

## HIGHER MINERAL ARSENIDES OF COBALT, NICKEL, AND IRON

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## ABSTRACT

X-ray, microscopic, microchemical, contact-print, and mineral synthesis techniques have been applied to the problem of the relationships of the higher natural arsenides of cobalt, nickel, and iron. The data obtained have been correlated with a review of existing analyses.

Both the isometric and "orthorhombic"<sup>1</sup> groups exhibit limited isomorphism in regard to the three metals, and the two groups appear to be essentially complementary. The isometric members form a single group of triarsenides with the skutterudite structure. The long-held assumption that published analyses indicate the existence of an isometric diarsenide series is not substantiated by a critical review of the analyses. Extensive arsenic deficiency shown by published analyses of isometric arsenides is due largely to mechanical inhomogeneity involving "orthorhombic" diarsenides, niccolite, and other minerals. Isomorphous substitution of metal for arsenic may contribute to the arsenic deficiency, but evidence for this was not obtained.

The lattice constants of the isometric arsenides are related to the ratio between the three metals, varying directly with increasing nickel, iron, or nickel and iron content. Variations in arsenic ratio do not appear to influence the lattice constants appreciably. The lattice constants range from 8.187 Å to 8.311 Å, an increase over that previously recorded (8.18 Å to 8.27 Å).

Isometric arsenide crystals are almost invariably zoned and inhomogeneous, containing both isometric and nonisometric constituents. Fine granular aggregates of "orthorhombic" diarsenides frequently occur in these complex cubic crystals

<sup>1</sup> The term "orthorhombic" in quotation marks is used as a group term for the nonisometric higher arsenides, all of which are orthorhombic with the exception of safflorite which Peacock (1944) considers monoclinic with rectangular axes.

and have probably often been overlooked since the anisotropism is weak. The inhomogeneous character of these zonal crystals could account for many of the reported compositional peculiarities of the isometric arsenides such as extensive arsenic deficiency and extreme variation in the cobalt-nickel-iron ratio.

Since there is no valid basis for an isometric diarsenide series, it is urged that the names smaltite, chloanthite, chathamite, and arsenoferrite, long associated with an alleged series of isometric diarsenides, be dropped. The single term skutterudite should be applied to all isometric arsenides of cobalt, nickel, and iron and in a restricted sense to those in which cobalt is dominant; the appropriate modifiers, nickelian and ferrian, would indicate dominance of nickel and iron respectively. Such a terminology is believed adequate since the isomorphism between cobalt, nickel, and iron in the isometric group is clearly limited, and only a single end member (cobalt) appears to exist.

The "orthorhombic" diarsenides exhibit both discontinuous and limited isomorphism between cobalt, nickel, and iron; those high in nickel are completely separated from the iron-bearing members by a broad wedge of isometric arsenides. The term rammelsbergite is retained for the common high-nickel member, and paramrammelsbergite for the rarer nickel-rich form. The term loellingite is applied to all iron-rich orthorhombic diarsenides and in a restricted sense to those with an iron ratio greater than 85. The group of iron-rich orthorhombic diarsenides with an iron ratio of less than 85 and with cobalt dominant over nickel may be termed cobaltian loellingite. The corresponding group with nickel dominant over cobalt is designated nickelian loellingite. Safflorite has been rather generally accepted for the cobalt end member of an allegedly unlimited isomorphous series of orthorhombic diarsenides, the other end members being loellingite and rammelsbergite. There is no evidence for the existence of such a cobalt end member of the "orthorhombic" series, either from the available data on natural material or from the experiments in synthesis. The plotting of the published analyses indicates a clustering of "orthorhombic" analyses in the mid-portion of the cobalt-iron edge of the diagram. The symmetry of these iron-cobalt arsenides is monoclinic according to (Peacock, 1944), justifying the retention of the name safflorite as a species distinct from loellingite. However it should be redefined as a monoclinic diarsenide of cobalt and iron in which the proportions of the two metals are approximately equal

#### PROBLEMS OF THE HIGHER ARSENIDES

The minerals studied are the so-called white arsenides of cobalt, nickel, and iron, distinguished by color from the reddish, lower arsenides such as niccolite and maucherite. They may also be referred to as the higher arsenides since all members have an arsenic content greater than that required for the composition  $RA_2As_3$ .

The extent of isomorphous substitution between cobalt, nickel, and iron furnishes a major problem of the isometric arsenide series. Substitution has been generally considered unlimited, even to the extent that cobalt, nickel, and iron end members have been reported. For many high-iron and high-nickel occurrences, originally cited as isometric, restudy of material from the localities in question and attention to the original descriptions reveal that the analyzed materials were often either "orthorhombic" arsenides, mistakenly identified as isometric, or inhomogeneous mixtures.

Variation in metal-arsenic ratio shown by published analyses of the isometric arsenides is a problem of considerable interest. The ratio of metal to arsenic in the 195 published analyses ranges from 1:1.12 to 1:3.68. This has been explained as

due either to mechanical inhomogeneity or isomorphous substitution of arsenic for metal or of metal for arsenic. Heretofore no extensive investigation of the problem has been attempted.

The remarkable zonal structure of the isometric arsenides was recognized long ago. Microscopic, analytical chemical methods and partial solubility techniques have been employed in earlier attempts to identify the individual components, but the identification of the constituents has not been checked by x-ray methods. The identity of the constituents in the zonal crystals is essential to the solution of the problem of isomorphous substitution among the three metals as well as that of metal-arsenic ratio.

Another problem concerns the variation in the lattice constants of the isometric arsenides, first noted by Oftedal (1926; 1928). He suggested that the differences are due to variations in metal-arsenic ratio or variations in the ratio of the three metals but left the problem unsolved. Oftedal (1926; 1928) recognized the apparently anomalous structural situation in which two parallel series of isometric arsenides, one of diarsenides (smaltite, *etc.*) and another of triarsenides (skutterudite, *etc.*) possess identical crystal structures. The solution is closely related to the problems of variation in metal-arsenic ratio and variation in lattice constants.

The long-held assumption that two parallel series of the arsenides of these metals exist, one isometric, the other "orthorhombic", each exhibiting unlimited isomorphous substitution between cobalt, nickel, and iron, is unsupported. Both isometric and "orthorhombic" arsenides containing all three elements exist, but the extent of isomorphous substitution within each group is open to question. The present view of unlimited solid solution is based largely on chemical analyses, most of which were made many years ago on material whose homogeneity had not been ascertained and whose structural identity as isometric or "orthorhombic" had not been established.

Emphasis has been placed on the problems relating to the isometric arsenides; however, two problems of the "orthorhombic" series have been given consideration; the extent of isomorphous substitution between cobalt, nickel, and iron and the question of nomenclature. A number of changes in nomenclature and classification are found necessary. A classification and nomenclature of the higher arsenides is offered in Table I where comparison is made with the conventional classification of these minerals used by many authors in recent years and with that employed in the new 7th edition of Dana's *System of Mineralogy* (Palache, Berman, and Frondel, 1944). The relations of the minerals under discussion are shown diagrammatically in Figure 1. The conventional classification assumes the existence of three distinct mineral series. Most authors imply that each series exhibits unlimited isomorphous substitution between cobalt, nickel, and iron. Restudy supports the view that the isometric diarsenides are nonexistent and that all isometric members are essentially triarsenides. These may be represented by a triangular diagram (Fig. 1a) in which (cobaltian), nickelian, and ferrian skutterudite form the three segments. The "orthorhombic" diarsenides comprise discontinuous and limited units (Fig. 1b) which together are essentially complementary to the isometric arsenides.

TABLE 1.—Classification and nomenclature of the higher arsenides of cobalt, nickel and iron

Conventional classification prevailing in mineralogical literature	Classification in 7th edition of Dana's System, Palache, Berman, and Frondel (1944)	Revised classification
SKUTTERUDITE SERIES (ISOMETRIC TRIARSENIDES)	SKUTTERUDITE SERIES	SKUTTERUDITE SERIES
	ISOMETRIC ARSENIDES— $RA_{3-x} = .0$ to $.5$	ISOMETRIC TRIARSENIDES— $RA_3$
Skutterudite $CoAs_3$ (Dana, 1932) Nickel-skutterudite $(Ni, Co, Fe)As_3$ (Dana, 1932) Ferriferous skutterudite $(Co, Ni, Fe)As_3$ (Short, 1940)	Skutterudite $(Co, Ni)As_{3-x}$ Nickel-skutterudite $(Ni, Co)As_{3-x}$ Ferrian skutterudite $(Fe, Ni, Co)As_{3-x}$	Skutterudite (cobaltian) $(Co, Ni, Fe)As_3$ and $CoAs_3$ Nickelian skutterudite $(Ni, Co, Fe)As_3$ (End member doubtful) Ferrian skutterudite $(Fe, Ni, Co)As_3$ (End member doubtful)
SMALTITE-CHLOANTHITE SERIES (ISOMETRIC DIARSENIDES)	ISOMETRIC ARSENIDES— $RA_{2-x} x = .5$ to $1.$	The above terms provide an adequate nomenclature for all isometric higher arsenides of these elements. The application of special names to varieties whose analyses exhibit deviations in arsenic ratio from the theoretical composition $RA_2$ are unnecessary since in many cases this is due to mechanical inhomogeneity. Structurally they are all triarsenides of the skutterudite type even though the arsenic deficiency may in some cases be due in part to substitution of metal for arsenic.
Smaltite $CoAs_2$ (Short, 1940) Chloanthite $NiAs_2$ (Short, 1940) Chathamite $“(Fe, Ni, Co)As_2”$ (Dana, 1892)	Smaltite $(Co, Ni)As_{2-x}$ Chloanthite $(Ni, Co)As_{2-x}$ Chathamite $(Fe, Ni, Co)As_{2-x}$	
Arsenoferrite $FeAs_2$ (Dana, 1932)	Arsenoferrite (?) $FeAs_2$	
ORTHORHOMBIC DIARSENIDES	ORTHORHOMBIC DIARSENIDES	“ORTHORHOMBIC” DIARSENIDES
Rammelsbergite $NiAs_2$ (Dana, 1932) Loellingite $FeAs_2$ (Dana, 1932) Safflorite $CoAs_2$ (Dana, 1932)	Rammelsbergite $NiAs_2$ Pararammelsbergite $NiAs_2$ Loellingite $FeAs_2$ Safflorite $CoAs_2$ “with considerable iron (4-16%)”	<i>Orthorhombic</i> Rammelsbergite $(Ni, Co, Fe)As_2$ and $NiAs_2$ Pararammelsbergite $(Ni, Co, Fe)As_2$ and $NiAs_2$ Loellingite $(Fe, Co, Ni)As_2$ with Fe > 85% and $FeAs_2$ Cobaltian loellingite $(Fe, Co, Ni)As_2$ with Fe < 85% and cobalt > nickel Nickelian loellingite $(Fe, Ni, Co)As_2$ with Fe < 85% and nickel > cobalt <i>Monoclinic</i> Safflorite $(Co, Fe)As_2$ deviation from 1:1 ratio not known.

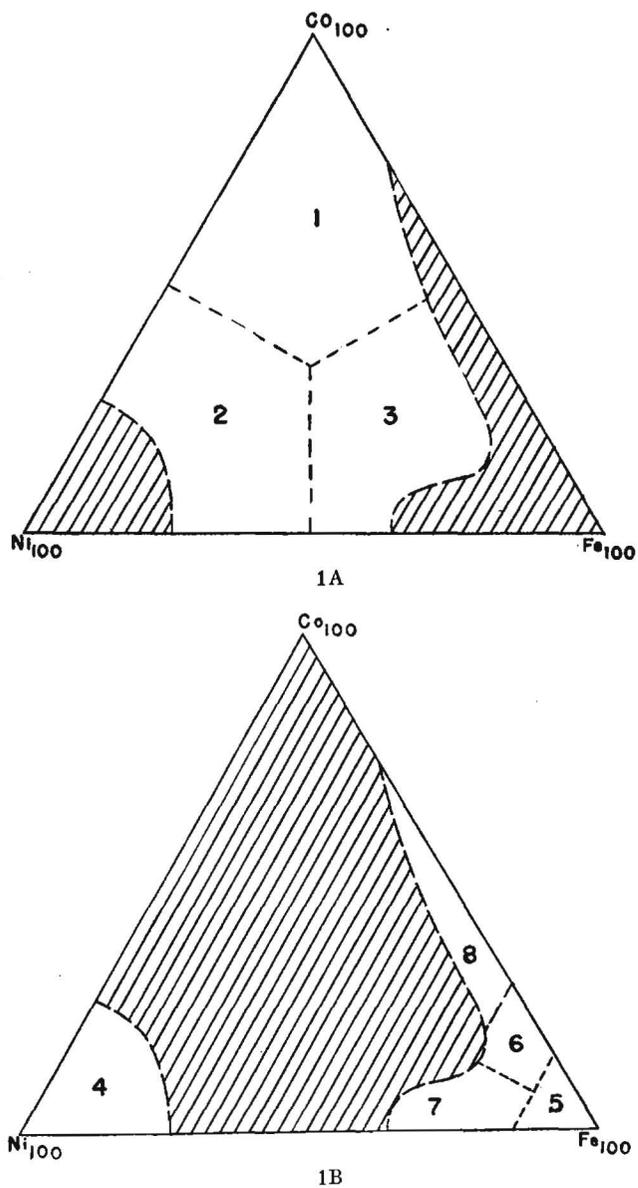


FIGURE 1.—Relation of composition to crystallization in the higher arsenides.

- (a) Isometric triarsenides
1. (Cobaltian) Skutterudite
  2. Nickelian Skutterudite
  3. Ferrian Skutterudite

- (b) "Orthorhombic" diarsenides
- Orthorhombic
4. Rammelsbergite and Pararammelsbergite
  5. (Ferrian) Loellingite
  6. Cobaltian Loellingite
  7. Nickelian Loellingite
- Monoclinic
8. Safflorite

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Although most of the specimens employed were obtained from the Egleston Collection of Columbia University, many were secured from the United States National Museum through the courtesy of Dr. William F. Foshag and Mr. Edward P. Henderson. Additional material has been supplied by Mr. Lawson H. Bauer, chief chemist, New Jersey Zinc Company, Dr. H. V. Ellsworth, Geological Survey of Canada, Mr. Samuel Gordon, Philadelphia Academy of Sciences, Professor Harry H. Hess, Princeton University, Dr. V. Ben Meen, Royal Ontario Museum, Toronto, Professor Charles Palache, Harvard University, Dr. Charles F. Park, U. S. Geological Survey, Professor M. A. Peacock, University of Toronto, and Dr. Waldemar T. Schaller, U. S. Geological Survey.

## MICROSCOPIC INVESTIGATIONS

The microscopic methods used follow the standard practices developed by Schneiderhöhn and Ramdohr (1931; 1934), Short (1940), and others in the investigation of the opaque ore minerals.

Surfaces of two types were employed: standard bakelite mounts polished on a Graton-Vanderwilt machine and hand-polished surfaces. Unmounted, hand-polished specimens are preferred as they are prepared more rapidly, larger specimens may be polished, and the electrolytic contact-print method is more readily applied. To use the electrolytic contact-print method on specimens mounted in bakelite blocks, one must drill through the bakelite to make contact with the metallic specimen. If the sample contains considerable gangue, several holes may be drilled before a suitable contact is established.

An electrically driven flexible shaft drill was used to obtain material to be used in microchemical testing and in the preparation of x-ray samples. The drill is similar to that described by Harcourt (1937) but differs in two respects: (1) It is mounted on a Leitz "manipulator" permitting easy and accurate control in one vertical and two horizontal directions; (2) two interchangeable clamps permit the use of both ordinary dental drills and needles.

The chemical methods used were entirely qualitative. The lack of homogeneity

revealed by microscopic observation indicates that comparatively few specimens of these minerals offer the possibility of securing sufficient material of acceptable purity for standard quantitative analysis. The contact-print technique of Gutzeit (1942a), especially the electrolytic variation was used extensively. The limitations of the contact-print method in the case of certain minerals exceptionally resistant to attack necessitated the use of microchemical tests following the technique of Short (1940). Etching with  $\text{HNO}_3$  was employed to develop zonal and other structures. Often the surfaces were strongly etched during the preparation of contact prints, and further etching was unnecessary.

#### CONTACT-PRINT STUDIES

The contact print provides a permanent record of the distribution of a particular element throughout the area of a polished surface. Examples of such prints are shown in Plate 1. The principle of the method was first employed by the metallurgists Baumann (1906) and Heyn (1906). Niessner (1929) and Glazounov (1929) revived interest in it. This renewed interest is undoubtedly due to the development of "spot testing" by Feigl (1935; 1937; 1943) during the period 1920–1930 which provided specific color reactions for most of the elements. The first application of the contact-print method to minerals appears to be that of Jirkovsky (1932). From 1932 to 1937 Gutzeit and his coworkers at the University of Geneva, Switzerland, developed the application of the method to minerals. Although 13 years have elapsed since the publication of the first paper by Gutzeit, Gysin, and Galopin (1933) use of the method seems to have been limited. The short papers of Gutzeit (1942a; 1942b), especially the former, provide an excellent summary.

The basic principle is the same as that underlying spot testing. Spot testing depends on the use of so-called specific reagents which produce a characteristic color in the presence of a particular element. Spot tests can be used as an adjunct to reflecting microscope methods in the same manner as the usual microchemical reactions. A small amount of the mineral is chiseled or drilled out of the polished surface and is dissolved by an attacking reagent. A drop of this solution is placed on a piece of white filter or blotting paper. A drop of the appropriate specific reagent is then applied to the center of the spot. In the case of nickel, using dimethylglyoxime, the customary pink reaction is observed. However, with both spot testing and orthodox microchemical testing the presence of an element is established only at a particular point on the surface.

The simple contact-print method consists of two operations as in spot testing: (1) the application of the attacking reagent, and (2) the application of the specific reagent. Gelatin-coated photographic paper from which the silver salts have been removed is prepared in advance and dried, or gelatin-coated paper free from silver salts can be secured from the Eastman Kodak Co. Pieces of this paper cut to a size slightly larger than the specimen are soaked for several minutes in an appropriate attacking reagent acids or strong bases). The excess reagent is removed by pressing the sheet between two pieces of white blotting paper. This paper, saturated with the attacking reagent, is placed with the gelatin side against the polished surface, good contact being assured by applying pressure. The length of attack varies from

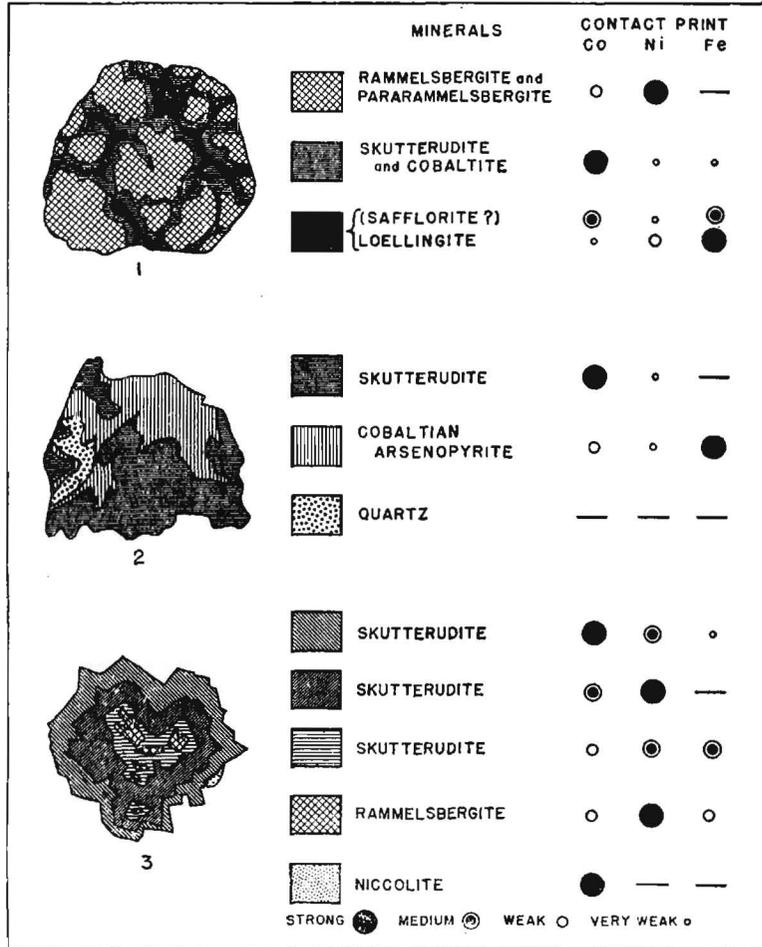
a few seconds to several minutes depending on the minerals involved. The paper is stripped from the surface and placed immediately in the specific reagent, (mostly complex organic compounds). A color pattern develops showing the distribution of the element in question throughout the entire area of the polished surface. Reagents such as  $\text{NH}_4\text{OH}$ , although ineffective under ordinary conditions, readily dissolve a sufficient quantity of material from a polished mineral plate to yield a specific reaction. This unusual solubility is believed due to mechanical disruption of the surface layers as a result of polishing. Successive prints become increasingly weaker unless the surface is repolished. The most complete treatment of the simple contact-print method is given by Gutzeit and Galopin (1934) and Gutzeit (1942a).

An electrolytic variation of the method devised by Glazounov (1929), and first used on minerals by Jirkovskiy (1932), was further developed by Hiller (1937). The procedure follows that of the simple contact-print method just described, but a current of 4–16 volts and less than 50 milliamperes obtained from a battery of 6 to 10 dry cells is employed during the attacking operation. The specimen is brought into contact with the (+) pole of the battery, and a sheet of aluminum attached to the (–) pole is placed below the gelatin paper. Anodic dissociation takes place on the mineral surface, and the (+) ions set free are trapped in the gelatin on their way through to the (–) aluminum sheet. By means of this device the time of attack is greatly decreased. Minerals essentially insoluble under the conditions of the simple contact-print method can be investigated, and the rapidity of the reaction results in sharper prints since lateral diffusion is reduced. Prints showing the distribution of negative elements such as sulphur and antimony or arsenic can be prepared by reversing the (+) and (–) leads from the battery. This method is limited to the investigation of minerals that are conductors, and cannot be used when the mineral occurs as isolated crystals in a nonconducting gangue. If the specimen is mounted in bakelite it is necessary to bore a hole through the bottom of the block so that a needle attached to the lead from the battery can be brought into contact with the specimen.

Caution must be exercised in attempting to make quantitative estimates by the use of the contact-print method since the depth of color obtained is proportional to the amount of material dissolved rather than the amount of the element present. Hence the relative solubility of the various minerals and potential effects influence the intensity of the color.

Reference to the use of the contact-print method with the isometric arsenides of cobalt, nickel, and iron is made in the following papers: Gutzeit and Galopin (1934); Wenger, Gutzeit, and Hiller (1934); Galopin (1936); Hiller (1937); Gutzeit (1942a; 1942b). In all cases these are descriptions of technique; the minerals merely serve as examples of the application of the method. Gutzeit and Galopin (1934) observed that specimens of the isometric arsenides high in cobalt and iron were less soluble than high nickel members. Apparently no use has heretofore been made of the method in attempting to solve any of the problems of this group.

The method proved helpful in establishing the distribution of cobalt, nickel, and iron. After a little experience it was found that much time was saved in mineral identification by preparing a set of contact prints of each polished surface before making observations under the microscope.

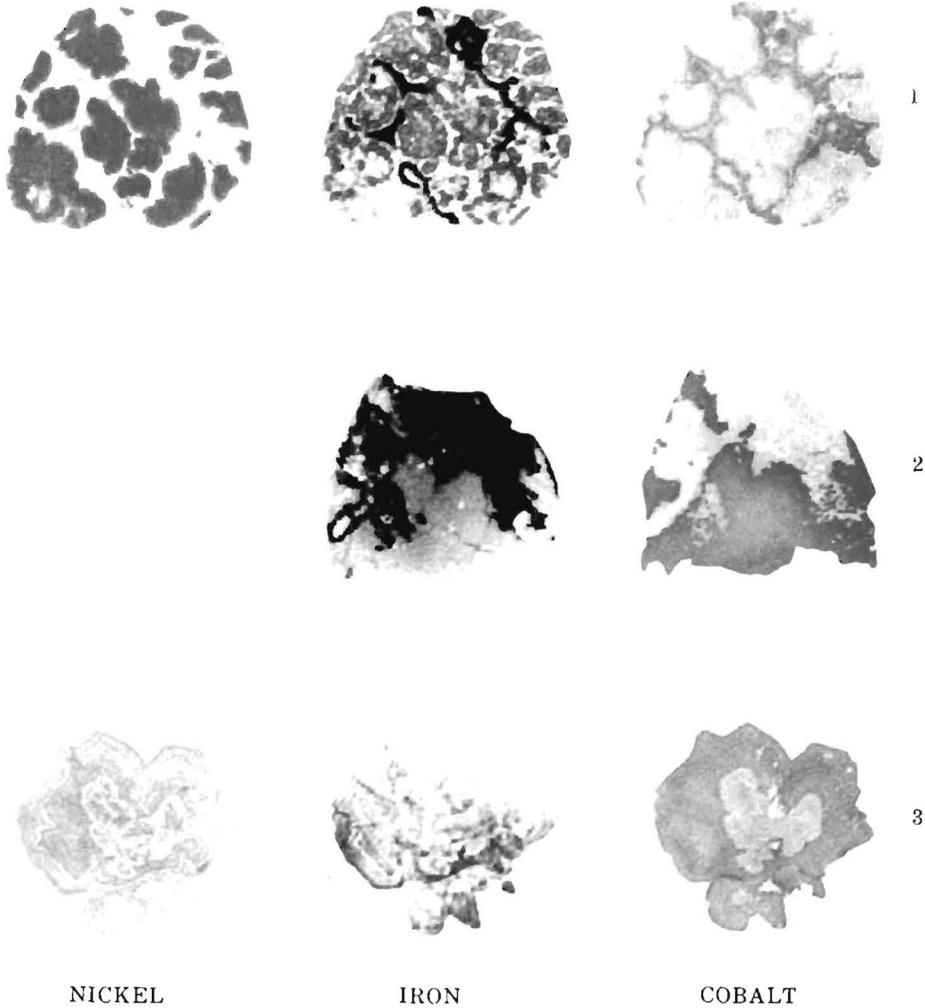


## EXPLANATION OF PLATE 1

Specimen No. 1—Cobalt, Ontario—Complex nodular aggregate of nickel-rich arsenides, rammelsbergite and pararammelsbergite, rimmed by successive narrow cobalt-rich zones of skutterudite and cobaltite. These are followed in turn by bands of an iron-cobalt nonisometric arsenide (safflorite ?) and finally by loellingite.

Specimen No. 2—Skutterud, Norway—Massive skutterudite, nearly devoid of nickel and iron, intergrown with cobaltian arsenopyrite (danaite). Intricate boundary relations of the two minerals are brought out clearly by the prints.

Specimen No. 3—Schneeberg, Saxony—Intergrown cubes of skutterudite, illustrating frequently observed inhomogeneous and zonal character of isometric arsenide crystals. Orthorhombic nickel arsenide rammelsbergite forms core of each crystal. This is surrounded by successive shells of the isometric arsenide, skutterudite. Variable cobalt-nickel-iron ratio of the several zones of isometric material evident in prints. Niccolite on the surface of the isometric crystals is additional complication. Such niccolite masses frequently observed within zonal isometric crystals.



#### CONTACT PRINTS OF COBALT - NICKEL - IRON ARSENIDES

Prints obtained from polished plates of representative minerals of this group to illustrate the application of the contact-print method in determining the distribution of elements in a complex mineral assemblage. Dimethylglyoxime used in the localization of nickel provides the well known pink reaction. The orange-brown cobalt prints are secured by the use of alpha-nitroso-beta-naphthol. The blue and green colors indicating iron are due to potassium ferrocyanide. The pale-gray and pale-brown prints provided respectively by cobalt-and nickel-rich minerals in the presence of potassium ferrocyanide do not mask the iron reaction.

## SYNTHESIS OF THE HIGHER ARSENIDES OF COBALT, NICKEL, AND IRON

## GENERAL STATEMENT

The uncertainty regarding much of the existing chemical data rendered it necessary to attempt the synthesis of as many of the higher arsenides as possible. The following section is a review of previous attempts at synthesis, a description of the experimental technique, and the correlation of experimental data with x-ray diffraction analysis. The experiments in mineral synthesis were undertaken in order to prepare arsenides of known composition as an aid in investigating the isomorphism of this group. No attempt was made to conduct a systematic study of the system cobalt-nickel-iron-arsenic. The experiments differ from previous attempts in two respects. They were not confined to the synthesis of single-metal arsenides. Both intermediate bi-metal and more complex tri-metal arsenides were investigated. The products of synthesis were examined for homogeneity, and the phases were identified by powder x-ray methods.

## PREVIOUS SYNTHESIS OF THE HIGHER ARSENIDES

*General statement.*—With few exceptions only lower arsenides (with a metal-arsenic ratio of 1:1 or less) have been obtained in previous experiments. Only two attempts have been made to investigate systems involving more than one metal, and both resulted in the production of lower arsenides. Observations on the higher arsenides are less numerous because they do not ordinarily form under the conditions commonly employed. The methods most frequently followed have been either “wet” chemical reactions in dilute solutions or “dry fusions” of arsenic and the appropriate metal under a protective cover of molten flux. Under such conditions the mono-arsenide seems to be the highest phase obtainable. The higher arsenides apparently form only under conditions of dry fusion or gaseous diffusion in a saturated arsenic atmosphere.

All previous syntheses of the higher arsenides of these metals were carried out prior to 1917, and all were concerned with simple two-component systems (Co-As, Ni-As, and Fe-As). The identity and composition of the product is open to question in every case since these earlier investigators assumed that bringing the powdered metal to a condition of “constant weight” by heating in an arsenic atmosphere provided a single-phase, homogeneous product whose composition could be determined by quantitative analysis of the bulk sample or by comparison of the weight of the product and the original metal sample. Unfortunately the reaction is that of arsenic vapor on solid metal particles hence an impervious coat of higher arsenide tends to form around a core of lower arsenide or metal, protecting the latter from further effective reaction with the arsenic vapor. Consequently the sample appears to have reached “constant weight”, although it is not a homogeneous single phase. Furthermore, enough free arsenic may become mixed with the arsenide, at times, to be detected in x-ray diffraction patterns. The identity and composition of the products of such reactions cannot be established by quantitative chemical methods unless the homogeneity of the sample is first established by x-ray or microscopic examination. In none of the previous investigations has either the reflecting-polarizing microscope

or the x-ray diffraction method been employed to determine the homogeneity of the product or to identify the phases. The results of earlier experiments in the synthesis of the higher arsenides of cobalt, nickel, and iron are outlined in Table 2. The production of the following phases has been claimed:  $\text{Co}_2\text{As}_3$ ,  $\text{CoAs}_2$ ,  $\text{Co}_2\text{As}_5$ ,  $\text{CoAs}_3$ ,  $\text{Ni}_2\text{As}_3$ ,  $\text{NiAs}_2$ , and  $\text{FeAs}_2$ .

*Previous syntheses of the higher arsenides of cobalt.*—The arsenides of cobalt occurring in nature, unlike those of nickel, all have a metal-arsenic ratio greater than 1:1. No natural cobalt equivalent of niccolite or any lower arsenide is known. The generally recognized natural arsenides of cobalt as well as the crystallization and composition usually assigned to them follow:—skutterudite ( $\text{CoAs}_3$ ) isometric, smaltite ( $\text{CoAs}_2$ ) isometric, and safflorite ( $\text{CoAs}_2$ ) orthorhombic. Synthesis of the following higher arsenides of cobalt has been reported:  $\text{CoAs}_3$ ,  $\text{Co}_2\text{As}_5$ ,  $\text{CoAs}_2$ .  $\text{Co}_2\text{As}_3$  has not been reported as occurring in nature, and  $\text{Co}_2\text{As}_5$  only by Beutell and Lorenz (1915) as a hypothetical constituent of smaltite-chloanthite.

Durocher (1851, p. 825) mentions the synthesis of "cobalt arsenical en hexaedre" but gives no data on the identity of the product. Fouqué and Lévy (1882, p. 276), Palache, Berman and Frondel (1944, p. 345), and others credit him with the synthesis of smaltite  $\text{CoAs}_2$ , but the basis for this seems doubtful. Ducelliez (1907) described in detail the synthesis of a series of cobalt arsenides which he later summarized Ducelliez (1908). He claimed the production of  $\text{Co}_2\text{As}_3$  and  $\text{CoAs}_2$  by passing a stream of hydrogen carrying either arsenic or arsenic chloride vapor over the powdered metal at high temperatures. The product was removed and weighed at intervals until a condition of constant weight was attained after which it was analyzed. Beutell and Lorenz (1916) and Beutell (1916a) used a sealed tube technique. They claim the production of four higher cobalt arsenides,  $\text{CoAs}_3$ ,  $\text{Co}_2\text{As}_5$ ,  $\text{CoAs}_2$ ,  $\text{Co}_2\text{As}_3$ , of which only  $\text{CoAs}_3$  is confirmed by the present study and is believed to have been synthetic skutterudite. When constant weight was achieved the composition was calculated by comparing the weight of the arsenide with that of the original powdered metal. Beutell (1916a) varied this procedure by grinding the material repeatedly, reducing the time required to bring the sample to "constant weight". In addition to the synthesis of cobalt arsenide from pure cobalt and arsenic, Beutell and Lorenz (1916) and Beutell (1916a) carried out similar experiments on *Speiskobalt* (smaltite-chloanthite) which they had first reduced to an approximate composition  $\text{RAs}_1$  by heating in a vacuum. This is not a true synthesis. Ramsdell (1927), in an abstract, mentions the production of a material "similar to artificial smaltite with a composition nearer  $\text{Co}_2\text{As}_5$  than  $\text{CoAs}_2$ " but does not elaborate.

*Previous syntheses of the higher arsenides of nickel.*—The natural compounds of nickel and arsenic are more numerous than those of cobalt and comprise both lower and higher arsenides. The lower arsenides are represented by such minerals as niccolite  $\text{NiAs}$  and are not considered here. The generally accepted higher arsenides of nickel are rammelsbergite ( $\text{NiAs}_2$ ) orthorhombic, pararammelsbergite ( $\text{NiAs}_2$ ) orthorhombic, and chloanthite ( $\text{NiAs}_2$ ) isometric. The term nickel skutterudite

TABLE 2.—*Previous syntheses of the higher arsenides of cobalt, nickel, and iron*

COBALT ARSENIDES						
Author	Date	Method	Co <sub>2</sub> As <sub>3</sub>	CoAs <sub>2</sub>	Co <sub>2</sub> As <sub>5</sub>	CoAs <sub>3</sub>
Ducelliez	1907 and 1908	AsCl <sub>3</sub> vapor on Co in H <sub>2</sub> , "constant weight," at- mospheric pressure	400°- 600°C.	—	—	—
Ducelliez	1907 and 1908	As vapor on Co in H <sub>2</sub> , "constant weight," at- mospheric pressure	400°- 600°C.	Below 400°C.	—	—
Beutell and Lorenz Beutell	1916  1916A	As vapor on Co in sealed tubes (tube in tube), "constant weight"	345°- 365°C.	385°- 405°C.	415°- 430°C.	450°- 618°C.

NICKEL ARSENIDES						
Author	Date	Method	Ni <sub>2</sub> As <sub>3</sub>	NiAs <sub>2</sub>	Ni <sub>2</sub> As <sub>5</sub>	NiAs <sub>3</sub>
Vigouroux	1907B and 1908	As vapor on Ni in H <sub>2</sub> , "constant weight," at- mospheric pressure	400°- 600°C.	300°- 400°C.	—	—
Beutell	1916A	As vapor on Ni in sealed tubes (tube in tube), "constant weight"	—	400°- 450°C.	—	—

IRON ARSENIDES						
Author	Date	Method	Fe <sub>2</sub> As <sub>3</sub>	FeAs <sub>2</sub>	Fe <sub>2</sub> As <sub>5</sub>	FeAs <sub>3</sub>
Richardson by Percy	1864	As vapor on Fe in H <sub>2</sub> , at- mospheric pressure	—	Red heat	—	—
Vigouroux	1907A	As vapor on Fe in H <sub>2</sub> , "constant weight," at- mospheric pressure	—	300°- 400°C.	—	—
Vigouroux	1907A	As vapor on Fe in sealed tubes, "constant weight" also As vapor on Fe in H <sub>2</sub>	—	300°- 400°C.	—	—
Hilpert and Dieckman	1911	As vapor on Fe in sealed tubes, then heated to constant weight in H <sub>2</sub> , atmospheric pressure	—	700°C.	—	—

has been used for the high nickel equivalent of cobalt triarsenide, but no pure NiAs<sub>3</sub> has ever been reported. Beutell and Lorenz (1915) apparently considered a compound Ni<sub>2</sub>As<sub>5</sub> to be one of the components of smaltite-chloanthite.

The synthesis of only two higher arsenides of nickel ( $\text{NiAs}_2$  and  $\text{Ni}_2\text{As}_3$ ) has been reported. One of these,  $\text{Ni}_2\text{As}_3$ , has not been claimed to occur in nature, and one of those claimed to exist in nature,  $\text{Ni}_2\text{As}_5$ , has not been produced synthetically. Vigouroux (1907b; 1908) using the method employed by Ducelliez (1907; 1908) in producing cobalt arsenides claimed the synthesis of two higher arsenides of nickel,  $\text{Ni}_2\text{As}_3$  and  $\text{NiAs}_2$ . Beutell (1916a) reported the results of experiments conducted in the same manner as those in which he and Lorenz produced cobalt arsenides, but like Vigouroux, was unable to produce an arsenide of nickel higher than  $\text{NiAs}_2$ . The phase  $\text{NiAs}_2$  is confirmed in the present study and their material of this composition is believed to have been synthetic rammelsbergite.

*Previous syntheses of the higher arsenides of iron.*—Natural occurrences of lower arsenides of iron are not known, neither has any natural iron arsenide comparable with the triarsenide of cobalt, skutterudite, been reported. The higher iron arsenides claimed to occur in nature are loellingite ( $\text{FeAs}_2$ ) orthorhombic, arsenoferrite ( $\text{FeAs}_2$ ) isometric, and leucopyrite, orthorhombic. Leucopyrite has usually been considered a variety of loellingite but has at times been regarded as a distinct mineral with a composition  $\text{Fe}_3\text{As}_4$  or  $\text{Fe}_2\text{As}_3$ . The only higher iron arsenide whose synthesis has been claimed by previous investigators is  $\text{FeAs}_2$ . Richardson (Percy, 1864) prepared a series of arsenides of iron by heating the powdered metal in a stream of hydrogen and arsenic vapor at "red heat." He mentions the production of two higher arsenides  $\text{FeAs}_2$  and  $\text{FeAs}_4$  but questioned the latter pointing out that a similar experiment resulted in the production of  $\text{FeAs}_2$ . Vigouroux (1907a) produced the diarsenide employing the method he used in the production of nickel arsenides. He obtained the same result by heating a mixture of arsenic and iron in a sealed glass tube. Hilpert and Dieckmann (1911) produced  $\text{FeAs}_2$  by heating iron and excess arsenic in sealed Jena glass tubes, followed by reheating in a hydrogen atmosphere at atmospheric pressure until constant weight was attained. The average arsenic content of the product in four trials using this method is 73.82, the theoretical value for  $\text{FeAs}_2$ . The specific gravity (7.38) lies within the range assigned to natural  $\text{FeAs}_2$ , Loellingite (7–7.4). Beutell and Lorenz (1916) claim the production of  $\text{Fe}_2\text{As}_3$  and  $\text{FeAs}_2$  employing the same (tube-in-tube) methods they used in the production of cobalt and nickel arsenides. However, instead of pure iron they used powdered loellingite, which had been reduced to approximately  $\text{FeAs}$ , by heating in a vacuum. This is not a true synthesis. In the light of the present study the  $\text{FeAs}_2$  of these investigators was synthetic loellingite.

#### METHODS OF MINERAL SYNTHESIS OF THE HIGHER ARSENIDES

"Wet methods" depending on reactions in aqueous solutions have been employed by numerous investigators but have always resulted in the formation of lower arsenides. Only dry "thermal" methods consisting of a direct attack of arsenic on the metal at high temperatures were used in this investigation. Arsenic at elevated temperatures, unless retained under great pressure, passes directly into the gaseous state. Therefore the production of arsenides by dry "fusion" methods is in reality an attack of gaseous arsenic on solid or molten metal. This introduces

difficulties in attempts to prepare arsenides by thermal methods. Experiments conducted in open crucibles under a protecting cover of molten flux have always led to the formation of lower arsenides. To produce the higher arsenides it is necessary to either use sealed containers or maintain an arsenic vapor atmosphere in an open system. At high temperatures the vapor pressure of arsenic results in frequent failure of sealed glass containers. Maintenance of an arsenic vapor atmosphere in an open system is dangerous and difficult. The problem of containers and furnace linings is also complicated due to the readiness with which arsenic attacks most metals.

Powdered C. P. cobalt, nickel, iron, and arsenic were used in the production of the monometallic arsenides. Some intermediate arsenides involving two or all three metals were prepared from these powdered metals, but most of them were obtained by using previously prepared alloy ingots. In many cases attempts to produce intermediate arsenides containing two or all three metals resulted in a mechanical mixture of two or more phases. It was hoped this could be avoided by insuring an intimate mixing of the metals before "arseniding". Small ingots of alloys containing the desired proportions of the metals were prepared in an induction furnace. The swirling motion imparted to the melt by the eddy currents in such a furnace favors uniform mixing but coring develops on cooling so that the ingots were annealed (homogenized) for 10 days at 1000°C. Fragments cut from the ingots were then treated in the same manner as the metal powders.

Two tubular resistance furnaces were used for most of the work. These consisted of an 18-inch spirally grooved core of alundum on which nichrome wire was wound and covered with 4 inches of insulation. The length of these furnaces insures a fairly uniform temperature for a distance of about 6 inches in the center. The furnaces were used in a vertical position to permit rapid quenching of samples. Temperature control was achieved by means of resistance mats to which leads could be clamped. No voltage control or other temperature regulating device was available, hence it was not possible to maintain the temperature closer than  $\pm 15^\circ\text{C}$ . due to fluctuations in the line current. Temperatures were determined by means of a Brown portable pyrometer employing a calibrated Pt-Pt<sub>90</sub>Rh<sub>10</sub> thermocouple.

Two different methods of synthesis were employed. Most of the experiments were carried out in sealed glass tubes, but some were conducted at atmospheric pressure in the presence of hydrogen. Some samples were prepared using sealed tubes containing a mixture of the powdered elements in the correct proportions. For work lower than 600°C. pyrex tubes were employed, and fused quartz (silica glass) for all work above this. Above 1200°C. silica-tubing disintegrates so that one is limited to lower temperatures. Failure of both pyrex and silica tubes was frequent. A modification of the sealed-tube method adapted from Beutell and Lorenz (1916) and referred to as the "tube in tube" technique was used extensively since it reduces the danger of contaminating the product with free arsenic. The powdered metal is placed in a small tube within a larger one containing excess arsenic. An opening in the small tube permits the arsenic vapor to come in contact with the metal yet keeps the excess arsenic separate from the product. After filling, the tube is attached by means of a two-way stopcock to a vacuum pump and hydrogen tank, permitting

alternate evacuation and introduction of hydrogen. This process is repeated two or three times, after which the tube is sealed off.

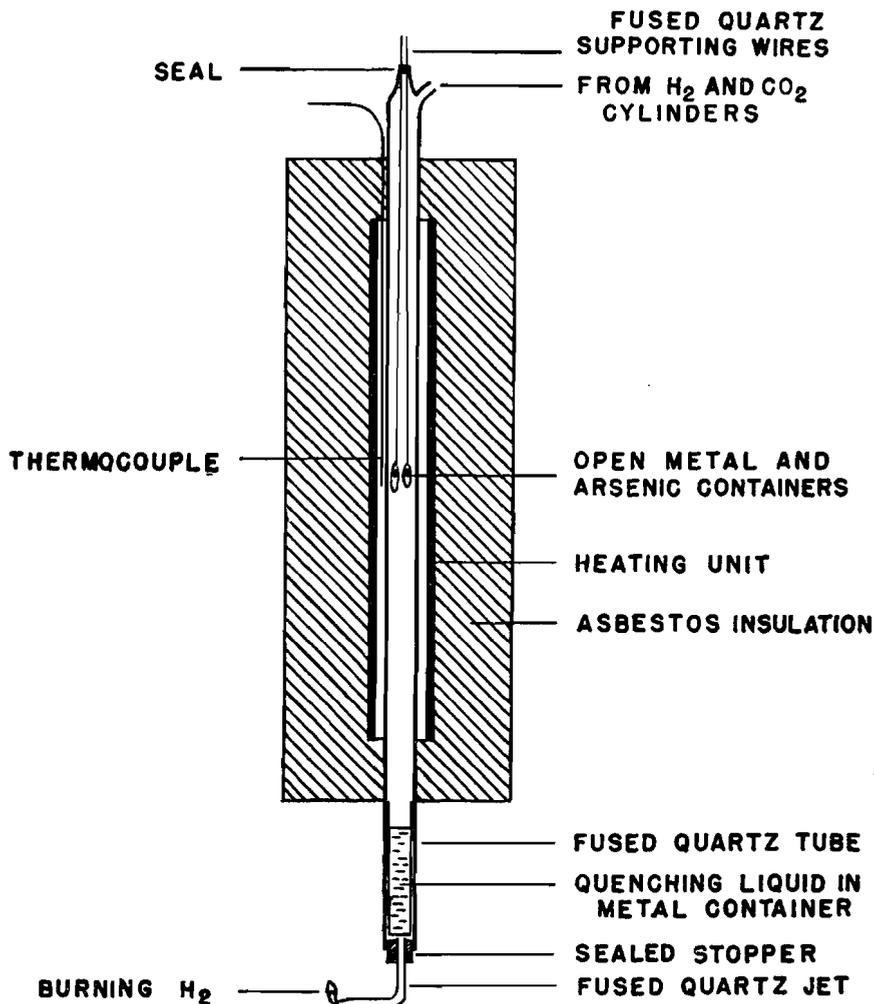


FIGURE 2.—Sectional view of electric resistance furnace used in the synthesis of the higher arsenides.

Synthesis by action of arsenic vapor on powdered metals in a hydrogen atmosphere; designed to permit rapid quenching of the sample.

Some of the experiments were carried out in a hydrogen-filled furnace at atmospheric pressure (Fig. 2). Two open containers are suspended at the center of this furnace, one holding arsenic, the other powdered metal. Since the entire furnace is filled with arsenic vapor, the supporting wires must be of pyrex or fused quartz depending on the temperature. The cylindrical fused-quartz lining projects well beyond the furnace. The furnace can be opened without cooling by replacing the atmosphere of hydrogen with one of carbon dioxide. Rapid quenching is accomplished by cutting the supporting wires allowing the tube to drop into a water-filled metal beaker at the bottom of the tube.

In all thermal methods there is a likelihood of inversion to another phase of the same composition or a breakdown into a mixture of two or more phases on cooling. The temperatures employed (350°–1050°C.) were below the melting point of the metals so that the reaction was one of arsenic vapor on solid metal particles. In such cases inhomogeneity may result from the formation of an impervious coat of higher arsenide which protects the metal, or low-arsenide center of each particle, from further reaction. This is especially true in the preparation of nickel arsenides as already noted by Beutell (1916a). In such cases frequent regrinding is necessary to permit the reaction to proceed to completion. The physical character of the product obtained by the methods of synthesis just described varies. Solid ingots of polycrystalline aggregates, masses of distinct crystals, sintered masses, and incoherent powders were obtained. Since repeated grinding and reheating was resorted to in most cases, the final product consisted of fine powders unsuited to microscopic examination. X-ray diffraction methods were used to identify the phases present and to determine the homogeneity of the sample. The chemical composition of the products established as homogeneous by x-ray methods was determined by comparing the final weight with that of the original metal sample. The method is subject to error since there is a slight loss in regrinding. No chemical analyses of the final products were made. Although desirable they were not considered essential in establishing the conclusions as set forth and are significant only if the product is homogeneous.

#### RESULTS OF EXPERIMENTS IN SYNTHESIS

*General statement.*—A summary of the results of the experiments in synthesis and the relation of the phases obtained is shown in Figure 3. The heavier broken-line boundaries indicate the limits of isomorphous substitution of cobalt, nickel, and iron in both the isometric and "orthorhombic" arsenide series, based on the experiments in synthesis and the data on natural material. These boundaries are approximate. One source of uncertainty regarding their position is the limited number of compositions synthesized and the lack of homogeneity of the product in certain cases. More precise limits might be drawn by conducting an extensive program of synthesis employing many samples of various compositions.

The symbols at the three corners of the triangle represent the product obtained using the single metals, cobalt, nickel, and iron. Samples represented by points within or on the periphery of the triangle contain either two, or all three, metals; their positions indicate the relative amounts present. The compositions indicated are those of the original sample which is also that of the final product in those cases in which a homogeneous single phase was secured.

Symbols have been used to indicate the crystallization of the products of synthesis as determined by x-ray methods. A solid symbol indicates a product consisting essentially of a single homogeneous compound. Inhomogeneous products are represented by combinations of symbols in which the one representing the dominant or important constituent is shaded, and the minor or less important constituent is represented by an outline symbol. The positions of the symbols are determined by the composition of the original sample. Essentially homogeneous isometric arsenides of the skutterudite type resulted from the synthesis of melts with the original com-

position: 1— $\text{Co}_{100}$ , 2— $\text{Co}_{90}\text{Fe}_{10}$ , 3— $\text{Co}_{75}\text{Fe}_{25}$ , 4— $\text{Co}_{75}\text{Ni}_{25}$ , 5— $\text{Co}_{70}\text{Ni}_{15}\text{Fe}_{15}$ , 6— $\text{Co}_1\text{Ni}_1\text{Fe}_1$ , 7— $\text{Ni}_{50}\text{Fe}_{50}$ . An essentially homogeneous orthorhombic arsenide of the loellingite type was obtained in the case of 8— $\text{Fe}_{100}$ , and essentially homogeneous orthorhombic arsenides of both rammelsbergite and pararammelsbergite types in the

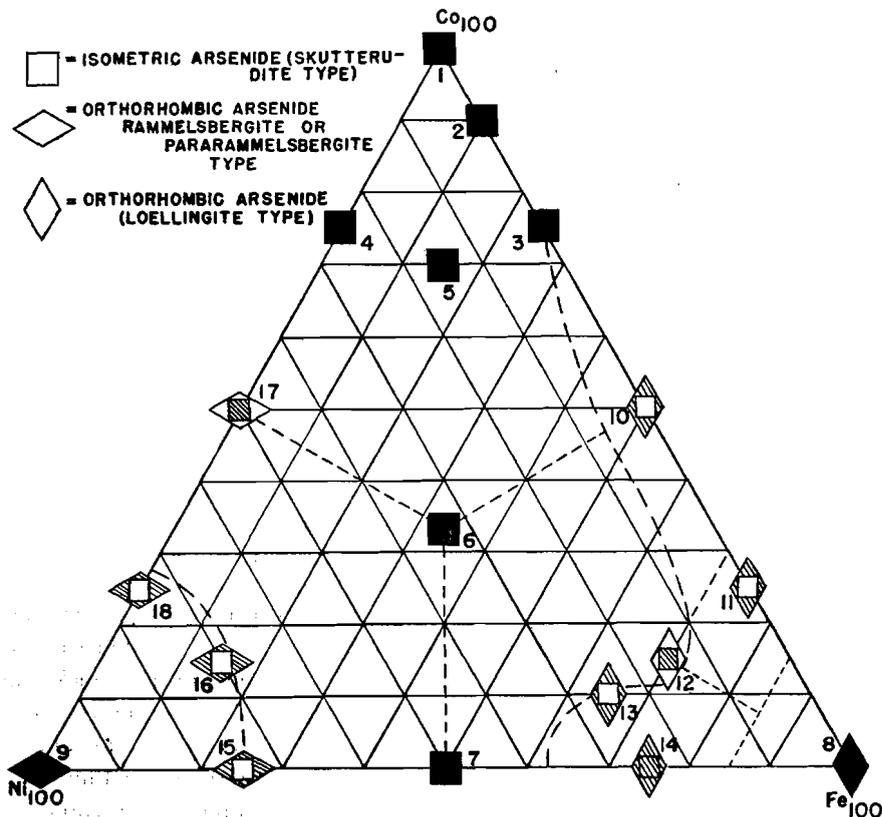


FIGURE 3.—Relation between crystallization and cobalt-nickel-iron ratio in the synthetic higher arsenides.

case of 9— $\text{Ni}_{100}$ . The remaining melts 10— $\text{Co}_{60}\text{Fe}_{50}$ , 11— $\text{Co}_{25}\text{Fe}_{75}$ , 12— $\text{Fe}_{70}\text{Ni}_{15}\text{Co}_{15}$ , 13— $\text{Co}_{10}\text{Ni}_{25}\text{Fe}_{65}$ , 14— $\text{Ni}_{25}\text{Fe}_{75}$ , 15— $\text{Ni}_{75}\text{Fe}_{25}$ , 16— $\text{Ni}_{70}\text{Co}_{15}\text{Fe}_{15}$ , 17— $\text{Co}_{80}\text{Ni}_{50}$ , and 18— $\text{Ni}_{75}\text{Co}_{25}$  resulted in the production of mixtures of isometric and orthorhombic compounds (rammelsbergite or loellingite) as indicated.

*Synthesis of the higher arsenides of cobalt (skutterudite, smaltite, and safflorite).—*Experiments in synthesis were undertaken primarily to determine whether the isomorphism between the elements cobalt, nickel, and iron in the isometric series is unlimited. The only monometallic triarsenide of this group reported in nature is the cobalt mineral skutterudite. The synthesis of this compound was the first attempted. Since two other cobalt arsenides, smaltite and safflorite, isometric and “orthorhombic” diarsenides respectively, have been described as existing in nature, the synthesis of these was also attempted. Cobalt arsenides were prepared by all three

methods described above, using various temperatures from 500°C. to 1050°C. Fluxes were used in some cases in the hope that certain phases might develop which otherwise would not form.

An isometric triarsenide of cobalt essentially identical with the mineral skutterudite, from Skutterud, Norway, was obtained whenever arsenic was present in sufficient amount. Neither technique nor temperature seems to influence the formation of  $\text{CoAs}_3$ . It was produced by all three methods both with and without fluxes and throughout the temperature range employed. Since a possible explanation for the variations in the lattice constants of the isometric triarsenides is metal for arsenic substitution, attempts were made to prepare skutterudite, both with excess arsenic and with arsenic deficiency. No phase with an arsenic content greater than  $\text{CoAs}_3$  was obtained. Samples deficient in arsenic prepared by the tube-in-tube method failed to provide a product exhibiting a measurable variation in lattice constant from that of material corresponding to the composition  $\text{CoAs}_3$ .

Attempts to synthesize cobalt diarsenides either isometric (smaltite) or "orthorhombic" (safflorite) resulted in the production of an inhomogeneous product providing x-ray patterns in agreement with that of the triarsenide (skutterudite) but with additional lines due to a lower arsenide. None of the patterns of such products contain lines agreeing with those in patterns of natural safflorite. This confirms the available analytical data on natural material which shows that no pure cobalt "orthorhombic" arsenide has been reported and that most analyses with a high cobalt content approach the R:As<sub>3</sub> ratio.

X-ray patterns of mineral specimens labelled smaltite yield the skutterudite pattern. A slight shift in line positions indicating a larger lattice constant is given by those in which nickel or iron replaces cobalt. Since no pure cobalt phase was produced with a lattice constant different from that of  $\text{CoAs}_3$ , no evidence for the existence of isometric  $\text{CoAs}_2$  (smaltite) was found. In spite of repeated attempts, varying the conditions of temperature and using different fluxes, no higher cobalt arsenide other than skutterudite  $\text{CoAs}_3$  was obtained. Hence the existence of the higher arsenides of cobalt,  $\text{Co}_2\text{As}_3$ ,  $\text{CoAs}_2$ , and  $\text{Co}_2\text{As}_6$ , claimed by Ducelliez (1908), Beutell (1916a) and Beutell and Lorenz (1916) is not confirmed. These alleged phases were probably inhomogeneous mixtures of  $\text{CoAs}_3$  and lower arsenides resulting from incomplete reaction. Such mixtures were frequently encountered in the present study.

*Synthesis of the higher arsenides of nickel (rammelsbergite, pararammelsbergite, chloanthite, and nickel skutterudite).—*Although the nickel end member of the isometric triarsenide series is unknown in nature, an isometric nickel-rich triarsenide known as nickel skutterudite has been reported. Two orthorhombic nickel diarsenides, rammelsbergite and pararammelsbergite, are also recognized. An isometric diarsenide, chloanthite, has long been regarded as the principal natural higher arsenide of nickel.

Synthetic nickel arsenides were prepared using the same methods and conditions employed in the synthesis of cobalt arsenides, except that the temperature range was extended downward to 350°C. Higher arsenides of nickel are more difficult to pre-

pare than those of cobalt. The production of the higher arsenides of nickel is preceded by the conversion of the powdered metal into a lower arsenide. A homogeneous monoarsenide with the hexagonal structure of niccolite can be produced readily, the reaction proceeding to completion without regrinding. However, the diarsenide of nickel is exceptionally impervious to arsenic vapor. Consequently the reaction proceeds to partial completion, then comes to a halt, and the coating of impervious diarsenide effectually shields the monoarsenide core. Grinding and reheating facilitate the reaction, but this must usually be repeated many times before an essentially homogeneous higher arsenide phase is produced. This is especially true in the preparation of pararammelsbergite which formed only at temperatures below 400°C. The vapor pressure of arsenic is very low at this temperature, and the reaction is extremely slow. Nature apparently has the same difficulty since it is commonly observed that niccolite masses have a narrow selvage or crust of rammelsbergite or pararammelsbergite. This difference between the permeability of the higher arsenides of cobalt as contrasted with those of nickel may explain the nonexistence in nature of a cobalt equivalent of niccolite.

Three natural polymorphous forms of nickel diarsenide have been recognized, chloanthite (isometric) and rammelsbergite and pararammelsbergite (both orthorhombic). Material labelled chloanthite provides the same type of x-ray pattern as that of skutterudite  $\text{CoAs}_3$ , with a slight shift in the lines indicating a larger lattice constant. No arsenide providing the skutterudite type of x-ray pattern was obtained when the proportions of the metals present approached those of the nickel end member. This investigation yields no evidence for the existence of a nickel end member of the isometric triarsenide (skutterudite) series or for any nickel arsenide higher than  $\text{NiAs}_2$ . Although over 40 experiments were performed in attempting to produce an isometric nickel arsenide, they consistently resulted in the production of the orthorhombic phases. Temperatures from 350° to 1050°, various fluxes, and all the variations in technique described did not produce a single sample providing an x-ray pattern of the skutterudite type. The experiments in synthesis lend no support to the existence of an isometric arsenide of nickel corresponding either to a diarsenide (chloanthite) or a triarsenide (nickel skutterudite). The present study confirms the work of Vigouroux (1908) and Beutell (1916a) who failed to produce a nickel arsenide higher than  $\text{NiAs}_2$ . The phase  $\text{Ni}_2\text{As}_3$  claimed by Vigouroux is believed to have been a mechanical mixture of niccolite and rammelsbergite, a combination frequently encountered in the present study.

Synthetic rammelsbergite providing an x-ray diffraction pattern in agreement with that of rammelsbergite from Schneeberg, Saxony, and other localities was produced at temperatures above 400°C. In sealed tubes synthetic rammelsbergite forms at all temperatures from 400°C. up to 1050°C. and was the only higher arsenide of nickel produced in this way. In an open system in an arsenic-hydrogen atmosphere, rammelsbergite forms between 400°C. and 575°C. Above approximately 575°C. the highest arsenide obtained is the monoarsenide, niccolite, followed by maucherite  $\text{Ni}_3\text{As}_2$  at still higher temperatures. This confirms Vigouroux's (1908) observation that in an open system arsenic content decreases with increasing temperature. When sealed tubes are used, temperature appears to have no influence on arsenic content.

Below 400°C., synthetic rammelsbergite passes into a different phase which provides an x-ray pattern corresponding to that of pararammelsbergite from Cobalt, Ontario. It forms during attempts to produce rammelsbergite at temperatures as high as 575°C., but it is believed that the pararammelsbergite forms at temperatures lower than this during cooling, since the amount produced seems to depend on the rate of cooling. Even rapid quenching fails to prevent the partial conversion of rammelsbergite into the lower-temperature form, when the material is produced in an open system in an arsenic-hydrogen atmosphere. However, the conversion does not take place when rammelsbergite is formed in sealed tubes. Pararammelsbergite either does not form directly by the attack of arsenic vapor on nickel powder, or the reaction at the low temperature employed (350°–375°C.) is so slow as to be negligible. It was obtained by first producing rammelsbergite. The powdered rammelsbergite was sealed in a tube-in-tube device with excess arsenic and heated at 350°–375°C. with occasional regrinding. After treating a sample in this way for 4 months, the last traces of rammelsbergite had not yet been removed. This intimate association of the two orthorhombic arsenides is also observed in the natural occurrence of the mineral. Specimens from Cobalt, Ontario; Franklin, New Jersey; and Riechelsdorf, Hesse are mechanical mixtures of rammelsbergite and pararammelsbergite. The pararammelsbergite from Tilt Cove, Newfoundland, is the only occurrence of this mineral found to be free of rammelsbergite.

*Synthesis of the higher arsenides of iron (loellingite, arsenoferrite iron skutterudite).—*The recognized higher mineral arsenides of iron are loellingite (orthorhombic  $\text{FeAs}_2$ ) and arsenoferrite, a doubtful isometric diarsenide. No isometric iron triarsenide end member occurs in nature, but considerable quantities of iron are reported in some skutterudites. Attempts were made to synthesize loellingite, arsenoferrite, and the theoretical iron end member of the isometric triarsenide series. The conditions and methods of formation were the same as those used in the synthesis of the cobalt arsenides, the temperature range being 535° to 1050°C. No arsenide higher than  $\text{FeAs}_2$  was obtained; hence there is no evidence from the present investigation for the existence of an iron-end member of the isometric triarsenide series.

Eight attempts under different conditions made to produce an isometric arsenide of iron resulted in the production of the orthorhombic diarsenide or a mixture of this and free arsenic. The x-ray pattern of the orthorhombic diarsenide obtained agrees with that of loellingite from the type locality at Lölling in Styria and that from Franklin, New Jersey. No evidence for the existence of an isometric diarsenide (arsenoferrite) was secured, confirming Buerger's (1936) belief based "on certain structural considerations" that an isometric diarsenide of iron is nonexistent. Evidence from synthesis points to the existence of a single higher arsenide of iron, the orthorhombic phase of  $\text{FeAs}_2$  (loellingite).

*Syntheses of intermediate members of the isometric (skutterudite) group.—*The isometric cobaltian end member, skutterudite, was successfully synthesized, but repeated efforts failed to produce an isometric nickel or iron end member. The synthesis of both bi-metal and tri-metal arsenides containing various amounts of cobalt, nickel, and iron was then attempted, in order to establish the limits of isomorphous substitution among the three metals in the isometric arsenide series.

The intermediate arsenides were produced in sealed tubes (tube-in-tube technique) with arsenic in excess of that required for  $RA_s_3$ . Some were prepared from mixtures of the powdered metals, but the majority were made from previously prepared alloys containing the desired proportions of the metals. Improved results were obtained in this way. Various temperatures between  $550^\circ$  and  $1050^\circ\text{C}$ . were employed, but experience showed that equally good results were obtained in the lower temperature range so that most of the work was carried out at temperatures between  $550^\circ$  and  $600^\circ\text{C}$ . Although some homogeneous single-phase arsenides were obtained, many of the products were inhomogeneous, consisting of an isometric arsenide of the skutterudite type and an orthorhombic arsenide of rammelsbergite type in the case of samples high in nickel, or of loellingite type in the case of samples high in iron.

The lattice constants of isometric arsenides obtained from samples containing nickel, iron, or nickel and iron in addition to cobalt and those containing nickel and iron without cobalt were measurably different from those of pure  $CoAs_3$ . This difference in lattice constant, compared with  $CoAs_3$  increased with increasing amounts of nickel, iron, or nickel and iron.

In many cases it was not possible to determine the metal-arsenic ratio of the resulting isometric arsenide since the product was not homogeneous, but the composition of homogeneous samples approached  $RA_s_3$ , and, in the case of the inhomogeneous products, the bulk metal-arsenic ratio was in all cases well above  $RA_s_2$ . The formation of an inhomogeneous product introduces uncertainty regarding the exact composition of the isometric phase present. The synthesis of the arsenide containing equal amounts of cobalt and nickel ( $Co_{50}Ni_{50}$ ) is a case in point. Some of the nickel, and probably a little cobalt, separated out as rammelsbergite. Consequently there is doubt as to the exact proportions of cobalt and nickel in the remaining phase which crystallized as the isometric triarsenide. Some estimate of the magnitude of this effect can be obtained from a consideration of the relative intensities of the lines in the x-ray pattern, but this can be, at best, only an approximation. Some of the data, for this reason, are not precise and further experiments in synthesis will be necessary to fix the limits of isomorphous substitution. However, sufficient data have been assembled to outline the relations and to confirm the view that the isomorphism is limited. The data also indicate that the dominant factor influencing variations in the lattice constants of the isometric arsenides is the ratio between the three metals. The evidence from these experiments indicates that isometric arsenides containing only nickel and cobalt may exist, carrying at least 50% nickel, but an isometric arsenide with a nickel content as high as 75% seems unlikely.

Intermediate cobalt-iron arsenides of four compositions were investigated, two of which, ( $Co_{90}Fe_{10}$ ) and ( $Co_{75}Fe_{25}$ ), provided essentially homogeneous isometric phases. Those higher in iron, ( $Co_{50}Fe_{50}$ ) and ( $Co_{25}Fe_{75}$ ), provided a mixture of orthorhombic  $FeAs_2$ , an isometric arsenide (skutterudite), and a third unidentified phase. Traces of this phase were observed in other high iron samples, but the lines are few and weak, and its identity is uncertain. This phase neither belongs to the isometric series, nor do the lines agree with those of safflorite. The evidence from synthesis establishes the existence of isometric cobalt-iron arsenides with an iron content as high as approximately ( $Co_{75}Fe_{25}$ ). The lattice constants of the isometric phase produced

from melts of  $(\text{Co}_{50}\text{Fe}_{50})$  and  $(\text{Co}_{25}\text{Fe}_{75})$  were only slightly different from  $(\text{Co}_{75}\text{Fe}_{25})$ , suggesting that the limit for iron in the isometric series is close to  $(\text{Co}_{75}\text{Fe}_{25})$ .

Cobalt-nickel arsenides of three intermediate compositions were investigated. Only  $(\text{Co}_{75}\text{Ni}_{25})$  provided an essentially homogeneous product. The two with a higher nickel content provided inhomogeneous mixtures containing both the isometric arsenide and an orthorhombic arsenide of the rammelsbergite type. The existence of an isometric arsenide  $(\text{Co}_{75}\text{Ni}_{25})$  appears established. Likewise an isometric arsenide  $(\text{Co}_{50}\text{Ni}_{50})$  or one close to that composition exists since the amount of nickel separating out as rammelsbergite in this sample was small. In samples of composition  $(\text{Co}_{25}\text{Ni}_{75})$  rammelsbergite was the major constituent.

Nickel-iron arsenides of three compositions were investigated.  $(\text{Ni}_{50}\text{Fe}_{50})$  provided a homogeneous isometric arsenide, while the other two did not. The synthesis of the (Ni-Fe) series reveals a strange situation in which two metals, nickel and iron, neither of which seems to form isometric arsenides when present alone, readily form isometric triarsenides of the skutterudite type when both are available in approximately equal proportions. The existence of isometric arsenides containing only nickel and iron ranging in composition from about  $(\text{Ni}_{30}\text{Fe}_{70})$  to approximately  $(\text{Ni}_{70}\text{Fe}_{30})$  appears likely. No natural cobalt-free nickel-iron arsenides have been reported but the experiments in synthesis indicate that they could exist.

Arsenides of five compositions, containing all three metals, were synthesized. Two of these,  $(\text{Co}_{70}\text{Ni}_{15}\text{Fe}_{15})$  and  $(\text{Co}_1\text{Ni}_1\text{Fe}_1)$ , provided essentially homogeneous single phases. The high-nickel and high-iron samples gave inhomogeneous products consisting of an isometric and a nonisometric component. Since the isometric phase was dominant in sample  $(\text{Fe}_{70}\text{Ni}_{15}\text{Co}_{15})$  isometric arsenides close to this composition are probably possible. The principal component of the sample  $(\text{Ni}_{70}\text{Co}_{15}\text{Fe}_{15})$ , is the orthorhombic nickel diarsenide rammelsbergite, suggesting that the nickel limit for orthorhombic arsenides may be below 70.  $(\text{Co}_{10}\text{Ni}_{25}\text{Fe}_{65})$  provided an orthorhombic arsenide of the loellingite type with extra lines due in part to a constituent whose identity was not ascertained and in part to an isometric arsenide of the skutterudite type.

## X-RAY DIFFRACTION STUDIES

### PREVIOUS X-RAY DIFFRACTION STUDIES

*Isometric arsenides.*—Since the pioneer work of Ramsdell (1925), considerable x-ray data on isometric arsenides of cobalt, nickel, and iron have been published. Ramsdell (1925) showed that Debye patterns of smaltite and chloanthite are essentially alike and incompatible with the structure of the pyrite group to which they had long been assigned. He was unable to establish the crystal structure as he assumed a composition  $\text{RA}_2\text{S}_2$  and found that no space group compatible with such a composition could be reconciled with the spacing and intensities of the lines. He computed an approximately correct lattice constant (8.28 Å) but rejected it, as a cell of this size gave an irrational cell content, assuming a composition  $\text{RA}_2\text{S}_2$ . A pattern of skutterudite proved to be identical with those of smaltite and chloanthite, so he concluded that the specimen was a mislabelled smaltite. Samdahl (1926), at the instigation of

Goldschmidt, analyzed a specimen of skutterudite from Skutterud. The only reference to x-ray work is the mention of the preparation of an x-ray pattern which "confirmed the chemical analysis completely and proved the impossibility of nickel". Oftedal published a preliminary paper in English (1926) followed by an exhaustive detailed study in German (1928) in which the crystal structure of skutterudite was established for the first time. He noted that skutterudite ( $\text{CoAs}_3$ ) gave a good Laue pattern, whereas it was impossible to obtain satisfactory Laue patterns of the so-called diarsenides, smaltite, and chloanthite. He concluded that the skutterudite crystals were unit crystals, whereas the apparent single crystals of smaltite and chloanthite were multicrystalline aggregates. Oftedal looked upon smaltite and chloanthite as varieties of skutterudite ( $\text{RAs}_3$ ), whereas Ramsdell had considered skutterudite a variant of smaltite-chloanthite ( $\text{RAs}_2$ ). The behavior of the three minerals in the Laue camera and the essential identity of their Debye patterns led Oftedal to the conclusion that the lattice-forming substance in all three was  $\text{RAs}_3$  ["die kristallisierte (gitterbildende) Substanz  $\text{RAs}_3$  sein muss" Oftedal (1928) p. 543]. He found that space group  $T_h^6$  not only accounted for all details of spacing, intensity, and extinctions but was also compatible with a composition  $\text{RAs}_3$ . Like Ramsdell he was unable to find any space group which would reconcile the x-ray data with a composition  $\text{RAs}_2$ . Skutterudite from Skutterud was found to be body-centered cubic with  $a_0 = 8.189 \pm .002 \text{ \AA}$ , with 8 molecules ( $\text{RAs}_3$ ) to the unit cube. Speiskobalt (smaltite) from Riechelsdorf proved to have the same structure with  $a_0 = 8.124 \pm .005 \text{ \AA}$ . In the detailed paper no lattice constant was given for the chloanthite from Schneeberg. This remains the only thorough structural study of the isometric arsenides. Goldschmidt (1926) in a paper on co-ordination numbers gives three lattice constants based on unpublished work of Oftedal. Holmes (1935) confirmed Oftedal's observation on the identity of Debye patterns of smaltite and chloanthite. Although the statement does not appear in the abstract, the identity of patterns of skutterudite with those of smaltite and chloanthite, except for slight differences in spacing, was pointed out in the oral presentation of this paper. Krieger (1935, p. 720) quotes Holmes to the effect that the nickel skutterudite from Bullards Peak, New Mexico (probably a portion of the type specimen of Waller and Moses) gave a Debye pattern of the skutterudite type. Buerger (1936) found that the material from Jachymov (St. Joachimsthal), Czechoslovakia, described by Foshag and Short (1930) as arsenoferrite, isometric  $\text{FeAs}_2$ , gave a Debye pattern of the loellingite type. On the basis of this and "certain crystal structure considerations" he concluded that the existence of an isometric  $\text{FeAs}_2$  was doubtful and that the name arsenoferrite should be discontinued. Peacock and Berry (1940) prepared powder patterns, presumably Debye, of eight samples of skutterudite, smaltite, and chloanthite from various localities. The patterns proved to be identical except for slight differences in spacing. A lattice constant  $a_0 = 8.18 \pm .01 \text{ \AA}$  was obtained for skutterudite from Cobalt, Ontario. Harcourt (1942, p. 77 and 98) prepared tables of "d" values from Debye patterns of skutterudite from Skutterud and smaltite-chloanthite from Schneeberg. In a preliminary paper dealing with the present investigation Holmes (1942) reported the results of correlated x-ray work on natural and synthetic isometric arsenides based on Debye and Phragmen powder patterns. Holmes (1945),

on the basis of Debye patterns, established the presence of skutterudite in the nickel-cobalt arsenide association at Franklin, N. J.

X-ray data have been published on isometric material from at least 10 localities. All the specimens investigated gave patterns of the skutterudite type pointing to the structural identity of the isometric arsenides. Three lattice constants in essential agreement are available for skutterudite from Skutterud and one for skutterudite from Cobalt (Table 3). The three lattice constants for smaltite from Riechelsdorf and the two for chloanthite from Schneeberg show considerable variation but are all larger than those of skutterudite from Skutterud. The arsenoferrite of Buerger (1936) is the only analyzed specimen used in any recorded x-ray study of the isometric group, and this proved to be a nonisometric arsenide. Hence no published x-ray data exist on analyzed specimens of isometric arsenides. A summary of the available x-ray data on the isometric arsenides from all the localities covered in the literature has been assembled in Table 3.

*“Orthorhombic” arsenides.*—Detailed structural studies based on single-crystal x-ray data have been carried out for natural loellingite, rammelsbergite, parammelsbergite, and safflorite. Apparently no x-ray work has been done on nickelian or cobaltian loellingite. The only reference to x-ray data on synthetic “orthorhombic” arsenides is that of Holmes (1942).

**LOELLINGITE:** The earliest x-ray data on loellingite is the Debye work of deJong (1926). He gave “d” values for material from Saxony (locality?), indexed the lines by analogy with patterns of marcasite, computed lattice constants, and assigned the mineral to space group  $V_h^{11}$ . He claimed that patterns of loellingite, rammelsbergite, and safflorite were indistinguishable and gave a single set of lattice constants for all three minerals. Buerger (1932) using single-crystal rotation and oscillation methods determined the structure of the loellingite from Franklin, New Jersey (Bauer and Berman, 1927). Three papers by Buerger and one by Huggins followed this. None of these contains new x-ray data, but they are devoted to interpretations of structure based on the data contained in Buerger’s original paper. Buerger (1934) showed that the most probable explanation for the arsenic deficiency of the Franklin loellingite is isomorphous substitution of iron for arsenic. Buerger (1937) proposed a new orientation for loellingite in order to make more evident the relation between the lattice of this mineral and that of arsenopyrite. This requires the following interchange of axes:  $a \rightarrow c$ ,  $b \rightarrow a$ , and  $c \rightarrow b$ . In a discussion of the relation of the structure of loellingite to that of marcasite and arsenopyrite, Buerger (1939) pointed out that the arsenopyrite lattice bears a superstructure relation to the simpler ones of the first two minerals. Huggins (1937) questioned certain of Buerger’s statements regarding details of the structure of loellingite. In an earlier reference Huggins (1922) had computed theoretical lattice constants for this mineral, but there is no evidence in the paper that these calculations were based on actual x-ray data. Holmes (1935) pointed out that Debye powder patterns of loellingite, rammelsbergite, and safflorite show sufficient variation to permit recognition of these minerals by x-ray methods. The “arsenoferrite” from Jachymov (St. Joachimsthal), Bohemia, described by Foshag and Short (1930) as isometric was found by Buerger (1936) to give a Debye

TABLE 3.—Existing *x*-ray data on the isometric higher arsenides

Mineral name	Locality	Investigator	Date	Type of pattern	Lattice constant (a <sub>0</sub> )
Skutterudite	Skutterud, Norway	Oftedal	1926	Skutterudite	8.17 Å
	Modum (Skutterud), Norway	Oftedal by Goldschmidt	1926	Skutterudite	8.18 ±015 Å
	Skutterud, Norway	Samdahl	1926	(?)	—
	Skutterud, Norway	Oftedal	1928	Skutterudite	8.18 ±01 Å 8.189 ±002 Å "d" values only
	Skutterud, Norway	Harcourt	1942	Smaltite-chloanthite	
	Skutterud, Norway	Holmes	1942	Skutterudite identical with synthetic CoAs <sub>3</sub>	—
	Cobalt, Ontario	Peacock & Berry	1940	Skutterudite	8.18 ±01 Å
	Franklin, N. J.	Holmes	1945	Skutterudite	—
	Nickel-Skutterudite	Bullards Peak, New Mexico	Holmes by Krieger	1935	Skutterudite
Smaltite	Riechelsdorf, Hesse	Oftedal	1926	Skutterudite	8.25 Å
	Riechelsdorf, Hesse	Oftedal by Goldschmidt	1926	Skutterudite	8.270 ±.015 Å
	Riechelsdorf, Hesse	Oftedal	1928	Skutterudite	8.240 ±.005 Å
	Riechelsdorf, Hesse	Peacock & Berry	1940	Skutterudite	—
	Hesse	Peacock & Barry	1940	Skutterudite	—
	Schneeberg, Saxony	Peacock & Berry	1940	Skutterudite	—
	Gowganda, Ontario	Peacock & Berry	1940	Skutterudite	—
	Huelva, Spain	Peacock & Berry	1940	Skutterudite	—
Irrtem, Morocco	Peacock & Berry	1940	Skutterudite	—	
Chloanthite	Schneeberg, Saxony	Oftedal	1926	Skutterudite	8.25 Å
	Schneeberg, Saxony	Oftedal by Goldschmidt	1926	Skutterudite	8.250 ±015. Å
	Schneeberg, Saxony	Oftedal	1928	Skutterudite	—
	Schneeberg, Saxony	Peacock & Berry	1940	Skutterudite	—
Smaltite-chloanthite	Schneeberg, Saxony	Harcourt	1942	"Identical to pattern of smaltite-chloanthite"	"d" values only
Arsenoferrite	Jachymov (St. Joachimsthal) Czechoslovakia	Buerger	1936	Loellingite	—

pattern agreeing with that of loellingite. Peacock (1941) published "d" values, intensities, and lattice constants for loellingite from Franklin, using material which he regarded as identical with that used by Buerger (1932). A set of "d" values and

intensities for loellingite from Silver Center, Ontario, based on Debye patterns, are included by Harcourt (1942) in his compilation of x-ray data on ore minerals. In a discussion of the results of synthesis of the higher arsenides Holmes (1942) pointed out that the Debye and focusing camera patterns of synthetic  $\text{FeAs}_2$  and natural loellingite are in agreement.

**RAMMELSBERGITE:** De Jong (1926) using material from Schlaggenwald, Bohemia, (not Styria) as stated in Peacock and Michener (1939), claimed that the rammelsbergite pattern was not measurably different from that of loellingite. Patterns of rammelsbergite are entirely different from those of loellingite, as pointed out by Holmes (1935; 1942) and shown by the powder data in Peacock (1940; 1941) and Harcourt (1942). Peacock carried out a detailed structural study of the orthorhombic nickel arsenides using both single-crystal and Debye methods. A preliminary abstract (Peacock, 1940) preceded the appearance of the detailed discussion of this work (Peacock and Dadson, 1940). Rammelsbergite from Schneeberg, Saxony, and two specimens from Eisleben, Prussia (not Thuringia), were investigated. Lattice constants were determined for one of the specimens from Eisleben, and the material was assigned to space group  $V_h^{12}$ . This, however, was not the material analyzed nor the one on which the density determinations were made. The essential x-ray data in this paper also were given by Peacock and Berry (1940), and a reproduction of the powder diagram of the Eisleben specimen is given by Peacock (1941). Harcourt (1942) gave "d" values and intensities for a Debye pattern of the Eisleben material. A comparison of Debye and Phragmen patterns of certain synthetic nickel diarsenides and those of natural rammelsbergite is discussed by Holmes (1942). Holmes (1935; 1945) on the basis of Debye patterns established rammelsbergite as the principal component of the white arsenide association at Franklin, N. J. (the cloanthite of Koenig, 1899).

**PARARAMMELSBERGITE:** Pararammelsbergite was first examined by x-ray methods by Peacock and Michener (1939). On the basis of powder, rotation, and Weissenberg patterns the identical character of the material from two Canadian localities was established, and the mineral was provisionally called rammelsbergite. Lattice constants were determined for the Elk Lake material, and the mineral was assigned to one of two possible space groups. The Canadian material was established as an independent species (pararammelsbergite) by Peacock as the result of a comparison of the diffraction data with those derived from specimens of rammelsbergite from two German localities (Peacock, 1940; Peacock and Dadson, 1940). The essential x-ray data are reproduced by Peacock and Berry (1940), and the powder diagrams of the materials from Elk Lake and Cobalt are reproduced by Peacock (1941). Harcourt (1942) on the basis of Debye patterns gave "d" values and intensities for "type material" from Elk Lake, Ontario. Holmes (1942) showed that synthetic  $\text{NiAs}_2$  produced at low temperatures provides a diffraction pattern agreeing with that of natural pararammelsbergite. Holmes (1945) identified pararammelsbergite in the nickel-cobalt association at Franklin, N. J., using Debye patterns.

**SAFFLORITE:** X-ray data on this mineral are meager. De Jong (1926) claimed that the Debye pattern of safflorite was identical with those of loellingite and rammelsbergite. Holmes (1935) pointed out that Debye patterns of safflorite are meas-

urably different from those of leellingite and rammelsbergite. This is confirmed by the published powder data on these minerals (Peacock, 1940; 1941; Harcourt, 1942). Harcourt (1942) published "d" values and intensities based on a Debye pattern for a safflorite from Quartzberg, Oregon. Holmes (1942) pointed out that patterns of certain synthetic iron-cobalt arsenides are of the safflorite-leellingite type but was unable to synthesize an orthorhombic arsenide of pure cobalt. Peacock (1944), on the basis of Weissenberg photographs of safflorite from Nordmark, Sweden, found the structure of the mineral to be monoclinic (with rectangular axes) rather than orthorhombic. This justifies the retention of the name safflorite, since on the basis of structure it is distinct from leellingite. Monoclinic symmetry results from the nonequivalence of the iron and cobalt atoms. He points out the close similarity of powder photographs of safflorite and leellingite.

Original cell-edge data or "d" values for "orthorhombic" arsenides are given by De Jong (1926), Buerger (1932), Peacock and Michener (1939), Peacock (1940; 1941; 1944), Peacock and Dadson (1940), and Harcourt (1942). The remaining papers are devoted to conclusions and interpretations based on x-ray studies. The only detailed structural studies are those of Buerger (1932) on leellingite, Peacock and Michener (1939) on pararammelsbergite, under the name rammelsbergite, and Peacock and Dadson (1940) on rammelsbergite. The available x-ray data establish the existence in nature of two distinct orthorhombic forms of nickel diarsenide and show that although leellingite and rammelsbergite belong to the same space group they have widely different lattice constants. The results of later investigators do not support the conclusions regarding the structure and relations of the "orthorhombic" arsenides offered by De Jong (1926). The available x-ray data on the "orthorhombic" arsenides are assembled in Table 4.

#### X-RAY DIFFRACTION METHODS

Extensive use was made of x-ray powder diffraction methods. Most of the work was done using iron radiation and cameras of the asymmetrical focusing type developed by Phragmen and based on a principle earlier employed by Seeman (1919) and Bohlin (1920). A set of three cameras covers the entire diffraction range. Although modelled after those designed by Phragmen, certain modifications were introduced, including an oscillating arm insuring uniform motion of the sample holder. The original Phragmen type cameras are briefly described by Westgren (1931). Conclusions concerning isomorphous substitution were based on patterns obtained in the outer Phragmen camera. Debye cameras with a radius of 57.3 mm. were used for routine identification. Debye pictures have the advantage in that the entire picture is obtained on a single film. However, the resolution or separation of any pair of lines on a focusing camera film is twice as great as with a Debye camera of the same radius because of the fundamental difference in the geometry of the camera which results from the position of the sample (at the center in a Debye camera but on the circumference of a focusing camera). In problems involving isomorphism, the solution hinges on the measurement or recognition of slight variations in the positions of corresponding lines in the patterns of specimens with slightly different composition.

TABLE 4.—Existing x-ray data on the "orthorhombic" higher arsenides

LOELLINGITE				
Locality	Investigator	Date	Lattice constants	and Space group
Saxony	deJong	1926	* $a_0 = 6.35$ , $b_0 = 4.86$ , $c_0 = 5.80$	$V_h^{11}$
Franklin, N. J.	Buerger	1932	* $a_0 = 2.85$ , $b_0 = 5.25$ , $c_0 = 5.92$	$V_h^{12}$
Franklin, N. J.	Peacock	1941	* $a_0 = 2.87$ , $b_0 = 5.28$ , $c_0 = 5.97$	$Pm\bar{m}n = (V_h^{12})$
Silver Center, Ont.	Harcourt	1942	"d" values and intensities only.	
RAMMELSBURGITE				
Locality	Investigator	Date	Lattice constants	and Space group
Schlaggenwald (Bohemia)	deJong	1926	* $a_0 = 6.35$ , $b_0 = 4.86$ , $c_0 = 5.80$	$V_h^{11}$
Eisleben, Prussia	Peacock	1940	* $a_0 = 3.53 \pm .01$ , $b_0 = 4.78 \pm .01$ , $c_0 = 5.78 \pm .01$	$D_{2h}^{12} = (V_h^{12})$
Schneeberg, Saxony	Peacock	1940	Pattern identical with that of Eisleben material	
Eisleben, Prussia	Harcourt	1942	"d" values and intensities only.	
PARAMMELSBURGITE				
Locality	Investigator	Date	Lattice constants	and Space group
Moose Horn Mine, Elk Lake, Ont.	Peacock and Michener	1939	* $a_0 = 5.74 \pm .01$ , $b_0 = 5.81 \pm .01$ , $c_0 = 11.405 \pm .03$	apparent space group $D_{2h}^{11}$ or $C_{2v}^3$
Hudson Bay Mine, Cobalt, Ont.	Peacock and Michener	1939	Pattern identical with that of Elk Lake material	
Keeley Mine, South Lorrain, Ont.	Peacock and Dadson	1940	Pattern identical with that of Elk Lake material.	
Moose Horn Mine, Elk Lake, Ont.	Harcourt	1942	"d" values and intensities only.	
SAFFLORITE				
Locality	Investigator	Date	Lattice constants	and Space group
Saxony	deJong	1926	* $a = 6.35$ , $b = 4.86$ , $c = 5.80$	$V_h^{11}$
Quartzberg, Grant Co., Ore.	Harcourt	1942	"d" values and intensities only.	
Nordmark, Sweden	Peacock	1944	* $a = 2.93$ , $b = 5.25$ , $c = 5.97$	$C_{2h}^1 = P2/m$

\* Orientation is that given in the original paper.

It is an advantage to use a camera in which the resolution or separation of lines is as great as possible. Asymmetrical focusing cameras have an additional advantage over Debye cameras of the same radius in providing sharp strong lines in the outer (high-angle) range which is the most sensitive to variations in cell-edge dimensions. X-ray data were obtained in this study for three purposes: identification of the minerals in natural material and the phases in the products of synthesis, determination of the lattice constants of natural and synthetic isometric arsenides, and correlation of synthetic and natural material.

## X-RAY AND MICROSCOPIC DATA ON NATURAL AND SYNTHETIC HIGHER ARSENIDES

More than 200 specimens from a large number of the known localities for these minerals have been examined by microscopic, contact-print, microchemical, and x-ray methods. Extensive inhomogeneity was frequently encountered, especially among the isometric arsenides; the majority of skutterudite crystals contain inclusions of nonisometric arsenides. This widespread inhomogeneity could account for much of the variation in arsenic ratio as well as the extreme variations in cobalt-nickel-iron ratio indicated by certain analyses. The correlated x-ray, optical, contact-print, and microchemical data on these specimens confirm the published analyses in establishing as isometric the high cobalt members and those containing considerable quantities of nickel or nickel and iron in addition to cobalt. The high-nickel, high-iron and iron-cobalt-low-nickel specimens proved to be "orthorhombic." The evidence points to limited isomorphous substitution among the three metals in both the isometric and "orthorhombic" series. In the isometric series a correlation between lattice constant and the ratio of the three metals is indicated.

The x-ray patterns confirm the results of earlier workers who found that all isometric arsenides of cobalt, nickel, and iron have the skutterudite structure. Powder patterns of three specimens of skutterudite from the type locality at Skutterud, Norway (two of crystals and one of massive material), were found to be of the same type and provided essentially identical lattice constants (8.187 Å). Ten lattice constants for isometric arsenides exist in the literature. These range from 8.17 to 8.270 Å. The value 8.17 of Oftedal was apparently regarded by him as a preliminary figure since he speaks of revised lattice constants in the detailed paper (Oftedal, 1928) and gives a value of  $8.189 \pm .002$  Å for the skutterudite from Skutterud. The present study reveals no value as low as 8.17 Å and extends the range upward to 8.311 Å. The lowest value obtained is that for synthetic  $\text{CoAs}_3$  and for skutterudite from Skutterud, Norway, both of which are 8.187 Å. A nickel-rich variety from Schneeberg, Saxony, provided the largest lattice constant, 8.311 Å. This confirms the data from other sources which indicate an inverse relation between lattice constant and cobalt content in the isometric arsenides.

Higher arsenides of the individual metals—cobalt, nickel, and iron—and intermediate ones containing various amounts of two or all three metals have been synthesized, and the products identified by x-ray diffraction methods. The data obtained confirm the limited character of the isomorphism of cobalt, nickel, and iron in both the isometric and "orthorhombic" groups and aid in outlining the limits of isomorphous substitution between the three metals in both series. Attempts to synthesize pure nickel or pure iron isometric arsenides in all cases resulted in the formation of "orthorhombic" phases. Likewise attempts to produce a pure cobalt "orthorhombic" arsenide resulted in the formation of an isometric product.

The following minerals have been synthesized, and the identity of the natural material and the artificial product has been established by means of powder x-ray methods: skutterudite (pure  $\text{CoAs}_3$  and phases containing various amounts of cobalt, nickel, and iron), rammelsbergite ( $\text{NiAs}_2$ ), paramrammelsbergite ( $\text{NiAs}_2$ ), and loellingite ( $\text{FeAs}_2$ ). Although previous claims have been made to the synthesis of cobalt triarsenide, nickel diarsenide, and iron diarsenide, the homogeneity and structural identity of the product had not been determined in the earlier experiments. X-ray

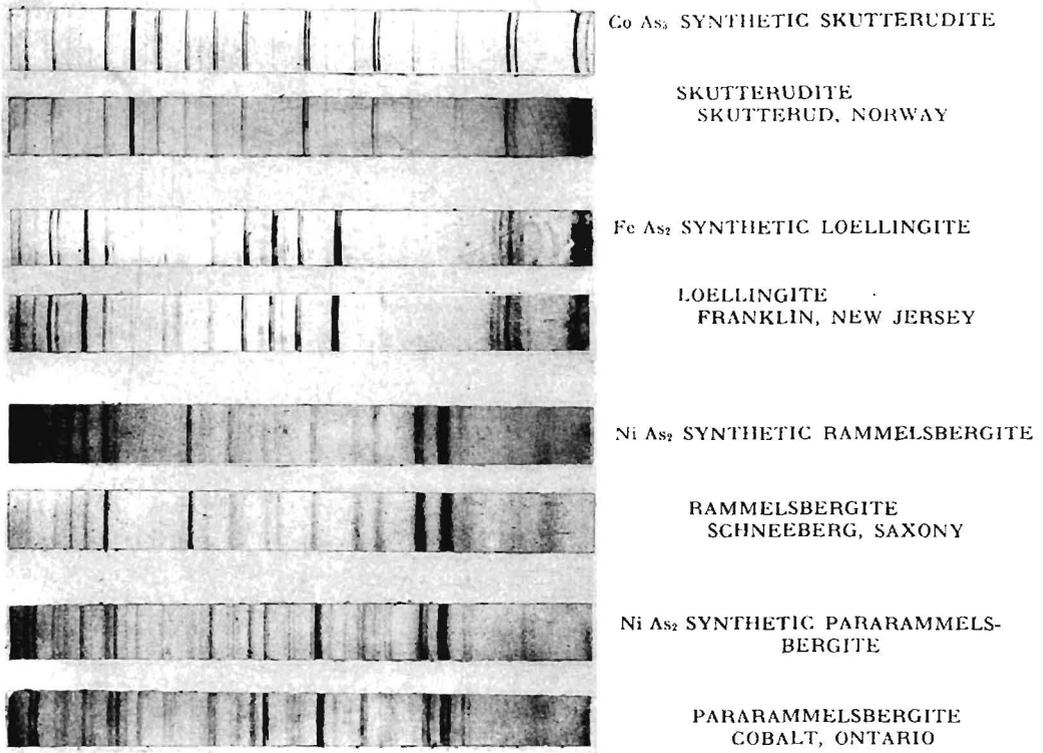


FIGURE 1. X-RAY DIFFRACTION PATTERNS OF THE PRINCIPAL MINERALS OF THE HIGHER ARSENIDE GROUP. They are compared with those of synthetic equivalents. All patterns were obtained in the outer phragmen asymmetrical focusing camera using unfiltered iron radiation.

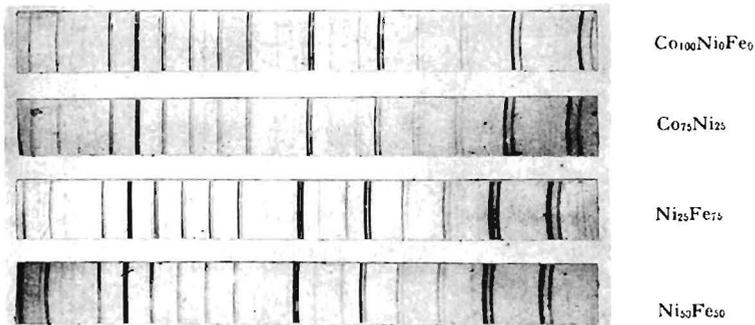


FIGURE 2. COMPARISON OF X-RAY DIFFRACTION PATTERNS OF SYNTHETIC ISOMETRIC ARSENIDES (SKUTTERUDITES)

Influence of variations in cobalt-nickel-iron ratio on lattice constants is indicated by a shift in the positions of corresponding lines. All patterns taken in the outer phragmen camera with unfiltered iron radiation. The compositions indicated are those of the original melt.

X-RAY DIFFRACTION PATTERNS

patterns of synthetic monometallic arsenides are compared with those of the natural minerals skutterudite, rammelsbergite, pararammelsbergite, and loellingite in Plate 2.

All synthetic isometric arsenides of these metals are essentially triarsenides with the skutterudite structure and are restricted in composition to those high in cobalt, those containing approximately equal quantities of nickel and iron, and those containing appreciable quantities of all three metals. No evidence for the existence of cobalt diarsenides, either isometric (smaltite) or "orthorhombic" (safflorite), was obtained. The existence of very high nickel or very high iron isometric arsenides is unlikely. No evidence for the existence of an isometric iron diarsenide (arsenoferrite) or iron triarsenide (iron skutterudite) was obtained; all pure iron arsenides give the orthorhombic loellingite diffraction pattern. No evidence for the existence of an isometric nickel diarsenide (chloanthite) or an isometric nickel triarsenide (nickel-skutterudite) was obtained; all pure nickel arsenides give diffraction patterns of either rammelsbergite or pararammelsbergite type. Nickel-free isometric arsenides with an iron ratio above 25 are also very doubtful. In all cases the isometric constituent of the synthetic product yielded the skutterudite type of pattern, with lattice constants varying inversely with cobalt content. The range of lattice constants of the synthetic and natural isometric arsenides are of the same order of magnitude and show the same trend. The range for natural material ( $a_0 = 8.187 \text{ \AA}$  to  $8.311 \text{ \AA}$ ) is greater than that of synthetics so far produced ( $a_0 = 8.187 \text{ \AA}$  to  $8.263 \text{ \AA}$ ). The upper synthetic limit ( $8.263 \text{ \AA}$ ) is that of the isometric constituent of the melt of composition  $\text{Co}_{15}\text{Ni}_{70}\text{Fe}_{15}$ . This melt however was inhomogeneous, an unknown amount of nickel having separated out as the orthorhombic phase rammelsbergite, so that the composition of the isometric phase providing the above lattice constant possessed a nickel ratio below  $\text{Ni}_{70}$ . The lower limit ( $8.187 \text{ \AA}$ ) is that of pure cobalt triarsenide.

#### LATTICE CONSTANT AND COBALT-NICKEL-IRON RATIO IN THE ISOMETRIC ARSENIDES

The lattice constants of the synthetic arsenides exhibit consistent variations which appear to be a function of the variation in the proportions of the three metals. Increasing amounts of nickel, iron, or nickel and iron result in an increase in the length of the cell edge. These variations in lattice constants confirm observations on the lattice constants of natural isometric arsenides in that the smallest is that of the pure cobalt triarsenide, whereas the largest is that of nickel-rich members. The same relation has been observed repeatedly in the zonal isometric crystals, in which material drilled from individual zones provided lattice constants correlating with cobalt-nickel-iron content as revealed by microchemical and contact-print methods.

Variations in the lattice constants of isometric materials are shown in a striking manner in x-ray patterns. There is a direct relation between a shift in lines to the left (Pl. 2, fig. 2) and increasing lattice constant; the size of the unit cell is at a minimum for pure  $\text{CoAs}_3$ . Figure 2 of Plate 2 shows that substitution of nickel, iron, or nickel and iron for cobalt in the isometric arsenides results in an increase in the lattice constant. The relation between lattice constant and cobalt-nickel-iron ratio for certain materials used in the present study is shown in Figure 4 and summarized in Table 5. It includes natural minerals for which analyses exist and synthetic isometric arsenides of known composition.



iron ratio of the isometric phase produced only when the product is homogeneous (Fig. 3).

Natural arsenides are represented by squares whose positions are determined by the Co-Ni-Fe ratio calculated from published analyses. Arrows are attached to the symbols representing synthetic materials whose compositions are questionable due to inhomogeneity of the product and to those of natural minerals shown to be inhomogeneous by optical or x-ray examination. The arrows attached to the symbols of these inhomogeneous specimens indicate the direction and approximate amount that the symbols should be moved in order to represent correctly the cobalt-nickel-iron ratio of the isometric constituent. In the synthetic material this is based on an estimation of the amount of inhomogeneity indicated by the relative strength of the lines in the x-ray pattern due to the admixed nonisometric phase. In the natural material it is based on similar x-ray evidence confirmed by microscopic observations.

The synthetic material (Fig. 4) is of two sorts. Melts of certain compositions supplied homogeneous isometric products which therefore have the composition of the original sample. An inhomogeneous product was obtained from some melts, consisting of a mechanical intergrowth of isometric and "orthorhombic" phases. In these, the composition of the isometric phase is known only approximately. Nevertheless the data obtained from the isometric constituents in these inhomogeneous materials support the relation between cobalt-nickel-iron ratio and lattice constant established by the homogeneous synthetic samples and the natural material of known composition.

Seven essentially homogeneous isometric arsenides (1—Co<sub>100</sub>, 2—Co<sub>90</sub>Fe<sub>10</sub>, 3—Co<sub>75</sub>Fe<sub>25</sub>, 4—Co<sub>75</sub>Ni<sub>25</sub>, 5—Co<sub>70</sub>Ni<sub>15</sub>Fe<sub>15</sub>, 6—Co<sub>1</sub>Ni<sub>1</sub>Fe<sub>1</sub>, 7—Ni<sub>50</sub>Fe<sub>50</sub>) were plotted. In addition the isometric components of the inhomogeneous products of the melts (8—Co<sub>50</sub>Ni<sub>50</sub>, 9—Co<sub>25</sub>Ni<sub>75</sub>, 10—Co<sub>15</sub>Ni<sub>70</sub>Fe<sub>15</sub>, 11—Ni<sub>75</sub>Fe<sub>25</sub>, 12—Ni<sub>25</sub>Fe<sub>75</sub>, 13—Co<sub>15</sub>Ni<sub>15</sub>Fe<sub>70</sub>, 14—Co<sub>25</sub>Fe<sub>75</sub>, 15—Co<sub>50</sub>Fe<sub>50</sub>) were used. The positions of the symbols for the latter group are only approximate. The general direction in which the symbol should be moved to indicate the correct cobalt-nickel-iron ratio of the isometric phase is indicated by an arrow. The length of the arrow indicates whether the necessary shift is great or small.

The minerals, with the exception of Nos. 16 and 17 (Fig. 4), are those for which portions of analyzed specimens were available for x-ray examination: No. 16 Skutterud, Norway (position of symbol based on essential absence of nickel and iron in three specimens used, which conforms with the published analyses of material from this locality); No. 17 Cobalt, Ontario (brilliant cubes in chlorite from Temiskaming Mine, which are apparently identical with those analysed by Walker, analysis No. 148). In agreement with Walker's findings, qualitative tests indicate very little nickel and iron; No. 18 Horace Porter Mine, Gunnison Co., Colo., analysis No. 172; No. 19 Schneeberg, Saxony, analysis No. 36; No. 20 Schneeberg, Saxony, analysis No. 37; No. 21 Bullards Peak, New Mexico (material in Columbia University Collection believed to be part of that analyzed by Waller and Moses), analysis No. 168; No. 22 Great Bear Lake, N.W.T., Canada, analysis No. 163. An arrow attached to the symbol of a natural material indicates that the specimen was found to be inhomogeneous on the basis of optical and x-ray examination, and the nature of the

inhomogeneity is such that the symbol should be moved in the direction indicated to represent correctly the cobalt-nickel-iron ratio of the isometric constituent. A single analyzed natural arsenide, No. 19, fails to conform to the general pattern outlined by all other natural and synthetic samples used. This specimen is considered in more detail in a later section.

#### LATTICE CONSTANT AND METAL-ARSENIC RATIO IN THE ISOMETRIC ARSENIDES

Evidence that variations in arsenic content have a measurable effect on the lattice constants of the isometric arsenides was not obtained. Attempts to produce synthetic skutterudite with a deficient or excess arsenic content failed to provide a material with a lattice constant measurably different from that of material with a metal-arsenic ratio between  $R:As_{2.55-3.00}$ . In all cases in which a homogeneous product was obtained, the arsenic ratio was above 2.6. There is similar evidence from natural material. The two analyzed specimens (Nos. 19 and 20) with alleged arsenic ratios of 1:1.43 and 1:2.46, respectively, gave closely similar lattice constants, 8.303 Å and 8.294 Å, whereas analyses No. 18 and 20, with closely similar metal-arsenic ratios, gave widely different lattice constants, 8.222 Å and 8.294 Å.

#### RECORDED ANALYSES OF THE HIGHER ARSENIDES

##### GENERAL STATEMENT

Since much of the uncertainty concerning mineral relationships in this group may be traced to published analyses, a review of all available analyses has been undertaken. Metal-arsenic ratios computed from the analyses of arsenides, described as isometric, range from  $R:As_{1.12}$  to  $R:As_{3.68}$ . This has been ascribed by some to extensive metal-arsenic substitution, by others to the existence of two distinct isometric series (diarsenides and triarsenides), each of which is alleged to exhibit considerable substitution between metal and arsenic. The present study confirms the existence of a single isometric series (triarsenides of the skutterudite type) and points to mechanical inhomogeneity as a principal cause of the reported variability in metal-arsenic ratio. The study also indicates that isomorphous substitution between the three metals is limited in both the isometric and "orthorhombic" series. These views are supported by the published analyses when they are examined in the light of the accompanying descriptions of the materials used.

Crystals of the isometric arsenides are usually zonal and mechanically inhomogeneous. In addition to the isometric constituent, shells of other minerals, especially "orthorhombic" diarsenides concentric with the zonal structure, are frequently encountered. Irregularly distributed grains and veinlets of niccolite and "orthorhombic" arsenides commonly occur. "Orthorhombic" arsenides also occur as radiating masses at the centers of zonal isometric crystals. Perfection of external crystal form is no guide to purity. Some of the best-developed crystals exhibit marked inhomogeneity. Some cubic crystals are mere shells of isometric material enclosing an aggregate of nonisometric constituents.

Most published analyses were made on material which had not been examined by microscopic methods or at least without due regard for anisotropism, the principal

optical property distinguishing the isometric and "orthorhombic" members of such allegedly dimorphous pairs as chloanthite-rammelsbergite, smaltite-safflorite, and arsenoferrite-loellingite. Even close attention to this property may at times not distinguish between isometric and "orthorhombic" members since the latter, when fine-grained, exhibit weak anisotropism. Only 18 of the 198 analyses appear to have been made on material observed under a reflecting polarizing microscope, and only 5 of the materials used, Nos. 49, 74, (100-101), 156, and 195 had been examined by x-ray diffraction methods. Apparently no analyses of isometric arsenides have been made on material whose identity and homogeneity have been established by x-ray methods except Nos. (100-101) and 195. In many cases there is no evidence that the crystallization or homogeneity of the analyzed material had been established by any method.

Inhomogeneity of the type observed in the isometric arsenides from many localities would yield analyses of widely varying arsenic content, lower than that called for by the skutterudite formula,  $R:As_3$ . The illusion of extensive isomorphism between the metals and arsenic is an obvious consequence. At the same time widespread inhomogeneity combined with occasional failure to recognize the non-isometric character of massive material has provided analyses suggesting unlimited isomorphism among the three metals in the isometric series.

#### TABULATED DATA RELATING TO PUBLISHED ANALYSES

In Table 6, 198 analyses of the higher arsenides of cobalt, nickel, and iron have been arranged. A tabulation of essential data relating to these analyses has been assembled in Table 7. With few exceptions the original paper has been examined to ascertain the basis on which the author's identification of the material depends and to check the analysis. Although most of the headings in Table 7 are self-explanatory, several call for special comment.

Column (5), "original description of analyzed material," comprises comments by the analyst or original author concerning crystal form, structure, or mode of aggregation of the material and statements concerning homogeneity and mineral association which help to explain the deviations in chemical composition.

To render the data comparable all analyses prior to the computation of the cobalt-nickel-iron ratio and metal-arsenic ratio have been recalculated to the basis of 100 per cent after eliminating "obvious" impurities. This includes gangue, "insoluble" residues, quartz,  $SiO_2$ ,  $CaCO_3$ ,  $MgCO_3$ , and silver and bismuth. It is assumed that these two elements are present in the native state. There is general agreement that the silver revealed by analysis of these arsenides is present as the native metal. The work of McCay (1883) and the frequently observed presence of native bismuth in polished plates supports the view that the bismuth is also due to mechanical intergrowth. McCay (1883), by treating the powdered mineral with mercury, demonstrated that the bismuth in the so-called *Wismuth-kobalterz* or cheleutite from Schneeberg is a mechanical intergrowth of a tri-arsenide of skutterudite type and native bismuth.

The cobalt-nickel-iron ratio (Column 6) has been computed for each analysis and is indicated by three percentage figures arranged in sequence (cobalt-nickel-iron).

TABLE 6.—*Published analyses of the higher arsenides of cobalt, nickel and iron*

	As	S	Co	Ni	Fe	Miscellaneous	Total
1	65.75	—	28.00	—	5.00	1.25 (Mn, Fe and Mn given as oxides.)	100.00
2	77.96	1.02	9.89	1.11	4.77	3.89 Bi, 1.30 Cu, trace Mn.	99.94
3	70.37	.66	13.95	1.79	11.71	.01 Bi, 1.39 Cu.	99.88
4	71.30	.14	—	28.14	—	2.19 Bi, .50 Cu.	102.27
5	71.08	trace	9.44	—	18.48	1.00 Bi, trace Cu.	100.00
6	66.02	.49	21.21	—	11.60	.04 Bi, 1.90 Cu.	101.26
7	75.85	—	3.32	12.04	6.52	.94 Cu.	98.67
8	(77.82)	—	3.38	11.57	6.35	.88 Cu.	100.00
9	74.80	.85	3.79	12.86	7.33	—	99.63
10	58.71	2.80	3.01	35.00	.80	Cu—trace.	100.32
11	73.55	.27	6.28	14.49	5.20	—	99.79
12	68.30	—	—	26.65	2.06	2.66 Bi, trace Cu.	99.67
13	75.73	.87	6.81	11.59	4.43	—	99.43
14	75.14	1.31	12.66	3.02	5.10	Insol.—.32, 1.65 Cu, .66 Bi.	99.86
15	75.05	1.30	12.27	3.00	5.23	Insol.—.52, 1.52 Cu, .90 Bi.	99.79
16	75.09	1.30	12.46	3.01	5.16	Insol.—.42, 1.58 Cu, .78 Bi.	99.80
17	76.00	1.32	12.61	3.05	5.22	1.60 Cu.	99.80
18	75.40	.73	3.42	11.90	7.50	.39 Cu.	99.34
19	68.40	1.06	4.20	24.95	.69	.21 Bi.	99.51
20	62.85	1.20	15.88	.90	6.42	Insol.—10.62, 1.44 Bi, .01 Cu.	99.32
21	71.53	1.38	18.07	1.02	7.31	.01 Cu.	99.32
22	45.30	1.10	8.42	2.18	3.08	Insol.—39.00, trace Bi, .72 Cu.	99.80
23	74.35	1.80	13.80	3.60	5.05	1.20 Cu.	99.80
24	66.33	.16	.64	27.76	trace	5.11 Bi.	100.00
25	69.90	.17	.67	29.26	trace	—	100.00
26	65.02	.49	16.00	trace	11.20	Insol.—5.82, .37 Bi, .65 Cu.	99.55
27	69.34	.51	17.06	—	11.95	.69 Cu.	99.55
28	70.36	.90	18.58	—	9.51	trace Bi, .62 Cu.	99.97
29	73.46	.61	2.03	19.88	.38	Pb .36, insol.—.12, .41 Bi.	97.25
30	73.53	.61	21.94	—	.37	Pb .37, insol.—.14, .31 Bi.	97.27
31	73.49	.61	21.90	—	.37	Pb .37, insol.—.14, .36 Bi.	97.24
32	75.78	.61	2.30	19.89	.47	Pb .01, insol.—.13, .16 Bi.	99.35
33	76.19	.61	21.71	—	.30	Pb .12, insol.—.16, .18 Bi.	99.27
34	61.59	.05	13.70	—	3.71	Pb .16, 20.17 Bi, .69 Cu.	100.07
35	75.85	.88	13.18	1.72	4.93	1.59 Bi, 1.42 Cu.	99.57
36	63.42	—	15.83	15.07	3.69	Insol.—.32, .86 Bi.	99.19
37	75.4	—	4.5	15.2	3.5	.7 Cu.	99.30
38	69.85	1.10	—	—	27.41	1.05 Sb.	99.41
39	61.62	6.84	—	—	31.20	—	99.66
40	61.18	6.63	—	—	31.20	—	99.01
41	61.40	6.73	—	—	31.20	—	99.33
42	58.94	6.07	—	—	32.92	1.37 Sb.	99.30
43	76.38	.11	1.60	18.96	2.30	.31 Sb, .34 Bi.	100.00
44	71.19	.30	21.19	—	1.35	4.58 Bi.	98.61
45	75.43	.30	22.24	—	1.22	.37 Bi.	99.56
46	71.47	.58	3.62	21.18	2.83	.29 Cu.	99.97
47	74.52	1.81	11.72	1.81	5.26	3.60 Bi, 1.00 Cu.	99.72
48	47.99	1.89	.93	.75	17.78	.47 Sb, .05 Pb, .12 Zn, .01 Cu, trace Bi, 30.15 SiO <sub>2</sub> .	100.14
49	66.84	1.08	—	—	24.88	.05 Pb, CaCO <sub>3</sub> 4.00, MgCO <sub>3</sub> 1.57, 1.34 Cu.	99.76
50	74.22	.89	20.31	—	3.43	.16 Cu.	99.01

TABLE 6.—Continued

	As	S	Co	Ni	Fe	Miscellaneous	Total
51	72.64	—	3.37	20.74	3.25	—	100.00
52	73.53	.94	9.17	14.06	2.24	—	99.94
53	76.09	—	4.56	12.25	6.82	—	99.72
54	60.42	2.11	10.80	25.87	.80	—	100.00
55	59.38	2.22	18.30	19.38	.72	—	100.00
56	68.73	—	16.37	12.15	2.30	.45 Cu.	100.00
57	77.32	.42	10.23	10.41	.78	.62 Sb, .13 insol.	99.91
58	77.10	.39	10.98	9.79	.75	.47 Sb, .56 insol.	100.04
59	72.97	1.70	10.88	9.41	2.78	1.31 Bi, .58 insol.	99.63
60	62.29	5.18	4.40	—	24.33	4.37 Sb, trace Mn.	100.57
61	69.70	4.71	10.11	8.52	5.05	trace Sb, .97 Bi, .94 Cu.	100.00
62	70.17	—	—	27.38	2.12	—	99.67
63	69.52	.32	22.11	1.58	4.63	.33 Bi, 1.78 Cu.	100.27
64	67.31	1.82	18.49	1.24	8.59	2.55 Cu.	100.00
65	68.50	7.00	9.60	—	9.70	1.00 Cu.	95.80
66	74.84	1.70	8.28	8.50	4.45	3.24 Cu.	101.01
67	61.46	2.37	14.97	—	16.47	4.22 Cu.	99.49
68	68.27	1.30	13.12	1.88	14.38	.26 Cu, 1.24 Bi.	100.45
69	69.12	1.32	13.29	1.90	14.56	.25 Cu.	100.45
70	70.34	—	—	28.40	trace	—	98.74
71	70.93	—	—	29.50	trace	—	100.43
72	74.47	1.53	19.73	—	4.27	—	100.00
73	75.04	1.61	10.93	6.12	5.22	.31 Cu, .70 insol.	99.93
74	70.13	.35	2.86	24.58	.03	.48 Sb, .56 Cu, trace Bi, 1.45 gangue.	100.44
75	55.00	8.35	—	—	36.44	.01 Ag.	99.80
76	70.59	1.65	—	—	28.67	—	100.91
77	53.64	7.66	—	—	38.70	—	100.00
78	58.75	1.40	—	—	26.70	.36 Sb, .44 CaO, .05 MgO, .19 H <sub>2</sub> O, .44 Al <sub>2</sub> O <sub>3</sub> , .92 SiO <sub>2</sub> , 10.28 insol.	99.53
79	55.85	6.24	11.85	26.04	.92	—	100.90
80	72.00	.43	1.94	7.00	17.39	—	98.76
81	49.85	2.65	.30	5.13	22.36	19.71 Sb.	100.00
82	59.96	3.19	—	—	26.89	9.96 Sb.	100.00
83	68.08	.84	—	—	27.32	4.03 Sb, .10 Cu, .10 SiO <sub>2</sub> .	100.47
84	70.16	1.20	4.13	.20	23.75	.29 Sb, trace Bi.	99.73
85	65.99	1.94	—	—	28.06	2.17 Serpentine.	98.16
86	65.88	1.77	—	—	32.35	—	100.00
87	63.14	1.63	—	—	30.24	3.55 gangue.	98.56
88	65.61	1.09	—	—	31.51	1.04 gangue.	99.25
89	66.57	1.02	—	—	31.08	.92 gangue.	99.59
90	61.52	.83	—	—	29.83	6.07 gangue.	98.25
91	66.59	1.93	—	—	28.28	2.06 gangue.	98.86
92	67.81	1.97	—	—	28.19	1.14 gangue.	99.11
93	68.21	1.32	—	—	29.05	1.21 insol.	99.79
94	68.38	1.32	—	—	28.86	1.21 insol.	99.77
95	68.52	1.95	—	—	27.96	1.75 gangue.	100.18
96	77.84	.69	20.01	—	1.51	trace Cu.	100.05
97	79.00	—	19.50	—	1.40	—	99.90
98	79.20	—	18.50	—	1.30	—	99.00
99	72.05	2.30	18.90	—	3.83	3.41 insol.	100.49
100	72.10	.97	18.60	—	2.64	5.63 insol.	99.94

TABLE 6.—Continued

	As	S	Co	Ni	Fe	Miscellaneous	Total
101	76.41	1.03	19.70	—	2.80	—	99.94
102	70.09	1.33	—	—	27.39	—	98.81
103	70.22	1.28	—	—	28.14	—	99.64
104	72.17	.37	trace	—	27.14	trace P.	99.68
105	71.13	.68	12.99	.20	15.28	.33 Cu and Pb.	100.61
106	69.46	.90	23.44	—	4.94	—	98.74
107	71.10	1.55	27.31	—	—	.02 Cu.	99.98
108	70.24	.57	27.83	—	—	.05 Bi, trace Cu, 1.26 insol.	99.95
109	71.09	trace	—	—	28.70	—	99.79
110	63.08	3.42	1.22	.29	28.95	.45 SiO <sub>2</sub> .	97.41
111	65.02	2.90	3.93	26.75	1.40	—	100.00
112	72.91	.14	8.09	12.25	4.70	2.42 Zn.	100.51
113	74.45	.72	16.47	—	3.90	4.40 Bi, .28 gangue.	100.22
114	71.10	—	—	—	28.90	—	100.00
115	71.70	—	—	—	28.30	—	100.00
116	68.12	1.40	6.65	11.37	9.88	2.09 Cu.	99.51
117	71.13	.36	6.94	11.87	9.70	—	100.00
118	70.11	.81	—	—	28.21	trace Bi.	99.13
119	76.78	1.67	7.78	12.94	1.04	.44 insol.	100.65
120	60.41	5.20	5.10	13.37	13.49	—	97.57
121	72.18	.70	—	—	26.48	—	99.36
122	58.92	2.77	—	—	25.63	6.34 Bi, 6.34 insol.	100.00
123	68.87	1.09	—	—	29.20	—	99.16
124	57.90	4.21	.34	—	31.46	Sb 3.49, 2.58 qtz.	99.98
125	63.21	trace	—	—	35.85	trace Ti.	99.06
126	68.00	.56	20.61	—	10.40	—	99.57
127	77.94	.51	3.69	12.01	5.07	—	99.22
128	78.26	—	15.05	—	6.69	—	100.00
129	66.84	.56	1.72	11.09	19.48	—	99.69
130	67.26	3.29	—	—	29.45	—	100.00
131	71.11	2.29	—	18.71	6.82	—	98.93
132	63.66	3.66	6.44	—	21.22	5.61 Sb.	100.59
133	66.90	2.36	4.67	—	21.38	3.59 Sb, 1.14 Cu.	100.04
134	52.43	.34	21.93	—	12.96	.67 Bi, .33 Cu, trace Mn, 5.19 CaCO <sub>3</sub> , 1.46 MgCO <sub>3</sub> , 4.99 insol.	100.30
135	61.54	.27	20.56	7.39	5.98	4.76 Bi.	100.50
136	76.55	.75	7.31	4.37	7.84	.32 Sb, 4.11 Zn, .22 Cu.	101.47
137	58.76	2.94	7.65	9.85	9.86	1.06 Sb, .72 Zn, 6.33 Pb, 2.14 gangue.	99.31
138	70.85	.81	2.88	.79	24.67	—	100.00
139	67.17	2.18	4.11	23.24	—	2.78 Ag.	99.48
140	71.61	.75	13.81	11.35	1.21	.96 Cu.	99.69
141	66.87	4.13	12.16	14.14	2.10	.40 Cu.	99.80
142	70.84	.82	5.62	—	22.18	trace Sb, .41 Cu.	99.87
143	69.08	.96	5.94	—	23.60	trace Sb, .38 Cu.	99.96
144	67.32	2.03	1.80	27.84	trace	.83 Sb.	99.82
145	68.78	2.02	19.99	—	7.97	—	98.76
146	74.72	1.25	20.57	1.31	2.35	—	100.20
147	72.71	.99	20.89	2.54	2.87	—	100.00
148	76.38	1.50	20.18	.11	1.84	—	100.01
149	66.12	2.45	2.61	26.47	.66	.60 Sb, .25 SiO <sub>2</sub> .	99.16
150	68.03	2.24	2.24	27.19	.44	.43 Sb.	100.57

TABLE 6.—Continued

	As	S	Co	Ni	Fe	Miscellaneous	Total
151	65.90	3.33	2.93	25.73	.78	.96 Sb, .32 SiO <sub>2</sub> .	99.95
152	66.60	2.97	2.70	26.21	.66	.85 Sb, .21 SiO <sub>2</sub> .	100.20
153	65.78	3.05	1.94	27.08	.56	.91 Sb, .16 Cu.	99.48
154	74.51	1.38	16.03	.89	6.89	.40 Sb.	100.10
155	75.02	1.51	17.60	.44	5.22	.56 Sb.	100.35
156	68.5	2.60	.40	28.10	—	—	99.60
157	68.84	.96	5.84	—	22.24	.26 Sb, 2.22 insol.	100.36
158	75.70	.66	17.66	.66	3.56	.06 Bi, 1.64 insol.	99.94
159	66.61	3.30	11.24	17.46	.73	.84 insol.	100.18
160	71.30	.92	12.56	.36	14.60	—	99.74
161	75.15	1.18	20.50	.20	.95	.16 CO <sub>2</sub> , .10 Cu, 1.22 insol.	99.46
162	67.67	2.06	6.10	19.23	1.09	3.53 insol.	99.68
163	76.63	1.20	16.59	4.11	1.42	.05 Cu.	100.00
164	76.20	1.39	19.27	.11	1.85	—	98.82
165	70.66	1.54	6.37	18.63	2.31	.89 CaCO <sub>3</sub> .	100.40
166	69.80	.21	—	—	29.40	—	99.41
167	74.04	.13	19.52	—	.44	.03 Pb, 4.78 Ag, .04 Cu, .09 CaO, .05 MgO.	99.12
168	67.37	—	5.13	11.12	2.64	trace Pb, 8.38 Ag, 1.04 Cu.	99.20
169	70.83	.77	—	—	27.93	trace Cu.	99.53
170	63.82	1.55	11.59	trace	(15.99)	2.05 Pb, trace Ag, 1.13 Bi, .16 Cu, 2.60 SiO <sub>2</sub> .	98.89
171	71.18	.56	4.37	.21	22.96	.08 Bi, .39 Cu.	99.75
172	75.30	—	10.98	5.14	5.82	1.44 Insol.	98.68
173	64.06	.57	14.88	1.12	11.14	6.34 CaCO <sub>3</sub> , 2.22 insol.	100.33
174	71.12	.76	13.75	—	13.85	—	99.48
174A	70.94	.96	—	—	27.89	—	99.79
174B	74.01	trace	—	—	26.30	—	100.31
174C	58.94	6.07	—	—	32.92	1.37 Sb.	99.30
175	70.00	—	1.35	12.16	17.70	—	101.21
176	70.11	4.78	3.82	9.44	11.85	—	100.00
177	67.44	5.62	3.85	10.17	12.92	—	100.00
178	66.20	1.10	—	—	27.60	5.10 gangue.	100.00
179	70.30	1.10	—	—	27.60	.20 Ag.	99.20
180	70.85	.08	24.13	1.23	4.05	.41 Cu.	100.75
181	71.58	.87	—	—	27.35	—	99.80
182	71.60	.60	17.64	—	4.93	1.19 Ag, 4.60 Cu.	100.56
183	60.30	—	15.80	11.40	6.20	3.20 Ag.	96.90
184	73.82	.20	15.90	5.16	2.61	2.06 Ag.	99.75
185	68.51	.70	15.16	2.62	7.16	—	94.15
186	56.40	2.30	—	35.10	1.40	4.70 gangue.	99.90
187	64.84	7.01	.13	—	24.35	Au and Ag .01, .11 Cu, .10 Bi, gangue 2.88.	99.43
188	69.32	1.38	9.42	—	19.18	—	99.30
189	64.50	1.00	13.25	3.50	3.50	O, H <sub>2</sub> O etc. 14.25, trace Cu.	100.00
190	74.02	1.94	12.82	3.96	5.54	.60 insol.	98.88
191	74.67	.84	19.91	.55	2.80	.40 insol.	99.17
192	77.64	.82	18.59	trace	2.29	—	99.34
193	67.64	1.08	—	—	29.31	1.86 Cu, .11 Sb.	100.00
194	71.36	1.46	—	—	27.83	.17 insol.	100.82
195	65.70	1.57	5.93	—	20.70	2.60 insol.	96.50

TABLE 7.—Data relating to published analyses of the higher mineral arsenides

No.	Locality (1)	Analyst (2)	Source of Data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
1	Schneeberg, Saxony	John	*John (1810) p. 236, Hintze (1904) p. 800		Fibrous; original source not seen, Fe and Mn given as oxides.	88.3- 0 -11.7	1:1.63	I?	<i>Speiskobalt</i>	?	Questionable analysis. Identity (?)
2	Schneeberg, Saxony	Kersten	Kersten (1826) p. 292	6.0-6.7	Massive, reticulated; Bi- in arsenide, no expl. of Cu; average of 4 anal.	61.7- 6.9-31.4	1:3.68	?	<i>Wismuth-Kobalterz</i>	?	Questionable analysis. Identity (?)
3	Sauschwart Mine, Schneeberg, Saxony	Hoffmann	Hoffmann (1832) p. 493	—	Massive; Cu- in Chalcocite, S- in Pyrite, Bi- native.	49.6- 6.4-44.0	1:1.93	IP	<i>Grauer Speiskobalt</i>	M?	Safflorite (?)
4	Schneeberg, Saxony	Hoffmann	Hoffmann (1832) p. 492	—	Massive; Cu- in Chalcocite, Bi- native.	0 -100 - 0	1:1.96	?	<i>Arseniknickel</i>	O?	Rammelsbergite (?)
5	Schneeberg, Saxony	Kobell	Kobell (1838) p. 300	6.95	Spherical, radial aggreg., prob. isometric; Bi- no expl.; (McKay (1885) p. 373 thinks Kobell switched Co and Fe).	32.6- 0 -67.4	1:1.93	IP	<i>Speiskobalt (Eisen Kobaltkies)</i>	M	Safflorite
6	Schneeberg, Saxony	Jaেকে	Rose (1852) p. 53	6.84	Fibrous, spherical radiating, massive (implied orthorhombic); Cu and S- no expl.	63.4- 0 -36.6	1:1.50	O	<i>Arsenikkobalt</i>	M	Safflorite
7	Schneeberg, Saxony	Bull	Rose (1852) p. 54	6.537	Massive (?); no descr.; Cu- no expl.	14.9- 51.2-30.9	1:2.58	I	<i>Chloanthit (Stängelkobalt)</i>	I	Nickelian skutterudite
	Schneeberg, Saxony	Bull	Rose (1852) p. 54	6.537	Same specimen; partial analysis; As calculated by difference.	15.6- 53.5-30.9	1:2.72	I	<i>Chloanthit (Stängelkobalt)</i>	I	Nickelian skutterudite
9	Schneeberg, Saxony	Karstedt	Rammelsberg (1853) p. 225	—	Crystallized; S- in arsenide.	15.5- 52.8-31.7	1:2.47	I	<i>Speiskobalt</i>	I	Nickelian skutterudite
10	Schneeberg (?), Saxony	Salvetat	Wertheim (1854) p. 79	—	Three analyses in original, all closely similar, "Physical character of smaltine."	7.7- 90.0- 2.3	1:1.32	?	Nickel Arsenical	?	Questionable analysis. Identity (?)
11	Daniel Mine, Schneeberg, Saxony	Lange	Rammelsberg (1860) p. 24	—	Crystalline; S- in arsenide.	23.8- 55.3-20.9	1:2.22	I	<i>Speiskobalt</i>	I	Nickelian skutterudite

12	Schneeberg, Saxony	Hilger	Sandberger (1871) p. 204	7.19	Spheroidal, radiating, needles, and columns; rhombic crystals; Bi- native.	0 -92.5 - 7.5	1:1.86	O	<i>Weissnickelkies</i> or <i>Rammelsbergit</i>	O	Rammelsbergite
13	Schneeberg, Saxony	Renetsky	Rammelsberg (1875) p. 44	—	"Regular" crystals; S- in arsenide.	29.4- 50.3-20.3	1:2.64	I	<i>Weissnickelkies</i> or <i>Speiskobalt</i>	I	Nickelian skutterudite
14	Neustädtel near Schneeberg, Saxony	McCay	McCay (1883) p. 28	6.30	Reticulated, massive; isometric; Cu and S in arsenide; Bi- native.	60.1- 14.4-25.5	1:2.74	I	<i>Cheleutit</i>	I	Skutterudite
15	Neustädtel near Schneeberg, Saxony	McCay	McCay (1883) p. 28	6.30	Same specimen.	59.0- 14.5-26.5	1:2.77	I	<i>Cheleutit</i>	I	Skutterudite
16	Neustädtel near Schneeberg, Saxony	McCay	McCay (1883) p. 28	6.30	Average of (14-15).	59.6- 14.4-26.0	1:2.75	I	<i>Cheleutit</i>	I	Skutterudite
17	Neustädtel near Schneeberg, Saxony	McCay	McCay (1883) p. 31	6.30	Same as 16 (-Qtz. and Bi)	59.6- 14.4-26.0	1:2.75	I	<i>Cheleutit</i>	I	Skutterudite
18	Gesellschaft Mine, Schneeberg, Saxony	McCay	McCay (1883) p. 40	6.54	Massive (twinned cryst. as descr. by Naumann); no expl. of Cu and S (prob. in arsenide).	14.7- 51.3-34.0	1:2.57	I	<i>Chloanthit</i> ( <i>Stängelkobalt</i> )	I	Nickelian skutterudite
19	Schneeberg, Saxony	McCay	McCay (1883) p. 39	6.44- 6.45	Spheroidal, radial, fibrous; niccolite inclusions but anal. material be- lieved pure; S- in arsenide; chloan- thite on basis of specific gravity alone.	14.0- 83.6- 2.4	1:1.86	I?	<i>Chloanthit</i>	O	Rammelsbergite
20	Schneeberg, Saxony	McCay	McCay (1883) p. 44	6.11	Massive, fine grained; Bi- native, S and Cu- no expl. (prob. in arsenide).	67.4- 3.8-28.8	1:2.19	I	<i>Grauer Smaltin</i>	I	Skutterudite
21	Schneeberg, Saxony	McCay	McCay (1883) p. 44	6.11	Same as 20 (-Qtz. and Bi).	67.4- 3.8-28.8	1:2.19	I	<i>Grauer Smaltin</i>	I	Skutterudite
22	Schneeberg, Saxony	McCay	McCay (1883) p. 34	6.35	Reticulated; Cu and S- in arsenide.	60.7- 15.9-23.4	1:2.59	I	<i>Cheleutit</i>	I	Skutterudite
23	Schneeberg, Saxony	McCay	McCay (1883) p. 34	6.35	Same as 22 (-Qtz.).	60.7- 15.9-23.4	1:2.59	I	<i>Cheleutit</i>	I	Skutterudite
24	Schneeberg, Saxony	McCay	McCay (1883) p. 8	6.90	Bi- native, S- in arsenide.	2.2- 97.8- 0	1:1.84	O	<i>Weissnickelkies</i>	O	Rammelsbergite
25	Schneeberg, Saxony	McCay	McCay (1883) p. 8	6.90	Same as 24 (-Bi).	2.2- 97.8- 0	1:1.84	O	<i>Weissnickelkies</i>	O	Rammelsbergite

\* Original reference not seen.

TABLE 7—Continued

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
26	Wolfgang Massen near Schneeberg, Saxony	McCay	McCay (1883) p. 19	7.28	Globular, radiating, massive, no cryst.; Bi-native, Cu and S in arsenide.	57.5- 0 -42.5	1:1.83	O	Safflorit	M	Safflorite
28	Schneeberg, Saxony	McCay	McCay (1885) p. 373	7.17	Massive; S and Cu in mineral. Smaltite cryst. on surface.	64.9- 0 -35.1	1:1.95	O	Safflorite ( <i>Schlacken-kobalt</i> )	M	Safflorite
29	Schneeberg, Saxony	Vollhardt	Vollhardt (1886) p. 14	—	Isometric crystals (cube and pyrit.); micro exam and etch—inhomog. Shell struct; prob. contains niccolite.	9.1- 89.1- 1.8	1:2.62	I	Speiskobalt	I	Nickelian skutterudite
	Schneeberg, Saxony	Vollhardt	Vollhardt (1886) p. 14	—	Same specimen.	Ni & Co not separated	1:2.63	I	Speiskobalt	I	Nickelian skutterudite
	Schneeberg, Saxony	Vollhardt	Vollhardt (1886) p. 14	—	Average of 29-30.	Ni & Co not separated	1:2.63	I	Speiskobalt	I	Nickelian skutterudite
	Schneeberg, Saxony	Vollhardt	Vollhardt (1886) p. 15	—	Same specimen after treatment with HCl and KClO <sub>4</sub> .	10.1- 87.8- 2.1	1:2.67	I	Speiskobalt	I	Nickelian skutterudite
33	Schneeberg, Saxony	Vollhardt	Vollhardt (1886) p. 16	—	Another portion same specimen after treatment with HCl and KClO <sub>4</sub> .	Ni & Co not separated	1:2.76	I	Speiskobalt	I	Nickelian skutterudite
34	Zschorlau near Schneeberg, Saxony	Frenzel	Frenzel (1896) p. 524	6.92	Crystals (Cube and oct.) and (Cube and Dod); Bi- in arsenide, Cu and S in chalcopyrite.	78.6- 0 -21.4	1:2.69	I	Bismutosmallin	I	Skutterudite
35	Schneeberg, Saxony	Frenzel	Hintze (1904) p. 810	—	No description; Cu and S- no expl.; Bi- in arsenide.	65.5- 8.6-25.9	1:2.86	I	Wismuthkobalters	I	Skutterudite
36	Schneeberg, Saxony	Fahey	Short (1930) p. 767	—	No description; micro exam. and etch-shell struct. (homog.); Bi- no expl.	45.4- 43.4-11.2	1:1.43	I	Smaltite	I ?	Skutterudite (?)
37	Schneeberg, Saxony	Fairchild	Short (1930) p. 767	—	No description; micro exam. and etch (homog.); Cu- no expl; no shell structure.	19.2- 65.1-15.7	1:2.46	I	Smaltite	I	Nickelian skutterudite

38	Breitenbrunn, Saxony	Behncke	Behncke (1856) p. 187	7.259	Needlelike, massive, rhombic; S- in arsenopyrite; Sb- in arsenide.	0 - 0 -100	1:1.99	O	<i>Arsenik Eisen</i>	O	Loellingite
39-41	Breitenbrunn, Saxony	McCay	McCay (1883) p. 45	6.580	Orthorhombic; S- in arsenide.	0 - 0 -100	1:1.85	O	<i>Geierit</i>	O	Loellingite
	Breitenbrunn, Saxony	McCay	McCay (1883) p. 45	6.580	Same sample.	0 - 0 -100	1:1.83	O	<i>Geierit</i>	O	Loellingite
	Breitenbrunn, Saxony	McCay	McCay (1883) p. 45	6.580	Average of 39 and 40	0 - 0 -100	1:1.84	O	<i>Geierit</i>	O	Loellingite
42	Geyer (Geier), Saxony	Behncke	Behncke (1856) p. 187	6.321	Massive and orthorhombic crystals; S- in arsenopyrite, Sb- in arsenide.	0 - 0 -100	1:1.39	O	<i>Arsenik Eisen</i>	O	Loellingite
43	Markus Röhling Mine, Annaberg, Saxony	Rammelsberg	Rammelsberg (1873) p. 283	5.734	Cubic crystals; S and Bi- in arsenide; (As- direct 73.8, As- by difference 76.38).	6.9- 82.6-10.5	1:2.53	I	<i>Speiskobalt</i>	I	Nickelian skutterudite
44-45	Wolkenstein, Saxony	Vollhardt	Vollhardt (1886) p. 19	—	Massive and crystals (cube and oct.); polished plate inhomog. after etching; (Baumbauer, 1886, fig. 1-2).	Ni & Co- Not sep.	1:2.50	I	<i>Speiskobalt</i>	I	Skutterudite (kind?)
	Wolkenstein Saxony	Vollhardt	Vollhardt (1886) p. 19	—	Residue of 44 after attack by HCl and KClO <sub>4</sub> .	Ni & Co- Not sep.	1:2.54	I	<i>Speiskobalt</i>	I	Skutterudite (kind?)
46	Geistergänger Erzbruch, St. Joachimstal, Bohemia	Marian	Vogl (1856) p. 143	6.89	Massive.	13.0- 76.3-10.7	1:2.04	O	<i>Weissnickelkies</i>	O	Rammelsbergite
47	St. Joachimstal, Bohemia	Marian	Vogl (1856) p. 148	6.807	Massive, isometric; Bi- in bismuthinite.	61.4- 9.5-29.1	1:3.02	I	<i>Speiskobalt</i>	I	Skutterudite
48	St. Joachimstal, Bohemia	Heuseler	Zuchert (1925) p. 82	?	Massive crystal; Zuchert doubts reliability of anal.	4.6- 3.7-91.7	1:2.02	O	<i>Loellingit</i>	O	Loellingite
49	St. Joachimstal, Bohemia	Foshag	Foshag & Short (1930) p. 429	—	Massive, fine grained; homog. and isotropic under refl. microscope; (Loellingite—Buerger (1936)).	0 - 0 -100	1:1.98	I	Arsenoferrite	O	Loellingite
50	Riechelsdorf, Hesse	Stromeyer	Stromeyer (1817) p. 715	6.449	Crystallized; Rose (1852, p. 51) questions lack of Ni.	84.9- 0 -15.1	1:2.50	I	<i>Speiskobalt</i>	I	Skutterudite
51	Riechelsdorf, Hesse	Booth	Booth (1835) p. 242	—	Isometric (cube- oct.- Dod.) also columnar-terminating in isom. forms; isom. crystal or columnar masses used in analysis?—apparently both; As by loss.	12.2- 75.4-12.4	1:2.07	I?	<i>Deutarseniuret of Nickel</i>	O	Rammelsbergite + skutterudite (nickelian?)

TABLE 7—Continued.

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
52	Riechelsdorf, Hesse	Sartorius	Genth (1848) p. 279	—	Isometric (cube-oct.-dod.); homog. under micro.	35.8- 55.0- 9.2	1:2.27	I	<i>Speiskobalt</i>	I	Nickelian skutterudite
53	Riechelsdorf, Hesse	Bull	Rose (1852) p. 52	—	Isometric crystals.	18.7- 51.3-30.0	1:2.50	I	<i>Chloanthit</i>	I	Nickelian skutterudite
54	Riechelsdorf, Hesse	Rammelsberg	Rammelsberg (1853) p. 226	6.374	Isometric (cube-oct.); As by difference, Sp. Gr. 4.374 in original, corrected in Rammelsberg (1875, p. 36).	28.7- 69.1- 2.2	1:1.29	I	<i>Speiskobalt</i>	I ?	Nickelian skutterudite (?)
55	Riechelsdorf, Hesse	Weber	Rammelsberg (1853) p. 226	6.374	Same specimen as 54.	40.3- 42.9-16.8	1:1.12	I	<i>Speiskobalt</i>	I ?	Nickelian skutterudite (?)
56	Riechelsdorf, Hesse	Klauer	Rammelsberg (1853) p. 225	—	Crystalline, isometric; aver. 2 anal.	52.8- 39.4- 7.8	1:1.72	I	<i>Speiskobalt</i>	I ?	Skutterudite (?)
57	Riechelsdorf, Hesse	Lorenz	Beutell & Lorenz (1915) p. 364	—	No description; 57, 58 and 59 made on 3 different specimens.	47.6- 48.6- 3.8	1:2.88	I	<i>Speiskobalt</i>	I	Nickelian skutterudite
58	Riechelsdorf, Hesse	Lorenz	Beutell & Lorenz (1915) p. 364	—	No description; another specimen.	50.9- 45.4- 3.7	1:2.87	I	<i>Speiskobalt</i>	I	Skutterudite
59	Riechelsdorf, Hesse	Lorenz	Beutell & Lorenz (1915) p. 364	—	No description; another specimen.	46.8- 40.6-12.6	1:2.60	I	<i>Speiskobalt</i>	I	Skutterudite
60	Wolfach, Baden	Petersen	Petersen (1869) p. 393	6.797	Massive, rhombic crystals; Sb and Co in arsenide.	14.7- 0 -85.3	1:2.08	O	<i>Geierit</i>	O	Loellingite
61	Gutes Gottes Mine, Wittichen, Baden	Petersen	Petersen (1868) p. 72	6.272	Isometric (cube-oct.); core of niccolite, chalcopyrite assoc.	42.1- 35.7-22.2	1:2.55	I	<i>Speiskobalt</i>	I	Skutterudite
62	Wittichen, Baden	Hilger	*(Original?) Quoted by McCay (1883) p. 9		No description, original source not seen.	0 - 92.5- 7.5	1:1.86	O ?	<i>Rammelsbergit</i>	O	Rammelsbergite
63	Dreikönigstern Mine, Rheinerzau Thal, Württemberg	Petersen	Sandberger (1868) p. 410	6.915	Nodular, needlelike, massive, rhombic; core of Bi, S- in arsenide; shells of <i>speiskobalt</i> inclosing radial <i>arsenkobalteisen</i> .	77.4- 5.5-17.1	1:1.81	O	<i>Arsenkobalteisen</i>	M	Safflorite

64	Auerbach, Hesse	Reinhardt	Harres (1881) p. 13	—	Massive, isom. crystals; chalcopyrite assoc.	64.2- 4.3-31.5	1:1.81	I	<i>Speiskobalt</i>	I ?	Skutterudite (?)
65	Bieber, Hesse	Laugier	*Laugier (1813) p. 34		Totals only 95.80; no description.	48.4- 0 -51.6	1:3.22	I ?	<i>Weisser Speiskobalt</i>	?	Questionable analysis. Identity (?)
66	Bieber, Hesse	Van Gerichten	Sandberger (1873) p. 137	7.1	Isometric (cube- oct.- dod.); chalcopyrite and niccolite assoc.—latter often included.	38.5- 39.7-21.8	1:2.53	I	<i>Speiskobalt</i>	I	Nickelian skutterudite
67	Bieber, Hesse	Van Gerichten	Sandberger (1873) p. 138	6.7	In druses on <i>speiskobalt</i> ; chalcopyrite and pyrite assoc.	46.3- 0 -53.7	1:1.45	O ?	<i>Spathiopyrit (Quirkies)</i>	M	Safflorite
68	Bieber, Hesse	McCay	McCay (1883) p. 21	7.26	Lenticular, radial, fibrous; with smaltite.	43.5- 6.2-50.3	1:1.84	O	<i>Safflorit</i>	M	Safflorite
69	Bieber, Hesse	McCay	McCay (1883) p. 21	7.26	Same analysis (-Bi).	43.5- 6.2-50.3	1:1.84	O	<i>Safflorit</i>	M	Safflorite
70	Kamsdorf near Saalfeld, Thuringia	Rammelsberg	Rammelsberg (1843) p. 15	6.735	No description; isometric-Rammelsberg (1845, p. 19).	0 -100 - 0	1:1.94	I ?	<i>Arseniknickel</i>	O ?	Rammelsbergite (?)
71	Kamsdorf near Saalfeld, Thuringia	Rammelsberg	Rammelsberg (1843) p. 15	6.735	Same specimen.	0 -100 - 0	1:1.88	I ?	<i>Arseniknickel</i>	O ?	Rammelsbergite (?)
72	Schweina-Glücksbrunn, Sachsen-Meiningen	Rammelsberg	Rammelsberg (1860) p. 24	—	Isometric (cube- oct.- dod).	81.4- 0 -18.6	1:2.53	I	<i>Speiskobalt</i>	I	Skutterudite
73	Schweina-Glücksbrunn, Sachsen-Meiningen	Krusch	Krusch (1902) p. 56	—	Isometric (cube and oct.) and massive.	48.4-27.2 -24.4	1:2.71	I	<i>Speiskobalt</i>	I	Skutterudite
74	Eisleben, Prov. of Saxony in Prussia (not Thuringia)	Int. Nickel Co.	Peacock & Dadson (1940) p. 572	6.97	Orthorhombic; Co in Rammelsbergite, Fe in loellingite, Bi native; Rf. micro. exam., aniso. intergrown with loellingite and Bi; X-ray.	10.4- 89.5- .1	1:1.99	O	Rammelsbergite	O	Rammelsbergite
75	St. Andreasberg in the Harz	Jordan	Jordan (1837) p. 439	—	Platy, orthorhombic	0 - 0 -100	1:1.65	O	<i>Arsenikeisen</i>	O	Loellingite
76	St. Andreasberg in the Harz	Illing	Illing (1854) p. 56	6.8	Massive; S- in <i>arsenikalkies</i> ; aver. 4 anal.	0 - 0 -100	1:1.94	O ?	<i>Arsenikalkies</i>	O	Loellingite
77	St. Andreasberg in the Harz	Illing	*Illing (1854A) p. 51 ? Hintze (1904) p. 871	—	Original source not seen.	0 - 0 -100	1:1.38	O ?	<i>Arsenikalkies</i>	O	Loellingite

TABLE 7.—Continued

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
78	St. Andreasberg in the Harz	Hahn	Streng (1861) p. 281	—	No description.	0 - 0 -100	1:1.74	O ?	<i>Arsenikalkies</i>	O	Loellingite
79	St. Andreasberg in the Harz	Hahn	Streng (1861) p. 281	—	No description; anal. in Hintze (1904) incorrect (no Cu).	30.4-67.1- 2.5	1:1.42	?	<i>Kupfernicksel</i> (1)	?	Questionable analysis. Identity (?)
80	St. Andreasberg in the Harz	Kobell	Kobell (1868) p. 403	6.6	Fine granular, massive (distinct from smalt.-chloan.) implies ortho.-"analogous to safflorite"; S- in arsenopyrite.	7.1-25.7- 67.2	1:2.10	O	<i>Chalthamit</i>	O	Nickelian loellingite
81	St. Andreasberg in the Harz	Rammelsberg	Rammelsberg (1873) p. 282	7.114	Surrounds <i>breithauptite</i> ; Co, Ni and 19.71 Sb in <i>breithauptite</i> .	1.1-17.7- 81.2	1:1.85	O	<i>Arsenikeisen</i>	O	Questionable analysis. Loellingite (?) + <i>breithauptite</i> .
	St. Andreasberg in the Harz	Rammelsberg	Rammelsberg (1873) p. 282	7.114	Surrounds <i>breithauptite</i> ; anal. #81 corrected by assigning all Co and Ni to <i>breithauptite</i> ; remaining Sb in arsenide.	0 - 0 -100	1:2.04	O	<i>Arsenikeisen</i>	O	Questionable analysis. Loellingite (?)
83	St. Andreasberg in the Harz	Loczka	Loczka (1886) p. 261	7.4746	Massive, platy.	0 - 0 -100	1:1.97	O	<i>Arsenikeisen</i>	O	Loellingite
84	Radauthal in the Harz	Kluss	Scheibe (1900) p. 119	—	Massive, rhombic, measured crystals; columnar; with galena, chalcopyrite and arsenopyrite; S in arsenide.	14.0- .7- 85.3	1:1.96	O	<i>Kobalt haltiger Arsenikalkies</i>	O	Loellingite
85	Reichenstein, Silesia	Hoffmann	Hoffmann (1832) p. 490	—	Orthorhombic, massive; S- in FeS <sub>2</sub>	0 - 0 -100	1:1.95	O	<i>Arsenikeisen</i>	O	Loellingite
86	Reichenstein, Silesia	Karsten	Karsten (1831) p. 579	—	Massive; S in <i>magnetkies</i> .	0 - 0 -100	1:1.61	O ?	<i>Arsenikalkies</i>	O	Loellingite
87	Reichenstein, Silesia	Meyer	Scheerer (1840) p. 154	—	Crystals.	0 - 0 -100	1:1.65	O	<i>Arsenikeisen</i>	O	Loellingite

88	Reichenstein, Silesia	Weidenbusch	Rose (1852) p. 54	—	Massive and crystalline in serpentine; S in FeAsS.	0 - 0-100	1:1.61	O	<i>Arsenikeisen</i>	O	Loellingite
89	Reichenstein, Silesia	Güttler	*Güttler (1870) p. 14, Hintze (1904) p. 872	7.41	Needle-like crystals; original source not seen.	0 - 0-100	1:1.65	O	<i>Arsenikeisen</i>	O	Loellingite
90	Reichenstein, Silesia	Güttler	*Güttler (1870) p. 12, Hintze (1904) p. 872		Original source not seen.	0 - 0-100	1:1.59	O?	<i>Arsenikeisen</i>	O	Loellingite
91	Reichenstein, Silesia	Güttler	*Güttler (1870) p. 12, Hintze (1904) p. 872	6.97	Massive; original source not seen.	0 - 0-100	1:1.87	O?	<i>Arsenikeisen</i>	O	Loellingite
92	Reichenstein, Silesia	Güttler	*Güttler (1870) p. 12, Hintze (1904) p. 872	7.05	Massive; original source not seen.	0 - 0-100	1:1.92	O?	<i>Arsenikeisen</i>	O	Loellingite
93	Reicher Trost Mine, Reichenstein, Silesia	Beutell & Lorenz	Beutell & Lorenz (1915) p. 372	—	No description; S-in arsenide; mixture of FeAs <sub>2</sub> and lower arsenides.	0 - 0-100	1:1.83	O?	<i>Löllingit</i>	O	Loellingite
94	Reicher Trost Mine, Reichenstein, Silesia	Beutell & Lorenz	Beutell & Lorenz (1915) p. 372	—	No description; S-in arsenide; mixture of FeAs <sub>2</sub> and lower arsenides.	0 - 0-100	1:1.85	O?	<i>Löllingit</i>	O	Loellingite
95	Reichenstein, Silesia	Palmer	Palmer & Bastin (1917) p. 211	—	Massive; S-in arsenopyrite.	0 - 0-100	1:1.95	O?	<i>Löllingit</i>	O	Loellingite
96	Skutterud, Norway	Scheerer	Scheerer (1837) p. 553	6.78	Isometric (cube-oct.-dod.-pyrit.) and massive(?); S & Fe in arsenide, Cu in chalcopyrite.	92.6- 0- 7.4	1:2.89	I	<i>Arsenikobaltkies</i>	I	Skutterudite
97	Skutterud, Norway	Wöhler	Wöhler (1838A) p. 290	—	Isometric (massive).	93.0- 0- 7.0	1:2.96	I	<i>Arsenikobaltkies</i>	I	Skutterudite
98	Skutterud, Norway	Wöhler	Wöhler (1838A) p. 290	—	Isometric (crystals).	93.2- 0- 6.8	1:3.14	I	<i>Arsenikobaltkies</i>	I	Skutterudite
99	Skutterud, Norway,	Lorenz	Beutell (1916) p. 214	—	Massive; S and Fe in arsenide; one half examined under refl. micro., other half analyzed. No mention of aniso.	82.4- 0-17.6	1:2.65	I	<i>Tesseralkies</i>	I	Skutterudite

TABLE 7.—Continued

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
100	Skutterud, Norway	Samdahl	Samdahl (1926) p. 72	—	Massive; specimen exam. under micro; no mention of aniso. Not clear if this was analyzed portion.	87.0- 0-13.0	1:2.74	I	Skutterudite	I	Skutterudite
101	Skutterud, Norway	Samdahl	Samdahl (1926) p. 72	—	Same analysis as 100 (-Qtz.)	87.0- 0-13.0	1:2.74	I	Skutterudite	I	Skutterudite
102	Sättersberg near Fossum in Modum, Norway	Scheerer	Scheerer (1840B) p. 536	7.09	Massive.	0- 0-100	1:1.99	O	<i>Arsenikeisen</i>	O	Loellingite
103	Sättersberg near Fossum in Modum, Norway	Scheerer	Scheerer (1840A) p. 156	—	Massive.	0- 0-100	1:1.94	O?	<i>Arsenikeisen in maximum</i>	O	Loellingite
104	Brevik in Modum, Norway	Nordenskiöld	Nordenskiöld (1875) p. 242	—	Twinned rhombic crystals.	0- 0-100	1:2.01	O	<i>Leucopyrit or Sättersbergit</i>	O	Loellingite
105	Ko Mine in Nordmarken, Sweden	Mauzelius	Sjögren (1894) p. 70	7.41	Massive and cryst.; ortho. (Pl. IV fig. 6); (measured cryst.) "chemically between löllingite and safflorite".	44.3- .7-55.0	1:1.94	O	<i>Safflorit</i>	M	Safflorite
106	Tunaberg, Sweden	Varrentrapp	Varrentrapp (1839) p. 505	7.131	Massive; intergrown with chalcopyrite and cobaltite; S- in cobaltite.	81.8- 0-18.2	1:1.97	I?	<i>Graver Speiskobalt</i>	M	Safflorite
107	Alvsbyn, Sweden	Bygden	Högbom (1929) p. 534	7.32	Orthorhombic cryst.; nodules, veinlets, radiating, plumose; Cu in chalcopyrite; Refl. pol. micro. exam.-aniso.	0- 0-100	1:2.04	O	<i>Löllingit</i>	O	Loellingite
108	Västersel, Sweden	Assarsson	Högbom (1929) p. 535	—	Massive (ortho.); Bi in bismuthinite, Cu in chalcopyrite.	0- 0-100	1:1.92	O	<i>Löllingit</i>	O	Loellingite
109	Sukula, Tamela, Finland	Makinen	Makinen (1913) p. 37	—	Crystals.	0- 0-100	1:1.85	O	<i>Löllingit</i>	O	Loellingite
110	Parainen (Pargas), Finland	Ingman	Laitakari (1921) p. 39	7.275	No crystals.	3.8- .9-95.3	1:1.74	O	<i>Löllingit</i>	O	Loellingite

111	Anniviers Thal, Switzerland	Berthier	Berthier (1837) p. 505	—	Mixture, separated from niccolite by hand picking; S in a sulpharsenide.	12.0- 83.0- 5.0	1:1.75	?	<i>Biarseniure de nickel</i>	O?	Rammelsbergite (?)
112	Grand Prat Mine, Anniviers Thal, Switzerland	Rammelsberg	Rammelsberg (1873) p. 283	6.765	Crystalline masses assoc. with niccolite.	32.0- 49.0-19.0	1:2.17	?	<i>Weissnickelkiess</i>	I?	Nickelian skutterudite (?)
113	Turtmannthal, Switzerland	Staudenmaier	Staudenmaier (1892) p. 469	—	Isometric crystals (cube-oct.-dod.); Bi as Bi <sub>2</sub> S <sub>3</sub> or free Bi; measured crystals.	Ni-Co not sep.	1:2.97	I	<i>Tesseralkies</i>	I	Skutterudite (kind?)
114	Binnenthal, Switzerland	Schneider	Baumhauer (1912) p. 144	—	Isometric crystals, (cube-oct.-dod.); "validity of species depends on finding better material"; anal. after elim. much Al <sub>2</sub> O <sub>3</sub> .	0- 0-100	1:1.83	I	<i>Arsenoferrit</i>	?	Questionable analysis Identity (?)
115	Binnenthal, Switzerland	Schneider	Baumhauer (1912) p. 144	—	Same specimen as 114.	0- 0-100	1:1.89	I	<i>Arsenoferrit</i>	?	Questionable analysis Identity (?)
116	Dobschau, Hungary	Löwe	Foeterle (1850) p. 363	6.057	Cu in bornite. Remaining S in arsenide.	23.0- 40.0-37.0	1:1.85	I?	<i>Grauer speiskobalt</i>	I?	Nickelian skutterudite (?)
117	Dobschau, Hungary	Löwe	Löwe (1862) p. 25	6.057	No descr.; same anal. with Cu assigned to chalcocopyrite	23.8- 41.0-35.2	1:1.95	I?	<i>Grauer speiskobalt</i>	I?	Nickelian skutterudite (?)
118	Dobschau, Hungary	Niedzwiedzki	Niedzwiedzki (1872) p. 161	7.15	Massive, fine grain; S in arsenopyrite.	0- 0-100	1:1.90	O	<i>Löllingit</i>	O	Loellingite
119	Orawicza, Hungary	Graham	Thomson (1930) p. 81	6.551	Isometric crystals (cube and oct.) and pseudoprismatic; S in pyrite; zonal crystal on polished surfaces (resistant rim-Ni free), isotropic.	35.6- 59.4- 5.0	1:2.90	I	Nickel skutterudite	I	Nickelian skutterudite
120	Schladming, Austria	Hoffmann	Hoffmann (1832) p. 491	—	Massive; S in pyrite; (anal attrib to Weyde (error); McCay, 1883, p 42)	15.6- 41.0-43.4	1:1.74	O?	<i>Arsenikeisen</i>	O?	Nickelian loellingite(?)
121	Schladming, Austria	Weidenbusch	Rose (1852) p. 54	8.67- 8.71	Massive and prismatic crystals; S in arsenopyrite.	0- 0-100	1:2.08	O	<i>Arsenikeisen</i>	O	Loellingite
122	Hüttenberg, Austria	Weyde	Zepharovich (1868) p. 87	7.10 Av. of 3	Porous masses, platy, radiating, needle-like ortho. crystals; S in arsenopyrite, Bi-native.	0- 0-100	1:1.88	O	<i>Löllingit</i>	O	Loellingite

TABLE 7.—Continued

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
123	Hüttenberg, Austria	McCay	McCay (1883) p. 43	6.752 Av. of 3	No descr.; calculated (-Bi).	0- 0-100	1:1.82	O?	<i>Hüttenberit</i>	O	Loellingite
124	Schwarzgrubnergang, Pribram, Bohemia	Mrazek	Mrazek (1864) p. 373	6.6	Nodular, platy, fine grained, bladed, massive; Sb and Co in arsenide, S in arsenopyrite; this is Hintze's anal. #21 not corrected for Qtz.	0- 0-100	1:1.64	O	<i>Leukopyrit (Arsenikalkies)</i>	O	Loellingite
125	Pribram, Bohemia	Broz	Broz (1869), p. 359	—	Curved plates with pyrite.	0- 0-100	1:1.31	O?	<i>Löllingit</i>	O	Loellingite
126	Markirch, Alsace	Carriere	*Voltz (1828) p. ? Dürr (1907) p. 228	—	Original source not seen.	65.2- 0-34.8	1:1.73	I?	<i>Speiskobalt</i>	M?	Safflorite(?)
127	Markirch, Alsace	Vollhardt	Vollhardt (1886) p. 22	6.32	Isometric (cube-oct.); homog. on etching; surrounded by radiating spathio-pyrite.	17.5- 57.1-25.4	1:2.95	I	<i>Speiskobalt</i>	I	Nickelian skutterudite
	Markirch, Alsace	Vollhardt	Vollhardt (1886) p. 22	6.32	Same specimen as 127.	Co-Ni not sep.	1:2.79	I	<i>Speiskobalt</i>	I	Nickelian skutterudite
129	Gabe Gottes Mine, Markirch, Alsace	Dürr	Dürr (1907) p. 232	7.51	Spherical fibrous masses; mixed with leucopyrite or lower NiCo arsenide; notes similarity to chathamite from Chatham, Conn.	5.0- 33.0-62.0	1:1.60	O	<i>Rammelsbergit</i>	O	Nickelian loellingite
130	Gabe Gottes Mine, Markirch, Alsace	Dürrfeld	Dürrfeld (1910) p. 308	—	Orthorhombic crystals with rammelsbergite; S in pyrite.	0- 0-100	1:1.99	O	<i>Arseneisen (Löllingit)</i>	O	Loellingite
131	Allemont, France	Rammelsberg	Rammelsberg (1849) p. 8	6.411	No description.	0- 78.7-21.3	1:2.32	?	<i>Arseniknickel</i>	I?	Nickelian skutterudite (?)
132	Chalanche, France	Frenzel	Frenzel (1875) p. 677	6.34	Ortho. crystals (obs. and meas.) but massive material used, low sp. gr. due to "earthy" impurities.	22.3- 0-77.7	1:2.06	O	<i>Löllingit</i>	O	Cobaltian loellingite

133	Guadacanal, Spain	Senfter	Sandberger (1870A) p. 232	7.181	Orthorhombic crysts. and nodular fine-grained aggregates with tetrahedrite and stibnite.	17.1- 0-82.9	1:2.08	O	<i>Glaukopyrit</i>	O	Cobaltian loellingite
134	Badeni-Ungureni, Romania	Saligny	Saligny (1886) p. 56	5.224	Sp. Gr. low, due to gangue	61.6- 0-38.4	1:1.17	?	Cobalt arsenical	?	Questionable analysis Identity (?)
135	Badeni-Ungureni, Romania	Poni	Poni (1901) p. 29	7.104	Granular, fibrous, no statement on syst.; S and Bi in mineral.	60.0- 21.6-18.4	1:1.43	?	<i>Badenite</i>	?	Questionable analysis Identity (?)
136	Usseglio, Italy	Rammelsberg	Rammelsberg (1873) p. 284	6.498	Isometric crysts. (cube-oct.).	36.6- 22.0-41.4	1:2.59	I	<i>Speiskobalt</i>	I	Ferrian skutterudite
137	Niddoris, Sardinia	Fassolo	Lovisato (1894) p. 88	—	Botryoidal, massive, platy; no expl. of obvious & excessive inhomogeneity.	27.4- 35.4-37.2	1:1.72	?	<i>Minerale bianca argentina</i>	?	Questionable analysis Identity (?)
138	Galway, Peterborough Co., Ontario	Johnston	Hoffmann (1895) p. 19	7.028	With pyrrhotite.	9.7- 2.7-87.6	1:1.93	O	Cobaltiferous löllingite	O	Loellingite
139	La Rose Mine, Cobalt, Ontario	Burrows(?)	Miller (1905) p. 14	—	Nodular, massive.	15.0- 85.0-0	1:2.07	I?	Chloanthite	O	Rammelsbergite
140	Foster Mine, Cobalt, Ontario	Ellsworth	Ellsworth (1916) p. 220	—	Crysts. (cube-oct.-dod.); inhomog.—at least four constituents; poor zonal structure	52.1- 43.1-4.8	1:2.11	I	Smaltite & Chloanthite	I	Skutterudite + (?)
141	Foster Mine, Cobalt, Ontario	Ellsworth	Ellsworth (1916) p. 220	—	Massive; inhomog.—at least 4 constituents.	42.6- 49.7-7.7	1:2.08	I?	Smaltite & Chloanthite	I?	(Nickelian ?) skutterudite + (?)
142	Kerr Lake Mine, Cobalt, Ontario	Ellsworth	Ellsworth (1916) p. 225	—	Fibrous, radiating, nonhomog.; S-in arsenopyrite and Cu mineral, Co in safflorite.	20.2- 0-79.8	1:2.02	O	Löllingite	O	Loellingite + (safflorite?)
143	Kerr Lake Mine, Cobalt, Ontario	Ellsworth	Ellsworth (1916) p. 225	7.300	Same specimen as 142.	19.3- 0-80.7	1:1.80	O	Löllingite	O	Loellingite + (safflorite)
144	University Mine, Cobalt, Ontario	Ellsworth	Ellsworth (1916) p. 229	7.157	Fibrous, prismatic, ortho.; niccolite accounts for low As; S, and Co may be in cobaltite; obs. under refl. micro	6.0- 94.0-0	1:1.92	O	Rammelsbergite	O	Rammelsbergite
145	Buffalo Mine, Cobalt, Ontario	Palmer	Palmer and Bastin (1917) p. 209	—	Massive.	Ni & Co not sep.	1:2.03	I?	Smaltite	?	Questionable analysis Identity (?)

TABLE 7.—Continued

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
146	Temiskaming Mine, Cobalt, Ontario	Walker	Walker (1921) p. 55	6.79	Crystals (cube-oct.-dod.-trap); no expl. of S; mechanical mixture of RAs <sub>2</sub> and RAs <sub>3</sub> ; bulk anal. of cryst.	84.4- 5.4- 10.2	1:2.51	I	Skutterudite & Smaltite-chloanthite	I	Skutterudite
147	Temiskaming Mine, Cobalt, Ontario	Walker	Walker (1921) p. 55	—	Nonresist. fract., after treatment HNO <sub>3</sub> , anal. of solution; same specimen as 146.	78.9- 9.6- 11.5	1:2.23	I	Smaltite-chloanthite	I	Skutterudite
148	Temiskaming Mine, Cobalt, Ontario	Walker	Walker (1921) p. 55	—	Crystals (cube-oct.-dod.-trap); resist. fract. calc. by difference (not a true anal.). Same specimen as 146.	90.8- .5- 8.7	1:2.83	I	Skutterudite	I	Skutterudite
149	Silver Bar Mine, Cobalt, Ontario	Todd	Walker & Parsons (1921) p. 28	7.00	Radiating prismatic cryst. (orth.), (cobaltite and niccolite (nipped off); arsenopyrite, cobaltite, gersdorffite, ullmannite, niccolite present; obs. under refl. micro.	8.7- 88.9- 2.4	1:1.90	O	Rammelsbergite	O	Rammelsbergite
150	Silver Bar Mine, Cobalt, Ontario	Todd	Walker & Parsons (1921) p. 29	—	Same material as 149, second sample; (anal. of solution) after treatment with HNO <sub>3</sub>	7.5- 91.0- 1.5	1:1.93	O	Rammelsbergite	O	Rammelsbergite
151	Silver Bar Mine, Cobalt, Ontario	Todd	Walker & Parsons (1921) p. 29	—	Same material as 149, second sample; (anal. of residue) after treatment with HNO <sub>3</sub> .	9.9- 87.3- 2.8	1:1.97	O	Rammelsbergite	O	Rammelsbergite
152	Silver Bar Mine, Cobalt, Ontario	Todd	Walker & Parsons (1921) p. 29	—	Same material as 149, second sample; (average of solution and residue).	9.1- 88.6- 2.3	1:1.96	O	Rammelsbergite	O	Rammelsbergite
153	Hudson Bay Mine, Cobalt, Ontario	Todd	Walker & Parsons (1921) p. 30	7.02	Radiating prismatic rounded masses, dendritic, ortho.; with cobaltite and gersdorffite; examined under refl. micro.	6.5- 91.5- 2.0	1:1.88	O	Rammelsbergite (Pararammelsbergite) (Pea. & Dad. (1940), p. 573)	O	Pararammelsbergite
154	La Rose Mine, Cobalt, Ontario	Todd	Walker & Parsons (1924) p. 10	6.84	Rims around löllingite; S in CoAsS inhomog., löllingite (25.34%) and cobaltite (7.14%)	66.2- 3.8- 30.0	1:2.54	I	Skutterudite and smaltite Chloanthite	I	Skutterudite + löllingite

155	La Rose Mine, Cobalt, Ontario	Todd	Walker & Parsons (1924) p. 10	6.94	Rims around löllingite; S in CoAsS inhomog., löllingite (19.16%), cobaltite (7.80%).	74.7- 1.9 -23.4	1:2.64	I	Skutterudite	I	Skutterudite + loellingite
156	Moose Horn Mine, Elk Lake, Ontario	Rogers	Peacock & Michener (1939) p. 99	7.12	Crude platy structure, ortho.; with cobaltite and niccolite, aniso. under refl. micro.; x-ray.	1.4-98.6 - 0	1:2.05	O	Rammelsbergite (Pararammelsbergite Pea. & Dad. (1940) p. 573)	O	Pararammelsbergite
157	Keeley Mine, South Lorrain, Ontario	Todd	Bell & Thomson (1924) p. 32	6.979	Radiating, fibrous, rhombic; inhomog., 11% smaltite, 5% cobaltite, obs. under refl. micro.	19.9- 0 -80.1	1:1.91	O	Löllingite	O	Loellingite + skutterudite
158	Keeley Mine, South Lorrain, Ontario	Todd	Bell & Thomson (1924) p. 33	6.582 av. of two	Cubic crystals. inhomog.—13% löllingite; 3% cobaltite-gersdorffite; obs. under refl. micro.	80.0- 3.0 -17.0	1:2.75	I	Skutterudite	I	Skutterudite + loellingite
159	Keeley Mine, South Lorrain, Ontario	Rickaby	Walker (1925) p. 53	6.734	Rhombic radiating; inhomog.—18% safflorite; 3% löllingite; 17% cobaltite; obs. under refl. micro.	38.0- 59.3- 2.7	1:1.98	O	Rammelsbergite (Pararammelsbergite, Pea. & Dad. (1940) p. 573)	O	Pararammelsbergite + (safflorite, + cobaltite?)
160	Keeley Mine, South Lorrain, Ontario	Rickaby	Walker (1925) p. 51	—	Radiating, nodular, concentric masses; inhomog.—54% löllingite; 35% safflorite; 6% skutterudite; 5% cobaltite; obs. under refl. micro.	44.3- 1.3-54.4	1:2.04	O	Löllingite (& Safflorite ?)	O	Questionable analysis Identity(?)
161	Frontier Mine, South Lorrain, Ontario	Rickaby	Walker (1925) p. 50	6.519	Cubic crystals. inhomog.—6% cobaltite-gersdorffite; 3.5% löllingite.	94.5- .9- 4.6	1:2.81	I	Skutterudite	I	Skutterudite
162	Eldorado Mine, Gt. Bear Lake, N.W.T., Canada	Rothwell	Thomson (1932) p. 46	—	Zoned cubic crystals; smaltite and skutterudite, cobaltite also present.	23.0- 72.7- 4.3	1:2.15	I	Chloanthite	O?	Rammelsbergite(?) and skutterudite
163	Eldorado Mine, Gt. Bear Lake, N.W.T., Canada	Ellsworth	Spence (1932) p. 88	—	Massive (?), zonal; skutterudite and smaltite-chloanthite and probably cobaltite; obs. under refl. micro. (?).	74.7- 18.6- 6.7	1:2.81	I	Skutterudite	I	Skutterudite
164	Eldorado Mine, G. Bear Lake, N.W.T., Canada	Haycock	Spence (1932) p. 88	—	Massive (?) no description; obs. under refl. micro. (?).	90.3- .6- 9.1	1:2.93	I?	Skutterudite	I	Skutterudite
165	Trotter Mine, Franklin, N. J.	Koenig	Koenig (1889) p. 185	6.8334	Isometric crystals; massive material, mostly prismatic; assoc. with niccolite; (anal. on isom. crystal or massive material or both?).	23.2- 68.0- 8.8	1:2.12	I	Chloanthite	O	Rammelsbergite + pararammelsbergite + skutterudite (nickelian?)

TABLE 7.—Continued

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name			
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)	
166	Franklin, N. J.	Bauer	Bauer & Berman (1927) p. 43	—	Rhombic cryst., measured; "As deficiency due to 14% Leucopyrite molecule."	0 - 0 -100	1:1.78	O	Löllingite	O	Loellingite
167	Rose Mine, Grant County, New Mexico	Hillebrand	Hillebrand (1888) p. 46	6.644	Pyritohedral cryst.; high As due to Triarsenide or native As; (mixture?).	Co-Ni not sep.	1:2.91	I	Argentiferous arsenide of Co + Ni	I	Skutterudite (nickelian?)
168	Bullards Peak Dist., Grant Co., N. Mex.	Waller & Moses	Waller & Moses (1892) p. 50	—	Massive, associated with arborescent silver.	26.9- 58.5- 14.6	1:2.78	I	Nickel skutterudite	I	Nickelian skutterudite
169	Drums Farm, Alexander Co., N. C.	Genth	Genth (1892) p. 384	7.031	Massive with scorodite.	0 - 0 -100	1:1.94	O	Löllingite	O	Loellingite
170	Gothic, Gunnison Co., Colo.	Iles	Iles (1882) p. 380	—	Massive (?); error in anal. (Total 98.89 but adds up to 94.89.) (Fe increased to 15.99 following Dana (1892) p. 88.) 11.99 Fe in original.	40.7- 0 - 59.3	1:1.79	I?	Smaltite	M?	Safflorite (?)
171	Teocalli Mt., Gunnison Co., Colo.	Hillebrand	Hillebrand (1884) p. 353	7.4	Radial ortho. crystals and massive; (mixed with safflorite and chalcopyrite?); micro. exam. (Kind?).	15.1- .8- 84.1	1:1.96	O	Löllingite	O	Cobaltian loellingite
172	Horace Porter Mine, Gunnison Co., Colo.	Fairchild	Short (1930) p. 767	—	Homog. under micro., not zonal; no mention of anisotropism or inclusions.	49.3- 23.2- 27.5	1:2.66	I	Skutterudite	I	Skutterudite
173	Standard Mine, Prairie City, Grant Co., Ore.	Burrows	Miller (1905) p. 61	—	Massive, acicular, fine columnar.	53.6- 4.0- 42.4	1:1.85	I?	Smaltite	M	Safflorite
174	Grafton, N. H.	Palmer	Palmer & Bastin (1917) p. 215	7.08	Massive—safflorite on basis of Sp. Gr.; fractional solution proved S in arsenopyrite.	48.5- 0 - 51.5	1:2.02	O	Safflorite	M	Safflorite
174A	Center Stratford, N. H.	Gonyer	Switzer (1938) p. 817	—	Orthorhombic crystals and massive.	0 - 0 -100	1:1.96	O	Loellingite	O	Loellingite

174B	Peerless Mine, Keystone, S. D.	Beach	Landes (1928) p. 555	—	Long tabular crystals.	0 - 0 -100	1:2.10	O	Löllingite	O	Loellingite
174C	Etta Mine, Keystone, S. D.	Beach	Landes (1928) p. 555	—	Massive; S in arsenide, no expl. of Sb.	0 - 0 -100	1:1.67	O ?	Geyerite	O	Loellingite
175	Chatham, Conn.	Shepard	Shepard (1844) p. 158	6.226	Orthorhombic, massive; with arsenopyrite and niccolite.	4.2- 37.9- 57.9	1:1.71	O	Chathamite	O	Nickelian loellingite
176	Chatham, Conn.	Genth	Genth (1854) p. 28	—	Minute grains and powder in gneiss.	12.0- 29.8- 58.2	1:2.01	I ?	Cloanthite	O	Nickelian loellingite
177	Chatham, Conn.	Genth	Genth (1854) p. 28	—	Sample different from #176; washed sample of ore. Minute grains and powder in gneiss; As by loss.	13.9- 36.9- 49.2	1:2.29	I ?	Cloanthite	O	Nickelian loellingite
178	Descubridora, Carrizo, Chile	Domeyko	Domeyko (1846) p. 467	—	No description.	0 - 0 -100	1:1.86	?	<i>Arseniure de Fer pur</i>	O ?	Loellingite (?)
179	Descubridora, Carrizo, Chile	Domeyko	Domeyko (1879) p. 162	—	Orthorhombic.	0- - 0 -100	1:1.97	O	<i>Leucopyrit</i>	O	Loellingite
180	Atacama, Chilè	Smith	Smith (1855) p. 85	—	"Agrees with description of smaltin."	81.4- 4.2- 14.4	1:1.86	I ?	Smaltene	I ?	Skutterudite (?)
181	La Loreto, Chanarcillo, Chile	Domeyko	Domeyko (1879) p. 162	—	Orthorhombic, fibrous, radial.	0 - 0 -100	1:2.01	O	<i>Leucopyrit</i>	O	Loellingite
182	Punta Bravo, Copiapo, Chile	Domeyko	Domeyko (1879) p. 178	—	Massive	77.3- 0 - 22.7	1:2.12	I ?	<i>Smaltit</i>	I ?	Skutterudite (?)
183	Punta Bravo, Copiapo, Chile	Domeyko	Domeyko (1879) p. 178	—	Fills fractures, massive.	46.7- 33.9- 19.4	1:1.40	I ?	<i>Smaltit</i>	I ?	Skutterudite (?)
184	Bandurrias, Copiapo, Chile	Domeyko	Domeyko (1879) p. 178	—	Massive.	66.7- 21.7- 11.6	1:2.45	I	<i>Smaltit</i>	I	Skutterudite
185	Emilia Mine, Cabeza de Vaca, Chile	Domeyko	Domeyko (1879) p. 178	—	Platy.	59.8- 10.4- 29.8	1:2.18	I ?	<i>Smaltit</i>	I ?	Skutterudite (?)
186	Portezuelo del Carrizo, Huasco, Chile	Domeyko	Domeyko (1879) p. 186	—	Orthorhombic, massive, platy, bladed.	0 - 96.0- 4.0	1:1.32	O	Rammelsbergite	O	Rammelsbergite

TABLE 7.—Continued

No.	Locality (1)	Analyst (2)	Source of data (3)	Sp. Gr. (4)	Original description of analyzed material including comments on homogeneity & explanation of deviations from theoretical composition (5)	Co-Ni-Fe Ratio (6)	R:As Ratio (7)	Crystallization and Mineral Name				
								Assigned to material in original source (8)		Assigned to material on basis of present study (9)		
187	La Paz, Bolivia	Winkler	Breithaupt (1866) p. 167	6.297-6.303	Platy, rhombic; Au, Ag, and Bi native.	.5- 0 -99.5	1:2.46	O	<i>Pazit</i>		O	Loellingite
188	Andahuaylas, Peru	Raimondi	Raimondi (1878) p. 190	—	Radial, fibrous; S in arsenopyrite.	32.9- 0 -67.1	1:1.89	I ?	<i>Esmaltina ferrifera</i>		M	Safflorite
189	Bou Azzer, Morocco	?	Glasser (1934) p. 371	—	No description (massive ?); impure, oxidized.	64.8- 17.2-18.0	1:2.57	I	Smaltine		I	Skutterudite
190	Bou Azzer, Morocco	Orcel and Jouravsky	Orcel and Jouravsky (1935) p. 209	—	Isometric, massive material selected free of safflorite; similar material in micro. photo is zonal with incl. niccolite and aniso. cryst. of (safflorite?).	56.6- 17.5-25.9	1:2.73	I	Smaltite		I	Skutterudite
191	Bou Azzer, Morocco	Orcel and Jouravsky	Orcel and Jouravsky (1935) p. 209	6.639	Isometric, zonal cryst. material selected free of safflorite; micro. photo of similar material is zonal with incl. niccolite and aniso. cryst. of (safflorite?).	85.0- 2.4-12.6	1:2.57	I	Smaltite + Skutterudite		I	Skutterudite
192	Bou Azzer, Morocco	Orcel and Jouravsky	Orcel and Jouravsky (1935) p. 210	6.696	Same material as #191 after treatment with HNO <sub>3</sub> .	88.5- 0 -11.5	1:2.98	I	Skutterudite		I	Skutterudite
193	San Mauricio, Mine, Camarines Norte, Luzon, Philippine Islands	Gonyer	Murdoch & Gardner (1942) p. 74	6.9	Orthorhombic crystals. Other crystals (not analyzed) were aniso under rfl. micro.; S, Cu, and Sb in arsenide.	0 - 0 -100	1:1.69	O	Löllingit		O	Loellingite
194	Dalnich Borů, Czechoslovakia	Rzihek (?)	Vysloužil (1928) p. 84	7.091	S in arsenopyrite.	0 - 0 -100	1:2.00	O	<i>Löllingit</i>		O	Loellingite
195	Little Gem Claim, Lilloet Mining Div. British Columbia	Bell	Warren and Thompson (1945) p. 11	7.1-7.2	S in Danaite. 2.60 loss = soluble gangue; aniso-rfl. micro.; X-ray.	21.4- 0 -78.6	1:1.96	O	Loellingite safflorite		O	Cobaltian loellingite

The relation between the ratio of the three metals and crystallization is shown graphically in Plates 3 and 4 where each analysis is represented by a symbol indicating crystallization. The position of the symbol on these plates is determined by the ratio of the three metals.

The metal-arsenic ratio (Column 7) has been calculated for each analysis. Sulphur and antimony have been arbitrarily included in the arsenic total, and metallic elements such as copper and more rarely others have been grouped with cobalt, nickel, and iron. This data is given as a ratio R:As. The relation between arsenic content and the ratio of the three metals is shown graphically in Plate 5.

A few of the 198 analyses have not been plotted on the diagrams or used in the computations. Nickel and cobalt are not separated in 9 analyses (Nos. 30, 31, 33, 44, 45, 113, 128, 145, and 167), hence these cannot be used in a discussion involving cobalt-nickel-iron ratios. Eight analyses (Nos. 17, 21, 23, 25, 27, 69, 101, and 117) represent recalculations, by the original author, after eliminating "obvious impurities" (quartz, bismuth, *etc.*). Each of these is identical with a corresponding uncorrected analysis in the ratios of the three metals and the metal-arsenic ratio. The 8 listed above correspond respectively with Nos. 16, 20, 22, 24, 26, 68, 100, and 116. Each pair is represented on the triangular diagrams by one symbol.

In some cases a single material or specimen is represented in the original paper by more than one analysis. These multiple analyses represent in part, determinations made on different portions of the same specimen or on several specimens described as representing the same material. A few were made on fractions of a single specimen obtained in the course of selective solubility experiments. If the compositions shown by these multiple analyses are nearly the same, the group is represented on the diagrams by a single symbol: (29-32), (39-40-41) (70-71), (114-115), and (150-152). If there are appreciable differences, the analyses are plotted individually: (7-8), (14-15), (54-55), (142-143), (146-147-148), (149- (150-152)), and (191-192). Analyses (16-17) are averages of others, hence were not used.

Column (8) contains the mineral name and system of crystallization for each analyzed specimen, as they appear in the source. The letters (I) isometric and (O) orthorhombic indicate the crystallization implied by the mineral name assigned to the material by the original author. A letter alone is used if the crystallization implied by the mineral name is supported by accompanying physical, chemical, x-ray, or optical data, such as crystal form, crystal habit, mode of aggregation, anisotropism, high specific gravity ("orthorhombic" arsenides), or very high arsenic ratio (isometric arsenides). A question mark following the letter indicates that the crystallization implied by the assigned mineral name is unsupported by accompanying data, either because the original source lacks any description of the material used or contains data of a conflicting nature. A question mark replacing the letter indicates that there is no evidence of the author's view concerning crystallization, either expressed in the description of the analyzed material or implied in the mineral name.

In a corresponding column (9) a revised interpretation of the crystallization and nomenclature is given. This is based on the original description of the analyzed material, in many cases supported by microscopic and x-ray data obtained in the course of the present study on material from the locality in question. The letters

I, O, and M are used to represent respectively isometric, orthorhombic and monoclinic members. A letter alone indicates that the identity and crystallization of the material is reasonably certain. A question mark follows the letter if the identity and crystallization of the material are in doubt. A question mark alone indicates

TABLE 8.—*Relation between crystallization and cobalt-nickel-iron ratio for the materials used in the published analyses plotted on Plates 3 and 4*

Area	(Pl. 3) Crystallization according to original author				(Pl. 4) Crystallization on basis of present investigation			
	Isom.	"Or- tho."	Syst. (?)	Total	Isom.	"Or- tho."	Reject	Total
<i>I. Isometric area</i>								
A. Skutterudite								
1. Skutterudite (cobaltian).....	43	1	2	46	41	2	3	46
2. Nickelian skutterudite.....	19	1	2	22	19	2	1	22
3. Ferrian skutterudite.....	3	2	1	6	1	4	1	6
Total—Isometric area.....	65	4	5	74	61	8	5	74
<i>II. Nonisometric "orthorhombic" areas</i>								
A. Rammelsbergite and pararammelsbergite (orthorhombic)...								
	7	11	4	22	3	18	1	22
B. Loellingite (orthorhombic)								
1. Loellingite (ferrian).....	2	48	1	51	0	50	1	51
2. Cobaltian loellingite.....	0	7	0	7	0	7	0	7
3. Nickelian loellingite.....	0	3	0	3	0	3	0	3
Total—Loellingite area.....	2	58	1	61	0	60	1	61
C. Safflorite (monoclinic).....								
Total—iron-cobalt nonisometric area.....	9	66	2	77	0	73	4	77
Total—Nonisometric areas.....	16	77	6	99	3	91	5	99
Total—All analyses.....	81	81	11	173	64	99	10	173

that the analysis has been rejected as questionable either because it is believed to be unreliable or because of gross inconsistency in the available data on the analyzed material.

#### RELATION OF COBALT-NICKEL-IRON RATIO TO CRYSTALLIZATION IN THE HIGHER ARSENIDES

*General statement.*—Data on the relation between the cobalt-nickel-iron ratio and the crystallization of the materials represented by the published analyses are summarized in Plates 3 and 4 and in Tables 8 and 9. Broken-line boundaries on the triangular diagrams indicate probable limits of composition of the several minerals of the group, based on a review of published analyses and the results of the experiments in synthesis. Isometric arsenides are limited to the single large skutterudite area. The "orthorhombic" members are restricted to two isolated groups—(1) rammelsbergite-pararammelsbergite and (2) loellingite-safflorite. Distribution of

TABLE 9.—*Relation between crystallization and cobalt-nickel-iron ratio for the materials used in the published analyses plotted on Plates 3 and 4\**

Area	(Pl. 3) Crystallization according to original author			(Pl. 4) Crystallization on basis of present investigation		
	Isom.	"Orth."	Syst. (f)	Isom.	"Orth."	Reject
<i>I. Isometric area</i>						
A. Skutterudite						
1. Skutterudite (cobaltian).....	1		2		63	1
	106	63	135	—	106	2
						135
2. Nickelian skutterudite.....	165	159	79	112	159	
			112		165	79
3. Ferrian skutterudite.....	176	120	137	—	120	137
	177	175			175	
					176	
					177	
<i>II. "Orthorhombic" areas</i>						
A. Rammelsbergite and pararammelsbergite (orthorhombic).....						
	19		4	(29-32)	4	10
	(29-32)	—	10	43	19	
	43		111	131	51	
	51		131		(70-71)	
	(70-71)				111	
	139				139	
	162				162	
B. Loellingite (orthorhombic)						
1. Loellingite (ferrian).....	49		178	—	49	(114-115)
	(114-115)				178	
2. Cobaltian loellingite.....	—	—	—	—	—	—
3. Nickelian loellingite.....	—	—	—	—	—	—
C. Safflorite (monoclinic).....						
	3	160	134	—	3	65
	5				5	134
	65				126	160
	126				170	
	170				173	
	173				188	
	188					

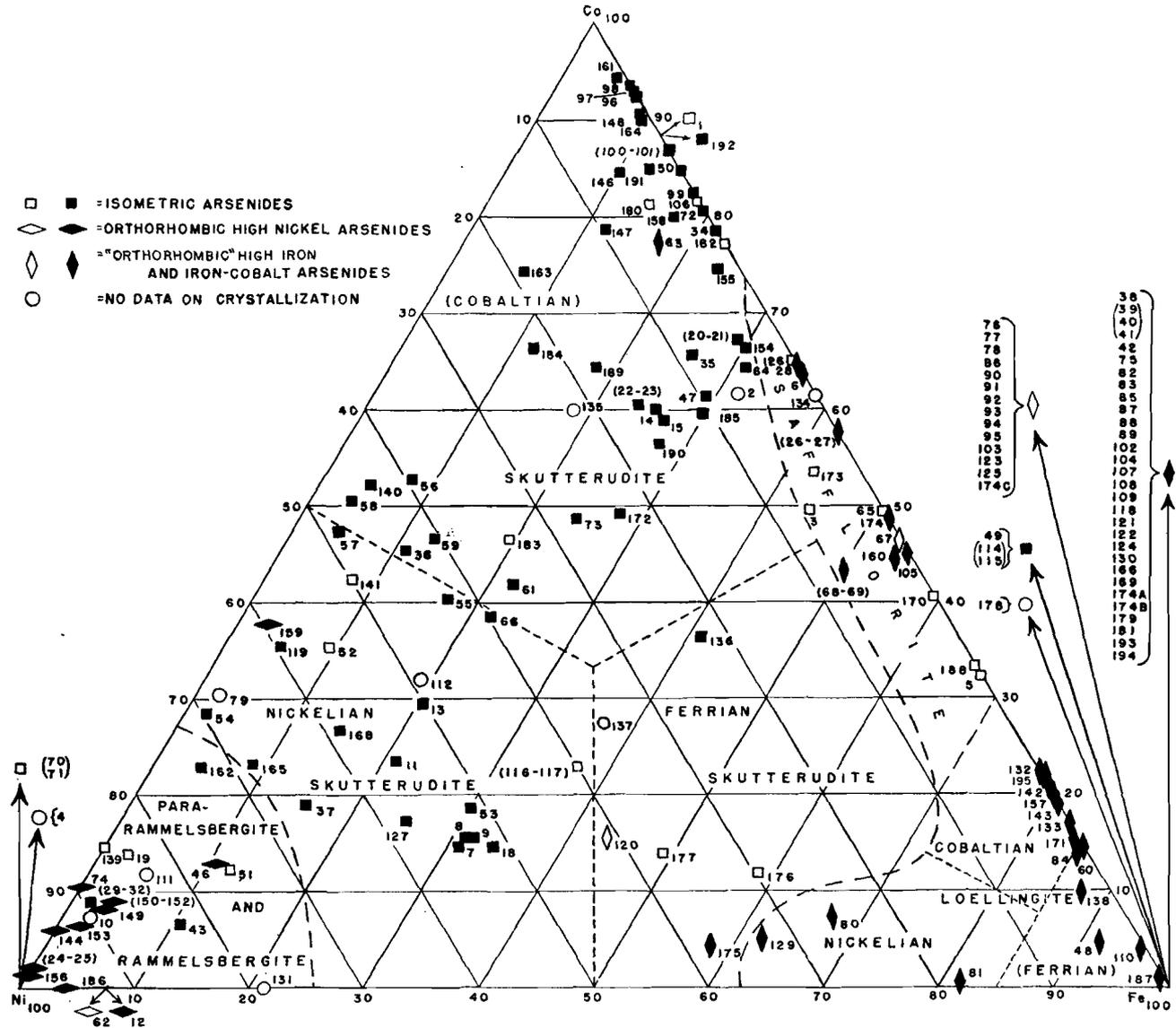
\* Disposition of nonconforming analyses and those unaccompanied by data on crystallization or of doubtful reliability. The numbers are those of the analyzed materials listed in Table 7.

available analyses and Peacock's work on safflorite suggest that the latter may comprise two discontinuous units. The position of each analysis on Plates 3 and 4 is determined by the cobalt-nickel-iron ratio. Two or more specimens have the same ratio and the same crystallization, the numbers representing them have been bracketed. Numbers enclosed in parentheses indicate that the symbol represents more

than one analysis on the same sample. Plate 3 is based on the analyst's or original author's interpretation of the crystallization. The symbols used in Plate 4 represent a revised interpretation of the crystallization based on the present study.

In Plate 3 each of the three major mineral groups—skutterudite, rammelsbergite-pararammelsbergite, and loellingite-safflorite is represented by a distinctive symbol. The solid symbol indicates that specific statements in the original paper confirm the crystallization implied by the assigned mineral name. This may consist of a description of crystal forms observed, optical data such as the presence of anisotropism, physical data such as unusually high specific gravity, a characteristic of the "orthorhombic" arsenides, or other evidence distinguishing isometric from nonisometric phases. An open symbol indicates that the original description contains no reference to the crystallization of the analyzed material or contradictory data in which case the symbol used is based solely on the crystallization implied in the assigned mineral name, as given in the original source. A few analyses are not only unaccompanied by data on crystallization but were assigned mineral names such as "arseniknickel" without implication of any one crystal system. In other cases the assigned name can be interpreted as referring either to an isometric or "orthorhombic" mineral. For example the term rammelsbergite in the middle of the nineteenth century was used by certain mineralogists for the supposed isometric diarsenide of nickel, while others applied it to the orthorhombic form. It is not always clear which usage a particular author had in mind. All such analyses are represented by circles.

The identity and crystallization of the material represented by the published analyses have been reviewed in the light of the accompanying description of the specimens used. Additional data obtained in the course of the present investigation, on specimens from the localities in question, have also been considered. The symbols in Plate 4 are based on the present study and have a somewhat different connotation from those used in Plate 3. The solid symbol indicates that the identity and crystal system of the material is accepted as reasonably well established. An open symbol indicates that the assigned system is probably the correct one, but the evidence is inconclusive or contradictory. A circle represents an analysis rejected either because it is believed to be unreliable or because of strong doubt concerning the crystallization of the material used, due to lack of data or inconsistencies in the original description. Arrows are attached to certain symbols on Plate 4 to show that the cobalt-nickel-iron ratio calculated from the analysis is misleading due to inhomogeneity, the nature of which is described in the original paper or seems reasonably certain from other evidence. For example, the material used for analysis No. 159 which lies in the midst of the isometric arsenides was described as rammelsbergite (orthorhombic). Examination of the published description, however, reveals that the author recognized the analyzed material to be intergrown with appreciable amounts of safflorite and cobaltite. Obviously the nickel ratio of the rammelsbergite itself is much higher than the position of the symbol on the diagram indicates. The arrow indicates the direction in which the symbol should be moved to portray the true cobalt-nickel-iron ratio of the mineral represented. Unfortunately, the amount of inhomogeneity is not often stated by the author so that only the direction of movement can be indicated.



RELATION OF CRYSTALLIZATION TO COBALT-NICKEL-IRON RATIO ACCORDING TO ORIGINAL SOURCE

Published analyses are plotted against cobalt-nickel-iron ratio to show the relation between composition and crystallization among the higher arsenides of these metals. The crystallization is that claimed in the original source.

*Solid*—Symbol based on crystallization implied by the mineral name assigned in the original source, supported by data contained in the description of the analyzed material.

*Outline*—Symbol based solely on crystallization implied by the mineral name assigned; description of the analyzed material containing conflicting data on crystallization or none at all.

*Circle*—Evidence of crystallization neither expressed in the description of the analyzed material nor implied in the mineral name assigned.

*Broken-line boundaries*—Limits of cobalt-nickel-iron ratio for each of the mineral groups based the present study.

Table 8 summarizes the data of Plates 3 and 4. The predominance of arsenides of a particular crystallization in each of the areas outlined is evident. The figures referred to in the following discussion are taken from this tabulation.

Table 9, a supplement to Table 8, lists (1) analyses of doubtful reliability, (2) analyses made on materials of unknown crystallographic character, and (3) those whose original crystallographic classification seems questionable. The figures given are the numbers of the analyses. It summarizes the disposition made of analyses, concerning which there was question. This table indicates that a number of specimens claimed to be isometric are more likely orthorhombic when consideration is given to the descriptions of analyzed material, but in no case is the reverse true. Reference to Plates 3 and 4 and Tables 8 and 9 will aid in following the discussion of the relation between cobalt-nickel-iron ratio and crystallization.

*Isometric arsenides (skutterudite).*—Eighty-one of the 173 specimens for which published analyses exist were alleged by the original authors to represent isometric material. Sixty-five of these fall within the limits, established on the basis of the present study for isometric arsenides, while 16 lie within the limits assigned to "orthorhombic" arsenides (Table 8). Twelve of these 16 specimens alleged to be isometric, but falling outside the isometric limits, are believed to be "orthorhombic" minerals misidentified as isometric (Table 9). Although 8 arsenides accepted as "orthorhombic" occur within the isometric area, the descriptions of the analyzed material in every case provide evidence of misleading cobalt-nickel-iron ratios due to inhomogeneity. On the basis of restudy, 64 of the 173 specimens are accepted as isometric, 61 of which fall within the limits set for the isometric group. Whether one accepts the crystallization of the analyzed material as set forth in the original source (Pl. 3), or as revised on the basis of the present study (Pl. 4), the majority of isometric arsenides fall within the limits outlined for this group. Most of the few exceptions can be satisfactorily explained. These are considered in some detail, and their disposition is summarized in Table 9.

Eight specimens accepted as "orthorhombic" fall within the isometric area. The materials used in four analyses, Nos. 63, 120, 159, and 175, occurring within the isometric zone were described as orthorhombic by the original authors. Four others, Nos. 106, 165, 176, and 177, although considered isometric by the original author are believed to be "orthorhombic" on the basis of the descriptions of the analyzed material and other information obtained in the present study. All but two of these (Nos. 120 and 159) are very close to the isometric "orthorhombic" boundary. All eight, either on the basis of the published descriptions or on the basis of data obtained in the present study, bear evidence of mechanical inhomogeneity resulting in fictitious cobalt-nickel-iron ratios. The correct position for each symbol would be close to, if not well within, areas assigned to "orthorhombic" arsenides. These analyses are treated in more detail in the discussion of the "orthorhombic" areas.

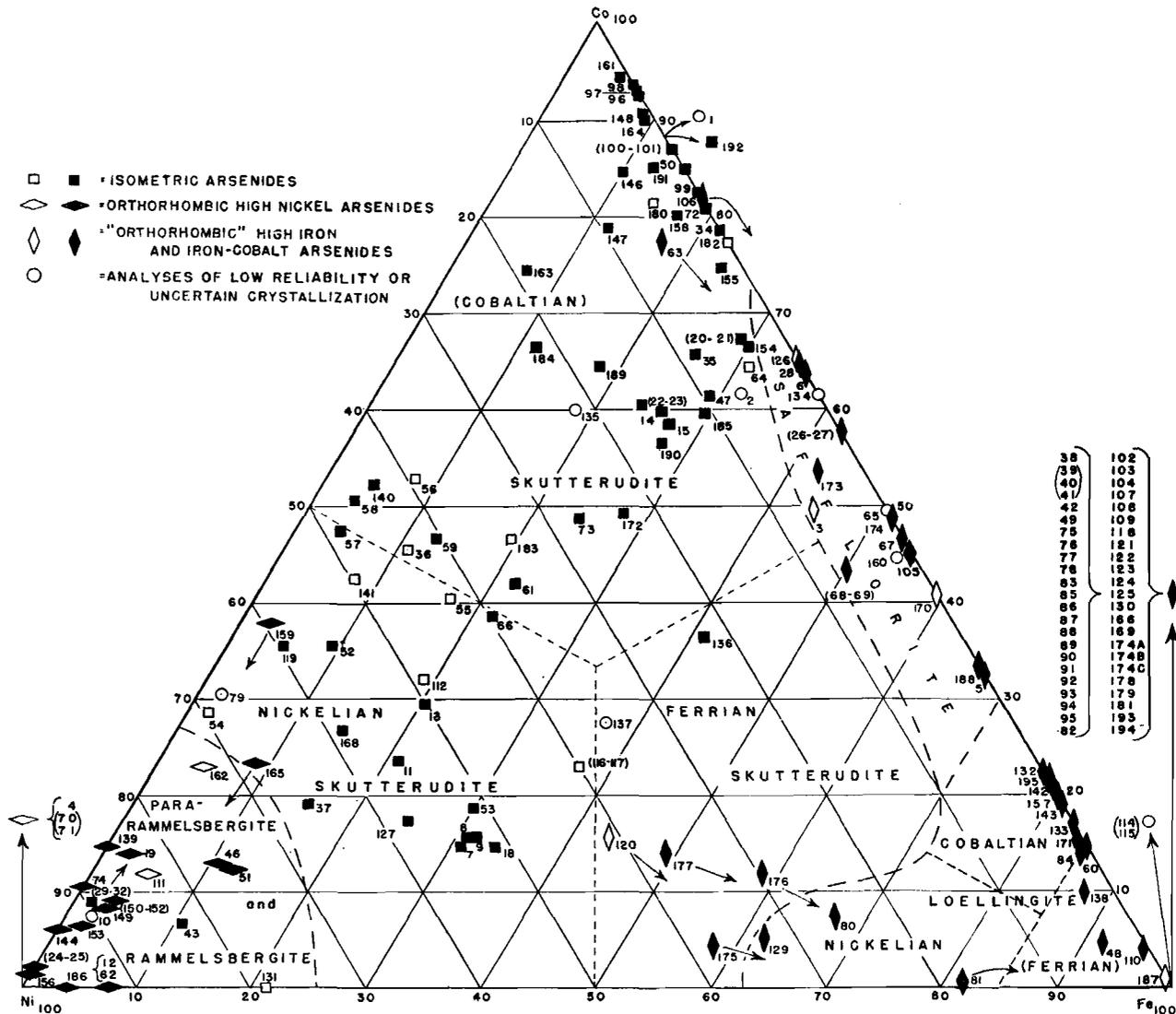
Five analyses, Nos. 2, 79, 112, 135, and 137, for which essentially no data on crystallization are available occur within the isometric area and are represented by circles on Figure 4. Analyses Nos. 1, 2, 79, 135, and 137 have been rejected, and

their positions on Plate 4 are indicated by a circle. Analysis No. 1, dated 1810 (the earliest known analysis of *Speiskobalt* (smaltite) is rejected as unreliable. Analysis No. 2 of *Wismuthkobalterz*, analyzed by Kersten, (1826), has a questionable arsenic ratio of 3.68 entirely out of line with that of all other reported occurrences of these arsenides. Analysis No. 79 made on material described by the original author (Streng, 1861) as Kupfernicker (niccolite) is included because Hintze (1904, p. 811) cites it as an analysis of *Speiskobalt* with an extremely low arsenic content. Analysis No. 135 was made on "badenite", a material shown by Petruilian (1936) to be a mechanical mixture of several minerals. No. 137 is an analysis of a very impure specimen identified by the original author as "*minerale bianca argentina*". These five analyses may be justifiably eliminated as serving no useful purpose in the present study. Analysis No. 112 has not been rejected since the high metal-arsenic ratio suggests isometric material, although no data on crystallization accompanied it.

Sixteen analyses alleged to be isometric by the original authors lie within the "orthorhombic" areas. Seven of these occur within the high nickel area, seven in the safflorite area, and two in the high-iron loellingite area. Twelve of these are almost certainly "orthorhombic" minerals if the descriptions of the analyzed materials are considered. Two have been rejected as unreliable, leaving two isometric arsenides, both in the high-nickel orthorhombic area, whose presence outside the field assigned to the isometric members requires explanation.

Two of the seven arsenides described as isometric which occur within the high-nickel orthorhombic area (29-32), and 43, in addition to the undescribed material used in analysis 131, are accepted as isometric. The remaining 5, Nos. 19, 51, (70-71), 139, and 162, are believed to be orthorhombic and will be discussed under that heading. The *Speiskobalt* on which analyses (29-32) (Vollhardt, 1886) were made was described as inhomogeneous, probably containing niccolite which could account for the unusually high nickel ratio, 89.1. The correct position for the symbol would be in the low-nickel direction bringing it close to, or within, the isometric area. Analysis 43 on *Speiskobalt* with a nickel ratio of 82.6 is not accompanied by any description (Rammelsberg, 1873). It is a questionable analysis since nothing is known of the analyzed material and it was made long before any method of ascertaining the homogeneity of opaque minerals was available. Analysis 131 of *Arseniknickel*, although made on undescribed material is accepted as isometric since it has a high arsenic content. The specimens represented by analyses (29-32), 43, and 131 are the only arsenides with a nickel ratio greater than 69.1 for which strong evidence of orthorhombic crystallization is lacking.

Two analyses of arsenides alleged to be isometric fall within the high-iron area. Both are pure iron arsenides described as arsenoferrite. One of them, analysis 49, is that of the material from St. Joachimsthal, assumed by Foshag and Short (1930) to be isometric arsenoferrite, on the basis of apparent isotropism, and shown by Buerger (1936) as the result of x-ray work to be loellingite, (orthorhombic). Analyses (114-115) were made on the type specimen of arsenoferrite from the Binnenthal. The material was described as exceedingly impure by the original author who proposed the name, tentatively, admitting that the validity of the species depended on finding more satisfactory material. Apparently the material from this locality has



RELATION OF CRYSTALLIZATION TO COBALT-NICKEL-IRON RATIO BASED ON THE PRESENT STUDY

The symbols on this diagram are based on a reinterpretation of the crystallization of the same materials shown in Plate 3. This reinterpretation involves a consideration of the original description of the analyzed material combined in many cases with data obtained in the present study on similar material from the locality in question.

*Solid*—Identity and crystallization accepted as reasonably certain.

*Outline*—Identity and crystallization uncertain. In the absence of evidence to the contrary crystallization as implied by the mineral name assigned in the original source.

*Circle*—Analysis of doubtful reliability or material of very questionable crystallization.

*Broken-line boundaries*—Limits of cobalt-nickel-iron ratio for each of the mineral groups, based on the present study.

Arrows attached to analyses of certain inhomogeneous specimens indicate the direction in which the symbol should be moved in order to correctly represent the cobalt-nickel-iron ratio of the principal constituent whose crystallization is indicated by the symbol.

never been re-examined. These analyses have been rejected and are represented by a circle on Plate 4. They constitute the available evidence for an isometric iron arsenide and the only evidence for an isometric arsenide with an iron ratio greater than 67.4. An isometric arsenide of pure iron or even one with a high iron ratio is very doubtful.

Seven analyses (Nos. 3, 5, 65, 126, 170, 173, 188) of the 16 falling within the safflorite area were made on material claimed by the original authors to be isometric. However, attention to the descriptions of the analyzed material, indicates that 6 of the 7 represent "orthorhombic" rather than isometric minerals and these will be described in the "orthorhombic" section. The seventh, analysis 65, made on '*Weisser Speiskobalt*' (Laugier, 1813), has been rejected as unreliable.

*Orthorhombic arsenides.*—The recorded data on published analyses fails to support the widely accepted assumption that the "orthorhombic" arsenides exhibit unlimited isomorphous substitution among the three metals. Isomorphism between cobalt, nickel, and iron is not only limited in the "orthorhombic" group, as in the isometric, but is discontinuous. The evidence suggests a complementary relationship between the two series which is apparent in Plates 3 and 4. The "orthorhombic" arsenides are clustered about the nickel and iron corners and the mid-portion of the cobalt-iron edge of the diagram, so that the high-nickel unit is completely separated from the larger group of iron-bearing members. The latter is divided into two areas, loellingite and safflorite. This restricted distribution is apparent regardless of whether the data on crystallization used are those of the original authors (Pl. 3) or the revised data based on the present study (Pl. 4). Seventy-seven of the 81 arsenides claimed to be orthorhombic by the original authors and 91 of the 99 accepted as "orthorhombic" on consideration of all available data occur within the limits assigned to "orthorhombic" arsenides on the basis of the present study.

ORTHORHOMBIC HIGH-NICKEL ARSENIDES (RAMMELSBURGITE AND PARARAMMELSBURGITE): An isolated area of orthorhombic high-nickel arsenides is indicated by the published analyses. Eleven of the 12 high-nickel arsenides claimed to be orthorhombic, and all but two of those accepted as orthorhombic in the present study, fall within the limits outlined for this group. Five of the seven allegedly isometric arsenides lying within this area are believed to be more likely orthorhombic when the published descriptions of the analyzed material are reviewed in the light of data obtained on similar specimens from the same localities. The remaining two, both very old and of questionable reliability, have been accepted as isometric for lack of evidence to the contrary. The presence of two accepted orthorhombic high-nickel arsenides within the adjacent isometric area has been accounted for.

Seven arsenides claimed to be isometric occur within this "orthorhombic" area, five of which—19, 51, (70-71), 139, and 162—are believed to be orthorhombic rather than isometric on the basis of the descriptions of the analyzed material. The remaining two specimens—(29-32) and 43—are accepted as probably isometric, and their positions outside the isometric limits have already been discussed. Analysis 19 was made on material called chloanthite by the original author solely because of the

low specific gravity—scarcely a sufficient basis, since the homogeneity of such material could not have been ascertained in 1883. Furthermore, it was described as radial and fibrous—structures associated with the rhombic nickel arsenides. Evidence favors an orthorhombic crystallization for this material. The specimen used in analysis 51, called “Deutarseniuret of nickel”, was described as radial, and columnar masses terminated by isometric crystals. Material of this description from the same locality, examined in the present study, proved to be rammelsbergite or intergrowths of rammelsbergite and pararammelsbergite capped by skutterudite. This analysis is believed to have been made on material consisting largely of an orthorhombic nickel arsenide. Analyses 70 and 71 were made by Rammelsberg (1843) on undescribed material with a fairly high specific gravity. Although he gave it the noncommittal name *Arseniknickel*, the same author (1845, p. 19) states that these analyses were made on isometric material. There is no more evidence for isometric than for orthorhombic crystallization for this material, and the high specific gravity suggests the latter. These two analyses, although made on the same material show considerable differences in metal-arsenic ratio, an indication that the specimen was inhomogeneous and the analyses of questionable reliability. Analysis 139 was made on material from cobalt called chloanthite and described as having a nodular structure, a characteristic of the orthorhombic nickel arsenides from this locality. It was made more than 10 years before orthorhombic nickel arsenides were recognized in the ores of the Cobalt District. Nodular material from Cobalt answering this description is largely an intergrowth of rammelsbergite and pararammelsbergite. Analysis 162 was made on chloanthite from the Eldorado Mine, Great Bear Lake. On the basis of Thomson’s description and observations on similar material made in the present study, it was probably largely an aggregate of rammelsbergite in a shell of skutterudite.

Two orthorhombic high-nickel arsenides occur within the skutterudite area. One high-nickel arsenide, No. 159, within the isometric areas was considered orthorhombic by the original author, and another, No. 165, although called isometric by the analyst is believed to have consisted largely of orthorhombic material. Analysis 159 from South Lorrain, said to be orthorhombic, lies well inside the isometric field. The analyzed material is described as rammelsbergite with approximately 18 per cent safflorite and 17 per cent cobaltite, the latter minerals raising the cobalt and iron ratio at the expense of nickel. The correct position for the symbol representing the composition of the rammelsbergite component lies closer to the high-nickel end of the diagram, probably well within the orthorhombic limits. Analysis 165, described as chloanthite from Franklin, New Jersey, is probably that of a mixture. Specimens from this locality proved to be an intergrowth of rammelsbergite and pararammelsbergite with a narrow outer selvage of skutterudite or cobaltite-gersdorffite. The latter minerals would lower the nickel ratio, thereby bringing the symbol into the isometric arsenide zone. A very slight increase in the nickel ratio would throw it into the orthorhombic field.

Four analyses—4, 10, 111, and 131—are unaccompanied by any statements regarding crystal system and were assigned noncommittal names by the original authors. The first of these, No. 4, is Hoffman’s (1832) analysis of the *Arseniknickel*

from Schneeberg. Although there is no statement regarding crystallization, this has long been regarded as the earliest analysis of rammelsbergite and is so accepted here. Orthorhombic nickel arsenides were not recognized until 1845, hence arsenides rich in nickel analyzed prior to this were either regarded as isometric (whether or not isometric crystals were observed) or were given such noncommittal names as *Arseniknickel* without implication of crystallization. Analysis 10 is of questionable value and has been rejected. It is unaccompanied by any description and even the locality is in doubt. Analysis 111 is accepted as more probably orthorhombic than isometric on the basis of the low metal-arsenic ratio. There is actually no valid evidence for any assumption regarding the crystallization of this specimen. Analysis 131, *Arseniknickel*, made on undescribed material (Rammelsberg, 1849), is accepted as probably isometric on the basis of the high metal-arsenic ratio and the low specific gravity.

IRON-BEARING "ORTHORHOMBIC" ARSENIDES (LOELLINGITE AND SAFFLORITE): This, the larger of the two separate areas of "orthorhombic" arsenides, is completely separated from the high-nickel orthorhombic area by the extension of the isometric arsenide zone which reaches the mid-portion of the nickel-iron edge of the diagram. This "orthorhombic" area centers about the high-iron corner but has two extensions, a very narrow one along the iron-cobalt edge and a second, broader, but much shorter, zone along the iron-nickel edge. Sixty-six of the 77 analyses in this area were alleged to have been made on "orthorhombic" specimens, and, when the descriptions of analyzed material are considered, 73 of the 77 are accepted as "orthorhombic". Furthermore, no accepted isometric analysis falls within this area. Seven of the 9 alleged to have been isometric are probably "orthorhombic", and the remaining 2 have been rejected as unreliable. Six arsenides, accepted as "orthorhombic" on the basis of the description of analyzed material or other data, lie just outside the limits assigned to the iron-bearing nonisometric group, but their presence here can be explained. This appears to be a single unit, although the analyses tend to cluster at the iron corner and the mid-portion of the iron-cobalt side of the triangle. The differentiation of the members of this group is difficult, especially since their x-ray diffraction patterns are so similar. For this reason and because there is no evidence for the existence of an "orthorhombic" cobalt end member, Holmes (1942) proposed that the term safflorite be replaced by cobaltian loellingite, the entire group of iron-cobalt "orthorhombic" arsenides being considered a single species. However, Peacock (1944) on the basis of Weissenberg single-crystal studies on a specimen of safflorite from Nordmark, Sweden (analyzed?) states that cobalt-iron arsenides with approximately equal amounts of the two metals are monoclinic with rectangular axes. This would establish a group of cobalt-iron monoclinic arsenides distinct from the orthorhombic iron-rich ones, justifying the retention of the term safflorite. The extent to which the two metals can deviate from the 50-50 ratio without disturbing the monoclinic symmetry is not known. The boundary between safflorite and loellingite has been arbitrarily placed at the 70 per cent iron line. The iron-rich loellingite area has been subdivided into three units: the 85 per cent iron line was selected as the boundary for loellingite proper, or (Ferrian) loellingite. The cobalt-bearing (cobaltian loellingite) area and the nickel-

bearing (nickelian loellingite) area are separated from each other by the line representing equal amounts of cobalt and nickel.

ORTHORHOMBIC IRON-RICH ARSENIDES—FERRIAN, COBALTIAN, AND NICKELIAN LOELLINGITE: Forty-eight of the 51 specimens in this area were claimed to be orthorhombic; 50 of the 51 are accepted as orthorhombic. Two arsenides in this area were alleged to be isometric and have been discussed under isometric arsenides. Analysis 178 on *Arseniure de Fer Pur*, although unaccompanied by data on crystallization, is accepted as probably orthorhombic.

The orthorhombic iron-rich arsenides with cobalt in excess of nickel and an iron ratio of less than 85 per cent are described here as cobaltian loellingite. The boundary between the safflorite and cobaltian loellingite areas is arbitrarily placed at the 70 per cent iron line. The seven analyses within this area were all considered orthorhombic by the original authors and are so regarded here. No analyses in the adjacent isometric area are believed to belong to this group.

The nickelian loellingite area is the smallest of all the areas. Only 3 analyses occur within the limits set, but 4 analyses—120, 175, 176, and 177—within the adjacent isometric, ferrian skutterudite area are accepted as orthorhombic on the basis of the present study and are considered nickelian loellingite. Analyses 176 and 177, just outside the boundary, were alleged to have been made on isometric material. These are the 2 analyses of Genth, made on impure material from Catham, Connecticut. Both the ratio of the 3 metals and the metal-arsenic ratio of the 2 are quite different, yet the analyses were said to represent the same mineral. It was described as disseminated grains and impalpable powder, and, although it was claimed to be isometric (chloanthite), no evidence of crystallographic character was presented. Shepard who first described the mineral chathamite from the type locality (analysis 175) described it as orthorhombic, and data obtained in the present study on material from Chatham confirm his view and show that chathamite is an iron-nickel low-cobalt arsenide of loellingite type intergrown with a nickel-bearing member of the cobaltite-gersdorffite series and nicolite. In view of this, analyses 175, 176, and 177 are believed to represent mixtures of an orthorhombic iron-nickel arsenide (nickelian loellingite) intergrown with nicolite and cobaltite-gersdorffite. Intergrowth with the sulpharsenide would account for the high sulphur content of Genth's analyses and the high nickel and cobalt ratio which places them within the isometric area beyond the nickelian loellingite limits. The cobalt ratio of these three varies with the sulphur content confirming the belief that the cobalt is at least in part due to the admixed sulpharsenide. Analysis 120 was made on impure material from Schladming called *Arsenikeisen*. It was described as massive with a sulphur content of 5.20 per cent. Examination of specimens from this locality reveals a high iron-nickel, low-cobalt orthorhombic arsenide (nickelian loellingite) intimately associated with gersdorffite, an association very similar to that at Chatham. It is believed that this analysis represents a mixture of these two minerals. The gersdorffite accounts for the high sulphur content and the high nickel ratio which places the symbol within the isometric area as in the case of the specimens from Chatham. Analysis 81 on material from St. Andreasberg has a misleading high nickel content due to the presence of breithauptite. The original author believed the orthorhombic arsenide to be nickel

and cobalt free. However, contact prints of similar material from the locality show small amounts of both elements in the orthorhombic arsenide. It is undoubtedly a high-iron (ferrian) loellingite rather than a nickelian loellingite.

**MONOCLINIC IRON-COBALT ARSENIDES—SAFFLORITE:** The peripheral character of the distribution of the iron-bearing nonisometric arsenides is especially evident in the case of the iron-cobalt (safflorite) group. The cobalt ratio of the 16 analyses in this area varies from 32.6 to 65.2 per cent, yet the nickel ratio does not exceed 6.2 per cent. Peacock claims that the nonisometric arsenide with approximately equal amounts of cobalt and iron is monoclinic, but the extent to which the cobalt-iron ratio can deviate is not known. The tentative assumption is made that it can vary over a considerable range, and on this basis the safflorite area has been extended from the vicinity of  $\text{Co}_{30}$  to  $\text{Co}_{70}$ . The boundary, as placed, excludes the two analyses of "orthorhombic" minerals highest in cobalt, Nos. 63 and 106. Since the homogeneity of these two is questionable and they are considerably removed from the next nearest "orthorhombic" analysis, the boundary of the group has been placed between these two and the main concentration of minerals of this group.

The importance of considering the descriptions of analyzed material in evaluating published analyses is more evident in this group than in any other. Of the 16 analyses included in this area, 8 were claimed to have been made on orthorhombic material, 7 on isometric, and 1 on material for which no data on crystallization was given. On the basis of the descriptions of analyzed material and other data obtained in the present study, 13 of the 16 are believed to be "orthorhombic", while the remaining 3 have been rejected as unreliable. None of the 7 allegedly isometric arsenides within this area has been accepted as such after the available data contained in the descriptions of the analyzed material have been taken into account.

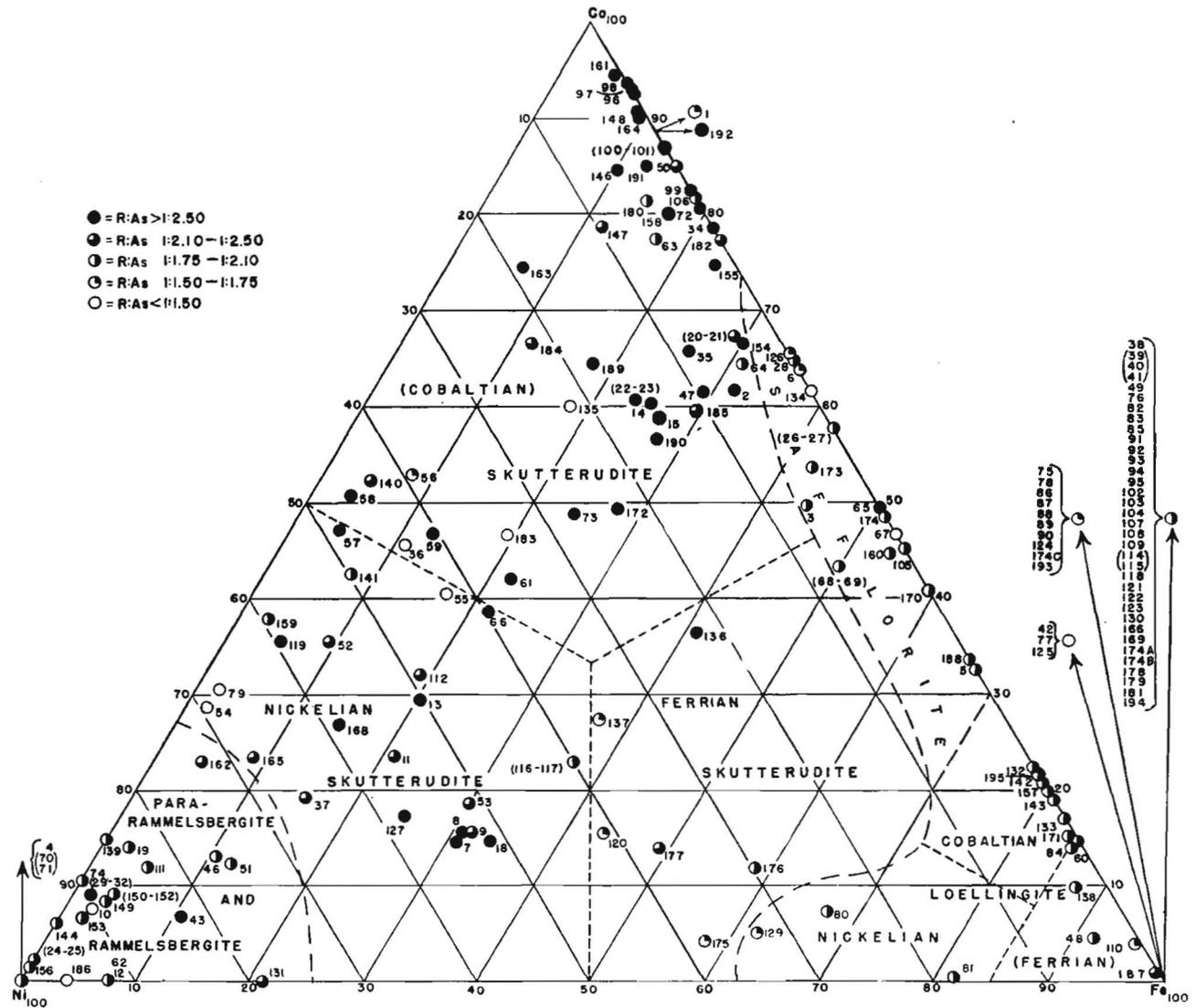
Six (Nos. 3, 5, 126, 170, 173, and 188) of the 7 allegedly isometric arsenides within this area are believed to be "orthorhombic", the remaining one, No. 65, has been rejected. Analysis 3 was made on massive *Grauer Speiskobalt* from Schneeberg before "orthorhombic" cobalt-iron arsenides were recognized and has a metal-arsenic ratio below  $\text{R}:\text{As}_2$ . The *Grauer Speiskobalt* from Schneeberg has been generally recognized as "orthorhombic" by later workers, and this is confirmed by the present study. Analysis 5 on material said to be probably isometric—*Speiskobalt (Eisen-Kobaltkies)*—but described as spheroidal radiating, is another analysis of material whose structure points to its nonisometric character. Analysis 126 is of material from Markkirch called *Speiskobalt* by Dürr (1907) and credited by him to Carriere (Voltz, 1828). The obscure volume on Alsace containing this analysis could not be located. No description of the material accompanies Dürr's mention of the analysis. On the basis of its low arsenic ratio and the prevalence of "orthorhombic" arsenides in specimens from this locality, it is believed to be an analysis of safflorite rather than an isometric material. "Orthorhombic" cobalt-iron arsenides were not yet recognized in 1828. Analysis 173 was made on material from Prairie City, Oregon, described as smaltite, with an acicular and columnar structure. The arsenide from this locality proves to be safflorite; no isometric arsenide has been observed on several specimens examined in the present investigation. Analysis 170 (Gunnison Co., Colorado) was made on material described as massive smaltite.

The author offers no evidence of crystallization. The low arsenic ratio and the cobalt-iron-low nickel content suggest that it is safflorite. There is a typographical error in the original paper. The total is given as 98.89, but the figures add up to only 94.89. Dana (1883) believed the error to be in the cobalt and increased this to 15.59, but later (1892) he assigned the error to iron and raised that to 15.99. Analysis 188 was made on material from Andahuaylas, Peru, called *esmaltina ferrifera* but described as having a radial fibrous structure which points to a nonisometric crystallization. These 6 analyses are believed to represent nonisometric material. They show strikingly the tendency in the period prior to the introduction of the reflecting microscope to call any material maltite which did not exhibit recognizable or measurable "orthorhombic" crystals. Microscopic and x-ray examination of arsenides exhibiting such nodular, radiating, and fibrous structures show that they are almost always nonisometric. Analyses 65, 134, and 160 have been rejected as unreliable and are represented by circles on Plate 4. Analysis 65, made on *Weisser Speiskobalt* in 1813, is an unreliable analysis with an arsenic ratio of 3.22. Analysis 160, although described as that of loellingite, was said to contain 35 per cent safflorite and other impurities. It has been rejected on the basis of excessive inhomogeneity. Analysis 134 was made on material from Badeni-Ungureni, Romania. Such material from this locality was later described by Poni (1900; 1901) as Badenite which, on the basis of microscopic work by Petruian (1936), was shown to be an intimate mixture of several minerals.

Two "orthorhombic" arsenides occur in the high-cobalt isometric area just outside the safflorite boundary. Analysis 63, considered to be that of an orthorhombic material *Arsenkobalteisen* by the analyst, and another, 106, alleged to be isometric *Grauer Speiskobalt* by the original author but having a specific gravity of 7.131, are both accepted as safflorite. As already pointed out, the boundary of the safflorite area has not been made to include them. The exact location of this boundary at the high cobalt end is open to question. However, these two "orthorhombic" arsenides lie near the boundary as drawn and were described as intimately intergrown with *Speiskobalt* in the case of No. 63 and with cobaltite in the case of No. 106, partly accounting for their high cobalt content. If the cobalt ratio of the "orthorhombic" component in each case were known, the symbol would move toward the iron end of the diagram, bringing them both closer to, if not within, the boundary as drawn.

*Bearing of the data from published analyses on the problem of cobalt-nickel-iron ratio in the isometric and "orthorhombic" series.*—The evidence from published analyses points clearly to the limited character of the isomorphism between the three metals in both the isometric and "orthorhombic" series, and furthermore, the two series appear to be essentially complementary in this respect. The isomorphism in the "orthorhombic" series is not only limited but is discontinuous as well. Non-isometric analyses are restricted to two completely separated areas, centered respectively about the iron and nickel corners of the diagram.

Only 11 of the 163 analyzed specimens whose crystallization is accepted fall beyond the limits of the appropriate area. The anomalous positions of 9 of these are due to the presence of mechanically admixed impurities whose presence is admitted by



RELATION OF METAL-ARSENIC RATIO TO COBALT-NICKEL-IRON RATIO

Based on the original analyses after eliminating gangue, silver, and bismuth, on the assumption that the last two are present as mechanically admixed native elements. Sulphur and antimony when present have been grouped with arsenic in the computation of the metal-arsenic ratios. Likewise copper and other metals have been included in the metal totals.

the original author, or is rendered reasonably certain from other data. The remaining two, No. 43, Rammelsberg (1873) and No. 131, Rammelsberg (1849), are unaccompanied by any data on homogeneity, hence their apparent anomalous position cannot be explained for lack of evidence.

RELATION BETWEEN METAL-ARSENIC RATIO, COBALT-NICKEL-IRON RATIO AND CRYSTALLIZATION AS SHOWN BY PUBLISHED ANALYSES

*General statement.*—If the arsenic ratios of specimens, for which published analyses exist, are considered in relation to the ratio of the three metals, a correlation between metal-arsenic ratio, cobalt-nickel-iron content, and crystal system is apparent. Specimens high in cobalt and those containing appreciable amounts of nickel, or nickel and iron in addition to cobalt tend to be isometric and have metal-arsenic ratios well above  $R:As_2$ , often approaching closely  $R:As_3$ , whereas those high in nickel or high in iron and the iron-cobalt-low nickel members tend to be “orthorhombic” and have a metal-arsenic ratio close to, or below,  $R:As_2$ .

A triangular diagram (Pl. 5) shows the relation of arsenic content to cobalt-nickel-iron ratio. Comparison of this diagram with Plates 3 and 4 will show the relation of arsenic ratio to crystallization. The position of each symbol on these diagrams is based on the cobalt-nickel-iron ratio of the analysis. A series of circular symbols have been used on Plate 5, representing five ranges of metal-arsenic ratios. The intervals selected are irregular. The metal-arsenic ratios of the published analyses of both isometric and “orthorhombic” materials vary from 1.12 to 3.68. As the recognized minerals are considered to be either diarsenides or triarsenides, the relation of the arsenic ratios to the values  $R:As_2$  and  $R:As_3$  are of particular interest. Only four analyses exceed  $R:As_3$ , and comparatively few reach it. All those with a metal-arsenic ratio greater than 2.50 are represented by a solid black circle. A half black circle has been allotted to the range (1.75 to 2.10), which includes most of the “orthorhombic” diarsenides. The range (2.10–2.50) is shown by a three-quarter black circle. Most of the materials in the two groups above the 2.10 ratio are isometric. The analyses with very low arsenic ratios have been divided into two groups. The larger of these covers the range (1.50–1.75) and is shown by a quarter black circle. An open circle represents the few remaining analyses with exceptionally low metal-arsenic ratios (below 1.50). The diagram is divided into three areas on the basis of crystallization. Since each area is assumed to be restricted to either isometric triarsenides or “orthorhombic” diarsenides, any considerable deviation in arsenic ratio from that proper for a given area requires explanation. Analyses whose arsenic ratios deviate widely from the two theoretical values,  $R:As_2$  and  $R:As_3$ , are discussed below.

Plates 3, 4, and 5, Tables 8, 9, and 10, and the preceding section on cobalt-nickel-iron ratios supplement the following detailed discussion. Table 10 summarizes the distribution of the analyses shown in Plate 5. It contains, in addition, a tabulation of average metal-arsenic ratios which have been calculated for each mineral group. The predominance of high arsenic ratios in the isometric areas and of diarsenide or lower ratios in the “orthorhombic” ones tends to confirm the essentially complementary relationship of these two groups.

TABLE 10.—Relation between crystallization and metal-arsenic ratio of the higher arsenides of cobalt, nickel and iron as shown by published analyses

<i>Isometric areas</i>									
Area	Number of analyses within each of the five R:As ranges						Average metal-arsenic ratios for analyses within areas indicated		Average metal-arsenic ratios for all analyses of materials accepted as isometric on the basis of the present study, including those in adjacent "orthorhombic" areas
	>2.50	2.10-2.50	1.75-2.10	1.50-1.75	<1.50	total	All analyses in area	Analyses of materials accepted as isometric on the basis of the present study.	
Skutterudite (Cobaltian).....	30	7	4	2	3	46	2.48 (46)	2.53 (41)	2.53 (41)
Nickelian Skutterudite..	9	7	3	0	3	22	2.30 (22)	2.37 (19)	2.39 (22)
Ferrian Skutterudite ...	1	1	1	3	0	6	2.01 (6)	2.59 (1)	2.59 (1)
Total—Isometric ....	40	15	8	5	6	74	2.38 (74)	2.48 (61)	2.48 (64)
<i>Nonisometric "orthorhombic" areas</i>									
Area	Number of analyses within each of the five R:As ranges						Average metal-arsenic ratios for analyses within area indicated		Average metal-arsenic ratios for all analyses of materials accepted as "orthorhombic" on the basis of the present study including those in adjacent isometric areas
	>2.50	2.10-2.50	1.75-2.10	1.50-1.75	<1.50	total	All analyses in area	Analyses of materials accepted as "orthorhombic" on the basis of the present study.	
Rammelsbergite and Pararammelsbergite..	2	2	16	0	2	22	1.96 (22)	1.91 (18)	1.92 (20)
Loellingite (Ferrian) ...	0	1	36	11	3	51	1.86 (51)	1.86 (50)	1.86 (50)
Cobaltian Loellingite ...	0	0	7	0	0	7	1.97 (7)	1.97 (7)	1.97 (7)
Nickelian Loellingite ...	0	0	2	1	0	3	1.85 (3)	1.85 (3)	1.90 (7)
Total—Loellingite ...	0	1	45	12	3	61	1.87 (61)	1.87 (60)	1.87 (64)
Safflorite.....	1	0	11	2	2	16	1.88 (16)	1.82 (13)	1.83 (15)
Total—Fe-bearing "Orthorhombic"...	1	1	56	14	5	77	1.87 (77)	1.86 (73)	1.87 (79)
Total—"Orthorhombic".....	3	3	72	14	7	99	1.89 (99)	1.87 (91)	1.88 (99)

*Arsenic ratios of the isometric arsenides—(skutterudite).*—This area is regarded as one of isometric triarsenides, hence the presence within it of minerals with unusually low metal-arsenic ratios calls for explanation. The almost universal inhomogeneity of the isometric arsenides revealed by the present study and the observations of others makes it almost certain that the arsenic ratio of most analyses of isometric triarsenides will fall below the R:As<sub>3</sub> ratio due to mechanical inhomogeneity involving "orthorhombic" diarsenides, niccolite, and other minerals. Possibly substitution of metal for arsenic is a factor affecting variations in the metal-arsenic ratio, although no evidence for this was secured in the present study. For this

reason no attempt will be made to account for the arsenic deficiency of analyses in the isometric areas with a ratio appreciably higher than R:As<sub>2</sub> (above 2.10).

The great majority of the 74 specimens represented in this area are isometric arsenides with a high arsenic content; the average metal-arsenic ratio is 2.38. Elimination of the 8 analyses believed to represent "orthorhombic" material and the 5 rejected as unreliable provides a revised ratio of 2.48 for those accepted as isometric. If the separate subdivisions are considered, the cobalt-rich area is found to have an average arsenic ratio of 2.53, the nickel-rich area 2.37, and the iron-rich area 2.59. The last named contains only a single, questionable analysis so that this value has little significance. Inclusion of the 3 analyses accepted as isometric, but occurring in the adjacent "orthorhombic" area, does not change this ratio for all accepted isometric arsenides. The accepted isometric members have an average arsenic ratio (2.48), well above R:As<sub>2</sub>, in spite of widespread inhomogeneity of the analyzed material, recognized by the analyst in many cases, and almost certainly present in others. There is no valid evidence for an isometric diarsenide series. The average arsenic ratio of the isometric components in analyzed materials is appreciably above 2.50. Furthermore, there is little evidence of extreme variability in arsenic ratio. The 3 analyses with an arsenic ratio greater than R:As<sub>3</sub> were all made prior to 1856, and one of these has been rejected as unreliable. Six of the 19 analyses in the isometric area having an arsenic ratio lower than 2.10 represent "orthorhombic" arsenides. Four have been rejected as unreliable, leaving 9 accepted as isometric. Five of these are accompanied by data indicating that the material used was inhomogeneous, and 3 others made prior to 1880 are unaccompanied by any data on homogeneity. Thus, only a single analysis with an arsenic ratio lower than 2.10 (No. 36) deserves serious consideration as evidence of widespread substitution of metal for arsenic to explain the extreme variation in metal-arsenic ratio shown by published analyses.

Thirty-seven of the 46 analyses in the (cobaltian) skutterudite area have an arsenic ratio greater than 2.10, 30 above 2.50, and 3 above 3.00; the average is 2.48. Forty-three of the materials used in these analyses were regarded as isometric by the original authors; 1 was considered orthorhombic, and 2 were unaccompanied by any reference to crystallization. Forty-one of the 46 have been accepted on the basis of the present study as definitely or probably isometric with an average arsenic ratio of 2.53. Two are believed to be "orthorhombic", and 3 have been rejected as unreliable. As no analyses in the adjacent nonisometric area are accepted as isometric, the ratio for all accepted cobalt-rich isometric arsenides is 2.53.

Nine of the 46 analyses in the cobalt-rich isometric area have a metal-arsenic ratio below 2.10 as follows:

<i>Number of analysis</i>	<i>Date</i>	<i>As ratio</i>	<i>Remarks</i>
106	1839	1.97	"ortho"
180	1855	1.86	no data
63	1868	1.81	"ortho"
64	1881	1.81	inhomo.
56	1853	1.72	no data
1	1810	1.49	reject
36	1930	1.43	(?)
135	1886	1.43	reject
183	1879	1.40	no data

The low arsenic ratios of some of these can be accounted for. Analyses 63 and 106 are almost certainly those of "orthorhombic" diarsenides which accounts for their low metal-arsenic ratios. Analysis 64 was made on inhomogeneous material containing chalcopyrite which could account in part for the low arsenic ratio. Analyses 56, 180, and 183 were made on material accompanied by descriptions containing no data on homogeneity or explanation for the low arsenic content. Analyses 1 and 135 have been rejected because of very questionable reliability. There remains a single analysis, one of smaltite from Schneeberg (No. 36). Although made by Fahey (Short, 1930) on material described as homogeneous and isometric on the basis of microscopic examination, it has one of the lowest metal-arsenic ratios reported for an isometric arsenide (1.43). Through Dr. Charles F. Park, Short's original surface (U. S. N. M. No. 4564) (U. S. G. S. Ref. 259) was made available. This has been re-examined by both x-ray and reflecting microscope methods in the present study and was found to be slightly inhomogeneous. The constituent present in addition to the isometric arsenide appears to be a cobaltian loellingite. However, the inhomogeneity (in the surface examined) is insufficient to account for the excessive arsenic deficiency shown by the analysis. Mr. Edward P. Henderson of the U. S. National Museum reports that the original specimen cannot be located. As this is the only modern analysis of an isometric arsenide providing an arsenic ratio lower than  $R:As_2$ , the material should be carefully examined for homogeneity and re-analyzed. Two of the 9 analyses with an arsenic ratio below 2.10 owe their low arsenic content to orthorhombic crystallization. Two have been rejected as unreliable. The material used in No. 64 was described as inhomogeneous, and that used in No. 36 although described as homogeneous was found to carry inclusions of a diarsenide. Three analyses lack data accounting for the low ratio. The homogeneity of all specimens is under suspicion since, with the exception of No. 36, the analyses were made prior to 1881 on material not examined by microscopic methods.

Three analyses with an arsenic ratio above 3.00 occur in this area:

<i>Number of analysis</i>	<i>Date</i>	<i>As ratio</i>	<i>Remarks</i>
2	1826	3.68	Reject
98	1838	3.14	(?)
47	1856	3.02	—

The deviation of No. 47 is too slight to justify consideration. Analysis 2 has been rejected as unreliable. The data in the description of 98 do not suggest an explanation of the excessive arsenic content, but the date of the analysis casts doubt on its reliability. No isometric arsenides analyzed since 1856 have provided arsenic ratios above 3.00.

The nickelian skutterudite area contains the analyses of 22 specimens with an average arsenic ratio of 2.30, well above  $R:As_2$ . Sixteen of the 22 have a ratio above 2.10, 9 a ratio above 2.50, leaving only 6 with a ratio lower than 2.10 and none above 3.00. Nineteen of the 22 were regarded as isometric by the original authors, and the same number are accepted as isometric. Two (Nos. 159 and 165) are believed to be "orthorhombic", and one (No. 79) has been rejected as unreliable.

All six specimens with an arsenic ratio below 2.10 can be accounted for either on the basis of their being orthorhombic diarsenides whose location within this area can be explained, or as due to inhomogeneity rendering the analyses of low reliability. If these six analyses are eliminated the recalculated arsenic ratio becomes 2.37 compared with a ratio of 2.30 for the group as a whole. The evidence from published analyses points to the isometric, high arsenic, character of the minerals in this area. If analyses (29-32), 43, and 131, accepted as isometric but occurring in the adjacent orthorhombic area, are included, the average arsenic ratio for all accepted nickelian skutterudites is 2.39. Six analyses with an arsenic ratio lower than 2.10 occur in this area.

<i>Number of Analysis</i>	<i>Date</i>	<i>As ratio</i>	<i>Remarks</i>
159	1925	1.96	"ortho"
79	1861	1.42	reject
(116-117)	1850	1.85	inhomo.
141	1916	2.08	inhomo.
54	1853	1.29	inhomo.
55	1853	1.12	inhomo.

Analysis No. 159 was made on an "orthorhombic" arsenide. Two analyses, Nos. 54 and 55, claimed to have been made on the same material, clearly demonstrate the inhomogeneity of the sample since they exhibit great variation both in the ratio of the three metals and in the metal-arsenic ratio. Consequently, their arsenic ratios are of little significance. Analysis No. 79 is a rejected analysis of material described by the original author as consisting largely of niccolite, which accounts for its low arsenic content. Analyses 116 and 117 are of questionable merit. The material used was admittedly inhomogeneous, and there is apparent uncertainty as to the nature of the inhomogeneity; it is described as chalcopyrite in one place (Foeterle, 1850) and bornite in another (Lowe, 1862). The material used for analysis 141 was described by the original author as inhomogeneous consisting of no less than four minerals.

The ferrian skutterudite area is one of limited extent and few analyses. According to the original authors, 3 of the 6 analyses were made on isometric material, 2 on orthorhombic. The one remaining, No. 137, was made on material called *minerale bianca argentina*, and the description carries no data on crystallization. One (No. 136) is accepted as isometric, and No. 137 has been rejected as unreliable. Analyses 120, 175, 176, and 177 are accepted as representing mixtures consisting principally of orthorhombic diarsenides with lesser amounts of isometric sulpharsenides and niccolite, accounting for the low arsenic ratio. The niccolite and cobalt-nickel sulpharsenide components give a fictitious high nickel ratio to the analyses, placing them in the isometric area. The average arsenic ratios for this group are of little significance. The low ratio of 2.01 for all analyses in the area is due to the predominance of orthorhombic members. When these are eliminated, the ratio of the remaining specimen in this area accepted as isometric is 2.59. As there are no arsenides in the adjacent "orthorhombic" areas accepted as isometric, this analysis

remains the only example of an accepted ferrian skutterudite. The arsenic ratios of four analyses in this group fall below 2.10:

<i>Number of Analysis</i>	<i>Date</i>	<i>As ratio</i>	<i>Remarks</i>
120	1832	1.74	"ortho"
175	1844	1.71	"ortho"
176	1854	2.01	"ortho"
137	1894	1.72	reject

The low arsenic ratio of the first three is accounted for by the orthorhombic character of the material. Analysis 137 has been rejected as unreliable.

*Arsenic ratios of the "orthorhombic" arsenides.*—Two separate groups of "orthorhombic" arsenides centering about the nickel and iron corners of the diagram appear to exist in nature. The data on metal-arsenic variations among the "orthorhombic" arsenides is summarized, and the presence of analyses with metal-arsenic ratios appreciably greater than  $R:As_2$  in the "orthorhombic" area is accounted for in most instances. The average arsenic ratio for all 99 analyses within the "orthorhombic" areas is 1.89. A revised ratio of 1.87 is obtained for the 91 accepted as "orthorhombic" in the present study. If consideration is given to the 8 "orthorhombic" arsenides whose analyses fall outside the limits for this group, the average arsenic ratio for all accepted "orthorhombic" arsenides is 1.88. The average arsenic ratio for the 77 analyses in the iron-bearing "orthorhombic" area is 1.87. A revised ratio of 1.86 is obtained for the 72 accepted as "orthorhombic". The average arsenic ratio for all 79 accepted iron-bearing "orthorhombic" arsenides, including the 6 lying beyond the limits for this group, is 1.87. The average ratio for the 22 analyses in the nickel-rich "orthorhombic" area is 1.96 and for the 18 accepted as "orthorhombic" in this area, 1.91. If the analyses of the 2 accepted as "orthorhombic" but lying within the adjacent isometric area are included, an arsenic ratio for all nickel-rich orthorhombic arsenides of 1.92 is obtained. Clearly the areas outlined as "orthorhombic" on the triangular diagrams are predominantly occupied by "orthorhombic" minerals whose average arsenic ratios are just below that required for the composition  $R:As_2$ . Ninety-two of the 98 analyses have an arsenic ratio below 2.10.

The present study is not concerned with the problem of arsenic deficiency in the "orthorhombic" group. In the case of loellingite and safflorite, true arsenic deficiency apparently exists since there is no known lower arsenide of cobalt or iron occurring in nature whose presence could account for the low arsenic ratios. Arsenic deficiency in nickel-bearing members is always open to question unless the absence of niccolite or maucherite has been established by microscopic or x-ray methods.

Evidence from published analyses indicates a clear relation between arsenic ratio, the ratio of the three metals, and crystallization. The high cobalt members and those containing nickel or nickel and iron in addition to cobalt have an arsenic ratio averaging well over  $R:As_2$  and are isometric, whereas the high nickel, high iron, and the iron-cobalt members have an average arsenic ratio of  $R:As_2$  or lower and are predominantly "orthorhombic". This confirms the view that the substitution among

the three metals in the isometric and "orthorhombic" arsenide series is limited and that the two groups are complementary.

HIGH-NICKEL "ORTHORHOMBIC" ARSENIDES (RAMMELSBURGITE AND PARARAMMELSBURGITE): Arsenides high in nickel are essentially diarsenides; 16 of the 22 lie in the range 1.75–2.10, and the average arsenic ratio is 1.96. Only 4 analyses in this group have an arsenic ratio above 2.10. Since it is contended that the high-nickel area is one of orthorhombic diarsenides, an explanation is required for the presence here of specimens deviating appreciably from this composition or claimed to be isometric. Analyses (19, 29–32, 43, 51, 70–71, 139, and 162) were made on material claimed to be isometric. Five are believed to represent orthorhombic material when all available data are considered. If the rejected analysis No. 10 and the 3 accepted as isometric are eliminated, the metal-arsenic ratio for the remaining 18 analyses accepted as definitely or probably orthorhombic is 1.91. The arsenic ratio for all 20 accepted high-nickel orthorhombic arsenides including the two in the adjacent isometric area is 1.92. Four analyses in this group have an arsenic ratio above 2.10 and two fall below 1.75 as follows:

<i>Number of Analysis</i>	<i>Date</i>	<i>As ratio</i>	<i>Remarks</i>
10	1854	1.32	reject
186	1879	1.32	no data
29–32	1886	2.62	iso.
131	1849	2.32	iso.
43	1873	2.53	iso.
162	1932	2.15	inhomo.

Of the 2 analyses falling below the 1.75 ratio, No. 10 has been rejected as unreliable, and No. 186 dated 1879 is not accompanied by any data on homogeneity. Analysis 162 probably represents a mixture of isometric and orthorhombic arsenides. The three remaining analyses with an arsenic ratio above 2.10 are accepted as isometric and except for analysis (29–32) made on material containing niccolite, their positions in this area cannot be explained on the basis of available data. The dates of these analyses and the absence of data on homogeneity render them of questionable value.

IRON-BEARING "ORTHORHOMBIC" ARSENIDES (LOELLINGITE AND SAFFLORITE): This area is separated from the high-nickel orthorhombic one just described. It has been subdivided into an iron-rich orthorhombic (loellingite) area and an iron-cobalt, monoclinic (safflorite) area. The loellingite group is subdivided into (1) (ferrian) loellingite, (2) cobaltian loellingite, and (3) nickelian loellingite. This is essentially an area of "orthorhombic" diarsenides, the arsenic ratio in practically all cases being at or below  $R:As_2$ .

Of the 51 specimens in the ferrian loellingite area, 44 are pure iron arsenides containing neither cobalt nor nickel. Only 12 exceed the  $R:As_2$  ratio and only one, No. 187, has an arsenic ratio greater than 2.10. Fourteen have an arsenic ratio lower than 1.75. If (114–115), rejected as unreliable, is eliminated, the arsenic ratio of the remaining 50 accepted as orthorhombic is 1.86. Since the boundaries of this area are purely arbitrary and adjoin other orthorhombic areas, there are no outlying members of the group; hence the average arsenic ratio for all ferrian loel-

lingite analyses is the same as above (1.86) Fourteen analyses in this area fall below the 1.75 limit, and one lies in the range above 2.10.

<i>Number of Analyses</i>	<i>Date</i>	<i>As Ratio</i>
187	1866	2.46
42	1856	1.39
75	1837	1.65
77	1854	1.38
78	1861	1.74
86	1832	1.61
87	1840	1.65
88	1852	1.61
89	1870	1.65
90	1870	1.59
110	1921	1.74
124	1864	1.64
125	1869	1.31
174C	1928	1.67
193	1942	1.69

Only a single analysis, No. 187, has an arsenic ratio above 2.10, and this is an inferior analysis published by Breithaupt (1866) apparently on inhomogeneous material carrying 7.01 per cent sulphur. The description of the analyzed material offers no explanation for the high arsenic or high sulphur content.

The nickelian loellingite area is the smallest subdivision of the iron-bearing "orthorhombic" arsenides; it contains only three analyses, all claimed to represent orthorhombic material—and accepted as such. The average arsenic ratio for the three specimens in this area is 1.85. Four analyses, Nos. 120, 175, 176, and 177, lying just outside this area, are probably "orthorhombic" and belong in this group. If they are included, an arsenic ratio of 1.90, for all accepted nickelian loellingites, is obtained. Analysis 129 has an arsenic ratio below 1.75 which may be due to inhomogeneity involving a lower arsenide of nickel as suggested by the author.

The seven analyses in the cobaltian loellingite area were described as orthorhombic and are so regarded here. In all cases, the arsenic ratios lie in the 1.75–2.10 range; the average is 1.97. Since all the analyses in this area are accepted as orthorhombic, and since there are no analyses in the adjacent isometric area believed to be those of cobaltian loellingite, 1.97 is the average arsenic ratio for all accepted cobaltian loellingites. Sixteen analyses occur within the area, which comprises the iron-cobalt-low nickel arsenides of the safflorite type. Thirteen of the 16 have been accepted as definitely or probably "orthorhombic". The average metal-arsenic ratio is 1.88 with only 3 greater than 2.00 and only 1, No. 65, above 2.10. Seven of the 16 analyses in this area were called isometric by the original authors, but no supporting evidence was offered. When reviewed in the light of the published descriptions and other data, 6 of the 7 are found to be "orthorhombic" rather than isometric, and the seventh, No. 65, has been rejected as unreliable. The average arsenic ratio for all analyses in the safflorite area is 1.88. If the 3 rejected analyses are eliminated, the arsenic ratio of the accepted "orthorhombic" arsenides in this area is 1.82. If the two "orthorhombic" arsenides in the adjacent isometric area, Nos. 63 and 106, are

included, the arsenic ratio for all safflorites is 1.83. Evidence from published analyses confirms the nonisometric diarsenide character of the iron-cobalt-low nickel arsenides. Analyses with arsenic ratios outside the 1.75–2.10 range as follows:

<i>Number of Analysis</i>	<i>Date</i>	<i>As Ratio</i>
65	1813	3.22
134	1886	1.17
6	1852	1.50
67	1873	1.45
126	1828	1.73

The only analysis with an arsenic ratio above 2.10 is No. 65 which has been rejected along with two others in this area, Nos. 134 and 160. Four analyses have unusually low arsenic ratios, Nos. 6, 67, 126, and 134; No. 134 has been rejected as unreliable. The remaining three have been accepted as safflorites. As pointed out earlier no attempt is made to account for arsenic deficiency in the "orthorhombic" arsenides.

## NOMENCLATURE OF THE HIGHER ARSENIDES OF COBALT-NICKEL AND IRON

### HISTORICAL BACKGROUND

The history of the classification and nomenclature of these minerals has been amply treated by Hintze (1904) and will be given only sufficient consideration here to provide a background for the changes proposed.

During the first quarter of the nineteenth century the composition and relations of the members of this group were very poorly understood. They were not only confused with each other, but were not clearly separated from related minerals such as arsenopyrite and cobaltite. At the end of this period only two distinct higher arsenides were recognized, an isometric cobalt diarsenide, *Speiskobalt*, and an orthorhombic iron diarsenide, *Arsenikeisen*. These are the materials later referred to as smaltite (*smaltine*, Beudant, 1832) and loellingite (*Löllingit*, Haidinger, 1845) or leucopyrite, Shepard, 1835).

During the second quarter of the century it was shown that the minerals of this group were more numerous and their relations more complex than earlier workers had realized. Hoffmann (1832) and Booth (1835) analyzed nickel diarsenides from Schneeberg and Riechelsdorf, respectively, which proved to be essentially cobalt free. Booth believed his material to be a nickel equivalent of the isometric cobalt diarsenide, *Speiskobalt* (smaltite) and called it *deutarseniuret of nickel*. Hoffmann gave no indication of the crystallization and assigned his material the noncommittal name *Arsenik-Nickel*. Breithaupt (1835) recognized the orthorhombic character of an iron-cobalt arsenide which he called *Safflorit*. In 1845 Breithaupt, who had earlier suspected the rhombic nature of certain high-nickel specimens stated clearly his belief in the dimorphism of  $\text{NiAs}_2$ , a view rigidly adhered to ever since. He assigned the name *Chloanthit* to the isometric nickel equivalent of *Speiskobalt* (smaltite) and *Weissnickelkies* to the orthorhombic form (present rammelsbergite). Almost simultaneously Haidinger (1845) who had not yet recognized orthorhombic nickel arsenides proposed the name *Rammelsbergit* for the isometric nickel equivalent of *Speiskobalt* (Breithaupt's *Chloanthit*). In an appendix (Haidinger, 1845) the

priority of Breithaupt's *Chloanthit* is recognized, but Haidinger proposed that it be reassigned to the orthorhombic member retaining his name, *Rammelsbergit*, honoring the mineral chemist, C. F. Rammelsberg, for the isometric one. This proposal resulted in widespread confusion which is traceable throughout the latter part of the nineteenth century. Dana (1854) reversed Haidinger's terms using chloanthite for the isometric and rammelsbergite for the orthorhombic member, and this nomenclature has been consistently followed in recent times. This complex stage in the history of the nomenclature of the nickel arsenides can be best understood by reference to the following tabulation:

Crystal System	Breithaupt (1845)	Haidinger (1845)	Haidinger (1845) (Revised)	Dana (1854)
Isometric	Chloanthite	Rammelsbergite	Rammelsbergite	Chloanthite
Orthorhombic	Weissnickelkies	—	Chloanthite	Rammelsbergite

By the middle of the nineteenth century two isometric and four orthorhombic diarsenides had been recognized. The isometric cobalt diarsenide (smaltite) and its nickel equivalent (chloanthite) seemed well established, but no corresponding isometric iron diarsenide had yet been reported. The orthorhombic members, rammelsbergite, loellingite, and safflorite, had been recognized and described as nickel, iron, and iron-cobalt diarsenides, respectively. In addition, an iron-nickel-cobalt diarsenide had been described as orthorhombic by Shepard (1844) and called chathamite. Breithaupt recognized the rhombic character of safflorite as early as 1835, and others confirmed this during the middle of the century. Dana steadfastly considered it to be an isometric iron-bearing smaltite. However it is accepted as a distinct orthorhombic mineral in the sixth edition of the *System of Mineralogy* (Dana E. S., 1892). He likewise never recognized the rhombic character of Shepard's chathamite which is still generally regarded as isometric, on the strength of Dana's authority. Although Breithaupt emphasized the "iron-cobalt" character of his *Safflorit* and no orthorhombic arsenide of even approximately pure cobalt composition has ever been reported, mineralogists extended the name safflorite to include a theoretical pure cobalt orthorhombic diarsenide. This view has persisted until the present as a glance at most mineralogical works, including the new seventh edition of Dana's system (Palache, Berman, and Frondel, 1944) will show. Hence by the middle of the nineteenth century unlimited isomorphism among the three metals in the orthorhombic series had been widely accepted, and names had been assigned to what were believed to be the three end members. An isometric iron diarsenide was not reported until well into the twentieth century. With the discovery of an alleged iron end member (arsenoferrite) of the isometric series (Baumhauer, 1912), the existence of a dual series of diarsenides appeared to have been established—one isometric (smaltite, chloanthite, arsenoferrite), and another orthorhombic (safflorite, rammelsbergite, loellingite). Each series was assumed to exhibit unlimited isomorphous substitution between cobalt, nickel, and iron.

The picture is complicated further as a result of the recognition of *Tesseralkies* from Skutterud, Norway (Breithaupt, 1827), as distinct from *Speiskobalt* (smaltite). Scheerer (1837) established this material as an isometric cobalt triarsenide, naming it *Arsenikkobalikes*; later it was called *Skutterudite* by Haidinger (1845). Toward the end of the century a nickel-rich triarsenide was described by Waller and Moses (1892) as nickel-skutterudite. Since this contained considerable iron as well as nickel and cobalt, the isometric triarsenide series appeared to offer another example of unlimited isomorphous substitution. No claim has ever been made for the existence of an essentially pure isometric iron triarsenide, although such terms as "ferriferous skutterudite (Short, 1940), imply extensive if not unlimited isomorphism.

Since comparatively few analyses of isometric arsenides reach the  $R:As_3$  ratio, skutterudites (prior to the advent of x-ray methods) were relegated to an inferior position. They were usually regarded as arsenic-rich smaltite-chloanthites. Oftedal (1926; 1928) in a detailed x-ray study, established the structural identity of smaltite, chloanthite, and skutterudite and demonstrated that the structural composition of all three is  $R:As_3$  (skutterudite). However, mineralogists have been reluctant to recognize skutterudite fully. Even in the new edition of Dana where the name skutterudite is assigned to the entire group of isometric arsenides, the old terms smaltite, chloanthite, and arsenoferrite are retained, but the iron diarsenide is here considered to be entirely unrelated to this group. Added complications are involved in the recognition of an additional orthorhombic diarsenide of nickel, parammelsbergite (Peacock, 1940) and the determination of monoclinic symmetry for safflorite (Peacock, 1944).

Many other names have been proposed for higher arsenides of this group which later work has shown to be either of doubtful validity or merely varieties of those already mentioned. The prevailing classification and nomenclature of the higher arsenides, is summarized in Table 1 and compared with the revised nomenclature proposed on the basis of the present study.

#### NOMENCLATURE OF THE ISOMETRIC ARSENIDES (SKUTTERUDITE)

The nomenclature of the isometric arsenides has been complicated by a long-held belief in the existence of a dual series, one of diarsenides (smaltite, chloanthite, arsenoferrite) and another of triarsenides (skutterudite, nickel-skutterudite, "iron skutterudite"). The available data on both natural and synthetic material does not support belief in a series of isometric diarsenides of these elements; it establishes the isometric members as essentially triarsenides. This confirms the crystal-structure studies of Oftedal who found that the diffraction data indicated a space group incompatible with a structural composition,  $R:As_2$ . All isometric arsenides of these elements both natural and synthetic observed in the present study gave diffraction patterns of the skutterudite type, hence only a single structure type is involved whose structural formula has been established as  $R:As_3$  (Oftedal, 1926; 1928). Thus, it does not matter how the metal-arsenic ratio varies. Deviations from the theoretical arsenic ratio  $R:As_3$ , shown by published analyses are a consequence either of mechanical inhomogeneity or isomorphous substitution of some sort. In either case the essential character of the mineral is unchanged, remaining fundamentally

a triarsenide of the skutterudite type. Hence all these materials should be regarded as skutterudites regardless of variations in arsenic content.

A nomenclature based on arsenic variation confuses the relationships of what is actually a comparatively simple group. Quantitative analysis alone can establish the arsenic content since the metal-arsenic ratio apparently does not appreciably affect the optical or x-ray diffraction behavior of the isometric arsenides. Furthermore, analyses are significant only when material of established homogeneity is available. Arsenic variations should not be considered as a factor in establishing a system of classification and nomenclature for the isometric arsenide series since, in most cases, it remains an extremely uncertain or even unknown value, and the available evidence indicates that the deviation from the theoretical  $R:As_3$  ratio is much less than the published analyses would suggest. On the other hand the measurable effect that variations in the ratio of the three metals have on the lattice constants makes it possible to determine, without quantitative analyses, and in spite of the widespread inhomogeneity of the material, the approximate cobalt-nickel-iron ratio of an unknown sample in order to classify it according to the system proposed.

Study of a large number of specimens combined with experiments in synthesis and a critical review of published analyses indicates that much of the alleged arsenic deficiency of the isometric arsenides is due to mechanical inhomogeneity. Whether or not the arsenic variation shown by published analyses is due entirely to inhomogeneity or in part to metal for arsenic substitution, the retention of the names (smaltite, chloanthite, and arsenoferrite) seems inadvisable. They have long been associated with alleged isometric diarsenides. Since the nonexistence of an isometric diarsenide series seems well established, neither the retention of these names with their present meanings nor the redefinition of them serves a useful purpose; their retention confuses the nomenclature.

For more than a century the name skutterudite has been associated with the isometric triarsenide of cobalt, and is named after the type locality for this mineral. The triarsenide of cobalt is the most firmly established, and the only monometallic end member of the isometric series known to exist in nature and the only one produced artificially. Appropriately, therefore, this name should be retained for the entire isometric arsenide group.

The isomorphism among the three metals in the isometric series is limited, but continuous, hence it is not possible to subdivide this group except in a purely arbitrary manner. It is essentially a unit with only a single known end member,  $CoAs_3$ . Consequently it seems unnecessary to assign special names to any portion of it.

It is believed that a satisfactory solution to the nomenclatural difficulties of the isometric arsenide series is to assign the name skutterudite to the entire group as already proposed by Peacock and adopted in the new edition of Dana's *System*. On the basis of cobalt-nickel-iron ratio, three subdivisions may then be recognized. The name skutterudite, in a restricted sense, or (cobaltian) skutterudite, preferably the former, would serve for the isometric arsenides in which cobalt is dominant, while the names nickelian skutterudite and ferrian skutterudite would apply to those members in which nickel and iron respectively dominate. This nomenclature

is structurally and chemically sound since all members of the group are essentially triarsenides with the skutterudite structure differing in cobalt-nickel-iron ratio. It has the further merit of simplicity and emphasizes the limited nature of the isomorphism by suggesting the less important character of the nickel- and iron-rich groups. It is believed that there is little justification for the use of more than a single name in cases where an isomorphous series contains only a single known end member. By rejecting the names (smaltite, chloanthite, arsenoferrite, and chathamite) long associated with a series of alleged isometric diarsenides, believed to be non-existent, and substituting the well-established name skutterudite which has at all times been associated with isometric triarsenides, the chemical and structural unity and limited character of the isomorphism of the isometric arsenide group is emphasized.

In a personal communication following the appearance of a preliminary abstract of the present study (Holmes, 1942), Fleischer stated objections to this proposed nomenclature, suggesting the use of individual names for the theoretical end members as follows: skutterudite-cobalt-dominant, chloanthite-nickel-dominant, and chathamite-iron-dominant. Available data on natural and artificial material provides no evidence for the existence of even approximately pure nickel and iron end members. If evidence for the existence of all three end members were at hand, the use of three mineral names would be advisable. Since only a single end member is known to exist, it is believed that the use of a single term with appropriate modifiers gives a clearer picture of the relations.

If separate names were to be employed for the nickel-rich and iron-rich members, objections to those suggested by Fleischer exist. The term chloanthite has been consistently applied for approximately a century to an isometric nickel *diarsenide*, one of the minerals chiefly responsible for the present confused state of the nomenclature of this group. Since valid evidence for the existence of an isometric nickel diarsenide is lacking, it would seem that the elimination rather than redefinition of the term chloanthite is the wisest course, especially since the well-established name nickel skutterudite (Waller and Moses, 1892) is available for isometric arsenides in which nickel is dominant. The name chathamite is objectionable because its origin is of doubtful validity. Shepard (1844) who applied this name to the high iron-nickel-low cobalt arsenide from Chatham, Conn., believed the material to be orthorhombic and later he claimed that he had observed orthorhombic crystals (Shepard, 1857). Similar material from Schladming, St. Andreasberg, and Markirch has been considered orthorhombic by other workers and has been correlated with the Chatham mineral. X-ray data confirms the non-isometric character of the nickel-bearing iron-rich material at these localities. Dana insisted that the Chatham mineral was isometric although he offered no evidence in support of this, and on his authority it is still generally regarded as an iron-rich chloanthite. Since the original author used this name for an orthorhombic mineral whose rhombic character has been amply verified in the present study it seems inappropriate and confusing to retain the name for an isometric material. Fleischer raises the question, "If the term nickelian-skutterudite refers to the mineral with nickel predominating, how is one to label the mineral with Co:Ni-3:2?" If, by

definition, the term skutterudite (*sensu stricto*) or cobaltian skutterudite covers all isometric arsenides in which cobalt dominates, the name of a material with composition Co: Ni-3:2 is automatically cared for.

#### NOMENCLATURE OF THE "ORTHORHOMBIC" ARSENIDES

*General statement.*—The limited and discontinuous character of the isomorphism between the three metals in the "orthorhombic" arsenide series, the reported monoclinic structure of safflorite, and the presence of two orthorhombic forms of  $\text{NiAs}_2$  complicate the nomenclature of this group. The "orthorhombic" arsenides are confined to two isolated groups; a fairly continuous iron-bearing unit is completely separated from the high-nickel group. The complete separation of the two groups is evident in the powder x-ray diffraction effect. Patterns of rammelsbergite and pararammelsbergite are entirely different from those of safflorite and loellingite. The distinction between safflorite and loellingite, however, is difficult; even the diffraction patterns are very similar.

*High-nickel orthorhombic arsenides—rammelsbergite and pararammelsbergite.*—The high-nickel orthorhombic arsenides (see Plates 3 and 4) appear to have a very limited range of composition. The group is complicated by the presence of the two orthorhombic dimorphous forms of nickel diarsenide, rammelsbergite and pararammelsbergite. Since most of the published analyses were made prior to 1940 when pararammelsbergite was first differentiated from rammelsbergite, it is impossible to tell which of these is represented by the published analyses. Without x-ray data, the identity of the analyzed material is open to question although most of the specimens examined in the present study proved to be rammelsbergite. No attempt has been made to prepare any but the pure nickel varieties of rammelsbergite and pararammelsbergite, so little is known of the range of the cobalt-nickel-iron ratio for these minerals from the standpoint of synthesis. However, the analyses of natural material indicate a high nickel ratio for both. This is confirmed by contact-print and microchemical data in which the pararammelsbergite from Cobalt, Ontario, Tilt Cove, Newfoundland, Franklin, New Jersey, and Riechelsdorf in Hesse, and rammelsbergite from many localities all proved to be very high in nickel and low in cobalt and iron.

The name rammelsbergite is retained for the orthorhombic nickel-rich diarsenide of common occurrence represented by the material from the type locality, Schneeberg, Saxony, a locality at which pararammelsbergite has not been observed. The term pararammelsbergite is retained for the material described from the Canadian localities by Peacock and Michener (1939) and observed at three new localities (Franklin, New Jersey; Riechelsdorf in Hesse; and Tilt Cove, Newfoundland) in the present study. The extent to which cobalt and iron substitute for nickel in these two minerals is not known, but on the basis of published analyses and the data from synthesis it appears to be slight. The boundary as drawn on the triangular diagrams probably represents a maximum in this respect.

*Iron-bearing "orthorhombic" arsenides (loellingite and safflorite).*—The high-iron and iron-cobalt "orthorhombic" arsenides occupy a restricted, but essentially con-

tinuous, area in that no wedge of isometric arsenides, natural or artificial, such as separates this series from the high-nickel "orthorhombic" group, cuts across any portion of it. Both minerals were formerly regarded as orthorhombic, and the difficulties encountered in distinguishing between them because of closely similar chemical, physical, optical, and x-ray diffraction properties resulted in a growing tendency to refer to such material as safflorite-loellingite. Holmes (1942) suggested substitution of the term cobaltian-loellingite for safflorite. However, the monoclinic structure of safflorite (Peacock, 1944) requires the recognition of this mineral as a species distinct from loellingite. The line of demarcation between the two must be arbitrary in the absence of data on the extent to which iron can substitute for cobalt in safflorite without affecting the monoclinic symmetry. It is not even clear whether the isomorphism is continuous from the pure iron end to the composition with approximately equal amounts of the two metals. It may be that safflorite and loellingite are two completely isolated groups. Analyses tend to cluster in the vicinity of the iron corner and the mid-portion of the cobalt-iron side of the diagram. However, scattered analyses occur between these two concentrations. It is assumed here that substitution between the two metals in the high-iron portion of the diagram is continuous, and the boundary separating safflorite and loellingite has been arbitrarily placed at the 70 per cent iron line.

**HIGH-IRON ORTHORHOMBIC ARSENIDES-LOELLINGITE:** The available evidence seems to favor the continuity of the entire iron-rich orthorhombic area. The group is a single unit exhibiting continuous, but limited, isomorphous substitution; hence it can be subdivided only arbitrarily. The entire group should be designated by the single name loellingite. The term loellingite (*sensu stricto*) or (ferrian) loellingite, preferably the former, is applicable to the members with an iron ratio greater than 85 per cent. Varieties with an iron ratio less than 85 per cent, in which cobalt is dominant over nickel, can be termed cobaltian loellingite, and the corresponding group, in which nickel is dominant over cobalt, nickelian loellingite.

The high-iron orthorhombic arsenides, loellingite, or (ferrian) loellingite was not distinguished from arsenopyrite until the latter part of the 18th century. Hintze (1904) credits Jameson with the separation of the iron diarsenide from the sulpharsenide. Jameson (1820) credited Moh with having called his attention to the essential difference between the two. However it is clear that such a distinction was recognized approximately a half century earlier and seems to have been overlooked by later writers, since Kirwan (1784) distinguishes *Mispickel*, *Speiss* of the Bohemians, mineralized by arsenic only (present loellingite) from white pyrites, *Giftkies*, *Arsenic Stein*, mineralized by sulphur and arsenic (present arsenopyrite). Many names were applied to materials, during the nineteenth century, which were later shown to be varieties of loellingite. Only one of these will be discussed here. Shepard (1835) applied the name leucopyrite to the common iron arsenide, and 10 years later Haidinger (1845) assigned the name *Löllingit* to the material from Lölling in Styria. Both names have persisted in the literature and have caused much confusion. The marked arsenic deficiency of the natural iron arsenide from many localities has given rise to the belief that two minerals are involved. In the first four editions of Dana's *System of Mineralogy* (1837; 1844; 1850; 1854), the term leucopyrite alone occurs, and the composition is said to be  $\text{FeAs}_2$ . In the fifth edition (1868) both leucopyrite ( $\text{FeAs}_2$ )

and löllingite ( $\text{FeAs} \cdot \text{FeAs}_2$ ) are recognized. In the appendix to the fifth edition this nomenclature is reversed; the term löllingite is assigned the formula  $\text{FeAs}_2$ , and leucopyrite ( $\text{FeAs} \cdot \text{FeAs}_2$ ). In the sixth edition (1892) only a single species, löllingite ( $\text{FeAs}_2$ ), is recognized; leucopyrite is regarded as a subspecies. Belief in the existence of a compound or "molecule" whose arsenic content is lower than  $\text{FeAs}_2$  has persisted up to the present. Bauer and Berman (1928) account for the arsenic deficiency of the Franklin loellingite by assuming the presence of a "leucopyrite molecule", and Short (1940, p. 161) places leucopyrite on an equal basis with loellingite and assigns it the composition  $\text{Fe}_3\text{As}_4$ .

Buerger (1932) showed that the diffraction pattern of the Franklin material indicates the presence of only a single phase with a structure based on a space group compatible with a composition  $\text{RAs}_2$ . On the basis of Buerger's work the term leucopyrite has been abandoned in the new seventh edition of Dana's *System* as representing a "nonexistent material". The data obtained in the present study on numerous specimens from many localities confirm Buerger's work on the Franklin mineral in showing that only a single component is present, providing diffraction patterns in essential agreement with those of the loellingite from Franklin and the type locality at Lölling in Styria. From this it would seem that the deviations in arsenic ratio in the natural iron arsenides are a consequence of metal for arsenic substitution as suggested by Buerger (1934). The situation is analogous to that of the isometric arsenides in which it has long been assumed that two distinct minerals, skutterudite ( $\text{CoAs}_3$ ) and smaltite ( $\text{CoAs}_2$ ), have existed. In both cases there is only a single compound involved (in each the one with higher arsenic content), hence there is no justification for the retention of the names applied to the materials with lower arsenic content whose existence as valid species is not verified by the available evidence. In the isometric arsenides the arsenic deficiency is in large part a consequence of mechanical inhomogeneity possibly further reduced by metal for arsenic substitution. In the case of the orthorhombic iron arsenides, metal for arsenic substitution must be the principal cause as no natural iron arsenide is known with an arsenic ratio lower than  $\text{R}:\text{As}_2$ .

The name leucopyrite, (Shepard, 1835) has priority over loellingite (Löllingit, Haidinger, 1845), but the latter has been consistently applied to the orthorhombic diarsenide of iron for so long that less confusion would result from the retention of this name, in preference to leucopyrite. No evidence was obtained in the present study for the existence of an iron arsenide structurally different from loellingite in the numerous natural specimens examined. Diffraction patterns of iron arsenides from the various localities are essentially alike although they exhibit some variation which may be correlated with variations in arsenic ratio, but this has not been verified. Since the structural composition established by Buerger is  $\text{FeAs}_2$ , and since the term loellingite has been applied to this mineral for a long period, this name alone should be retained. In keeping with the recommendation of the "Committee on Nomenclature"; the spelling loellingite rather than "löllingite" should be followed.

The name cobaltiferous loellingite was used by Hoffman (1895) for a loellingite with 9.7 per cent cobalt. This term, in the form of cobaltian loellingite modified in keeping with Schaller's suggestion concerning mineral nomenclature (Schaller,

1930), is used here as the name for orthorhombic arsenides with an iron ratio lower than 85 per cent and cobalt dominant over nickel. Six analyses fall in this area, and two others are practically on the loellingite-cobaltian loellingite boundary. The extent to which cobalt can replace iron in these orthorhombic iron-cobalt arsenides without reducing the symmetry to monoclinic is not known. The boundary between cobaltian loellingite and safflorite has been arbitrarily placed at the 70 per cent iron line.

The corresponding iron-nickel-low cobalt orthorhombic members (nickelian loellingite; chathamite of Shepard) are represented by few analyses. Four of the six analyses believed to represent this mineral group were made on material which the original authors considered to be orthorhombic. Two of these were called chathamite, one rammelsbergite, and one *Arsenikeisen*. Two additional analyses have been made on material from Chatham, considered to be isometric (iron-bearing chloanthite) by the analyst (Genth, 1854).

Chathamite was originally described by Shepard (1844) as an orthorhombic mineral distinct from the isometric smaltite-chloanthite group. Shepard (1857) reported orthorhombic crystals of this mineral similar in form and habit to those of arsenopyrite. Nevertheless, Dana in all editions of the *System* refused to accept the Chatham mineral as orthorhombic; he consistently regarded it as an iron-bearing chloanthite, and it is so described in the new seventh edition. Dana's stand appears to be based on Genth's statement that the Chatham mineral was a chloanthite. However, Genth admits in the original paper that the analyzed material was "massive granular," hence he had no basis for assuming it to be isometric rather than orthorhombic. Similar iron-nickel-low cobalt material has been described from St. Andreasberg in the Harz (Kobell 1868), Markkirch in Alsace (Dürr, 1907), and Schladming, Styria (Hoffman, 1832) as orthorhombic, and the similarity to chathamite from Chatham, Conn., was noted in the first two cases.

Eight specimens of chathamite from Chatham, Connecticut, were examined during the present study. No isometric arsenide was observed, but in each specimen the principal constituent was an anisotropic arsenide giving strong iron and nickel and weak cobalt reactions confirming Shepard's contention that the white arsenide from Chatham is a nonisometric mineral. The diffraction patterns of this material are in agreement with each other and are of the loellingite type. They agree with those of pure iron diarsenide more closely than do those of safflorite. The specimens from St. Andreasberg and Schladming give similar contact-print reactions and diffraction patterns of the same type, but differ slightly in spacing when compared with patterns of the Chatham material. Since the material from the type locality is nonisometric, as the original author contended it to be, it would seem that the name chathamite should be suitable for this group of orthorhombic arsenides. However, the name has been associated for so long with an isometric arsenide (iron-bearing chloanthite) that a return to its original meaning would add to confusion. Neither should the term chathamite be applied to an isometric arsenide since it was originally defined as the name of an orthorhombic material, and the nonisometric character of material from the type locality has been confirmed in the present study.

The apparent continuity of the nickelian loellingite area with that of the essen-

tially pure iron diarsenides (loellingite), removes any justification for the use of a specific name for this group. The limits separating this group from loellingite and from cobaltian loellingite are purely arbitrary. It is believed that the composition structure and relationships of this group are best expressed by the application of the name nickelian loellingite which is defined as an orthorhombic arsenide with an iron ratio less than 85 per cent and nickel dominant over cobalt.

**IRON-COBALT MONOCLINIC ARSENIDES—SAFFLORITE:** It has been assumed that there exists a pure cobaltorthorhombic arsenide, and the term safflorite has been widely and consistently used as the name of the cobalt end member of an allegedly unlimited isomorphous series of orthorhombic arsenides; the other end members are rammelsbergite and loellingite. However, no analyses of an "orthorhombic" arsenide with a cobalt ratio higher than 81.8 and only two with a cobalt ratio higher than 64.9 have been reported. This mineral was not recognized as distinct from *Speiskobalt* until Breithaupt (1835) established the *Faserigen Weissen Speiskobalt* as *wohl rhombisch* and assigned it the name *Safflorit*. The mineral has been known by other names such as *Eisenkobaltkies*, *Arsenkobalteisen*, *Eisenspeiskobalt*, and *Eisenkobalterz*, which clearly indicate the dominant or essential part iron plays in its composition.

The evidence from various sources points to the nonexistence of a pure cobalt "orthorhombic" arsenide. The data on published analyses offer no valid evidence for the existence of "orthorhombic" arsenides with a cobalt ratio much greater than 75 per cent. The two "orthorhombic" arsenides with a cobalt ratio greater than 64.9 are admittedly inhomogeneous with a fictitious high cobalt ratio. Not only do these cobalt-iron "orthorhombic" arsenides fail to reach the cobalt end of the diagram, but they are remarkable for their low nickel content. The nickel ratio in no case exceeds 6.2 per cent.

The name safflorite, as used here, applies to the iron-cobalt "orthorhombic" arsenides with approximately equal proportions of the two metals. Although there is a clustering of analyses of "orthorhombic" arsenides in the middle portion of the cobalt-iron side of the triangle, there are scattered analyses of these minerals over a considerable range on either side of the mid-point. Peacock (1944) has shown that the safflorite from Nordmark, Sweden, cobalt-nickel-iron ratio 44.3-.7-55.0 is monoclinic with rectangular axes. This is a safflorite with nearly equal amounts of cobalt and iron. How far the proportions of the two metals can deviate from equality without destroying the monoclinic symmetry is not known.

In the absence of available data on the extent of cobalt-iron substitution in these monoclinic arsenides the boundary between cobaltian loellingite and safflorite has been placed arbitrarily at the 70 per cent iron line. The cobalt limit has been drawn just beyond the 70 per cent cobalt line, embracing all but two of the known analyses of cobalt-rich "orthorhombic" arsenides.

*Use of hyphenated names for the "orthorhombic" arsenides.*—It has become common practice especially since the advent of the polarizing reflecting microscope to refer to an anisotropic arsenide for which no analysis is available as "safflorite-rammelsbergite," "safflorite-loellingite," or "a member of the safflorite-rammelsbergite

series". It is apparent that the use of these hyphenated terms involving the name rammelsbergite is in error since the rammelsbergite group is clearly distinct and separate from the iron-bearing orthorhombic arsenides, the isomorphism being discontinuous. Since the isomorphism is discontinuous, there is no such thing as a "safflorite-rammelsbergite" or "safflorite-rammelsbergite series". The tendency to use such terms as safflorite-loellingite indicates the lack of a clean-cut distinction between the minerals of these two groups. However, the recognition of the monoclinic character of safflorite precludes the use of such a hyphenated term for the members of the safflorite and loellingite groups.

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