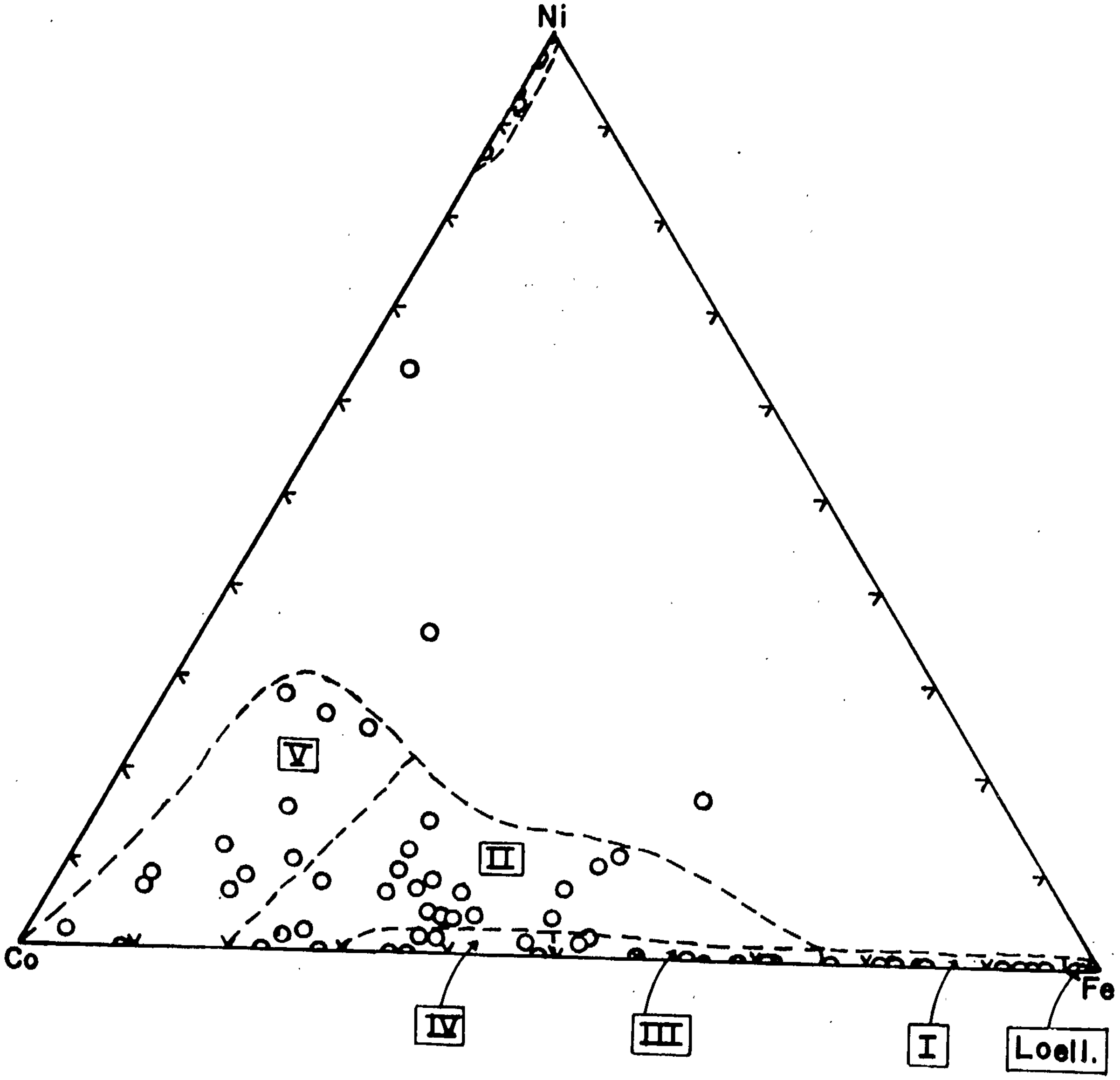

Figure 6. - The Composition of Safflorites I to V According to Radcliffe and Berry (20).

It is concluded from the above experiments that the decomposition temperature of cobaltite is above 850°C.

(ii) Arsenopyrite, FeAsS

The phase relations in the iron-sulphur-arsenic system have been extensively studied by Clark (25, 14); the diagram shown in Figure 7 was published in Kullerud's review paper (26). Four of the phases, viz., arsenopyrite, loellingite, pyrrhotite, and pyrite are shown by the following abbreviations, Asp, Lo, Po, and Py, respectively. The bulk composition of FeAsS is indicated as a small triangle on this diagram; the actual composition was shown to be $FeAs_{1.1}S_{0.9}$. Kullerud gives 702 ± 3°C as the temperature at which arsenopyrite, in the presence of vapour, melts incongruently to pyrrhotite, loellingite, and a liquid.

The thermal decomposition of arsenopyrite has been studied by Strathdee and Pidgeon (13), who found that arsenopyrite starts to decompose at about 500°C, yielding a distillate of arsenic and an arsenic-rich disulphide (As_2S_2), and leaving a residue of pyrrhotite ($Fe_{1-x}S$). At higher temperatures, the rate of reaction is greater but the products are the same.

(iii) Gersdorffite, NiAsS

The phase relations in the nickel-arsenic-sulphur system have been extensively studied by Yund (15); the diagram shown in Figure 8 was published in Kullerud's review paper (26). Five of the phases, viz., maucherite, niccolite, rammelsbergite, gersdorffite, and vaesite are shown by the following abbreviations: ma, nc, rm, gf, and va, respectively. It is seen that gersdorffite is a solid-solution series extending from $NiAs_{1.77}S_{0.23}$ to $NiAs_{0.77}S_{1.23}$. The decomposition temperature of gersdorffite was not given.

(d) Summary of Stability Ranges

The data on the thermal stabilities and on the compositional ranges of the various arsenides and sulpharsenides of cobalt, iron, and

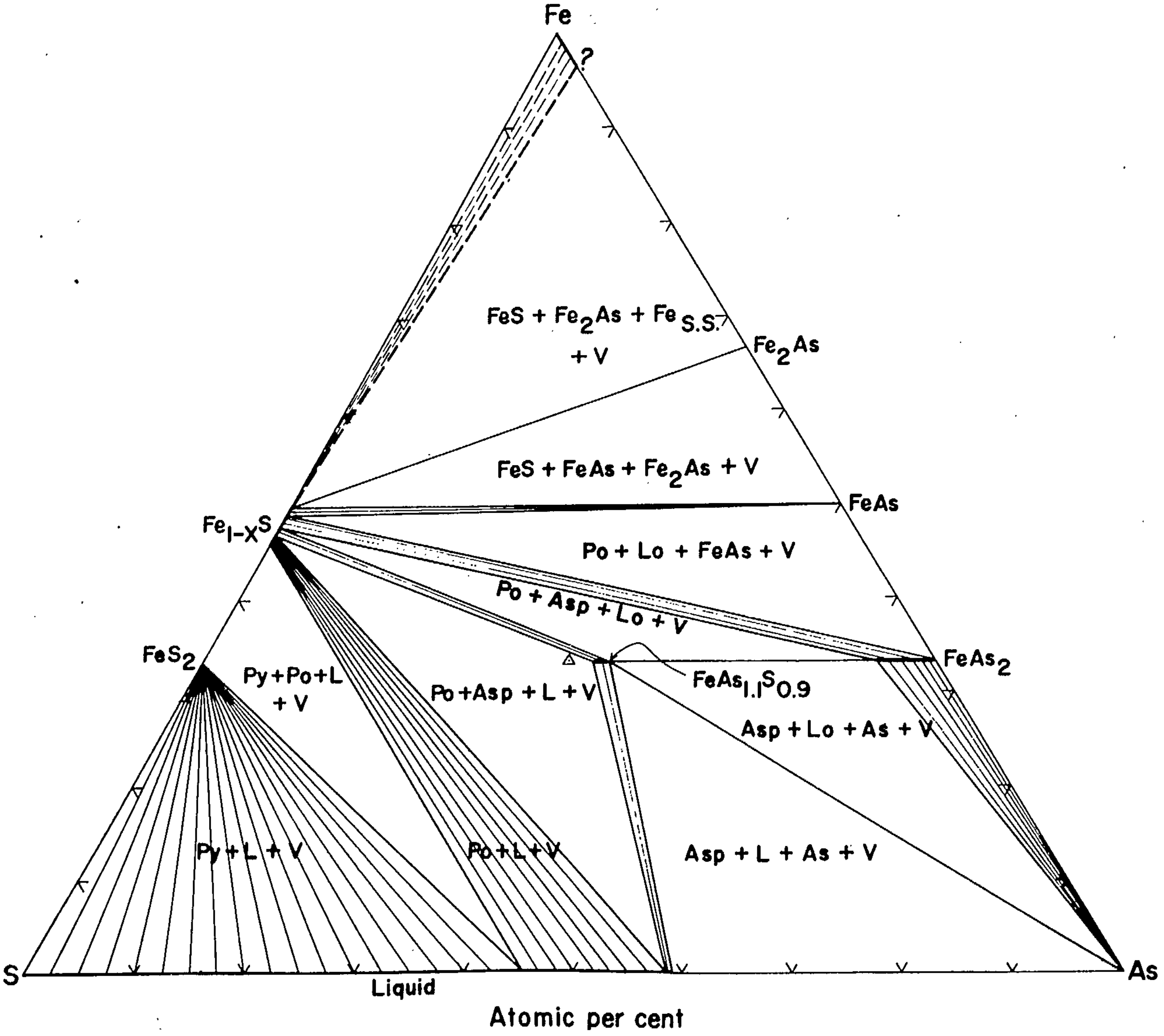

Figure 7. - Phase Relations in the Fe-As-S System at 600°C According to Clark (25), Published by Kullerud (26).

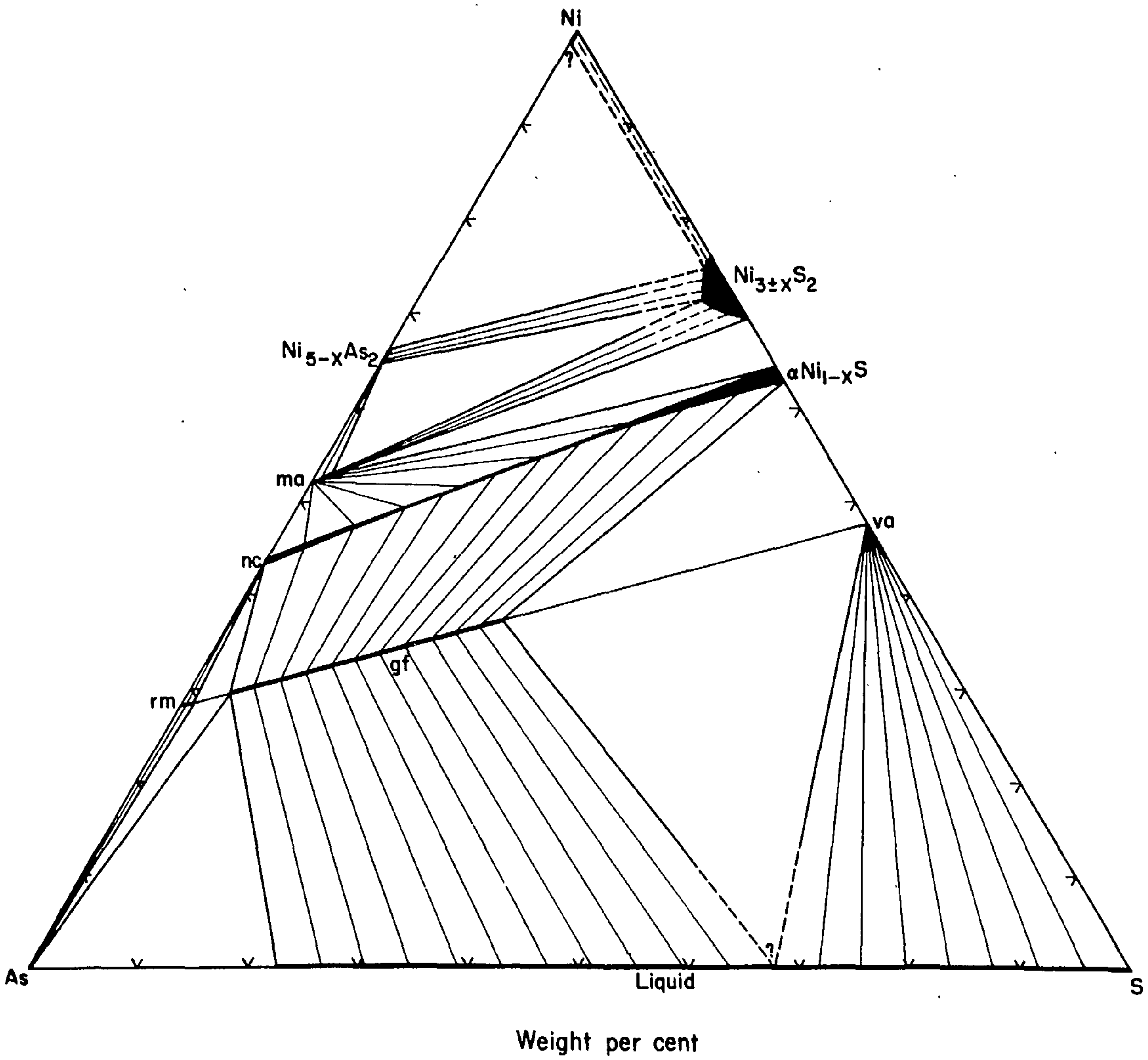

Figure 8. - Phase Relations in the Ni-As-S System at 600°C According to Yund (15), Published by Kullerud (26).

nickel presented in Figures 1 to 8 and in the comments pertaining to them, have been compiled in tabular form in Tables 3 and 4, respectively. The footnotes to Table 3 refer to the type of thermal stability being described. The references in Table 4 refer to the source of data for the compositional ranges of these compounds. Although these values vary, depending on experimental conditions, they do indicate the general stability of the compounds concerned.

ANALYSES

The various products obtained in the present study were not analysed as extensively as were ZnS (2) and the sulphides of cobalt, iron, and nickel (3); however, X-ray diffraction analyses have been indispensable for the identification of the phases present and are reported in context. Other physical analyses were used to solve specific problems. The use of the chemical method of oxidation of the products to oxides and the subsequent reduction to metallic state, which was successfully used in (1) and (2) to determine the composition of the products, was found not to be applicable to arsenides.

The various types of analysis performed in the laboratories of the Mineral Sciences Division, Mines Branch, are detailed in Table 5.

SOURCES OF MATERIALS

No commercial sources of cobalt, iron, and nickel arsenides or sulpharsenides were used in this study; therefore, all the arsenides and sulpharsenides used in the growth procedures were synthesized by the author by a direct union of the elements.

The source and the manufacturers' quoted purity of the elements used in the preparation and/or crystal-growth of the arsenides and sulpharsenides are shown in Table 6. The semi-quantitative spectrochemical analyses of the powder samples of cobalt and nickel, the millings

TABLE 3

Stability Range of Various Arsenides and Sulpharsenides

Formula	Mineral Name	Stability Range (°C)
α-Co_2As	---	R. T. -(400-500)(c)
β-Co_2As	---	(400-500) - 958 (d)
α-$CoAs$	Modderite	R. T. - 950 (c)
β-$CoAs$	Modderite	950 - 1180 (d)
$CoAs_2$	Safflorite	R. T. - $<$ 900 (a)
$(Co_{0.5}Fe_{0.5})As_2$	Safflorite	R. T. - $<$ 800 (a)
$CoAs_3$	Cobaltian Skutterudite	R. T. - $<$ 800 (a)
$FeAs$	Arseneisen	R. T. - 1030 (b)
$FeAs_2$	Loellingite	R. T. - $<$ 700 (a)
$NiAs$	Niccolite	R. T. - 970 (b)
α-$NiAs_2$	Pararammelsbergite	R. T. - 590 (c)
β-$NiAs_2$	Rammelsbergite	590 - $<$ 700 (e)
$Co_{0.8}Ni_{0.2}As$	Langisite	Not given
$CoAsS$	Cobaltite	R. T. - $<$ 850 (a)
$FeAsS$	Arsenopyrite	R. T. - 500 (a)
$NiAsS$	Gersdorffite	R. T. - $<$ 700 (a)

Note: R. T. = Room Temperature
(a) = Disproportionation
(b) = Melting Point
(c) = Transition
(d) = Transition (lower temperature) to Melting Point (higher temperature)
(e) = Transition (lower temperature) to Disproportionation (higher temperature)

TABLE 4

Compositional Range for Various Arsenides and Sulpharsenides

Mineral Name	Compositional Range	Reference
α-Co_2As	Stoichiometric	7
β-Co_2As	Stoichiometric	7
α-Modderite	Stoichiometric	7
β-Modderite	Stoichiometric	7
Safflorite (iron-and nickel-free)	$Co_{1.98}$ to $CoAs_{1.99}$	11
Safflorite (nickel-free)	$CoAs_2$ to $\sim Co_{0.8}Fe_{0.2}As_2$ (a)	20
	$\sim Co_{0.8}Fe_{0.2}As_2$ to $Co_{0.03}Fe_{0.97}As_2$ (b)	20
Skutterudite	$CoAs_{2.94}$ to $CoAs_{2.96}$	12
Arseneisen	Stoichiometric	7
Loellingite	$FeAs_2$ to $FeAs_{1.93}$	7
Niccolite	$NiAs$ to $Ni_{0.95}As$	17
Pararammelsbergite	Stoichiometric	10
Rammelsbergite	Stoichiometric	10, 11
Langisite	$Co_{0.84}Ni_{0.16}As_{1.04}$	16
Cobaltite	Stoichiometric	27
Arsenopyrite	$FeAs_{1.1}S_{0.9}$	14
Gersdorffite	$NiAs_{1.77}S_{0.23}$ to $NiAs_{0.77}S_{1.23}$	15

Note: (a) = Monoclinic structure

(b) = Orthorhombic structure

TABLE 5

Methods of Analysis of Cobalt, Iron, and Nickel Arsenides and Sulpharsenides at the Mineral Sciences Division Laboratories

Method of Analysis	Analyst
Chemical	The present author
Electron Microprobe	Dr. D.C. Harris Mr. D.R. Owens Mr. P.E. Porteous
Measurement of Interfacial Angles of the Crystals	Dr. E.H. Nickel
Semi-Quantitative Spectrochemical	Mr. G.L. Mason Mr. D.P. Palombo
X-Ray Diffraction (Powder)	Mr. E.J. Murray Mr. J.M. Stewart
X-Ray Fluorescence	Mrs. D.J. Reed
X-Ray Precession Diffraction Patterns	Dr. E.J. Gabe Mr. J.M. Stewart

Note: The above-mentioned personnel were all members of the staff of the Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, at the time of their involvement with this project.

of iron, and of arsenic crystals are shown in Table 7a. These results show that the main impurity in the cobalt and nickel is a little iron and that the iron millings and the arsenic crystals are of good quality except for the oxygen content which is not detectable by this means of analysis. The analyses of the high-purity sulfur are shown in Table 7b.

The powder samples of cobalt and nickel were used in the early experiments and the high-purity wire materials, obtained from Koch-Light, were used in the later ones.

PURIFICATION OF SOME ELEMENTS

(a) Metal powders

The following metal powders were purified by a hydrogen reduction to remove oxygen:

1. Cobalt powder (Fisher Scientific).
2. Iron millings (British Chemical Standards).
3. Nickel powder (Sherritt Gordon).

The results are shown in Table 8.

(b) Arsenic crystals

Freshly-reduced arsenic metal is re-oxidized when exposed to atmospheric conditions, as shown in Figure 9; three separate portions of arsenic were studied at different times. It appears that, after a period of about fifteen days, the black oxide film has become thick enough to retard further oxidation. The variation in the three curves is probably due to the size of the particles of arsenic composing the samples. After thirteen days, the average gain in sample weight was 1.3 per cent.

The purification of the arsenic used in the present study was made by one of two main methods.

(Continued on page 28)-

TABLE 6

The Source and Purity of the Elements Used in Synthesis and in Crystal Growth

Element or Compound	Physical Form	Source	% Purity (Suppliers' Data)
Co	Powder	Fisher	None given (b)
Co	Plate	---	99.9
Co	Wire	Koch-Light	99.99
Fe	Millings	British Chemical Standard	~99.93 (a) (b)
Ni	Powder	Sherritt Gordon	~99.5 (a) (b)
Ni	Wire	Koch-Light	99.99
S	Powder	ASARCO	99.999 (c)
As	Crystal	Fisher	None given (b)
I_2	Crystal	Anachemia	~99.9 (a)

Note:
(a) = Derived by subtracting the total quoted impurities from 100 per cent.
(b) = Additional analyses are in Table 7a.
(c) = Additional analyses are in Table 7b.

TABLE 7a

Semi-Quantitative Spectrochemical Analyses of Some Elements

Element or Compound	Physical Form	Semi-Quantitative Spectrochemical Analysis (% by weight)						
		Mn	Si	Fe	Mg	Cu	Ni	Co
Co	Powder	0.01	N.D.	0.2	N.D.	N.D.	N.D.	P.C.(a)
Fe	Millings	0.03	0.07	P.C.	0.1	N.D.	N.D.	N.D.(a)
Ni	Powder	N.D.	N.D.	0.4	N.D.	0.03	P.C.	N.D.(a)
As	Crystal	N.D.	N.D.	N.D.	0.01	0.006	N.D.	N.D.(b)

Note:
N.D. = Not detectable
P.C. = Principal constituent
(a) = Internal Report MS-AC 71-126
(b) = Internal Report MS-AC 71-211; in addition to the above elements, the following elements were reported as being not detectable by spectrographic means: Ba, B, P, Hg, Sb, Ge, W, Pb, Sn, Cr, Ga, Nb, Ta, Bi, Al, V, Sr, Zr, Ti, Zn, Na, Ag, In, Mo, Ca and Be.

NOTE: Recently, a second bottle of arsenic crystals was submitted for analysis. Internal Report MS-SC 72-235 indicated some 13 elements were present in varying minor amounts; therefore, this bottle of arsenic will require a purification before being used.

TABLE 7b

Analyses of Special High-Purity "ASARCO" Sulphur*

Source of Analysis	Na	Cl	Mg	Cu	O_2
			(In ppm)		
ASARCO (a)	1	1	N.D.	-	-
Mineral Sciences Division	N.D. (b)	-	80 (b)	400 (b)	55 (c)

*Special high-purity sulphur obtained from American Smelting and Refining Company (ASARCO). This sulphur was labelled 99.999 + per cent, Lot 5-64-1.

Note: (a) = 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.

(b) = 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, In, Ca, V, Zr, Ti, Ni, Co, Sr.

NOTE: 400 ppm Cu (0.04 per cent) is a somewhat high figure in view of the 99.999 per cent purity of this sulphur, claimed by the manufacturer.

(c) = Neutron-activation analysis, Internal Report MS-AC 68-642, from Mr. C. McMahon, Spectrochemistry Group, Mineral Sciences Division.

TABLE 8

Hydrogen Reduction of Metal Powders to Remove Oxygen

Metal	Temperature (°C)	Time (min)	$\%O_2$ (calc.) (a)
Cobalt	650	90	0.17
Iron	800	120	0.16
Iron	900	120	0.18
Nickel	900	90	0.19

Note: (a) = Calculated from weight loss.

The above value for oxygen in the nickel powder agrees with the value of 0.19 per cent obtained by Sherritt Gordon.

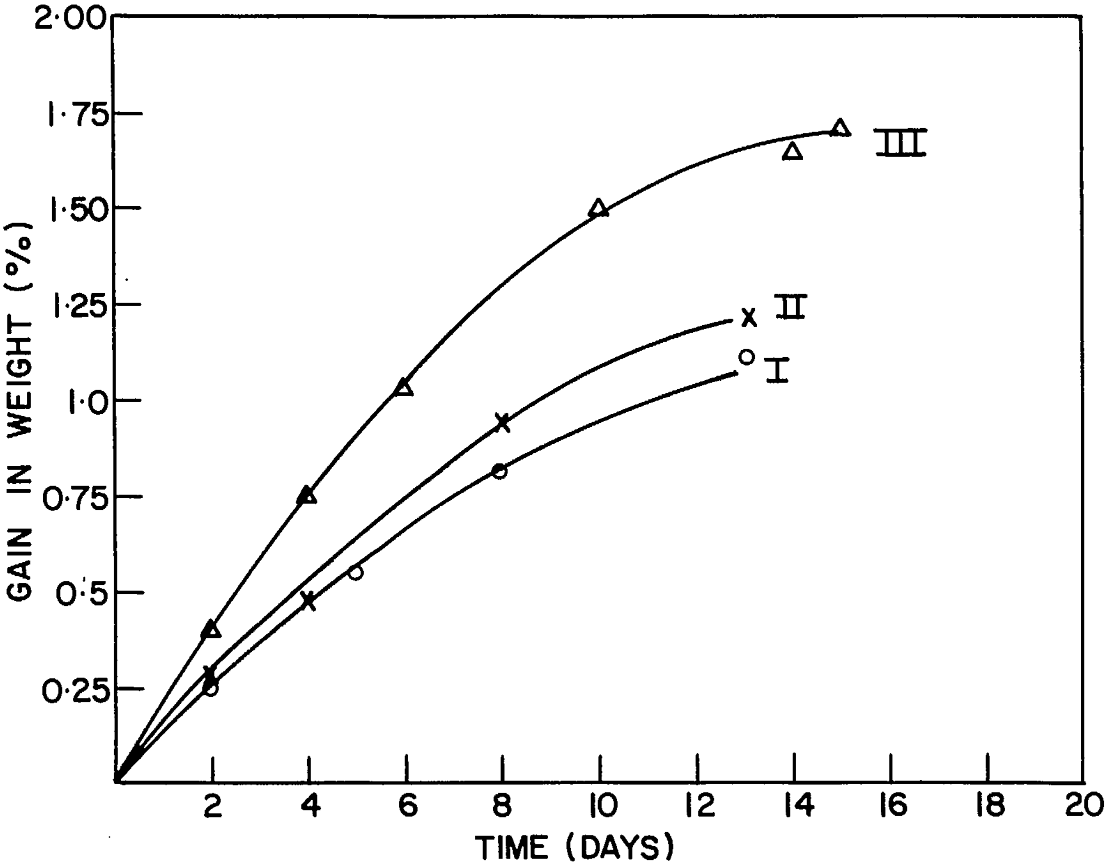

Figure 9. - The Re-oxidation of Freshly-Reduced Arsenic Metal on Exposure to Atmospheric Conditions.

(i) Distillation from a Lead-Arsenic Solution

This method was one of ten procedures described by Blum (6) in a review paper as being suitable for the purification of arsenic. Originally, this method was reported by Harman, Stambaugh, and Goering in a paper delivered to the Electrochemical Society, in Cleveland in 1956. The crude arsenic and twice its weight of high-purity lead are sealed in an evacuated quartz tube; the tube is heated at about 600°C for several hours to achieve solution; then the tube is re-positioned in the furnace to permit the arsenic to distil to the colder part of the tube.

The above method was tried once in the present study and a good-looking boule of arsenic was obtained. The recovery was 96.4 per cent of the starting weight.

(ii) Sublimation of the Arsenic Oxides from Arsenic

Blum (6) described two methods of purification, one based on the vacuum sublimation of arsenic and the other on the sublimation of arsenic in a hydrogen atmosphere. In both of these methods, the arsenic trioxide and trisulphide, which are more volatile than arsenic, are sublimed to a colder zone than that in which the arsenic condenses.

In the present study, a modification of this principle was used. The furnace temperature was controlled so that the arsenic trioxide and trisulphide would sublime from the arsenic, which was recovered in the reaction boat. There is no doubt that, as temperatures approaching 400°C were used, some of the arsenic was also sublimed, but this was considered to be minimal. The reaction boat, containing the crude arsenic, was placed in a process tube and heated in one of three flowing gas atmospheres: argon, helium, or hydrogen. Temperatures in the range of 280 to 400°C, the majority being 300°C, were used over one- to two-hour periods.

The recovery of arsenic from this procedure is shown in Table 9. The variation in these results is attributed, in part, to the size of arsenic particles, i.e., the surface area of the arsenic and, in part, to the sublimation of arsenic, which is assumed to be approximately one per cent.

TABLE 9

Recovery of Arsenic from Method (ii)

Gas Atmosphere (Flowing)	Recovery of Arsenic (a) (%)	Number of Determinations
Argon	94.08 ± 1.92	2
Helium	95.73 ± 1.45	12
Hydrogen	94.62 ± 1.97	4

Note: (a) = Based on the starting weight of crude arsenic.

The purified arsenic obtained from the above method was used immediately in the preparation and the growth experiments.

PREPARATION OF ARSENIDE AND SULPHARSENIDE MATERIAL

The preparation of some arsenides and some sulpharsenides has been accomplished by two main methods:

(i) direct combination of the elements, which has been achieved by several variations of the heating procedure, has produced some desirable products; however, this procedure usually yields a cluster of very small single crystals;

(ii) special crystal-growth procedures, of which the most widely used has been the chemical vapour transport technique using iodine as the carrier; larger crystals are usually obtained by this technique.

These methods of preparing arsenides and sulpharsenides will be dealt with separately. The former, the direct-combination preparation from the elements, will be dealt with in this section; and the latter, the various crystal-growth procedures, will be discussed later in this report (see page 55).

(a) Previous Syntheses by Direct Combination of the Elements

The synthesis of the arsenides and sulpharsenides of cobalt, iron, and nickel has been achieved by several researchers, and some useful references pertaining to previous studies, in which arsenides or sulpharsenides were prepared by direct combination of the elements, are shown in Table 10.

The basic procedure has been to seal the desired amounts of the elements in evacuated Pyrex or quartz capsules (depending on the temperatures used) and to heat them at optimium temperatures. Besides the above-mentioned glass capsules, Yund (8, 15) and Clark (14) used a second type of reaction vessel; it was a collapsible gold capsule the use of which eliminated the vapour phase in their preparations through the use of external water pressures as high as 2000 bars.

The monoarsenides are the easiest of all the arsenides to prepare and are stable to higher temperatures. The higher arsenides are more difficult to prepare because the reaction of arsenic vapour with solid metal particles tends to form an impervious coating of higher arsenides around a core of lower arsenides (9, 10, 11 and 12). This condition causes two problems: (i) it may preclude the reaction of all the arsenic with the metal and (ii) the reaction yields a product that is not homogeneous. The remedy for these problems has been to grind the intermediate product and reheat; this treatment has often been repeated several times.

Holmes (9) and Roseboom (11, 12) used a modification of the sealed-tube technique, a tube-in-tube system - the powdered metal being placed in a small capsule which has an orifice and is sealed inside a larger capsule that contained the arsenic. The arsenic vapour is able to come into contact with the metal but the excess arsenic is separated from the product. Unfortunately this technique does not prevent impervious coating of the core material; therefore, regrinding and reheating are often required.

The preparation of the sulpharsenides presents some problems distinct from those presented by the arsenides. Clark (14) has stated that the composition of arsenopyrite (approximately $FeAs_{1.1}S_{0.9}$)- in coexistence with liquid, arsenic, and vapour - is fixed at any given temperature. It is impossible to prepare pure arsenopyrite directly from a charge having the same bulk composition as the desired arsenopyrite.

Gersdorffite has been found by Yund (15) to be a solid solution of arsenic-rich $Ni(\underline{As}, S)$ and sulphur-rich $Ni(As, \underline{S})$ between the limits $NiAs_{1.77}S_{0.23}$ and $NiAs_{0.77}S_{1.23}$. A vapour is present over all concentrations of $NiAs_xS_{2-x}$ at temperatures above approximately 200°C. The compositions near the end members required a long period of heating (750 days) to ensure complete reaction.

TABLE 10

References to Previous Direct-Combination Preparations of Cobalt, Iron, and Nickel Arsenides and Sulpharsenides

Formulae	References	
Co_2As, CoAs	Heyding and Calvert	(7)
NiAs	Heyding and Calvert	(17)
CoAs, FeAs, NiAs	Remen, Nemoitin and Vaisburd	(28)
NiAs, $NiAs_2$	Yund	(8)
$FeAs_2$, $NiAs_2$, $CoAs_3$	Holmes	(9)
$Fe(Fe_xAs_{2-x})$, $CoAs_2$, $NiAs_2$, $CoAs_3$ (a)	Heyding and Calvert	(10)
$CoAs_2$, $FeAs_2$, $NiAs_2$, $(Co,Fe,Ni)As_2$	Roseboom	(11)
$CoAs_3$, $(Co,Fe,Ni)As_{3-x}$	Roseboom	(12)
CoAsS	None Available	----
FeAsS	Clark	(14)
NiAsS	Yund	(15)

Note: (a) = Heyding and Calvert (10), in discussing $Fe(Fe_xAs_{2-x})$, stated that x is probably equal to 0.04, and that some of the iron atoms are occupying arsenic lattice sites.

(b) Present Syntheses of Arsenides

(i) Direct Combination of the Elements

In the present study, the procedure involved the use of quartz capsules fashioned from tubing with a wall thickness of one millimetre and an inside diameter of either eleven or fourteen millimetres. The sealed capsules were usually fifteen centimetres long.

In the early experiments, freshly-reduced metal powders were used, but, in the later work, high-purity cobalt wire and nickel wire from Koch-Light were used. Throughout the study, the arsenic was purified immediately before use.

The preparative procedure has been to weight out stoichiometric amounts of the metal(s) and arsenic to yield the sought-after arsenide and to place them in a quartz capsule which was then evacuated to 10^{-4} mm Hg pressure and sealed.

The capsules were placed in a furnace so as to take advantage of its temperature profile to ensure that the colder end of the tube contained the metal-arsenic charge.

Most of the products were analysed by X-ray powder diffraction procedures. The patterns obtained were compared with the A.S.T.M. file of X-ray powder diffraction patterns and, in order to clarify some of the results, the A.S.T.M. card numbers are listed as references (33) through to (57); these will be used in the text and in the tables.

The conditions used for the direct combination of cobalt, iron, and nickel with arsenic are detailed in Table 11. The X-ray diffraction analyses of many of the products are recorded in Table 12.

It should be pointed out here that the prime interest in the direct preparation of arsenides and sulpharsenides has been to provide a source of nutrient material for crystal-growing experiments. Therefore, not all products were analysed, once the type of results that could be expected had been established from the earlier preparations; the products in the later preparations were utilized in growth precedures without being analysed.

(Continued on page 38)-

TABLE 11

Conditions Used for Direct Combination of Cobalt, Iron, and Nickel with Arsenic

Experiment Number	Metal	Metal:Arsenic Ratio	Temperature (°C)	Time (days)	Calculated Product
570	Cobalt	2:1	900	1	Co_2As
555	Cobalt	1:1	650	8	$CoAs$
529	Cobalt	1:2	680	6	$CoAs_2$
535	Cobalt	1:2	680	4	$CoAs_2$
554	Cobalt	1:2	700	9	$CoAs_2$
655	Cobalt	1:2	770	6	$CoAs_2$
677	#655 was ground and reheated		900	11	$CoAs_2$
543	Cobalt	1:3	630	23	$CoAs_3$
371	Iron	1:1	500	6	$FeAs$
556	Iron	1:1	1060 (melted)	1	$FeAs$
510	Iron	1:2	650	13	$FeAs_2$

(Continued on page 36)

TABLE 12

X-Ray Diffraction Analyses of the Two-Component Arsenides Described in Table 11

Experiment Number	Calculated Product	Phases Present	X-Ray Diffraction Report No.
570	Co_2As	α-Co_2As and a trace of unidentified "A"	69-444
555	CoAs	Major = α-Co_2As Minor = Skutterudite Trace of unidentified "A"	69-438
529	$CoAs_2$	Not analysed, tube not opened	--
535	$CoAs_2$	Not analysed, used in #538	--
554	$CoAs_2$	Transported = not analysed but assumed to be arsenic metal Untransported = Skutterudite (a = 8.20 Å)	-- 69-422
655	$CoAs_2$	Metallic portion = α-Co_2As and unidentified "A" Black powder = Skutterudite (a = 8.20 Å)	70-188 70-189
677	$CoAs_2$	$CoAs_2$ (37)	70-231
543	$CoAs_3$	Transported = Arsenic Untransported = Skutterudite (a = 8.19 Å)	69-392 72-359
371	FeAs	FeAs, Loellingite and possibly some α-Fe	69-110
556	FeAs	Not analysed, used in #807	--
510	$FeAs_2$	Not analysed, used in #524	--

Note: The unidentified "A" in #570 and in #555 have the same X-ray diffraction pattern.

(Continued on page 37) -

TABLE 11 (Concluded)

Experiment Number	Metal	Metal:Arsenic Ratio	Temperature (°C)	Time (days)	Calculated Product
412	Iron	1:2	430	4	$FeAs_2$
557	Iron	1:2	690	8	$FeAs_2$
574	Iron	1:2	840	4	$FeAs_2$
541	Nickel	1:1	950	1	NiAs
528	Nickel	1:2	700	16	$NiAs_2$
886	Nickel	1:2	800	2	$NiAs_2$

TABLE 12 (Concluded)

Experiment Number	Calculated Product	Phases Present	X-Ray Diffraction Report No.
412	$FeAs_2$	Not analysed, tube ruined	--
557	$FeAs_2$	Transported = Arsenic Untransported = Loellingite	69-374 69-373
574	$FeAs_2$	Not analysed, used in #575	--
541	NiAs	Niccolite	69-582
528	$NiAs_2$	Not analysed, used in #550	--
886	$NiAs_2$	Not analysed, used in #920	--

The X-ray diffraction analysis confirmed that, in some cases, chemical equilibrium had not been achieved. The remedial treatment generally used [(7) (9) (10) (11) (12) and (17)] was to grind the intermediate product and to reheat the sample. However, because some loss of material invariably occurs during grinding and handling which would cause a change in stoichiometry, this technique was not often used in the present study. A comparison of the results obtained in #655 and #677 (see Table 12) indicates that grinding certainly speeded up the achievement of chemical equilibrium in the $CoAs_2$ preparation.

A more detailed study of the results obtained in the preparation of cobalt arsenides indicates:

(1) α-Co_2As was not prepared in a pure form; a trace of an unidentified material was also present;

(2) CoAs was not obtained in any of the experiments;

(3) the skutterudite pattern (38) was obtained, along with either arsenic or α-Co_2As, in a number of cases; the materials balance in #543 and in #554 indicated that the untransported residues had a calculated gross composition of $CoAs_{2.91}$ and $CoAs_{1.89}$, respectively and had "a" values of 8.19 A and 8.20 A, respectively—this behaviour of skutterudite of showing a variable composition along with essentially constant "a" values was observed by Holmes (9); however, Roseboom (12) found that synthetic cobalt skutterudite did exhibit a small arsenic deficiency (even in the presence of crystalline arsenic), which was too slight to account for the analyses of naturally-occurring skutterudites.

The preparation of the iron and nickel arsenides showed the following results:

(1) FeAs had not achieved chemical equilibrium, whereas the NiAs was uniform in composition;

(2) neither $FeAs_2$ nor $NiAs_2$ was formed with stoichiometric compositions, excess arsenic being present after the heating period in all cases.

(ii) Melt-and-Anneal Procedure

This procedure, which was useful in the preparation of some sulphides (3), was tried in the preparation of some arsenides.

The technique involves the heating of the charge of metal and the chosen amount of arsenic until the intermediate product melts, and then annealing at a temperature lower than the melting point of the intermediate product to complete the reaction of this material with the balance of the arsenic.

The conditions used for the melt-and-anneal combination of cobalt, iron, and nickel with arsenic are detailed in Table 13. The X-ray diffraction analyses of the products are recorded in Table 14.

The preparation of four arsenides was attempted by this procedure: CoAs, $CoAs_2$, $FeAs_2$, and $NiAs_2$. In all cases, a button of the intermediate product and crystals arsenic were obtained. The annealing produced two types of results:

(1) in the case of CoAs, the annealing quickly yielded an uniform-appearing solid button and no residual arsenic; however, the X-ray diffraction and electron microprobe analyses (See Tables 14 and 34) showed the product to be a mixture of CoAs with some $CoAs_2$ and Co_2As;

(2) in each of the three diarsenide preparations, the intermediate buttons became brittle on annealing and soon were easily crumbled by shaking the capsule; however, even after extensive heating periods, residual arsenic was still present in the $FeAs_2$ and $NiAs_2$ preparations.

Disproportionation of the $FeAs_2$ and $NiAs_2$ was considered to be the reason for the incomplete reaction. The original capsules were opened and the gross composition of the intermediate products were found to be $FeAs_{1.25}$ and $NiAs_{1.10}$, respectively. These intermediate products and the corresponding unreacted arsenic were returned to their capsules and, before resealing, sealed inserts were placed within the capsules to reduce the free space. Additional annealing failed to accomplish complete reaction but the gross composition of the intermediate products had changed to $FeAs_{1.30}$ and $NiAs_{1.28}$, respectively.

An alternative procedure was then tried with the intermediate, $NiAs_{1.28}$: it was resealed, along with sealed inserts, in a capsule with the unreacted arsenic plus a little extra arsenic, to ensure an excess over the 1 : 2 ratio; the charge was not melted but was annealed at 590°C for 14 days. The resulting intermediate product had a gross composition of $NiAs_{1.38}$ and was composed of particles that had three degrees of hardness: easy to crush, moderately hard to crush, and very difficult to crush. The X-ray diffraction analyses of these materials showed that the softest and the slightly harder material consisted of a mixture of diarsenides, and that the hardest material contained maucherite ($Ni_{11}As_8$) and niccolite (NiAs).

The above results indicate that the direct combination of the elements to form arsenides is easiest with cobalt-arsenic compounds and most difficult with nickel-arsenic compounds. The ease of formation of the higher arsenides decreases as the arsenic content increases. In all cases, in order to achieve faster chemical equilibrium, it is evident that the intermediate products should be ground and reheated with the unreacted arsenic.

(c) Present Syntheses of Sulpharsenides

(i) Direct Combination of the Elements

The procedure used to prepare the sulpharsenides was similar to that described for the arsenides. Specific amounts of the selected metal (Co or Fe or Ni), along with calculated amounts of arsenic and sulphur, were sealed in evacuated quartz capsules and heated to yield the desired sulpharsenide. In some cases, excess arsenic and/or sulphur was added to the charge.

It is well known that arsenic and sulphur react to form two sulphides, As_2S_2 and As_2S_3; therefore, they will probably form intermediate compounds in the sulpharsenide preparation. The phase diagram (Figure 10) for the arsenic-sulphur system, as given by Hensen and Anderko (4), shows that the melting points for As_2S_2 and As_2S_3 are 321°C and 310°C, respectively. These sulphides are between orange and reddish orange in colour, depending

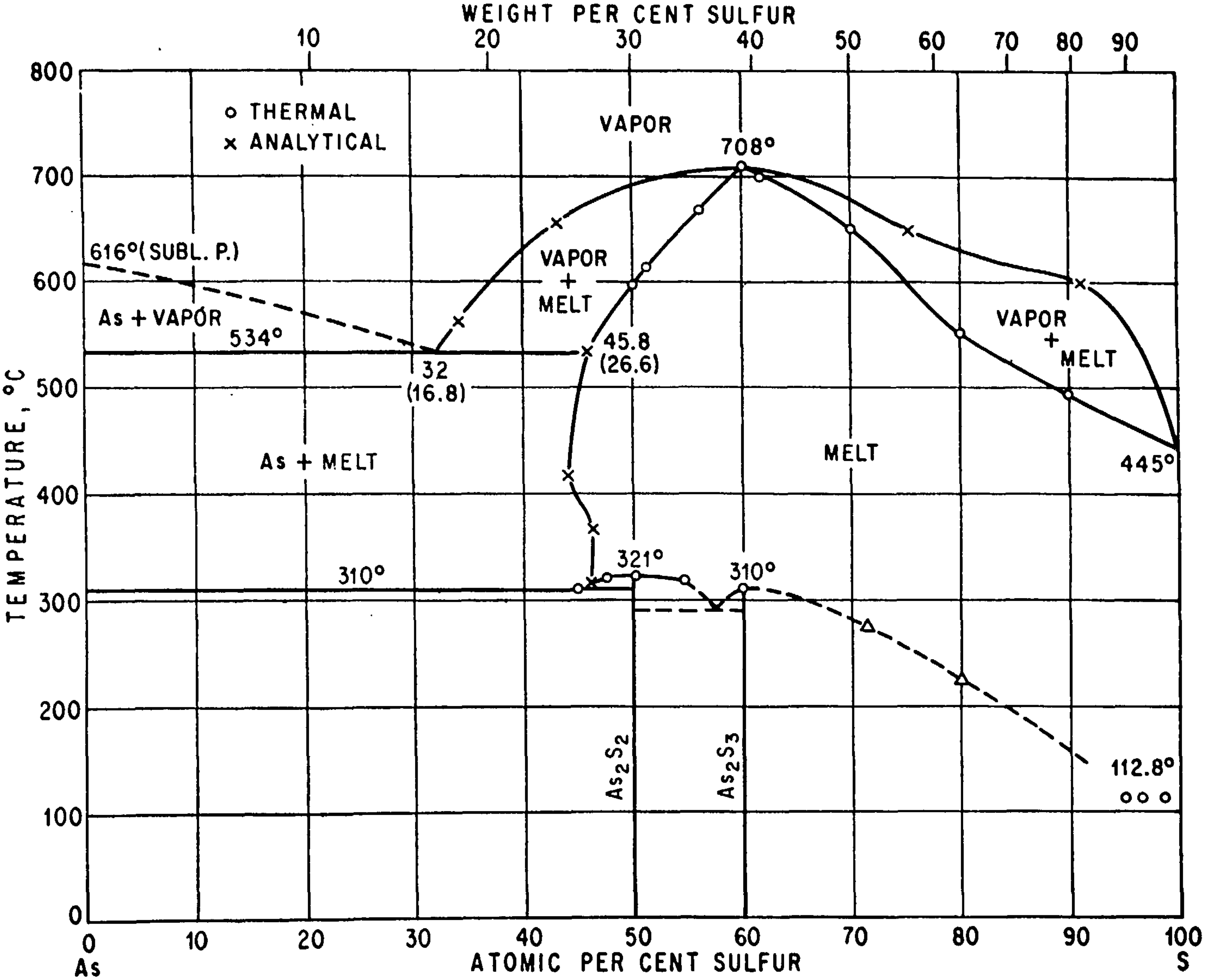

Figure 10. - Phase Diagram of the Arsenic-Sulphur System According to Hansen and Anderko (4).

TABLE 13

Conditions Used for the Preparation of Two-Component Arsenides by Melting and Annealing

Experiment Number	Metal	Metal:Arsenic Ratio	Melting Temperature (°C)	Annealing Temperature (°C)	Time (days)
888	Cobalt	1 : 1	1120	900	1
913	Cobalt	1 : 2	1200	650	3
911	Iron	1 : 2	1050	600→325 (a)	14
				400 (b)	20
912	Nickel	1 : 2	950	600→325 (a)	14
				400 (b)	20
921	Product from #912 and some additional (excess) arsenic.		Not re-melted	590	14

Note: (a) = The annealing temperature was lowered from 600°C to 325°C stepwise over 14 days.

(b) = The original ampoules were opened and the composition of the partly-reacted product was determined; then the total material (MAs_x and unreacted As) was re-sealed in a new ampoule and annealed at 400°C for an additional 20 days.

TABLE 14

X-Ray Diffraction Analyses of the Two-Component Arsenides Described in Table 13

Experiment Number	Phases Present	X-Ray Diffraction Report No.
888	CoAs (36) and minor of CoAs$_2$ (37) (e)	72-152
913	Skutterudite (38) ($a = 8.20\,\text{Å}$) and possibly a sl. minor of Co$_2$As	72-337
911 (a)	Transported = Arsenic Untransported = Unidentified material	72-335 72-336
912	Not Analysed	--
921 (b)	Rammelsbergite (45) and (NiAs$_2$) 12C (55)	72-358
921 (c)	Rammelsbergite (45) and Pararammelsbergite (46) and possibly (NiAs$_2$) 12C (55)	72-360
921 (d)	Maucherite (43) and Niccolite (44)	72-361

Note: (a) = The analysis was made on a crushed (uniform) product from the second annealing treatment.

(b), (c), and (d) = The product was composed of bead-like particles of various hardnesses between soft in (b) to very hard in (d).

(e) = See Table 34 for additional analyses.

on their composition and on their degree of crystallinity. It is assumed that the rapid cooling of molten As_2S_2 and/or As_2S_3 to room temperature would result in poorly-crystallized material which would give a very weak pattern in X-ray diffraction analysis; this may explain the nature of some of the unidentified material in Table 16.

The conditions used for the direct combination of cobalt, or iron, or nickel with arsenic and sulphur are detailed in Table 15. The X-ray diffraction analyses of several of the products are recorded in Table 16.

The rates of formation of the sulpharsenides are very slow; this is due, in part, to their decomposition temperatures being in the same range as the temperatures required to prepare these compounds.

It was stated on page 15 that Strathdee and Pidgeon (13) reported that arsenopyrite (FeAsS) starts to decompose at 500°C into arsenic and pyrrhotite ($Fe_{1-x}S$); if pyrite (FeS_2) were present it also would decompose, and the liberated sulphur and arsenic would combine to form the reddish orange condensate of As_2S_2.

A reddish orange condensate was encountered in the preparation of all three sulpharsenides, shown in Tables 15 and 16; in all cases, the X-ray diffraction analysis failed to identify it for reasons given above. It is obvious from Figure 10 that the composition of the condensate may well be $As_2S_{2\pm x}$; but, for the sake of simplicity, any reddish orange condensate obtained in the preparational experiments of sulpharsenides will arbitrarily be referred to as As_2S_2.

Seven attempts were made to prepare cobaltite (CoAsS), from three different ratios of the elements.

(1) Five experiments involved the elements in the ratio of 1:1:1. In #547, it was observed that a reaction temperature of 500°C was too low; also that some As_2S_2 was present at the conclusion of the experiment. In #370 and #536, the reactions appeared to have gone to completion; this is attributed to the use of cobalt powder, whereas, in #566 and #899, the incomplete reaction is assumed to be due to the different starting form of the cobalt used in these experiments, which were millings and wire, respectively. Some As_2S_2 was also present in these last two experiments.

(2) The use of excess arsenic in #585 did not eliminate the As_2S_2 formation.

(3) The technique of crushing the intermediate product and reheating was applied to #899. After six days, 46 per cent of the available (arsenic + sulphur) had reacted; after an additional nine days of heating the crushed product, 74 per cent of the available (arsenic + sulphur) had reacted. Although the experiment was terminated at this point, the results indicate that this technique could be expected to yield CoAsS if it were repeated several times.

(4) The use of CoS and arsenic as the nutrients in #564 did not appear to offer any advantage over the tri-element nutrient; As_2S_2 was formed during the reaction.

Five different approaches were tried in the preparation of arsenopyrite.

(1) The reaction temperature (400°C), in #508, appears to have been too low; some As_2S_2 was present at the end of the heating period.

(2) The use of excess As_2S_2 in #545 did not appear to be helpful.

(3) The use of a slight excess of arsenic in #586 gave a product that was assumed to be mixture of FeAsS and FeS (based on the fact that the transported material appeared to be only arsenic).

(4) The use of a large excess of arsenic in #654 did not eliminate, but did lessen, the concentration of As_2S_2 present.

(5) Sealed inserts were placed in the reaction capsule of #546 to minimize the free space; although this technique appears to be helpful, some unreacted arsenic was still present after 37 days of heating.

Two experiments were tried in the preparation of gersdorffite.

(1) Although the reaction temperature in #567 was only 400°C, some NiAsS (50) had formed along with NiAs and some As_2S_2.

(2) The technique of crushing the intermediate product and reheating was applied to #898. After six days, 48 per cent of the available (arsenic + sulphur) had reacted; after an additional nine days of heating the crushed product, 73 per cent of the available (arsenic + sulphur) had reacted.

(Continued on page 50)-

TABLE 15

Conditions Used for Direct Combination of the Sulpharsenides of Cobalt, Iron, and Nickel

Experiment Number	Nutrient	Temperature (°C)	Time (days)	Calculated Product (s)
370	Co, As, and S (1:1:1)	700	8	CoAsS
536	Co, As, and S (1:1:1)	650	3	CoAsS
547	Co, As, and S (1:1:1)	500	31	CoAsS
564	CoS and As (1:1)	500	35	CoAsS
566	Co, As, and S (1:1:1)	750	5	CoAsS
899	Co, As, and S (1:1:1)	650	6	
		700 (a)	9	CoAsS
585	CoAsS from #564 and As (1:0.07)	500	11	CoAsS and As
508	FeAs from #371 and S (1:1)	400	17	FeAsS
545	Fe, As, and S (1:1.1:1.1)	560	6	FeAsS and some As_2S_2
546 (b)	Fe, As, and S (1:1:1)	520	37	FeAsS

Note: (a) = After six days, the capsule was opened and the intermediate product was crushed and re-sealed for additional heating.

(b) = Sealed quartz capsules were used as inserts to minimize the free volume of the reaction capsule.

(Continued on page 48) -

TABLE 16

X-Ray Diffraction Analyses of the Sulpharsenides of Cobalt, Iron, and Nickel Described in Table 15

Experiment Number	Phases Present	X-Ray Diffraction Report No.
370	White material: CoAsS (49) Grey material : CoAsS (49) and a slight trace of unidentified material	68-0635 68-0635
536	Not opened	--
547	Transported : Unidentified material Untransported: CoAsS and Unidentified (but of the CoAs or CoS type, ?)	69-462 69-464
564	Not Analysed, used in #585	--
566	Not opened	--
899	Not analysed, used in #907	--
585	Shiny material: Similar to Co_4S_3 (56) Grey fines: $CoAs_3$ (38)	69-565 69-566
508	Not Analysed, used in #523	--
545	Not Analysed, used in #549	--
546	Transported: Arsenic Untransported: Major: Unidentified (similar to FeAsS but not close enough for identification) Minor: Pyrrhotite	69-500 69-501

(Continued on page 49) -

TABLE 15 (Concluded)

Experiment Number	Nutrient	Temperature (°C)	Time (days)	Calculated Product (s)
586	Fe, As, and S (1:1.08:1)	510	12	FeAsS and As
654	$FeS_{1.002}$ and As (1:2)	630	13	FeAsS and As
567	Ni, As, and S (1:1:1)	400	24	NiAsS
898	Ni, As, and S (1:1:1)	600	6	--
		600 (a)	9	NiAsS

<u>Note</u>: (a) = After six days, the capsule was opened and the intermediate product was crushed and re-sealed for additional heating.

TABLE 16 (Concluded)

Experiment Number	Phases Present	X-Ray Diffraction Report No.
586	Not Analysed	--
654	Not opened	--
567	Untransported: Shiny material - Unidentified	69-488
	Greyish material - NiAsS and NiAs	69-489
898	Not analysed, used in #906	--

These results parallel the results obtained with cobaltite and, as in that case, it is expected that this technique could yield NiAsS if it were repeated several times.

A survey of Table 16 and the various comments listed above, indicate that the intermediate product, formed in the preparation of the sulpharsenides from the elements, is composed of some of the sulpharsenide along with sulphide, an arsenide, and arsenic sulphide. The actual composition and concentration of these three compounds differ with each of the three metals (Co, Fe, Ni). Also, it appears that the sulphide, arsenide, and the arsenic sulphide are reacting slowly to form sulpharsenide.

(ii) Melting under Encapsulation

It was assumed that, if the direct combination of the elements to form sulpharsenides was restricted to as small a space as possible, the reaction would go to completion. A method that is often used to prevent the loss of volatile components from compounds during melting is the technique of Liquid Encapsulation. Usually, an inert liquid (e. g., B_2O_3) is used as a liquid seal over the molten charge; sufficient pressure must be maintained over the liquid B_2O_3 to prevent the volatile components from passing through the liquid seal and escaping.

During the present study, three experiments were attempted, as described in Table 17. In all cases, a quartz test-tube or a capsule was used; it was found that these vessels were shattered on cooling. In addition, it was found that the liquid encapsulation, under a helium atmosphere at one atmosphere pressure, failed to prevent the loss of sulphur and/or arsenic sulphide from experiment #682.

(d) Present Syntheses of Three-Component Arsenides

The term three-component arsenides is used here to mean either cobalt-iron or cobalt-nickel arsenides. These arsenides were prepared with some success by two methods.

TABLE 17

Conditions Used for the Attempted Melting of Arsenopyrite Under Liquid Encapsulation

Experiment Number	Nutrient	Temperature (°C)	Time (hr)	B_2O_3 (g)	Pressure (atm.)
663	$FeAs_2$ from #524 and FeS_2 from #611 (1:1)	560	1	4.3390	1 open
678	As in #663	500	3	9.502	1 open
682	Product from #678	710	1.5	16.0393	0.33 at R.T. sealed

Note: In all cases, the reaction tube cracked and shattered on cooling.

The helium at 1 atm did not contain the As_2S_2 or S, in experiment #682.

The B_2O_3 was pre-dried just prior to the experiment in #682.

TABLE 18

Conditions Used for the Preparation of Three-Component Arsenides by Melting

Experiment Number	Nutrient	Melting Temperature (°C)	Calculated Formula
530	Co, Ni, and As (0.8 : 0.2 : 1)	1030 (a)	$Co_{0.8}Ni_{0.2}As$
537	Co, Ni, and As (0.8 : 0.2 : 1)	1170	$Co_{0.8}Ni_{0.2}As$
540	Co, Ni, and As (0.8 : 0.2 : 1)	1150	$Co_{0.8}Ni_{0.2}As$
571	Co, Fe, and As (0.487 : 0.513 : 2.77)	975	$Co_{0.487}Fe_{0.513}As_2$ and As
573	Co, Fe, and As (0.486 : 0.514 : 2.0)	1095	$Co_{0.486}Fe_{0.514}As_2$

Note: (a) = This sample was not melted.

TABLE 19

X-Ray Diffraction Analysed of the Three-Component Arsenides Described in Table 18

Experiment Number	Phases Present	X-Ray Diffraction Report No.
530	Not analysed	--
537	Not analysed	--
540	Similar to langisite (16), but with a few extra unidentified lines present	69-527
571	Transported : assumed to be arsenic	--
	Untransported: similar to safflorite (57) and possibility of safflorite II (21)	69-507
573	Transported : assumed to be arsenic	--
	Untransported: shiny material - safflorite IV (21) and unidentified "A"	69-480
	dull material - loellingite (42) and unidentified "A"	69-481

Note: The unidentified "A" is the same in both portions of #573.

(i) Melting

The conditions used to prepare langisite ($Co_{0.8}Ni_{0.2}As$) and an iron-bearing safflorite ($Co_{0.5}Fe_{0.5}As_2$) are detailed in Table 18. The X-ray diffraction analyses are given in Table 19.

In these preparations, the elements were sealed in an evacuated quartz capsule, heated until melting had occurred, and then cooled.

The product of only one of the three experiments to produce langisite, #540, was analysed by X-ray diffraction analysis; the pattern was found to be similar to one published by Petruk et al (16), but a few extra lines that could not be identified were also observed.

Both preparations of safflorite, #571 and #573, were analysed by X-ray diffraction analysis but the results were inconclusive. In the former sample, the pattern was similar to a safflorite recorded as A.S.T.M. No. 12-575, a cobaltian loellingite containing about 6 per cent cobalt, along with a pattern of a large minor component similar to safflorite II (21); however, A.S.T.M. has recently deleted card No. 12-575. The pattern of the major portion of sample #571 does not agree with the remaining A.S.T.M. standards. The identification of #573 has shown it to be a mixture of arsenic, safflorite IV (21), loellingite (42), and an unidentified material.

The main conclusion obtained from the above results is that, in order to obtain uniform products, these preparational procedures should include a period of annealing.

(ii) Melting and Annealing

This technique was used in the preparation of langisite ($Co_{0.8}Ni_{0.2}As$) and of safflorite ($Co_{0.5}Fe_{0.5}As_2$). The conditions used in the preparation of these compounds are given in Table 20, and X-ray diffraction analyses are shown in Table 21.

The langisite preparation, #914, resulted in a good-looking button. The X-ray diffraction analysis gave a pattern similar to that obtained in #540 (Table 19) including the extra lines except that they are much weaker in the #914 sample. The results of an electron probe analysis will be presented later (see page 95).

The safflorite preparation did not go to completion; some unreacted arsenic was still present after 16 days of annealing. A calculation of the gross compositon of the intermediate product showed it to be $(Co,Fe)As_{1.88}$. The X-ray diffraction analysis showed this product to have segregated. The analysis of a small portion of the sample selected at random indicated that skutterudite was the principal phase, with smaller amounts of safflorite and the possibility of CoAs. However, the analysis of a representative sample, obtained by grinding of the balance of the product, indicated that the principal phase was safflorite I (this safflorite has the highest iron content, see Figure 6) with smaller amounts of skutterudite and the possibility of CoAs.

These results indicate that annealing gave a product that was closer to the sought-after phase than was achieved without it, (compare #573, Table 19, and #915, Table 21); however, a longer annealing time would be required to achieve a single-phased product.

PREPARATION OF ARSENIDES AND SULPHARSENIDES BY GROWTH PROCEDURES

(a) Previous Growth Procedures

The growth of arsenides and sulpharsenides by means of the well-known growth procedures has not been widely explored. Schäfer, in his book "Chemical Transport Reactions" (31), mentions the growth of indium arsenide and gallium arsenide (32) using chlorine or iodine carriers. It appears that growth procedures had been applied to only two of the sixteen arsenides and sulpharsenides discussed in this report, viz., loellingite and arsenopyrite. A chemical vapour transport, employing iodine as the carrier, was used; the references to these procedures are shown in Table 22.

TABLE 20

Conditions Used for the Preparation of Three-Component Arsenides by Melting and Annealing

Experiment Number	Nutrient	Melting Temperature (°C)	Annealing Temperature (°C)	Time (days)	Calculated Formula
914	Co, Ni, and As (0.8 : 0.2 : 1.0)	1210	1000	5	$Co_{0.8}Ni_{0.2}As$
915	Co, Fe, and As (0.5 : 0.5 : 2.0)	1140	600→300 (a)	16	$(Co,Fe)As_2$

Note: (a) = The annealing temperature was lowered from 600°C to 300°C stepwise over 16 days. There was excess arsenic present at the conclusion of the experiment; therefore, the product contains less arsenic than indicated by the calculated formula.

TABLE 21

X-Ray Diffraction Analyses of the Three-Component Arsenides Described in Table 20

Experiment Number	Phases Present	X-Ray Diffraction Report No.
914	Langisite (16) and a small minor amount of unidentified material	72-314
915	(a) Skutterudite (38) and a small minor amount of a safflorite and possibly some CoAs (36) (c)	72-331
	(b) Safflorite I (58) and a small minor amount of skutterudite and possibly some CoAs (36)	72-452

Note: (a) = This sample was a small portion of the product selected at random.

(b) = The balance of the product was ground to ensure uniformity and a small portion was removed for this analysis.

(c) = Some unreacted arsenic was also present at the termination of the experiment.

TABLE 22

References to Previous Growth Procedures for Cobalt, Iron, and Nickel Arsenides and Sulpharsenides

Growth Procedure	Formula	References
Chemical Vapour Transport (a)	$FeAs_2$	Rosenthal, Kershaw and Wold (29)
Chemical Vapour Transport (a)	FeAsS	Fushimi and Webster (30)

Note: (a) = Iodine was used as the carrier.

(b) Present Growth Procedures

Three growth procedures have been used in this study. The chemical vapour transport using iodine as the carrier was successful in several cases. The vapour transport and flux-growth procedures were only briefly explored. These methods will be discussed in turn.

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

This procedure is based on a reversible chemical reaction occurring in a closed system. In this study, iodine was used to generate intermediate volatile compounds.

The chemical reaction of iodine with arsenides or sulpharsenides can be ideally visualized as follows:

$$MAs_x + I_2 \rightleftarrows MI_2 + \frac{x}{4} As_4 \qquad \text{(Eq. 1)}$$

$$2MAsS + 2I_2 \rightleftarrows 2MI_2 + As_2S_2 \qquad \text{(Eq. 2)}$$

It must be pointed out that the decomposition products would play a part in the overall reaction.

The capsules were made of quartz and were fashioned as described on page 33; they were charged with products from the preparatory experiments (this included the unreacted arsenic or arsenic sulphides) and with iodine (usually 5 mg of iodine per cm^3 of the volume of the capsule were used). The capsules were then evacuated to 10^{-4} mm of Hg and sealed.

The capsule design and the chemical reaction, shown in Equation 1, for this technique is shown in Figure 11. The transport of sulpharsenides is assumed to occur in an analogous manner, based on Equation 2.

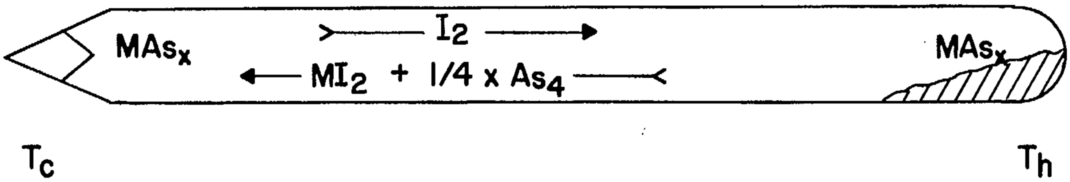

Figure 11. - Schematic Arrangement for Chemical Vapour Transport.

*The symbols T_h and T_c, used in this and subsequent diagrams, refer to the hot and cold zones of the capsule, respectively. The difference between T_h and T_c is the temperature gradient. A growing crystal is depicted in the cold zone.

The growth of arsenides and sulpharsenides will be discussed under separate headings.

(1) Arsenides

In Table 22, it is seen that Rosenthal, Kershaw and Wold (29) reported the transport of $FeAs_2$ by an iodine vapour transport method, from a nutrient temperature of 800°C to a growth temperature of 765°C, over a 10- to 16-day period.

When this experiment was tried in the present study in 1969, a nutrient temperature of 700°C and a growth temperature of 590°C were used for 13 days.

The conditions used in the above experiment, and for several other arsenides, are shown in Table 23. The X-ray diffraction analyses of these samples are shown in Table 24.

Some pertinent remarks should be made before assessing the results reported in these tables. The role of X-ray diffraction analysis in the present study has been to identify the products resulting from experiments; no effort has been made to verify the existing standard patterns. However, it is conceded that the field of cobalt, iron, and nickel arsenides and sulpharsenides has not been fully catalogued with regard to X-ray diffraction patterns.

It is well known that X-ray diffraction analysis is based on the crystal structure and not on the absolute chemical composition of the sample; this is particularly true with some arsenides and sulpharsenides. Holmes (9) stated that skutterudite was isometric, with essentially the same lattice constants over the compositional range of $\sim CoAs_2$ to $\sim CoAs_3$, and with some iron and/or nickel substitution. In another dimension of the problem, Radcliffe and Berry (20)(21) have divided the large compositional range of the safflorites $[(Co,Fe,Ni)As_2]$ into five main X-ray diffraction patterns as indicated in Figure 6.

Unfortunately, chemical analyses were not available in the present study to ascertain the actual compositions of any of the various samples submitted for X-ray diffraction analysis.

Returning now to Table 23, it is observed that seven experiments, involving various cobalt arsenides, are described.

(Continued on page 66)-

TABLE 23

Conditions Used for C. V. T. Growth of Cobalt, Iron, and Nickel Arsenides with Iodine Vapour

Experiment Number	Nutrient	Nutrient Temperature (°C)	Growth Temperature (°C)	Growth Rate (mg/ hr)	Time (days)
905	Co_2As from #570	1100	500	0. 13	6
538 (a)	$CoAs_2$ from #535	750	675	Very little growth	7
680	$CoAs_2$ from #677	900	850	0. 32	14
903	$CoAs_2$ from 538	800	500	0. 65	4
909	$CoAs_2$ from #903	1000	500	11. 27	4
568 (a)	$CoAs_3$ from #543	800	625	No growth	19
904	$CoAs_3$ from #568	800	500	2. 0 (b)	8
595 (a)	Fe and As (1 : 1)	1000	800	No growth	1
807	FeAs from #556	825	500	3. 8	5
901	$FeAs_{1.69}$ from #900	760	475	16. 82	5

Note: (a) = Quartz wool plugs were used in these experiments.

(b) = There were two transported products:

(i) arsenic, at the coldest part of the tube, and

(ii) crystals along the wall of the tube; the rate of growth refers to the crystals along the wall only.

(Continued on page 64) -

TABLE 24

X-Ray Diffraction Analyses of C. V. T. -Grown Arsenides of Cobalt, Iron, and Nickel

Experiment Number	Phases Present	X-ray Diffraction Report No.
905	Transported : CoAs (36) and a trace of Co_2As (33)	72-202
	Untransported: Co_2As (33) and a small minor of $CoAs_x$	72-203
538	Not Analysed - very little growth	--
680	Transported : $CoAs_2$ (37)	70-382
	Untransported: $CoAs_2$ (37)	70-383
903	Transported : $CoAs_2$ (37) and CoAs (36)	72-200
	Untransported: $CoAs_2$ (37)	72-201
909	Transported : skutterudite (a = 8.18Å) (38) and a small minor of Co_2As (35)	72-234
	Untransported: CoAs (36) and a possibility of σ-Co_2As (33)	72-235
568	Not analysed - no growth	--
904	Transported (1) : arsenic	72-223
	Transported (2) : skutterudite (a = 8.20Å) (38)	72-224
	Untransported : $CoAs_2$ (37)	72-225
595	Not analysed - no growth	--
807	Transported : FeAs (40) and $Fe_{1+x}As_{2-x}$ (41) (a)	72-180
	Untransported: FeAs (40)	72-181
901	Transported : $Fe_{1+x}As_{2-x}$ (41) (a)	72-193
	Untransported: FeAs (40)	72-194

Note: (a) = See page 65 for footnote.

(Continued on page 65) -

TABLE 23 (Concluded

Experiment Number	Nutrient	Nutrient Temperature (°C)	Growth Temperature (°C)	Growth Rate (mg/ hr)	Time (days)
524 (a)	$FeAs_2$ from #510	700	590	3.19	13
575 (a)	$FeAs_2$ from #574	750	675	2.49	22
594 (a)	Ni and As (1 : 1)	1000	800	No growth	1
809 (a)	Reheating #594	800	500	Arsenic deposited	3
810	$NiAs_{0.98}$ from #809	900	750	1.39	4
902	NiAs from #897	1000	400	0.76	4
550 (a)	$NiAs_2$ from #528	750	675	Arsenic deposited	15
656	Ni and As (1 : 2)	700	675	Arsenic deposited	30
897	Ni and As (1 : 2)	800	540	Arsenic deposited	5
920	$NiAs_2$ from #886	1000	500	1.42 (b)	4

Note: (a) = Quartz wool plugs were used in these experiments.

(b) = There were two transported products:

(i) arsenic at the coldest part of the tube, and

(ii) crystals along the wall of the tube; the rate of growth refers to the crystals along the wall only.

TABLE 24 (Concluded)

Experiment Number	Phases Present	X-Ray Diffraction Report No.
524	Transported : $Fe_{1+x}As_{2-x}$ (41) (a)	69-297
	Untransported: $Fe_{1+x}As_{2-x}$ (41) (a)	69-298
575	Transported : $Fe_{1+x}As_{2-x}$ (41) (a)	72-185
	Untransported: $Fe_{1+x}As_{2-x}$ (41) (a)	72-186
594	Not analysed - no growth	--
809	Not analysed - used in #810	--
810	Transported : $Ni_{11}As_8$ (43)	72-191
902	Transported : NiAs (44) and $NiAs_2$ (45)	72-197
550	Transported : arsenic	70-165
	Untransported: NiAs (44) and $NiAs_2$ (45)	69-581
656	Transported : **arsenic**	70-166
	Untransported: $NiAs_2$ (45)	70-167
897	Transported : arsenic	72-183
	Untransported: NiAs (44)	72-184
920	Transported (at tip of tube) : arsenic	72-332
	Transported (along walls of tube) : NiAs (44) and $NiAs_2$ (45)	72-333
	Untransported: NiAs (44)	72-334

Note: (a) = The X-ray diffraction pattern of $Fe_{1+x}As_{2-x}$ was reported by Peacock (58); the reported chemical analyses of his standard material yields a calculated value of 0.083 for x; the range of x values was not given. This material is still loellingite.

(1) Although a nutrient of Co_2As was used in #905, a growth product that was predominantly CoAs (36) with a trace of Co_2As (33) was obtained. This result violates the chemical balance of the elements, unless the crystal structure of CoAs is not stoichiometric and has instead a range of composition which approaches Co_2As.

(2) Four attempts to transport $CoAs_2$ gave four different results. In #680, good well-formed crystals (1 to 3 mm) of monoclinic $CoAs_2$ were obtained at a growth temperature of 850°C. A lower growth temperature of 500°C was used in #903; this resulted in a mixture of small crystals of monoclinic $CoAs_2$ and CoAs (36). In #909, a high nutrient temperature of 1000°C and a low growth temperature of 500°C produced a skutterudite, isometric $CoAs_{3-x}$, and a small amount of Co_2As (35).

The results of (1) and (2) suggest that the mechanism for the transport of cobalt arsenides is as follows:

$$CoAs_{1+x} \rightarrow CoAs + xAs \qquad \text{(Dissociation)} \qquad \text{(Eq. 3)}$$

$$CoAs + I_2 \rightleftarrows CoI_2 + As \qquad \text{(Transport)} \qquad \text{(Eq. 4)}$$

$$CoAs + xAs \rightarrow CoAs_{1+x} \qquad \text{(Association)} \qquad \text{(Eq. 5)}$$

And it appears that the isometric structure is more stable than the monoclinic form for the arsenic-rich cobalt arsenide grown at a growth temperature of 500°C.

(3) The very low growth rate in #538 is attributed to the presence of quartz wool plugs in the capsule. This implies that the growth mechanism is primarily by convection rather than by diffusion for $CoAs_2$.

Five experiments were attempted in the growth of iron arsenides.

(1) Two experiments with iron monoarsenide gave quite different results; in #807, the growth product was a mixture of small crystals of FeAs (40) and some $Fe_{1+x}As_{2-x}$ (41). On the other hand, in #595, no growth

occurred and this is again attributed to the use of a quartz wool plug. The chemical balance of the elements would suggest that $Fe_{1+x}As_{2-x}$ must have a range of composition which approaches the gross composition of FeAs.

(2) Three experiments were made in the growth of the higher arsenide of iron. The growth product was the same in all cases, namely, $Fe_{1+x}As_{2-x}$. The composition of the untransported residue was the same as that of the transported crystals in #524 and #575; in this case the iron:arsenic ratio in the capsule was essentially 1:2. However, in #901, the nutrient composition of iron:arsenic was 1:1.69, which resulted in a growth product of $Fe_{1+x}As_{2-x}$ and an untransported residue of FeAs. The growth products in all three cases were good-looking crystals (1 to 3 mm).

The results in (1) and (2) suggest that the mechanism for the transport of iron arsenides is similar to that of the cobalt arsenides as shown in Equations 3, 4, and 5.

(3) The presence of quartz wool plugs in #524 and in #575 slowed the rate of transport but did not stop it. Therefore, it is assumed that the mechanism of growth in this case is a blend of diffusion and convection processes.

Eight experiments were attempted in the growth of nickel arsenides.

(1) Four experiments were made in which the nutrient was essentially NiAs. Actually, only two different samples were involved because one sample was treated three successive times. The first sample (#594) was heated and no crystal growth occurred, the reasons for this being assumed to be the high temperature in the growth zone also the presence of the quartz wool plug in the capsule. The second treatment (#809) of the unopened capsule involved a lower temperature in the growth zone; only arsenic was sublimed, leaving a residue with a gross composition of $NiAs_{0.98}$. The third treatment (#810) involved re-sealing the above residue ($NiAs_{0.98}$) in another quartz capsule, this time without a quartz wool plug, and reheating at 900°C with the growth-zone temperature at 750°C; this time the transported product was maucherite ($Ni_{11}As_8$).

The other sample of NiAs (#902) was heated at a higher nutrient temperature with the growth temperature being lower than with the first sample; the transported product was a mixture of NiAs and some $NiAs_2$ (45).

(2) Four experiments were made in which the nutrient has the gross composition $NiAs_2$. In all cases, some arsenic was sublimed to the coldest part of the capsule. It was only in #920 that a nickel compound was transported; the higher nutrient temperature of 1000°C and the low temperature in the growth zone are credited with the transporting of NiAs, along with some $NiAs_2$.

The results in (1) and (2) suggest that the mechanism for the transport of nickel arsenides is more prone to temperature control that either the cobalt or the iron arsenides. It appears that the decomposition step (analogous to Equation 3) for nickel arsenides proceeds to a point at which the resultant arsenide is very nickel-rich; therefore, the mechanism is assumed to be:

$$NiAs_{1+x+y} \rightarrow NiAs_{1-x} + (2x+y)\,As \qquad \text{(Dissociation)} \qquad \text{(Eq. 6)}$$

$$NiAs_{1-x} + I_2 \rightleftarrows NiI_2 + (1-x)As \qquad \text{(Transport)} \qquad \text{(Eq. 7)}$$

$$NiAs_{1-x} + (2x+y)\,As \rightarrow NiAs_{1+x+y} \qquad \text{(Association)} \qquad \text{(Eq. 8)}$$

Although it appears that, for the most part, the growth products were mixtures of two or more arsenides, a highly successful growth-run of monoclinic safflorite ($CoAs_2$ in #680) and three successful runs of orthorhombic loellingite ($FeAs_2$ in #524, #575, and #901) were obtained. Good-looking 2-to 3-mm crystals were grown.

The results of additional physical analyses and related studies will be given later in this report.

(2) Sulpharsenides

In Table 22, it is seen that there is only one reference to the iodine vapour transport of a sulpharsenide; that was by Fushimi and Webster, who reported the transport of arsenopyrite from a nutrient of FeAsS and FeS_2 at a nutrient temperature of 650°C to a growth temperature of 575 to 610°C over a 7 to 20-day period.

Several attempts were made in the present study to grow cobaltite (CoAsS), arsenopyrite (FeAsS), and gersdorffite (NiAsS). The conditions used in these experiments are detailed in Table 25, and the X-ray diffraction analyses are shown in Table 26.

Three experiments involving the growth of cobaltite were made.

(1) Cobaltite was grown by the iodine vapour transport procedure, as shown in sample #907, but the crystals were extremely small.

(2) The use of excess sulphur in #813 seemed to prevent the growth of cobaltite, although the low temperature (300°C) in the growth-zone may have been partly responsible.

(3) Some As_2S_2 was usually present at the termination of the experiment, which suggests that the growth mechanism could be as shown in Equation 2, viz.,:

$$2CoAsS + 2I_2 \rightleftarrows 2CoI_2 + As_2S_2 \qquad \text{(Eq. (9)}$$

No explanation appears to be forthcoming from Equation 9 as to why a slight excess of sulphur should prevent the transport.

Seven experiments were attempted in the growth of arsenopyrite.

(1) It was only in #808 that any arsenopyrite was grown, and this was as a mixture with pyrrhotite.

(2) In some of the experiments, the growth products contained unidentified materials; in #523 and #583, the products were similar to arsenopyrite.

(3) The composition of the nutrient appears to be very important because the transported products varied depending on whether the nutrient

(Continued on page 74)-

TABLE 25

Conditions Used for C.V.T. Growth of Cobalt, Iron, and Nickel Sulpharsenides with Iodine Vapour

Experiment Number	Nutrient	Nutrient Temperature (°C)	Growth Temperature (°C)	Growth Rate mg/hr	Time (days)
804	CoAsS from #370	800	590	1.16	8
813	CoAsS from untrans. of #804 and S (1 : 0.1)	800	300	very slow growth	13
907	CoAsS from #899	900	400	0.91	17
523 (a)	FeAsS from #508	650	540	arsenic deposited	7
549 (a)	FeAsS containing As_2S_2 from #545	700	625	arsenic deposited	7
583	$FeAs_2$ from #524 and FeS_2 from #438 (1 : 1)	700	605	--	15
		and annealed at	650	0.04	14
667	$FeAs_2$ from #524 and FeS_2 from #438 (1 : 4)	730	460	0.35	14
802	FeAsS from untrans. of #583 and Fe (1 : 0.04)	700	590	2.2	6
647 (b)	$FeAs_2$ from #524 and FeS_2 from #611 (1 : 1)	500	445	no growth	13

Note: Footnote is on page 72.

(Continued on page 72) -

TABLE 26

X-Ray Diffraction Analyses of C. V. T.-Grown Sulpharsenides of Cobalt, Iron, and Nickel

Experiment Number	Phases Present	X-Ray Diffraction Report No.
804	Transported: CoAsS and a small minor of unidentified material	71-513
813	Not opened	--
907	Transported : cobaltite	72-264
	Untransported: cobaltite	72-265
523	Untransported: pyrrhotite and a trace of unidentified material	69-238
549	Transported : arsenic	69-455
	Untransported: pyrrhotite	69-456
583	Transported : pyrrhotite and a small minor of unidentified "X"	70-158
	Untransported: unidentified "X"	70-159
667	Transported : shiny material-unidentified material	70-281
	dull material-pyrite, pyrrhotite, and marcasite	70-282
	Untransported: pyrrhotite, pyrite, and a trace of unidentified material (a)	70-283
802	Transported : $FeAs_x$ (type) and arsenic	71-494
	Untransported: pyrrhotite and $FeAs_x$ (type)	71-495
647	Not analysed - no growth	--

Note: Footnote is on page 73.

(Continued on page 73) -

TABLE 25 (Concluded)

Experiment Number	Nutrient	Nutrient Temperature (°C)	Growth Temperature (°C)	Growth Rate mg/hr	Time (days)
808	FeAsS from #802 and S (1 : 0.14)	800	515	1.67 (c)	24
812	NiAsS from #567	800	540	4.2	15
906	NiAsS from #898	800	500	no growth	6

Note: (a) = Quartz wool plugs were used in these experiments.

(b) = Bromine was used instead of iodine in this experiment.

(c) = There were two transported products:

(i) arsenic at the coldest part of the tube, and

(ii) crystals along the wall of the tube; the rate of growth refers to the crystals along the wall only.

TABLE 26 (Concluded)

Experiment Number	Phases Present	X-Ray Diffraction Report No.
808	Transported : (1) arsenic and an unidentified material	72-263
	Transported : (2) pyrrhotite and arsenopyrite and a trace of unidentified material	72-262
812	Transported : (1) realgar	72-215
	Transported : (2) unidentified material	72-216
	Untransported: unidentified material (b)	72-217
906	Untransported: gersdorffite (a = 5.68Å)	72-252

Note: (a) = The unidentified material in the transported product is different from the unidentified material in the untransported product.

(b) = The unidentified material in the transported and the untransported products are similar.

contained excesses of either sulphur, pyrite, As_2S_2, or iron. However, it was only in #808, in which excess sulphur was used, that any arsenopyrite was obtained.

(4) The nutrient temperatures of the experiments fell into the range of 500 to 800°C; it was in #808 that this highest temperature was used.

(5) The growth-zone temperatures fell into the range of 445 to 650°C; in the most successful experiment (#808) it was 515°C.

(6) The use of bromine as the transporting agent was not successful under the conditions used in #647.

(7) It cannot be ascertained whether the use of quartz wool plugs in #523 and in #549 had any harmful effects in the growth mechanism; however, in these cases, only arsenic was transported.

(8) Because it appears that excess sulphur is necessary for the transport mechanism, it is conceivable that pyrrhotite is the key, and one possible route of the reaction that can be envisaged is a balance between the following two reversible reactions:

$$2(1-x)FeAsS + 2S \rightleftarrows 2Fe_{1-x}S + 1-x(As_2S_2) \qquad \text{(Eq. 10)}$$

$$Fe_{1-x}S + (1-x)I_2 \rightleftarrows (1-x)FeI_2 + \frac{1}{2} S_2 \qquad \text{(Eq. 11)}$$

Previously (3), it was stated that the rate of reaction of iodine with pyrrhotite increases from essentially zero when x is zero in the pyrrhotite formula ($Fe_{1-x}S$), to a significant figure when x is 0.1 at any given temperature in the range 800 to 1000°C; therefore, as the free sulphur in the system increases, so does the rate of reaction shown in Equation 11.

The main conclusion from these experiments is that the conditions used in #808 provide the basis for further investigations.

Only two experiments were attempted in the growth of gersdorffite.

(1) No evidence of gersdorffite having been transported was found in either of the two experiments.

(2) The difference between the products obtained in #812 and in #906 is attributed to a difference in the preparatory step (see Table 15); the unidentified transported material probably resulted from an intermediate product in #567 and not from the chemical vapour transport reaction in #812.

(3) The untransported product in #906 was found to be very good gersdorffite, as seen from the "a" value.

The product from #906, and any material prepared in the same manner, would be an ideal nutrient material for future growth investigations.

(3) Three-Component Arsenides

The chemical vapour transport technique was applied to only one compound of this class namely, safflorite ($Co_{0.5}Fe_{0.5}As_2$). The elements, Co, Fe, As, and I_2 were sealed in an evacuated quartz capsule; the capsule was heated slowly to allow the elements to combine. The temperature was then raised to the growth conditions, as described in Table 27. The X-ray diffraction analysis, as shown in Table 28, indicates that the growth product was loellingite and that the untransported residue was a mixture of skutterudite and CoAs. This type of result is consistent with previous experience. In Table 23, it was shown that the rates of growth of $FeAs_2$ and $CoAs_2$ were 3.19 and 0.65 mg/hr, respectively; however, it must be pointed out that the $CoAs_2$ experiment had a higher nutrient temperature and a lower growth-zone temperature than the $FeAs_2$ experiment, a condition which has inflated the above $CoAs_2$ growth rate over what it would be for similar growth parameters.

Therefore, this type of result can be expected from any multi-component system in which the rates of growth of the individual components are significantly different.

(ii) Vapour Transport (V.T.)

This technique relies on the sublimation of material from A, the warm zone of a sealed capsule, to the colder zone at B where a crystalline product is formed, as shown in Figure 12.

TABLE 27

Conditions Used for C.V.T. Growth of a Three-Component Arsenide with Iodine Vapour

Experiment Number	Nutrient	Nutrient Temperature (°C)	Growth Temperature (°C)	Growth Rate (mg/hr)	Time (days)
916	Co, Fe, and As (0.5 : 0.5 : 2.0)	800	500	7.4	8

TABLE 28

X-Ray Diffraction Analyses of the Three-Component Arsenide Described in Table 27

Experiment Number	Phases Present	X-Ray Diffraction Report No.
916	Transported : loellingite	72-324
	Untransported: skutterudite and a minor of CoAs	72-325

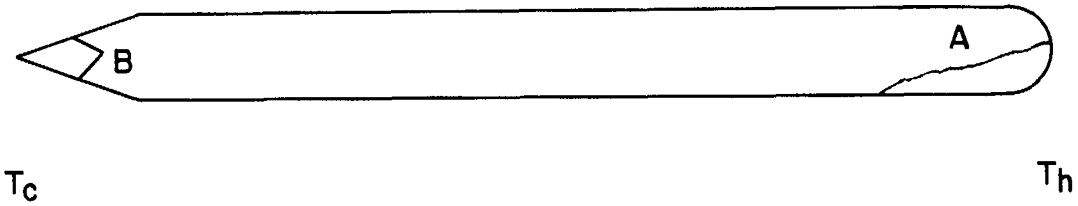

Figure 12. - Schematic Arrangement for Vapour Transport.

This technique was successfully used with several sulphides in (2) (3); it was hoped that it might work with arsenides, and possibly with sulpharsenides - particularly arsenopyrite - where the decomposition products are known (13) to be predominantly pyrrhotite and arsenic; both of these materials are transportable through vapour transport.

A new two-zone furnace assembly was constructed for this part of the project. The previous furnaces, described in (1), all gave a more or less gradually changing temperature profiles; whereas, two furnaces, separated by selected thickness of insulation, changed the temperature profile to the form shown in the schematic arrangement in Figure 13. This temperature profile permits the use of 15-cm capsules with a large temperature gradient between the ends of the capsule and a shallow gradient in the growth zone. Ideally, the sublimed arsenic is concentrated in the tip zone (B) and the resultant arsenic vapour pressure in the system can be controlled by the temperature at (B) and, when the other sublimate, pyrrhotite for example, reached zone (C), it could react with the arsenic vapour to form the desired product. The actual furnace design and the temperature profiles are given in the Appendix on pages 108 to 112.

The conditions used in the attempted sublimation of three materials are shown in Table 29. The X-ray diffraction analyses, given in Table 30, indicate that the rate of material deposited along the wall of the capsule was extremely slow. No iron arsenide was sublimed under the conditions used. The small amount of the unidentified material in #886 may have developed into a known material with a longer heating time. In #869, the desired pyrrhotite and arsenic sublimed, but failed to combine to form arsenopyrite.

(iii) Flux Growth

The technique of flux growth can be considered as the exsolution of a dissolved nutrient from a molten salt; if the temperature of the fusion mixture is lowered slowly, the dissolved nutrient is deposited as crystals.

The reaction mixture is contained in an evacuated quartz capsule, as shown in Figure 14, and placed in an oblique position in a furnace. This

(Continued on page 83)-

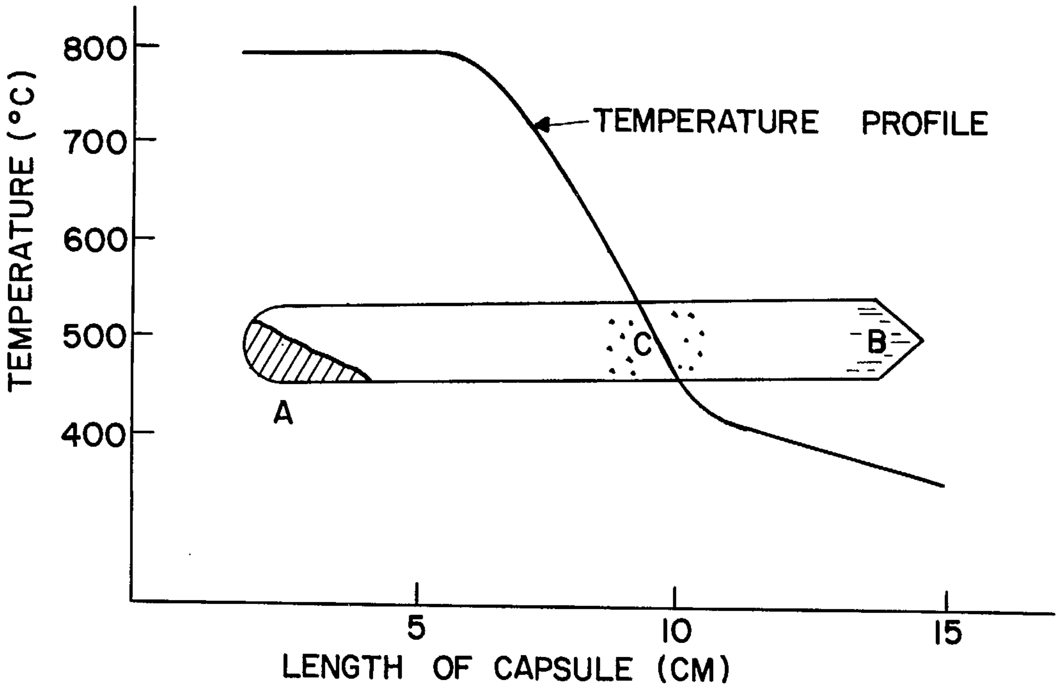

Figure 13. - Schematic Arrangement for a Vapour Transport in a Two-Zone Furnace.

TABLE 29

Conditions Used for Attempted V.T. Growth of Iron and Nickel Arsenides and Arsenopyrite

Experiment Number	Nutrient	Nutrient Temperature (°C)	Growth Temperature (°C)	Growth Rate (mg/hr)	Time (days)
900	$FeAs_{1.69}$	790	460	no growth	1
886	$NiAs_2$	800	500	(a)	2
869	$FeS_{1.1}$ and As (1 : 1.23)	900	400	(a)	12

Note: (a) = There were two transported products: (1), predominantly arsenic at the coldest part of the capsule (tip zone) and (2), a deposit along the wall of the capsule: This deposit was extremely small; therefore, no rate of growth was calculated.

TABLE 30

X-Ray Diffraction Analyses of the Attempted V. T. Growth of Iron and Nickel Arsenides and Arsenopyrite

Experiment Number	Phases Present	X-Ray Diffraction Report No.
900	Not analysed - no growth	--
886	Transported : (1) arsenic with a small trace of unidentified material	72-402
	Transported: (2) arsenic	72-403
869	Transported : (1) arsenic	72-405
	Transported : (2) pyrrhotite with a small amount of arsenic	72-406
	Untransported: pyrrhotite	72-404

Note: There were two transported products: (1), the deposit at the coldest part of the capsule part of the capsule (tip zone) and (2), the deposit along the wall of the capsule.

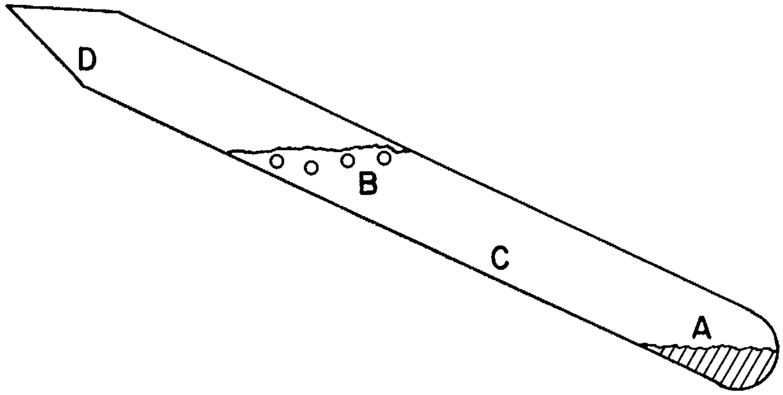

Figure 14. - Schematic Arrangement for Flux Growth.

keeps the molten salt, C, at the rounded end of the tube. If the crystals are to be grown in an atmosphere of excess arsenic, the pressure in the tube (and over the molten salt) is controlled by the temperature at D, the coldest part of the tube. The letters A and B show the location of undissolved nutrient and the growing crystals, respectively.

The conditions used in two unsuccessful attempts to grow arsenopyrite in two different flux media are shown in Table 31. The X-ray diffraction analyses of these attempts, as shown in Table 32, do not indicate whether future experiments might be successful or not.

SUMMARY OF CRYSTAL-GROWTH ACTIVITIES

The scope of the crystal-growing investigation, in terms of success in obtaining good crystalline material, is shown in Table 33. A successful growth (S) indicates that the growth product was a single component of the desired phase. A partly successful growth (P) indicates that the growth product was a mixture of the desired crystal with one or more other crystalline compounds. In the case of failure (F), the growth product (if there was one) did not contain the sought-after crystalline material. To complete Table 33, a dash (—) is used to show those systems that have not been attempted.

The two main goals were: firstly, to explore the total field within the confines of the 16 arsenides and sulpharsenides of cobalt, iron, and nickel (described in Table 2) so as to be prepared to supply any of those compounds in which the Sulphide Research Group in the Mineral Sciences Division had expressed interest at various times; secondly, to grow the crystals as large as possible and, eventually, to produce them in the cubic-centimetre size range if possible. However, none of the successes, marked S in Table 33, represent crystals as large as this. The two most successfully-grown crystals were: loellingite ($FeAs_2$) and safflorite ($CoAs_2$). Photographs of these crystals are shown on pages 87, 88 and 89.

TABLE 31

Conditions Used for Attempted Flux-Growth of Arsenopyrite

Experiment Number	Nutrient	Flux	Ratio of Flux to Nutrient	Conditions of Growth
515	Fe, As, and S (1 : 1 : 1)	KCℓ-LiCℓ (40 : 60)	0.32 : 0.036	(a)
688	FeS and As (1 : 2)	$PbCl_2$	0.048 : 0.0043	(b)

Note: (a) = The mixture was heated to 430°C and cooled 5°C per hour to 390°C; this temperature was held overnight, and the cooling was resumed at 5 °C per hour for two hours before cooling slowly to room temperature.

(b) = The mixture was heated to 550°C, held constant for 3 days then slowly cooled to room temperature.

TABLE 32

X-Ray Diffraction Analyses of the Products Obtained in Experiments Described in Table 31

Experiment Number	Phases Present	X-Ray Diffraction Report No.
515	Not analysed - tube cracked	--
688	Galena (PbS) and pyrrhotite ($Fe_{1-x}S$)	70-449

TABLE 33

Scope of Crystal-Growth Activities

Compound	Mineral Name	Success or Otherwise of Crystal Growth Technique					
		Direct Combination	Vapour Transport	Chemical Vapour Transport	Flux	Melt	Melt-and-Anneal
α-Co_2As	--	P	--	P	--	--	--
β-Co_2As	--	--	--	--	--	--	--
α-CoAs	Modderite	F	--	P	--	--	P
β-CoAs	Modderite	F	--	--	--	--	--
$CoAs_2$	Safflorite	S	--	S	--	--	P
$Co_{0.5}Fe_{0.5}As_2$	Safflorite	--	--	F	--	P	P
$CoAs_3$	Skutterudite	S	--	S	--	--	P
FeAs	Arseneisen	P	--	P	--	--	--
$FeAs_2$	Loellingite	S	F	S	--	--	--
NiAs	Niccolite	S	--	P	--	--	--
α-$NiAs_2$	Pararammelsbergite	F	--	--	--	--	P
β-$NiAs_2$	Rammelsbergite	F	F	P	--	--	P
$Co_{0.8}Ni_{0.2}As$	Langisite	--	--	--	--	P	P
CoAsS	Cobaltite	S	--	S	--	--	--
FeAsS	Arsenopyrite	F	F	P	F	--	--
NiAsS	Gersdorffite	P	--	F	--	--	--

Note: No hydrothermal growth experiments were made.

SIZE OF THE CRYSTALS

Photographs of representative crystals of three arsenides and one sulpharsenide are shown in Figures 15 to 18. The most successfully-grown arsenides are those shown in Figures 15 and 16. The growth details can be located in the Tables indicated in the captions. The scale divisions, shown underneath the crystals, represent 1 mm.

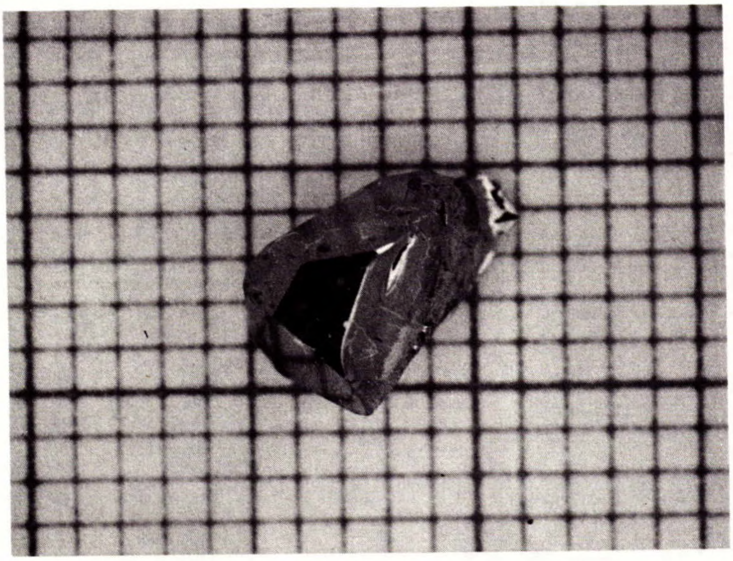

Figure 15. - Crystal of Loellingite, $FeAs_2$, Grown by Chemical Vapour Transport (Iodine) Technique, (Expt. #575, see Tables 23 and 24).

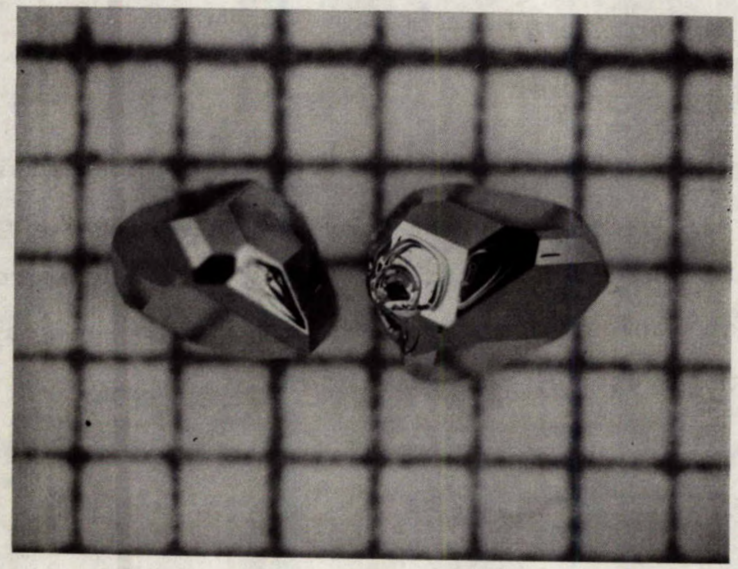

Figure 16. - Crystals of Safflorite, $CoAs_2$, Grown by Chemical Vapour Transport (Iodine) Technique, (Expt. #680, see Tables 23 and 24).

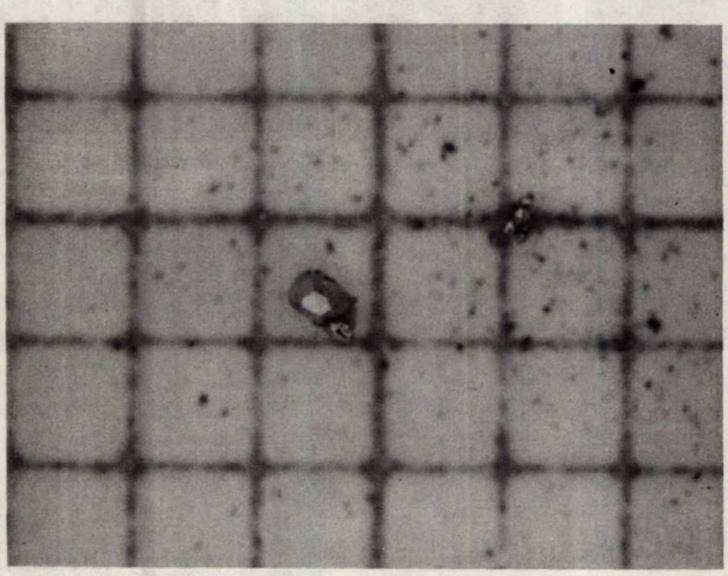

Figure 17. - Crystals of Skutterudite, $CoAs_{3-x}$, Grown by Chemical Vapour Transport (Iodine) Technique, (Expt. #904, see Tables 23 and 24).

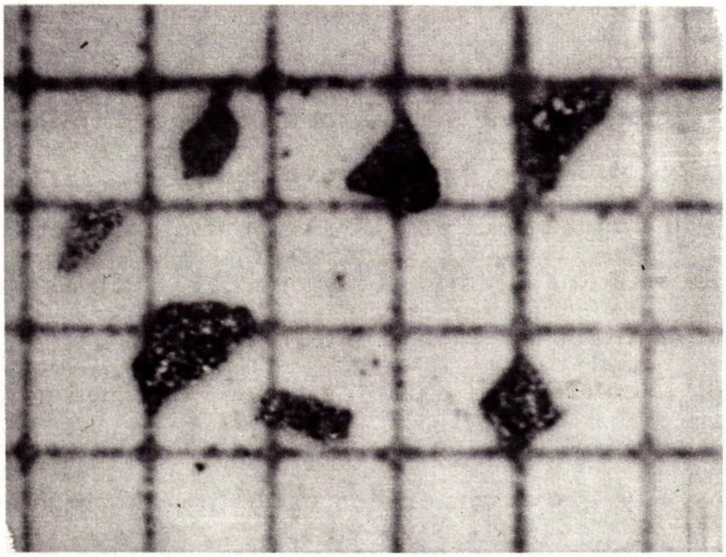

Figure 18. - Clusters of Cobaltite Crystals, CoAsS, Grown by Chemical Vapour Transport (Iodine) Technique, (Expt. #907, see Tables 25 and 26).

ANALYSES

Throughout the work described in this report, X-ray diffraction analysis has played a prominent role in identifying the phases present in the crystals and related materials. To a lesser extent, various other types of analysis have been used to identify trace impurities or to study the uniformity of the specimens.

(a) Electron Microprobe Analyses

The electron microprobe analyses have been very informative as to the uniformity of the matrix and in determining inclusions as well as impurities.

Four different arsenides were examined.

(1) The first arsenide examined, a melt-and-annealed cobalt monoarsenide, #888, that was prepared as shown in Table 13, is shown in Table 34. The microscopical examination of the sample showed it to contain only one phase, but upon coating with carbon, a second (minor) phase having the gross composition of $Co_{1.93}As$ was revealed. The X-ray diffraction analysed (Table 14) did not detect any Co_2As, but did detect $CoAs_2$. Therefore, because this sample was annealed for only one day, it is assumed that a longer annealing time might produce a uniform CoAs.

(2) The second set of samples to be examined consisted of two C.V.T.-grown diarsenides. These samples, which were representative of the most successfully-grown arsenides of the present project, were prepared as shown in Table 23. The lack of standardized materials in this compositional range was overcome through the use of synthetic standards. The results, as shown in Table 35, indicate several things. The specimen used in #524 was homogeneous, no iodine was detectable, and the composition was essentially stoichiometric for the diarsenide. The other set of results, obtained on a separate portion of #524 and analysed at a different time,agrees extremely well with the former results. The cobalt diarsenide, #680, was also of good quality.

Portions of these cobalt diarsenide and iron diarsenide samples have been accepted as standards for subsequent electron microprobe analyses.

(3) The third application of the electron microprobe analysis was a detailed analysis of the transported and the untransported products obtained from an experiment, #916, involving the C.V.T. of a nutrient that had the gross composition $Co_{0.5}Fe_{0.5}As_2$. Several portions of this sample were analysed as shown in Table 36.

The transported portion was composed of two crystal forms, a square grain and a dendritic grain; however, the analyses showed these two grains to be similar and quite homogeneous, except for a slight variation in the iron:cobalt ratio; the gross composition was $(Co,Fe)As_2$ with the cobalt concentration about 2 per cent or less of the iron content.

The dendritic form was essentially $FeAs_2$. No iodine was detectable in the transported crystals.

The untransported portion had one optically-invisible and three visible phases. The core was found to be homogeneous and had a gross composition of $(Co,Fe)_2As$, the iron concentration being less than 3 per cent of the cobalt content. The layer around the core was not homogeneous but had the general gross composition of (Co, Fe)As; again the iron concentration was only 1 per cent of the cobalt content. The rim around the outside of the material was a mixture of $(Co,Fe)As_2$ with traces of $(Co,Fe)As_3$; in both of these compounds, the iron concentration was less than 1 per cent of the cobalt content. Also, some iodine was detected in the fractures and pits of the untransported portion.

These results agree with the X-ray diffraction analyses shown in Table 28, except that the microprobe analyses give a clearer picture of the degree of the selective transport of iron over cobalt in the C.V.T., when iodine is used as the carrier.

(4) The final sample analysed was a melt-and-annealed langisite preparation $(Co_{0.8}Ni_{0.2}As)$. The results indicated that a fairly uniform product was obtained, except for a slight variation in the cobalt: nickel concentration. The results are shown in Table 37.

(b) Semi-Quantitative Spectrochemical Analyses

Only two samples were analysed by this technique. They were the most successfully-grown crystals of $CoAs_2$, #680, and of $FeAs_2$, #524. The results are shown in Table 38.

The level of impurities in these two samples is extremely low, only a trace of boron in the $CoAs_2$ and a trace of magnesium in the $FeAs_2$ being detected.

(c) Chemical Analyses

The chemical analyses by gravimetric means were attempted so as to complement the physical analyses. Two different problems were studied.

(Continued on page 96)-

TABLE 34

Electron Microprobe Analyses of Melt-and-Annealed Cobalt Monoarsenide

Experiment Number	Target Formula		Microprobe Analysis		Calculated Formula	Microprobe Report No.
			% Co	% As		
888	CoAs	Matrix	44.10	55.73	$Co_{1.005}As$	EP 72-42
		Inclusions	59.49	39.13	$Co_{1.93}As$	EP 72-42

Note: (1) Microscopical examination of the specimen showed it to be one phase only. However, upon coating it with carbon, a second (minor) phase was revealed.

(2) Sample #888 was prepared as shown in Table 13.

TABLE 35

Electron Microprobe Analyses of C.V.T.-Grown Cobalt and Iron Diarsenides

Experiment Number	Target Formula	Microprobe Analysis			Calculated Formula	Microprobe Report No.
		% Co	% Fe	% As		
680 (a)	$CoAs_2$	28.62	--	72.11	$CoAs_{1.982}$	EP 72-62
524 (a)	$FeAs_2$	--	27.60	72.81	$FeAs_{1.969}$	EP 72-62
524 (b)	$FeAs_2$	--	27.0	72.4	$FeAs_{2.0}$	EP 69-67

NOTE: (a) = The $CoAs_2$ and $FeAs_2$ were compared against standards As-1 and As-8, respectively.

(b) = Sample was analysed on one face and was found to be very homogeneous; no iodine was detectable.

Note: Samples #524 and #680 were prepared as shown in Table 23.

TABLE 36

Electron Microprobe Analyses of a C. V. T.-Grown Three-Component Arsenide

Experiment Number	Sample	Microprobe Analysis (c)			Calculated Formula
		% Co	% Fe	% As	
916 (a)	Transported : square small grain	0.69	26.66	72.57	$(Co_{0.024}Fe_{0.976})_{1.008}As_{2.00}$
(a)	Transported : dendritic grain	0.10	27.03	72.78	$(Co_{0.003}Fe_{0.997})_{0.998}As_{2.00}$
(b)	Untransported: rim of large grain	28.07	0.27	71.89	$(Co_{0.990}Fe_{0.010})_{1.002}As_{2.00}$
(b)	Untransported: inclusion in rim	20.55	0.05	78.80	$(Co_{0.997}Fe_{0.003})_{0.996}As_{3.00}$
(b)	Untransported: middle layer of large grain	43.44	0.49	55.06	$(Co_{0.988}Fe_{0.012})_{1.015}As_{1.00}$
(b)	Untransported: core of large grain	58.27	1.55	39.08	$(Co_{0.973}Fe_{0.027})_{1.949}As_{1.00}$

Note: (a) = The two small fragments of transported product are quite homogeneous, except for slight Fe:Co variations in the square grain. No iodine was detected in either grain.

(b) = The untransported product has three visible phases. These are: a white rim of $(Co,Fe)As_2$; a middle, darker layer of $(Co,Fe)As$; and a darker core of $(Co,Fe)_2As$. The white rim contains traces of $(Co,Fe)As_3$ which is not optically visible. The middle layer of $(Co,Fe)As$ was not homogeneous; however, the core was homogeneous. Iodine was detected in the fractures and pits.

(c) = Taken from Microprobe Report No. EP 72-80.

Note: Sample #916 was prepared as shown in Table 27.

TABLE 37

Electron Microprobe Analyses of a Melt-and-Annealed Three-Component Arsenide

Experiment Number	Target Formula	Microprobe Analysis			Calculated Formula	Microprobe Report No.
		% Co	% Ni	% As		
914	$Co_{0.8}Ni_{0.2}As$	35.4	8.9	56.5	$Co_{0.797}Ni_{0.201}As$	EP 72-65

Note: (1) There is a slight variation of the cobalt and nickel concentrations throughout the sample.

(2) Sample #914 was prepared as shown in Table 20.

(1) The first problem appears to be composed of two separate parts, but these are related through the decomposition of the arsenides. One part pertains to the decomposition temperature of iron or cobalt diarsenide. Previously-prepared iron diarsenide and cobalt diarsenide were sealed in evacuated quartz capsules and then heated slowly. The temperature at which arsenic was evolved was noted; on cooling (slightly) and annealing, the arsenic was reabsorbed. It was found, as shown in Table 39, that $CoAs_2$ and $FeAs_2$ start to decompose at 700°C and 300°C, respectively. The other part of this section involved heating iron or nickel monoarsenides to between 900 and 1000°C; the evolved arsenic was allowed to condense at a low temperature. These results are also shown in Table 39, the calculated composition of the residue indicating that a metal-rich material was obtained. These products were used in part (2) of this section.

(2) In previous Research Reports (2) and (3), a method was described whereby the chemical composition of the sulphides of zinc, cobalt, iron, and nickel were determined. This method involved the oxidation of the sulphide to the corresponding oxide and as a check, the oxide was usually reduced to the metal by means of hydrogen.

It was anticipated that this procedure could be used in the analysis of arsenides. In order to check this procedure, four samples of metal-rich cobalt, iron, and nickel arsenides were selected and finely ground before the oxidation step. It was soon established that the oxidation did not yield a stoichiometric oxide; the residual weight was too high, indicating that some arsenic was present; it then became apparent that hydrogen reduction of the resultant oxide residue did not yield a stoichiometric metal product. Additional oxidations or reductions of these residues, or of reground residue products, improved the stoichiometry only very slightly. An alternative approach was to treat a residue with hydrogen sulphide at high temperature in anticipation of converting the balance of the arsenide to a sulphide which could then be treated by an oxidation or reduction. This approach also failed to remove the residual arsenic. X-ray diffraction and X-ray fluorescence analyses confirmed the presence of arsenic in the residues tested.

TABLE 38

Semi-Quantitative Analyses of C. V. T.- Grown Cobalt and Iron Diarsenides

Experiment Number	Sample	% (by weight)					Internal Report No.
		As	Co	Fe	B	Mg	
680	$CoAs_2$	P. C.	P. C.	N. D.	0. 02	N. D.	MS-SC 71-210
524	$FeAs_2$	P. C.	N. D.	P. C.	N. D.	0. 2	MS-SC 71-210

Note: P. C. = Principal constitutuent N. D. = Not detectable

Note: Besides the above elements, the following elements were not detectable by spectrographic means; Ba, P, Mn, Sb, Ge, Pb, Sn, V, Cr, Si, Ga, W, Nb, Ta, Bi, Al, Sr, Ni, Ti, Zn, Na, Ag, Cu, Zr, In, Mo, Ca, and Be.

Note: Samples #524 and #680 were prepared as shown in Table 23.

TABLE 39

The Decomposition of Arsenides

Experiment Number	Nutrient	Nutrient Temperature (°C)	Cold Zone Temperature (°C)	Gross Composition of Residue
917	$CoAs_2$ from #913	700	< 100	(a)
918	$FeAs_2$ from #575	300	< 100	(a)
889	$FeAs_{1.1}$	1000	< 100	$FeAs_{0.53}$
887	$NiAs_{1.1}$	930	< 100	$NiAs_{0.87}$
892	NiAs	1000	< 100	$NiAs_{0.69}$

Note: (a) = These experiments were designed to determine the temperature of decomposition, which is the nutrient temperature in these cases; when it was reached, the samples were cooled somewhat and annealed to re-absorb the evolved arsenic.

Note: Samples #913 and #575 were prepared as shown in Tables 13 and 26, respectively. The nutrients used in #889, #887 and #892 were prepared by direct combination of the elements in the initial part of these experiments.

TABLE 40

Attempted Chemical Analysis of Arsenides

Experiment Number	Starting Gross Compositions	No. of Oxidations	No. of Reductions	No. of Hydrogen Sulphide Treatments	Calculated Final Composition
895	Co_2As from #570	3	3	--	$CoAs_{0.28}$ (a)
894	$FeAs_{0.53}$ from #889	2	3	--	$FeAs_{0.08}$
891	$NiAs_{0.87}$ from #887	4	6	2	$NiAs_{0.11}$ (b)
893	$NiAs_{0.69}$ from #892	3	2	--	$NiAs_{0.19}$

Note: (a) = The final product was composed of metallic-looking beads and a black powder; both fractions were analysed by X-ray diffraction procedure, which gave the following results:

Metallic Beads = major constituent-similar to β-Co_2As (34) and a small minor amount of cobalt.

Black Powder = same as metallic beads.

The X-ray diffraction Report numbers were 72-267 and 72-268, respectively.

(b) = After two oxidations, two hydrogen sulphide treatments, and four reductions, X-ray diffraction (Report number 72-153) indicated that the product was unidentified. However, X-ray fluorescence analysis showed arsenic to be present (Private communication from Mrs. D. J. Reed, Spectrochemistry Group, Mineral Sciences Division).

Note: The Co_2As was prepared as shown in Table 11, and the $FeAs_{0.53}$, $NiAs_{0.87}$, and the $NiAs_{0.69}$ were prepared as shown in Table 39.

It was observed that grinding of the residue at various stages of the oxidation-reduction sequence did not enhance the arsenic removal, perhaps because the powdered arsenide, on heating, melted to form a bead which probably became resistant to further reaction.

There was no evidence to suggest that the above chemical analyses could be made quantitative. Therefore, alternative means of chemical analysis should be explored.

CHARACTERISTICS OF SOME OF THE ARSENIDES

The two most successfully-grown arsenides covered by this report are: $CoAs_2$ (safflorite) and $FeAs_2$ (loellingite). Since it is believed that these diarsenides were the first ones ever to be synthesized by a C.V.T. growth, it was desirable to learn more about their crystal structure. Therefore, a brief account of two aspects of their crystal structure will now be given.

(a) Measurement of Interfacial Angles

Several crystals of $FeAs_2$ were submitted for this study. It was found that the exterior angles of $FeAs_2$ were in close agreement with previously-reported values; no formal report on this work has yet been released.

(b) Lattice Parameters

Several crystals of $CoAs_2$ and $FeAs_2$ were submitted for X-ray precession diffraction studies. It was anticipated that this study would shed some additional light on the exact structure of these pure end-members; as yet, no formal report has been released.

SUMMARY

During this study, much progress has been achieved in understanding some of the crystal-growth problems associated with the arsenides and sulpharsenides of cobalt, iron, and nickel.

Of the sixteen arsenides and sulpharsenides listed in Table 2, $CoAs_2$, $FeAs_2$, $CoAs_{3-x}$, and CoAsS have been obtained as good single crystals (see Figures 15 to 18). All the remaining arsenides and sulpharsenides were obtained as components of mixtures of compounds.

The chemical vapour transport technique was the prime growth method used; iodine was found to be a very useful carrier. Vapour transport and flux growth were not successful in the few cases in which were they were tried.

The future goals, in the field of arsenides and sulpharsenides, should be to grow larger crystals and to have them fully analysed by physical and chemical procedures.

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LGR/pg

APPENDIX

A Two-Zone Furnace

In Part I-"Background to Crystal Growth" (1), fifteen furnaces and temperature profiles were described. But, in spite of the variety of gradually-increasing temperature gradients offered by these furnaces, the need for a two-zone furnace was mentioned. The idea behind this two-zone furnace was that the temperature of each zone of the furnace could be controlled separately and, thereby, the rate of change in the temperature gradient could be made to increase or to decrease as desired.

The system explored involved two 30-cm, hinged-type, resistance-wound furnaces which were placed end-to-end. The 13-mm transite insulation was removed from the abutting ends of the two furnaces. Each of these furnaces was controlled by a separate thermo-electronic controller. To complete the system, a 25-mm quartz process tube was placed through the two furnaces.

A series of temperature profiles was made of the central portion of the system, when one furnace was held at a constant temperature and the other furnace was controlled at four different temperature, as shown in Figure 19.

Analogously, three other series of temperature profiles were obtained when the thickness of the insulation between the furnaces was increased to 6 mm, 13 mm, and 26 mm with transite, as shown in Figures 20, 21, and 22, respectively.

A survey of Figures 19 to 22 indicates that a wide range of temperature profiles is possible. The temperature profile selected for use in the vapour transport experiments was curve (d) on Figure 21.

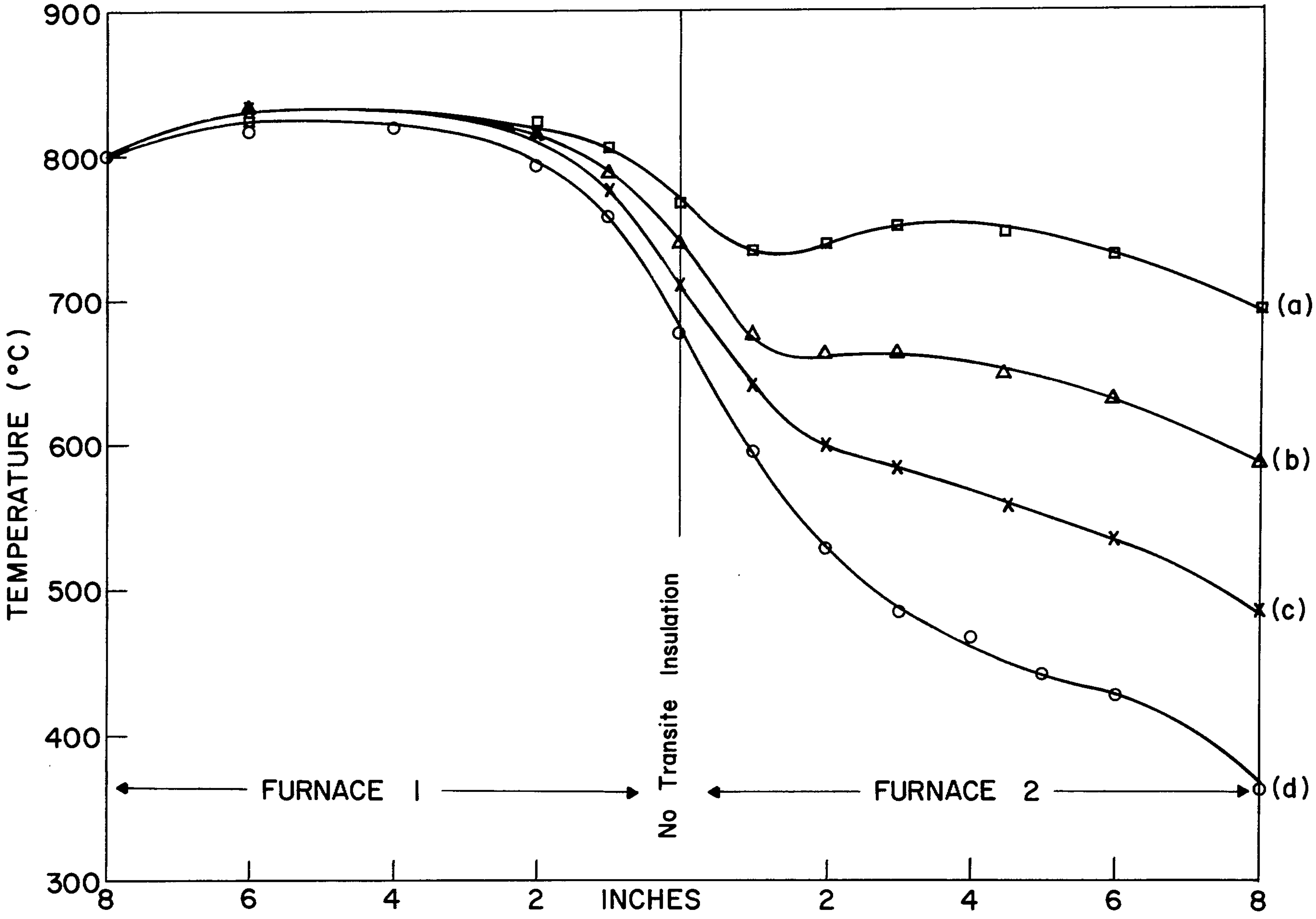

Figure 19. Temperature Profile of the Central Portion of a Two-Furnace (Two-Zone) System. No transite insulation is used between furnaces.

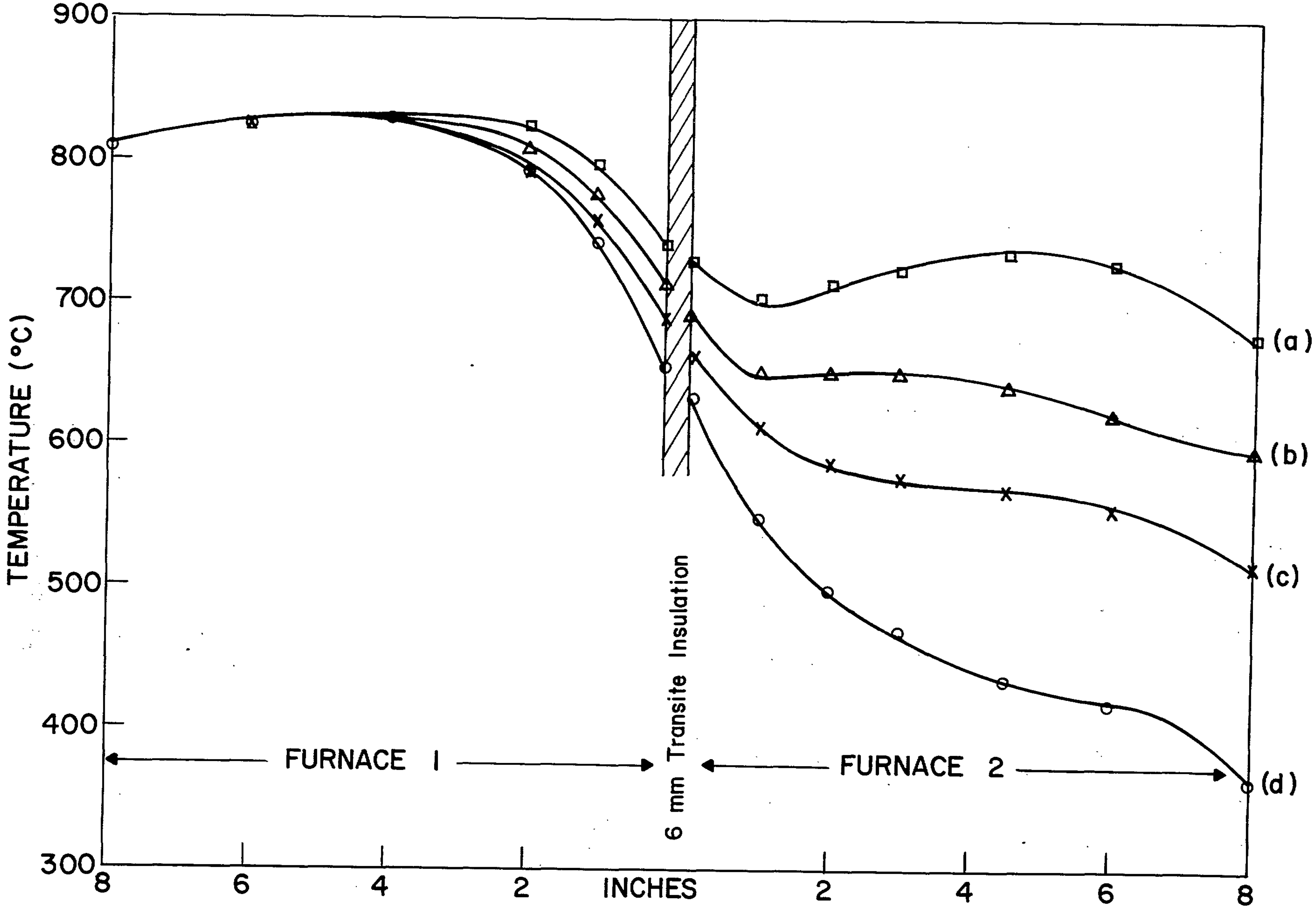

Figure 20. Temperature Profile of the Central Portion of a Two-Furnace (Two-Zone) System. A 6-mm transite insulation is used between furnaces.

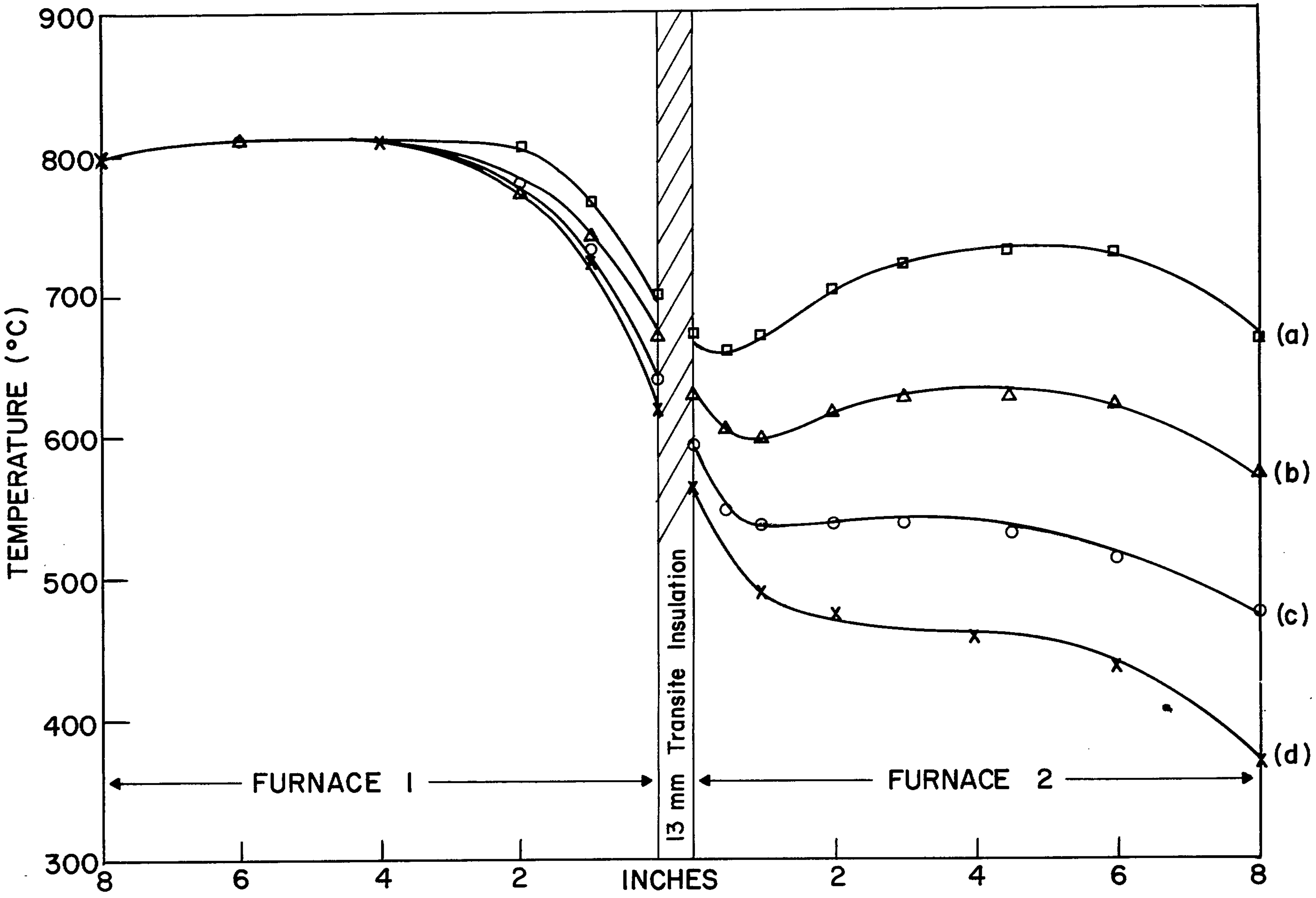

Figure 21. Temperature Profile of the Central Portion of a Two-Furnace (Two-Zone) System. A 13-mm transite insulation is used between furnaces.

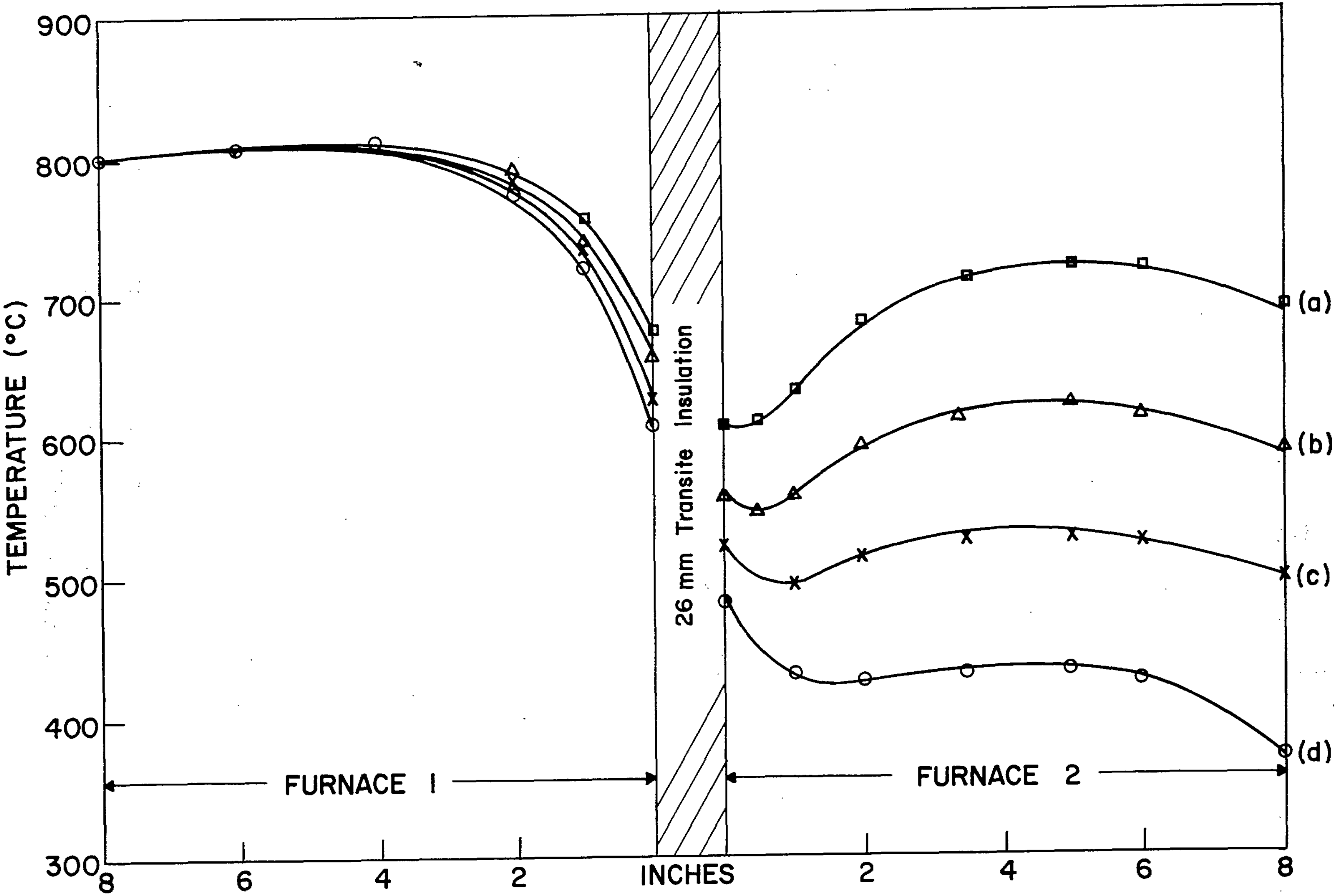

Figure 22. Temperature Profile of the Central Portion of a Two-Furnace (Two-Zone) System. A 26-mm transite insulation is used between furnaces.