

Co-Ni-Fe DIARSENIDES: COMPOSITIONS
AND CELL DIMENSIONS¹EUGENE H. ROSEBOOM, *U. S. Geological Survey, Washington, D. C.*²

ABSTRACT

Analyses of natural Co-Ni-Fe diarsenides have indicated two distinct compositional groups: the rammelsbergites (and pararammelsbergites), which are nickel-rich, and the loellingite-safflorite series, which are nickel-poor. The synthetic diarsenides show extensive solid solution at 800° C. A solvus interrupts the FeAs₂-NiAs₂ series near the NiAs₂ end and extends into the ternary solid solution toward CoAs₂. This solvus probably interrupts the NiAs₂-CoAs₂ series at temperatures well below 800° C. and hence explains the separation of rammelsbergites from the loellingite-safflorite series in nature.

At 800° C., synthetic rammelsbergite appears to be stoichiometric with the formula NiAs_{2.00}. Loellingite is homogeneous from FeAs₂ to FeAs_{1.98}. Homogeneous cobalt safflorite was made with the compositions CoAs_{1.99} and CoAs_{1.98} and appears to have monoclinic symmetry, in contrast to rammelsbergite and loellingite which are orthorhombic. Although the cell edges of the Co, Ni, Fe diarsenides vary as complex functions of the composition, the cell volumes vary as a linear function.

The cell edges of nine analyzed specimens of loellingite and safflorite show fair agreement with synthetic diarsenides of equivalent composition, after corrections are made for the effect of nickel and sulfur on the cell edges.

INTRODUCTION

In the course of an investigation of part of the system Co-Ni-Fe-As (Roseboom, 1957, 1958, 1959), the cell edges and composition ranges of synthetic triarsenides and diarsenides were determined. The triarsenides (skutterudites) were discussed in a previous paper (Roseboom, 1962). The data on the synthetic diarsenides and their correspondence to data for the natural diarsenides are the subject of the present paper.

The arsenides, of Co, Ni and Fe exhibit a wide range of solid solution. Figure 1 illustrates the nomenclature and the approximate extent of Co, Fe and Ni substitution in the diarsenides and triarsenides. The most recent and complete classification of the diarsenides of Co, Ni and Fe is that of Holmes (1947) which will be followed in this paper. In this classification, the nickel-rich diarsenides are the dimorphs, rammelsbergite and pararammelsbergite. The iron-rich diarsenides are called loellingite. Cobalt-iron diarsenides with a Co:Fe ratio of about 1:1 are called safflorite. Holmes arbitrarily placed the boundary between safflorites and loellingites at 70 mol per cent FeAs₂.

In addition to the Co, Ni and Fe substitutions, various workers have reported diarsenides with less arsenic than that required by the theo-

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² This work was begun at Harvard University as part of a Ph.D. thesis and continued at the Geophysical Laboratory, Carnegie Institute of Washington.

retical composition. For this reason the range of arsenic content in some synthetic diarsenides was also investigated.

No work was done on parammelsbergite, the low-temperature dimorph of rammelsbergite. Yund (1961) has investigated the parammelsbergite-rammelsbergite transition in detail.

ARSENIC CONTENT OF SYNTHETIC DIARSENIDES

Synthesis. The materials used and details of the experimental techniques have been discussed in a previous paper (Roseboom, 1962). In addition, spectrographic analyses are given by Swanson *et al.* (1960) of CoAs_2 , FeAs_2 , NiAs_2 and $(\text{Co}_{0.5}\text{Fe}_{0.5})\text{As}_2$ synthesized by Roseboom.

The maximum arsenic content of Ni diarsenide and Fe diarsenide was investigated by means of "tube-in-tube" runs. In these runs, iron or nickel was placed in a small open tube within the larger sealed tube. The larger tube contained sufficient arsenic to maintain a vapor phase in equilibrium with solid arsenic. The amount of arsenic that reacted with the iron or nickel was determined from the increase in weight of the inner tube. The sample was reground and the process repeated until a constant composition was obtained. Homogeneity of the phase was confirmed by means of the ore microscope.

The maximum arsenic content of Co diarsenide could not be deter-

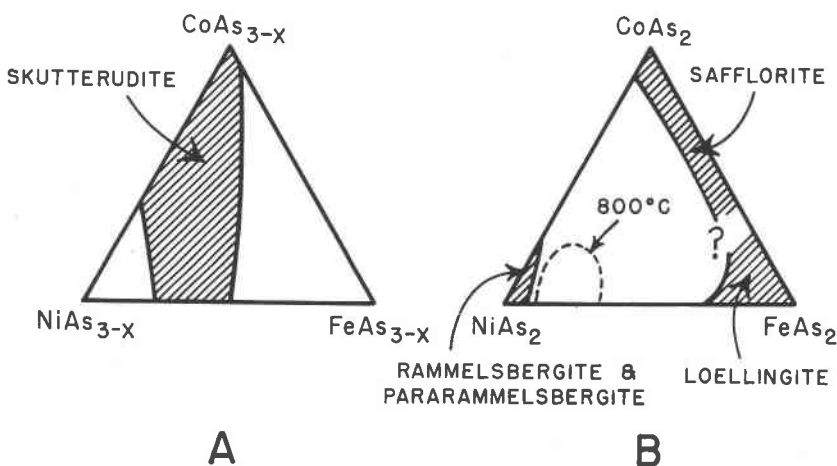


FIG. 1 (A). The extent of Co, Ni, and Fe substitution in synthetic skutterudite solid solution at 800° C. is shown by shading. Almost all analyzed natural skutterudites fall in or close to the shaded area.

FIG. 1 (B). The approximate extent of Co, Ni and Fe substitution in the natural diarsenides is shown by shading. At 800° C. the solid solutions cover all of the triangle except for an area approximately that shown by dashed lines.

mined in this manner because it is not stable in the presence of crystalline arsenic. Instead, samples of different arsenic content were annealed and the products examined to see whether or not any cobalt skutterudite (CoAs_{3-x}) was present. When cobalt skutterudite appeared in the sample, the arsenic content of the sample was greater than the maximum arsenic content of Co diarsenide.

The minimum arsenic content of Co, Ni and Fe diarsenides were determined in the same way as the maximum arsenic content of Co diarsenide. In this case, the presence of the monarsenide indicated when the arsenic content of the sample was less than the minimum arsenic content of the diarsenide.

Although pure Co and Fe diarsenides could be synthesized readily at 800°C ., some difficulty was experienced in forming homogeneous rammelsbergite. Niccolite (NiAs) formed first and then reacted with arsenic to make rammelsbergite. This resulted in grains with niccolite cores armored by rammelsbergite crystals. Similar inhomogeneity in synthetic Ni arsenides had been noted previously by Beutell (1916), Holmes (1947), and Heyding and Calvert (1960). In the present study, a single regrinding and reheating produced a homogeneous rammelsbergite, except for one very large sample which required additional grinding. In samples with arsenic in excess, a second regrinding and reheating caused no further increase in arsenic content of the rammelsbergite.

Range of arsenic content. The range in arsenic content for loellingite at 800°C . is at least $\text{FeAs}_{1.980\pm 0.002}$ to $\text{FeAs}_{2.000\pm 0.001}$. Three "tube-in-tube" runs with iron in the inner tube produced loellingite with the composition $\text{FeAs}_{1.995\pm 0.001}$ after 12 days, $\text{FeAs}_{2.001\pm 0.001}$ after 19 days, and $\text{FeAs}_{1.999\pm 0.001}$ after 27 days, respectively. The last of these was reground and heated for another 12 days with no further change in weight. Runs of $\text{FeAs}_{1.990\pm 0.002}$ and $\text{FeAs}_{1.980\pm 0.002}$ produced homogeneous loellingite, but runs of $\text{FeAs}_{1.970\pm 0.002}$ and lower in arsenic produced loellingite and an iron monarsenide phase. The limits on all of these compositions are based on the precision with which the samples could be weighed. Examination of polished sections of samples under the polarizing microscope would probably have detected one part in 10,000 of a second crystalline phase.

Heyding and Calvert (1960) sublimed excess arsenic from an alloy-arsenic mixture in the Fe-As system at 400°C . The final composition corresponded to $\text{FeAs}_{1.98}$. Assuming that their final product was completely homogeneous, this indicates that at lower temperatures a greater deviation from stoichiometric proportions is possible than at 800°C .

Rammelsbergite was found to be stoichiometric within the limits of errors of the investigation. "Tube-in-tube" runs with nickel in the inner tube contained niccolite armored by rammelsbergite crystals after 19

days at 800° C. Regrinding and six more days of heating at 800° C. gave compositions of $\text{NiAs}_{1.998 \pm 0.001}$, $\text{NiAs}_{1.999 \pm 0.001}$, and $\text{NiAs}_{2.001 \pm 0.001}$. A third grinding and seven more days of heating at 800° C. gave $\text{NiAs}_{1.999 \pm 0.001}$, $\text{NiAs}_{1.993 \pm 0.001}$, and $\text{NiAs}_{1.995 \pm 0.001}$, respectively, for the same three runs. Polished sections indicated that these runs were homogeneous. A large run containing almost a gram of Ni after two regrindings and reheatings had combined with more than 2 grams of arsenic to give a composition of $\text{NiAs}_{1.9993 \pm 0.0005}$. A simple sealed tube containing material of the composition $\text{NiAs}_{2.000 \pm 0.002}$ resulted in only rammelsbergite after two regrindings. A run of $\text{NiAs}_{1.990 \pm 0.002}$ and runs lower in arsenic content, after two regrindings and reheatings, still contained rammelsbergite and niccolite. Thus rammelsbergite is very near NiAs_2 in composition.

As explained above, simple sealed tubes were used for determining both maximum and minimum arsenic content of Co diarsenide. Runs of $\text{CoAs}_{1.990 \pm 0.002}$ and $\text{CoAs}_{1.930 \pm 0.002}$ compositions produced a single homogeneous phase. A run of $\text{CoAs}_{2.000 \pm 0.002}$ produced a diarsenide plus a trace of skutterudite while runs of $\text{CoAs}_{1.960 \pm 0.002}$ and lower arsenic content produced a diarsenide phase plus a cobalt monarsenide phase.

No change in d-values with the variation in arsenic content of loellingite could be detected. Four specimens of loellingite, one made with excess crystalline arsenic present, two with compositions of $\text{FeAs}_{1.99}$ and $\text{FeAs}_{1.98}$, and one sample with both loellingite and a trace of an iron monarsenide phase present, were measured as described in the section on x-ray measurements. The (120), (101), (210), and the (111) d-values were measured. If any systematic variation in d-value with arsenic content exists, it is too small to be detected when superimposed upon the random errors in measurement. Heyding and Calvert (1960) were also unable to detect any variation in d-values with arsenic content in loellingites.

Co:Ni:Fe RATIOS OF SYNTHETIC DIARSENIDES

Synthesis. Homogeneous Co-Fe and Fe-Ni diarsenide solid solutions were made from the elements or from mixtures of the end-member phases at 800° C. in runs ranging from 60 hours to 36 days. The Co-Ni diarsenide phases required one or two regrindings and reheatings before homogeneous phases were produced. Care was taken to keep the mechanical loss of material as small as possible. Because the samples were fine-grained mixtures of phases which were similar in their physical properties, any material that was lost would probably be of about the same composition as the bulk of the sample. Because of the difficulty mentioned above in making rammelsbergite, runs of CoAs_2 mixed with NiAs_2 produced homogeneous solid solutions more readily than the corresponding mixtures of pure elemental phases and were used throughout the Co-Ni

diarsenide series. Even in these runs, cobalt-rich skutterudite and niccolite formed metastably along with the stable Co-Ni diarsenide solid solution. With regrinding and reheating the skutterudite and niccolite first diminished and then disappeared. The diarsenide peaks did not change in position as the amounts of skutterudite and niccolite diminished. Thus the composition of the diarsenide should be about the same, whether or not a small amount of skutterudite and niccolite remained undetected.

Range in Co:Ni:Fe ratios. At 800° C there is extensive substitution of Co, Ni, and Fe among the diarsenides. Complete solid solution series exist between CoAs_2 and NiAs_2 and between CoAs_2 and FeAs_2 . The series between NiAs_2 and FeAs_2 is interrupted by a solvus, which probably extends into ternary compositions as shown in Fig. 2.

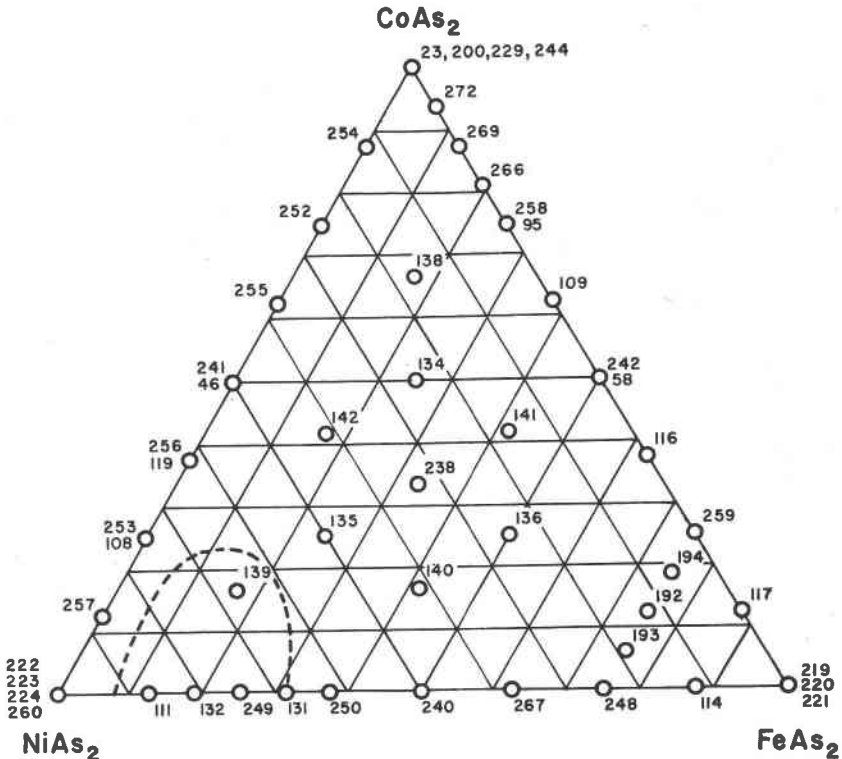


FIG. 2. Compositions investigated in the system CoAs_2 - NiAs_2 - FeAs_2 . Circles indicate composition of samples. Numbers correspond to sample numbers used in the text and in Table 2. The dashed line indicates the possible extent of the solvus at 800° C. The solvus is known to $\pm 1.0\%$ on the NiAs_2 - FeAs_2 side but its shape is only guessed at from the fact that d-values of two diarsenides appear in sample 139. The d-values of all other samples indicated a continuous solid solution outside of the solvus.

The evidence for the existence of the solid solution series consists of the fact that the dimensions of the interplanar spacings (and consequently the cell edges) are smooth and apparently continuous functions of composition. In Fig. 3, the d -values of the (120), (101), (210), and (111) x -ray diffraction peaks are plotted as a function of composition for the three binary series. The solid solution series between CoAs_2 and NiAs_2 and between CoAs_2 and FeAs_2 are complete as shown by the continuous change in d -values with composition. In the series between NiAs_2 and FeAs_2 , the d -values change continuously from 100 per cent FeAs_2 to 31 per cent FeAs_2 . Beyond this point, the d -values remain unchanged but the intensities of the diffraction peaks decrease toward NiAs_2 . In addition, the peaks of a different phase appear and increase in intensity toward NiAs_2 but have a constant d -value. If the curves of d -values versus composition are extrapolated from 31 per cent FeAs_2 to 100 per cent NiAs_2 as shown in Fig. 3, the d -values of the second phase would intersect them at about 7.5 per cent FeAs_2 .

The break in the NiAs_2 - FeAs_2 series at 800°C . was found to be smaller at 850°C . and wider at 750°C . Samples from the two-phase region were reheated at 750°C . and 850°C . for 18 days and 7 days, respectively. The

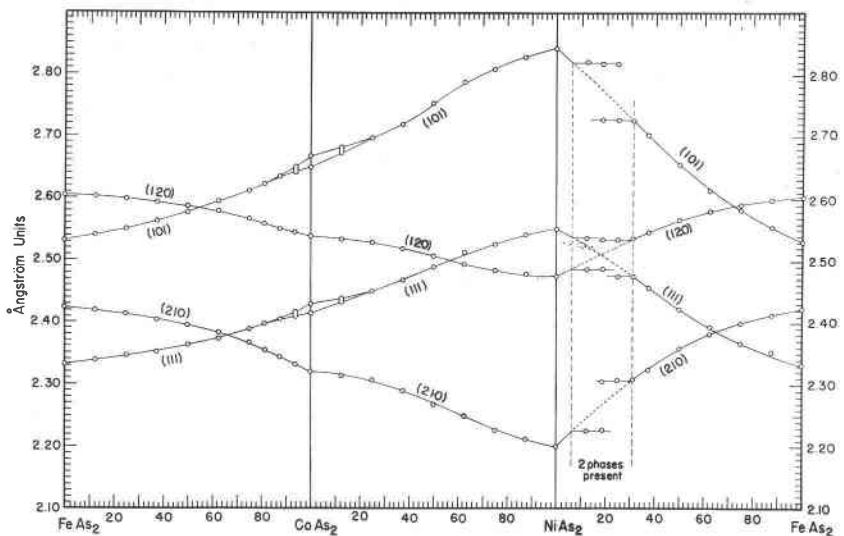


FIG. 3. The effect of composition on the (101), (111), (120), and (210) d -spacings of the Fe-Co, Co-Ni, and Ni-Fe diarsenides. Near CoAs_2 the (111) line splits into (111) and ($\bar{1}\bar{1}\bar{1}$) and the (101) line splits into (101) and ($\bar{1}\bar{0}\bar{1}$) as the symmetry changes from orthorhombic to monoclinic. Between NiAs_2 and FeAs_2 there is a two-phase region where rammelsbergite coexists with Ni-rich loellingite. All samples were heated at 800°C . and quenched. Compositions are in mol per cent.

d-values in the 750° C. sample correspond to two phases, one at 6.5 per cent FeAs₂ and the other at 33 per cent FeAs₂. The d-values in the 850° C. samples corresponded to a phase with the composition 8.5 per cent FeAs₂ and 26 per cent FeAs₂.

The fact that the extent of solid solution increased with rising temperature on both sides of the break in the series suggests to the writer a solvus rather than a transition loop. By projection, the crest of the solvus should lie near 900° ± 25° C. and 15 ± 5 mol per cent FeAs₂, the solid solution being complete above this temperature.

From the extensive solid solution in the binary systems, one would expect that at 800° C. there is also extensive solid solution among diarsenides containing all three metals, cobalt, iron, and nickel. The compositions shown in Fig. 2 were investigated. Homogeneous diarsenides were obtained from runs with the following ratios of Co:Ni:Fe: Run 238, 1:1:1; Run 192, 3:3:14; Run 193, 3:9:28; Run 194, 9:3:28. The last three were synthesized in the presence of solid arsenic. In addition, preliminary x-ray examination of seven other ternary compositions shown in Fig. 2 indicated a single diarsenide and a small amount of unreacted skutterudite. These ternary diarsenides also indicated a smooth change in d values with composition. Had these runs been reground and reheated, they would probably have also produced homogeneous diarsenides. Because of the solvus in the NiAs₂-FeAs₂ series, one would not expect every ternary composition to produce a homogeneous diarsenide. One run (No. 139) with a ratio of 1:4:1 produced two diarsenides not very different in d-values from those on the solvus in the series NiAs₂-FeAs₂. Thus the solvus extends at least beyond that composition toward the CoAs₂-NiAs₂ sideline.

X-RAY CRYSTALLOGRAPHY

Structures and space groups. All the Co, Ni, Fe diarsenides, with the exception of pararammelsbergite, probably possess the marcasite structure (C18 type) or some slight distortion of it. Buerger (1932) determined that loellingite had a marcasite structure with space group *Pnmm* (in the orientation used here). Peacock (1941) confirmed this space group and Peacock and Dadson (1940) found the same space group for rammelsbergite. Kaiman (1946) confirmed this space group for rammelsbergite and reported that it, like loellingite, had a marcasite structure.

Because complete solid solution series extend from NiAs₂ to CoAs₂ and from FeAs₂ to CoAs₂, CoAs₂ is almost certain to be isostructural with rammelsbergite and loellingite and thus have a marcasite structure also. In the case of CoAs₂ however, the marcasite structure is apparently distorted enough to change the orthorhombic symmetry to monoclinic.

Quesnel and Heyding (1962) report a space group of $P2_1/c$ for CoAs_2 (which would transform to $P2_1/n$ for the unit cell used in the present paper).

Peacock (1944) studied Weissenberg photographs of a natural safflorite intermediate in the CoAs_2 - FeAs_2 series and found the space group to be $P2/m$. He reported that it had monoclinic symmetry but with a β angle of 90° . The structure was probably analogous to that of loellingite and the lower symmetry was due to iron and cobalt not occupying equivalent sites. Berry and Thompson (1962, p. 129) noted that Peacock detected interplanar spacings which should be absent with space group $Pnmm$ and these spacings produce lines too weak to be observed by means of x -ray powder methods.

X-ray measurements. For measurements on the diarsenides, four of the strongest x -ray diffraction peaks were used: the (120), (101), (210), and (111) peaks. These four were chosen because they could be accurately measured for all compositions in the solid-solution series. All four peaks were between 30° and $41^\circ 2\theta$ for Cu radiation. The dimensions of the unit cells were calculated from the (120), (101), and (210) peaks. Different internal standards had to be used for different compositions to prevent diarsenide peaks from overlapping the peaks of the internal standards. The CoAs_2 - FeAs_2 series and the iron-rich half of the FeAs_2 - NiAs_2 series were run on the diffractometer at $\frac{1}{4}$ degree per minute, with quartz as an internal standard. The CoAs_2 - NiAs_2 series and the nickel-rich remainder of the FeAs_2 - NiAs_2 series were run at $\frac{1}{2}$ degree per minute, using either silicon or sodium chloride as an internal standard, the choice depending on the spacings in the individual cases. The cell edges used for the internal standards were those given by Parrish (1953) and are as follows: silicon (5.43062 Å), sodium chloride (5.63937 Å), quartz ($a=4.9131$ Å $c=5.4064$ Å). Two measurements were made on each line, one with the goniometer driving toward high 2θ angles and one with the goniometer driving toward low 2θ angles. The probable precision of measurement is discussed in the section titled "Cell edges and volumes of solid solutions."

Cell edges of CoAs_2 , NiAs_2 and FeAs_2 . X -ray data for the diarsenides show good agreement for the Co, Ni and Fe end-members. Table 1 summarizes the cell-dimension data for diarsenides in the literature for comparison with the results of the present work. The earliest work is that of de Jong (1926), who claimed that the patterns of loellingite, rammelsbergite and safflorite were identical. He gave a single set of lattice constants which failed to agree with those of subsequent workers on the three minerals. The cause of this discrepancy is unknown.

Peacock and Michener (1939) presented x -ray data for what they believed to be rammelsbergite. Later, however, Peacock and Dadson

TABLE 1. CELL DIMENSIONS (IN Å) OF RAMMELSBERGITE, LOELLINGITE, SAFFLORITE, AND COBALT DIARSENIDE

Reference	a	b	c	Material
Rammelsbergite—NiAs ₂				
deJong (1926)	4.87	5.81	6.36	Natural
Peacock and Dadson (1940)	4.79	5.79	3.54	Natural
Yund (1961)	4.757	5.793	3.544	Synthetic
Heyding and Calvert (1960)	4.76	5.79	3.54	Synthetic
Swanson <i>et al.</i> (1960)	4.759	5.797	3.539	Synthetic
Present work	4.755 ± 0.003	5.801 ± 0.004	3.542 ± 0.003	Synthetic
Loellingite—FeAs ₂				
deJong (1926)	4.87	5.81	6.36	Natural
Buerger (1932)	5.26	5.93	2.85	Natural
Peacock (1941)	5.29	5.98	2.87	Natural
Heyding and Calvert (1960)	5.300	5.982	2.882	Synthetic
Swanson <i>et al.</i> (1960)	5.300	5.983	2.882	Synthetic
Berry and Thompson (1962)	5.3023	5.9818	2.8802	Natural
Present work	5.301 ± 0.004	5.979 ± 0.005	2.882 ± 0.002	Synthetic
Cobalt Diarsenide—CoAs ₂				
Rosenqvist (1943)	5.08	5.89	3.10	Synthetic
Heyding and Calvert (1960)	5.005 ¹	5.87	3.11 ¹	Synthetic
Swanson <i>et al.</i> (1960)	5.047	5.872	3.127 ($\beta=90^{\circ}51'$)	Synthetic
Quesnel and Heyding (1962)	4.894 ²	5.885	3.167 ² ($\beta=90^{\circ}32'$)	Synthetic
Present work	5.051 ± 0.002	5.873 ± 0.002	3.127 ± 0.001 ($\beta=90^{\circ}27'$)	Synthetic

All measurements prior to 1946 were changed from kX units into Ångstrom units. Orientations are not always those of original papers but follow the recommendations of Buerger (1937). Measurements by Swanson *et al.* (1960) were made on materials synthesized by Roseboom. The \pm values for NiAs₂ and FeAs₂ are standard deviations as described in the text. The \pm values for CoAs₂ are standard errors of the means for four samples.

¹ These values are one-half the values given by Heyding and Calvert (1960) in their original paper.

² The original values of Quesnel and Heyding (1962) are $a=5.805$, $b=5.885$, $c=5.853$, $\beta=114^{\circ}11'$. Their cell can be transformed to that used by the writer by means of the matrix $(\bar{1}01/010/101)$.

(1940) compared these data with authenticated rammelsbergite from Iisleben and Schneeberg, Germany, and concluded that the material described in 1939 was actually an NiAs₂ polymorph which they named parammelsbergite. The measurements of Yund (1961), Heyding and Calvert (1960), and Swanson *et al.* (1960) on synthetic NiAs₂ are all within two standard deviations of the value obtained by the writer.

Buerger (1932) analyzed the structure of loellingite, and gave the cell edges listed in Table 1 for natural loellingite from Franklin, New Jersey. Peacock (1941) gave d-values and cell dimensions for a natural loellingite also from Franklin, New Jersey. Berry and Thompson (1962) gave cell edges on Franklin loellingite redetermined by R. J. Traill. These plus the measurements of Heyding and Calvert (1960) and Swanson *et al.* (1960) on synthetic material are all within two standard deviations of the value obtained by the writer.

Co diarsenide is apparently monoclinic. T. R. Rosenqvist (1953) in reporting the data of A. M. Rosenqvist (1943) gave only the cell edges which are listed in Table 1. Heyding and Calvert (1960) indexed CoAs₂

on the basis of an orthorhombic cell with the a and c edges (c and b in the orientation in the original paper) approximately twice those of the monoclinic cell. By using the larger orthorhombic cell, they obtained additional hkl 's to account for the lines which could not be explained by a smaller orthorhombic cell. However, even this larger cell only provided one hkl for the very strong line at 2.41 Å. This line, which they reported as broad, is actually two distinct lines as shown in Fig. 3. Swanson *et al.* (1960), starting with monoclinic cell dimensions given by the writer (Roseboom, 1958) indexed a sample of the writer's synthetic CoAs_2 and obtained the values given in Table 1. Quesnel and Heyding (1962) indexed CoAs_2 by direct comparison of the five or six strongest lines with RhP_2 and RhSb_2 . This produced a monoclinic cell which is related by a simple transformation matrix $(10\bar{1}/010/101)$ to the cell of Swanson *et al.* (1960) and the writer. Swanson *et al.* (1960) indexing accounts for all of the observed lines except six very weak ones. Quesnel and Heyding observed two of these six lines, their $(10\bar{2})$ and $(21\bar{3})$ lines. These indices transform by means of the above matrix to $(3/2\ 0\ \bar{1}/2)$ and $(5/2\ 1\ \bar{1}/2)$ which suggests that perhaps the a and c axes given in Table 1 should be doubled. However, the smaller cell of Swanson and the writer will be used in this paper to facilitate comparisons with the orthorhombic diarsenides. This cell is similar to the cells of the orthorhombic diarsenides but is slightly distorted ($\beta = 90^\circ 27'$). Unfortunately, no crystals of CoAs_2 suitable for single crystal studies were synthesized during the present study.

The present study indicates that although the Co-rich diarsenides are probably monoclinic, they form a complete solid solution with the orthorhombic Ni and Fe diarsenides at 800°C . The evidence for this was found in the solid solution series between FeAs_2 and CoAs_2 and between NiAs_2 and CoAs_2 . In both series, the (101) and the (111) peaks were observed to split into two peaks of equal intensity near the cobalt end of the series as shown in Fig. 3 and Table 2. In x -ray powder photographs of cobalt safflorite, the (101) and the (111) line each appeared as a single broad and somewhat diffuse line. However, with the x -ray diffractometer, split peaks of about equal intensity were clearly observed. One can interpret this splitting of lines as a degeneration of the orthorhombic cell to a monoclinic cell. Such a symmetry change would cause all peaks with the indices $(h0l)$ and (hkl) to split into $(h0l)$ and $(\bar{h}0l)$, (hkl) and $(\bar{h}kl)$, respectively. Thus the (101) peak of the orthorhombic phases would split into the (101) and $(\bar{1}01)$ peaks, and the (111) peak would split into the (111) and $(\bar{1}11)$. The size of the observed split would correspond to a β angle of about $90^\circ 27'$ for CoAs_2 . The accuracy of this figure for the β angle is uncertain due to the overlapping of the split peaks on the diffractom-

TABLE 2. Co-Ni-Fe DIARSENIDES; d-VALUES AND CELL DIMENSIONS

Run No.	Composition		d-values in Å with intensities ¹						Cell edges in Å				Duration of run ²	
	Co:	Ni:Fe	120	1	101	1	210	1	111	1	a	b		c
219	0:0:1		2.6040	6	2.5317	10	2.4230	3	2.3318	6	5.3007	5.9792	2.8816	19 days
117	2:0:14		2.6025	8	2.5404	10	2.4188	3	2.3382	8	5.2890	5.9786	2.8962	60 hrs
259	4:0:12		2.5974	7	2.5495	10	2.4131	4	2.3453	8	5.2768	5.9678	2.9119	17 days
116	6:0:10		2.5934	10	2.5625	7	2.4038	4	2.3512	8	5.2531	5.9643	2.9354	60 hrs
242	8:0:8		2.5873	10	2.5776	9	2.3947	—	2.3526	8	5.2312	5.9538	2.9668	4+6 days
109	10:0:6		2.5739	8	2.5739	10	2.3830	—	2.3726	8	5.2031	5.9402	2.9932	65 hrs
258	12:0:4		2.5665	10	2.6114	8	2.3672	3	2.3884	8	5.1664	5.9144	3.0264	17 days
266	13:0:3		2.5594	10	2.6227	10	2.3547	3	2.3970	8	5.1356	5.9039	3.0508	29 days
269	14:0:2		2.5516	10	2.6344	8	2.3441	3	2.4056	8	5.1104	5.8900	3.0744	2+15 days
272	15:0:1		2.5450	10	2.6472	8	2.3318	3	2.4131	8	5.0807	5.8810	3.1017	15 days
Ave. of 23, 200,229,244, 254	7:1:0		2.5341	10	{2.6495 ³ 2.6833 ³ 2.6726}	5	2.3190	2	{2.4301 ⁴ 2.4157 ⁴ 2.4384 ⁴ 2.4330}	5	5.0509	5.8730	3.1274	
							2.3147	2		9	5.0383	5.8637	3.1599	17+8 days
252	6:2:0		2.5289	9	2.6968	9	2.3068	2	2.4500	10	5.0198	5.8579	3.1973	23+14 days
255	5:3:0		2.5184	6	2.7239	9	2.2905	2	2.4685	10	4.9803	5.8381	3.2536	17+8 days
241	4:4:0		2.5074	7	2.7537	8	2.2686	2	2.4897	10	4.9261	5.8261	3.3210	486+6+17+8 days
256	3:5:0		2.4947	9	2.7879	9	2.2507	1	2.5135	10	4.8589	5.8140	3.4054	17+8 days
253	2:6:0		2.4847	10	2.8083	8	2.2278	1	2.5272	9	4.8163	5.8008	3.4567	17+8 days
257	1:7:0		2.4787	7	2.8286	7	2.2126	1	2.5411	10	4.7797	5.7984	3.5096	17+8 days
260	0:1:0		2.4756	9	2.8402	7	2.2015	1	2.5514	10	4.7546	5.8005	3.5416	10+14+10 days
131	0:11:5		2.5362	10	2.7259	10	2.3094	2	2.4660	8	5.0229	5.8765	3.2454	64 hrs.
250	0:10:6		2.5463	7	2.7039	10	2.3249	2	2.4577	9	5.0602	5.8931	3.1989	26+10 days
240	0:8:8		2.5679	10	2.6560	7	2.3589	2	2.4238	8	5.1424	5.9277	3.1017	4+6 days
267	0:6:10		2.5808	4	2.6143	10	2.3823	3	2.3945	5	5.2002	5.9453	3.0242	29 days
248	0:4:12		2.5916	8	2.5829	10	2.3994	2	2.3678	7	5.2422	5.9627	2.9682	28+10 days
114	0:2:14		2.5989	10	2.5544	9	2.4131	2	2.3524	5	5.2762	5.9726	2.9194	60 hrs.
238	1:1:1		2.5586	7	2.6556	10	2.3488	2	2.4226	6	5.1196	5.9080	3.1061	11+21+16 days
194	3:3:28		2.5959	6	2.5664	10	2.4056	2	2.3571	7	5.2568	5.9705	2.9407	10 days
192	3:3:14		2.5898	10	2.5736	7	2.4013	2	2.3654	7	5.2484	5.9551	2.9531	4 days
193	3:9:28		2.6084	8	2.5887	10	(2.3921)	2	(2.3738)	5	5.2381	6.0157	2.9778	4 days

¹ Intensities were estimated from relative heights of peaks on the diffractometer charts, the strongest peak being taken as 10.

² Plus sign indicates that tube was open and sample reground before next heating.

³ This line is indexed as 104.

⁴ This line is indexed as 111.

eter charts and the consequent uncertainty in locating the true position of their center lines. Swanson *et al.* (1960) indexing shows that in addition to the (101) and (111) peaks, the (121), (211), (221), (131), and the (122) peaks each split into (hkl) and ($\bar{h}kl$) of similar intensity.

The cell edges obtained by Swanson using a tungsten internal standard and a least squares fit for all of the indexed lines agree within two standard deviations of the cell edges obtained by the writer using only the (101), ($\bar{1}01$), (111), ($\bar{1}11$), (210) and (120) lines with quartz as an internal standard. Because the indexing of Quesnel and Heyding (1962) corresponds to that of Swanson (after transformation) on 25 lines and disagrees on only two lines, the measurements should have given closer agreement than that shown in Table 1.

Ventriglia (1957) presented an indexed set of d-values for what he believed was Co_2As_3 . However, the d-values are clearly those of CoAs_2 . His indexing is based on a hexagonal cell with $a = 6.16 \text{ \AA}$ and $c = 15.40 \text{ \AA}$. The writer could find no transformation relating this hexagonal cell to the two unit cells just described and believes that it is a fortuitous indexing made possible by the large value of c . In the present work it was found that runs of Co_2As_3 composition made at $500^\circ\text{--}800^\circ \text{ C.}$ produced a mixture of CoAs_2 and CoAs . Good evidence for the existence of the supposed phase Co_2As_3 is lacking.

Cell edges and volumes of solid solutions. The cell dimensions of the Fe-Co, Co-Ni, and Ni-Fe diarsenides as functions of composition are shown in Fig. 4. One interesting feature is the inverse relationship between the a and c dimensions. The rate of change of a with composition is about the same as that of c but opposite in sign. The b dimension follows the a dimension. Because of the inverse relationship, the d-values change rapidly with composition, some increasing and some decreasing. However, the maximum difference in volume is only about 7 per cent. The smallest cell volume is that of FeAs_2 , whereas the largest is that of NiAs_2 . The plot of measured cell volumes against composition in Fig. 4 suggests a straight-line relationship.

The hypothesis that there is a linear relationship between cell volume and composition was tested by fitting straight lines to the data by the method of least squares. The results were as follows:

- | | |
|------------------|--------------------------------|
| (2) Co-Fe series | $V = 0.0138X + 91.44 \pm 0.13$ |
| (3) Co-Ni series | $V = 0.0504Y + 92.76 \pm 0.07$ |
| (4) Fe-Ni series | $V = 0.0650Y + 91.23 \pm 0.11$ |

Where $V =$ cell volume in \AA^3 , $X =$ mol ratio, $100 \text{ Co}/(\text{Co} + \text{Ni} + \text{Fe})$ and Y is the mol ratio, $100 \text{ Ni}/(\text{Co} + \text{Ni} + \text{Fe})$. The last figure in each equation is the standard error of the estimate. The standard error of the estimate is:

$$\text{Standard error of estimate} = \sqrt{\frac{\sum R^2}{N - n}}$$

Where R is the difference between calculated and measured cell volume, N is the number of samples, and n is the number of constants in the equation. Thus $(N-n)$ equals number of degrees of freedom.

The linear relationship apparently holds for ternary compositions also. A least squares plane was fitted to the samples used in calculating equations (2), (3) and (4) above with the following result:

$$(5) \quad V = 0.0151X + 0.0642Y + 91.33 \pm 0.12$$

Equation (5) was then used to calculate cell volumes for samples No. 238, 194, 192, and 193 in Table 2. The measured cell volumes less the calculated cell volumes were -0.02 , $+0.15$, -0.22 , and $+0.95 \text{ \AA}^3$, respectively, for the four samples. The large difference for sample No. 193 is probably due to the overlapping (210) and (111) peaks.

Statistical treatment. An examination of the precision of the x-ray measurements on the diarsenides should answer two related questions. How much reliance can be placed on the data? Is there a linear relationship between cell volume and composition? If the hypothesis of a linear relation-

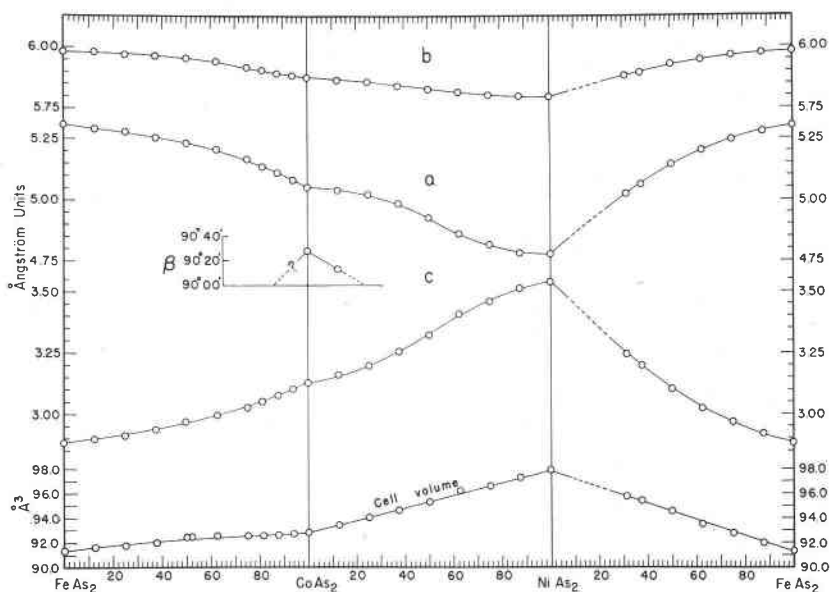


FIG. 4. The effect of composition on the cell edges and cell volumes of Fe-Co, Co-Ni and Ni-Fe diarsenides. Cell edges were calculated from the data illustrated by Fig. 1 and given in Table 2. Compositions are in mol per cent.

ship is correct, the amount of scatter in the cell volumes about the least squares plane should be approximately equal to the scatter in the cell volumes of a large number of samples with the same composition. Thus the standard error of the estimate of equation 5 should be about equal to the average standard deviation obtained when a number of different samples of diarsenides with the same composition are measured by the method described; that is, one complete oscillation of the diffractometer over the (120), (101) and (210) peaks.

Unfortunately, statistically rigorous conclusions cannot be drawn from the data because of the small number of repeated measurements and the many sources of error. However, the writer feels that an attempt to estimate the error is better than none at all. Some sources of error are certain to be relatively small when compared with others and will be neglected in the following analysis. With repeated measurements, each of the three internal standards would probably give slightly different average cell edges for the same diarsenide but these systematic errors are relatively small. If the errors in weighing out the materials altered the composition by as much as 0.05 per cent, the errors in cell edge that could result would range from about 0.0005 Å in the NiAs₂-FeAs₂ series to about 0.00002 Å. Thus, weighing errors might make a small, though noticeable contribution, to the scatter in the measurements of the *a* and *c* edges in some composition ranges. However, for simplification, all errors are assumed to be in the *x*-ray measurements. The relative intensity of the peaks varied to some extent with composition as can be seen from Table 2. Similarly, the background radiation was lowest with NiAs₂ and highest with CoAs₂. However, in all cases the peaks were strong and easy to measure.

Standard deviations for the *x*-ray data were estimated in three ways. Each of these estimates admittedly has some undesirable feature. The usual method of calculating a standard deviation was used for four samples of CoAs₂ and four samples of loellingite (but with different arsenic contents). These standard deviations do not involve factors such as weighing errors which would cause additional scatter in samples of solid solutions. Also, four samples are too few for a reliable estimate. The second method provides an average standard deviation based on all 32 samples of diarsenides. This average standard deviation can then be applied to individual samples if we assume that the standard deviation does not vary greatly with composition. The average standard deviation for the cell volumes can be compared with the standard error of the estimate of equation (5) to see if the cell volumes change linearly with composition. Finally, a maximum value for the average standard deviation for each cell edge and *d*-value can be derived from the standard error of the estimate of equation (5).

A standard deviation for the cell volume of CoAs_2 was obtained from measurements of four different samples, each sample having been given a single complete oscillation on the diffractometer. Standard deviations for the four oscillations across each peak were used to calculate standard deviations for the cell edges and the cell volume by the usual methods for combining independent random errors according to the law of propagation of errors (for example, Scarsborough, 1955, Beers, 1953). The results are shown in a of Table 3.

Four different samples of loellingite were handled in a similar way (see d of Table 3). The four samples of loellingite differed in arsenic content, ranging from $\text{FeAs}_{2.00}$ to between $\text{FeAs}_{1.98}$ and $\text{FeAs}_{1.97}$. However, as mentioned in the section on arsenic content, the d-values of these four did not differ significantly. A standard deviation calculated from these four specimens should be either equal to or larger than any standard deviation for stoichiometric loellingite, depending on whether or not the four samples really have the same cell edges.

Two methods of estimating an average standard deviation for all 32 samples were employed and both gave very similar results. Both methods

TABLE 3. ESTIMATED STANDARD DEVIATIONS (S.D.) FOR A SINGLE OSCILLATION OF THE DIFFRACTOMETER

(An oscillation consists of the average of two measurements, one with the goniometer driving toward larger values of 2θ and one toward smaller values)

	S.D. for d-values ($\times 10^{-3}$ A)			S.D. for cell edges ($\times 10^{-3}$ A)			S.D. for volume ($\times 10^{-3}$ A ³)
	(210)	(120)	(101)	<i>a</i>	<i>b</i>	<i>c</i>	
FeAs₂							
a. S.D. of 4 samples	0.43	0.86	0.65	1.3	2.6	1.0	55
b. Using average S.D.	0.59	0.58	0.57	1.6	1.9	0.9	48
c. Using standard error of estimate	1.48	1.45	1.43	4.0	4.8	2.3	120
CoAs₂							
d. S.D. of 4 samples	1.2	0.9	1.1	3.3	3.0	2.0	97
e. Using average S.D.	.53	.55	.62	1.6	1.9	1.1	51
f. Using standard error of estimate	1.24	1.29	1.46	3.8	4.5	2.6	120
NiAs₂							
g. Using average S.D.	.49	.53	.72	1.4	1.9	1.5	58
h. Using standard error of estimate	1.02	1.10	1.49	2.9	3.9	3.1	120

are described by Wilson (1952, p. 244–245). In the first method the relationship between range and standard deviation in a normal population is used. For a pair of measurements the standard deviation should be equal to 0.886 times the range. Although the range of individual pairs of measurements varies widely, an average value for the range can be calculated from the 32 samples. The second method makes use of a formula which for pairs of measurements reduces to:

$$\frac{1}{2} \sqrt{\frac{\sum D^2}{n}}$$

where D is the difference between the two measurements in each pair and n is the number of pairs. Inasmuch as this standard deviation applies to single measurements, it must be multiplied by $1/\sqrt{2}$ to obtain the standard deviation for a complete oscillation (two measurements).

The average standard deviations in degrees 2θ for the (210), (120) and (101) peaks were then converted into Angstroms for FeAs_2 , CoAs_2 and NiAs_2 , and standard deviations for the cell edges and volumes were calculated according to the law of propagation of error. The results are shown in b, e and g of Table 3. The above estimates of the average standard deviation are probably too low. Oscillation of a single slide produces a smaller scatter in the measurements than duplicate measurements of two different slides of the same sample. In 15 pairs of measurements on a synthetic digenite (Cu_9S_6), the writer found that remaking the slide after each measurement increased the standard deviation by about 50 per cent over that obtained from repeated oscillations of the same slide. Probably some similar factor should be applied to the values in lines b, e and g of Table 3.

In view of this and the additional sources of scatter previously mentioned, the differences between the estimated standard deviations of the volume (a, b, d, e, g, of Table 3) and the standard error of the estimate for the least squares plane are of doubtful significance. If the cell volumes do not vary linearly with composition, measurements of greater precision than those of the present study will be necessary to detect the discrepancy.

Maximum values for the standard deviation of the cell edges and d-values can be approximated by assuming that the standard error of the estimate for the cell volumes of 0.12 \AA^3 equals the average standard deviation; that is, all of the scatter is random error. The standard deviations of the (120), (101) and (210) peaks (and consequently the cell edges) should be in the same ratios as in b, e and g of Table 3. Consequently, the standard deviations in the cell edges and peaks that would produce a standard deviation in the volume of 0.12 \AA^3 (the standard error of the

estimate) can be easily determined. These values are given in c, f and h of Table 3. In Table 1, the standard deviations for the cell edges given for FeAs_2 and NiAs_2 correspond to c and h of Table 3, respectively. Those for CoAs_2 correspond to one-half of the values in d or f of Table 3 because these cell edges are the average values from four samples of the same composition.

Relationship to loellingite and marcasite structures. Buerger (1937) and Rosenqvist (1953) have recognized two distinct divisions of compounds with the marcasite structure, a marcasite group and a loellingite group.

The marcasite group all have c/b ratios of 0.60 to 0.63. Whereas the loellingite group all have ratios between 0.47 and 0.53, rammelsbergite belongs to the marcasite group with a ratio of 0.61. Cobalt safflorite has a ratio of 0.53 and belongs to the loellingite group if its small departure from orthorhombic symmetry is ignored. The ratios intermediate between the two groups fall in the region of the solvus in the Ni-Fe series and in the middle of the Co-Ni series. The solvus probably intersects the middle of the Co-Ni series at lower temperatures. Thus it appears that the phases with ratios intermediate between the loellingite and marcasite groups require higher temperatures to be stable than those within the groups.

NATURAL DIARSENIDES

Composition range. Some chemical analyses of natural diarsenides of Co, Ni, and Fe have indicated the presence of small amounts of S, Sb, Bi, Cu, Ag and Pb. Such "impurities" could be due to either the presence of small amounts of other minerals in the diarsenide or atoms of these elements proxying for other atoms in the structure. At present, only the substitution of S for As has been demonstrated. The remaining elements listed above rarely aggregate more than one or two weight per cent.

The extent of substitution of Co, Ni, and Fe among the natural diarsenides can be seen from Fig. 5 which contains the analyses collected by Holmes (1947), those made by Jouravsky (1959), and those summarized by Godovikov (1960). One group of analyses lie near the NiAs_2 corner. These represent the rammelsbergites and pararammelsbergites. The remaining analyses are distributed near the CoAs_2 - FeAs_2 side and represent safflorites and loellingites. No safflorites containing more than about 80 per cent CoAs_2 have been reported. All but one of the safflorites contain less than 8 mol per cent NiAs_2 , while a few loellingites apparently run as high as 30 per cent NiAs_2 , if one assumes that the analyzed material was homogeneous. The distribution of the analyses does not indicate a break between safflorite and loellingite. It was for this reason that Holmes'

placement of the boundary at the 70 per cent FeAs_2 line was necessarily arbitrary.

The natural separation of the diarsenides into rammelsbergites on the one hand and the loellingite-safflorite series on the other is probably due to the expansion at lower temperature of the solvus which was observed at 800°C . in the synthetic diarsenides. Assuming that the three determinations of the loellingite side of the solvus at 750° , 800° and 850° were near equilibrium, one could reasonable expect the loellingite field along the NiAs_2 - FeAs_2 side to extend from FeAs_2 to about $\frac{1}{3}$ to $\frac{1}{2}$ of the way to NiAs_2 at room temperature. The inversion of rammelsbergite to paramrammelsbergite might further reduce the loellingite field because the solubil-

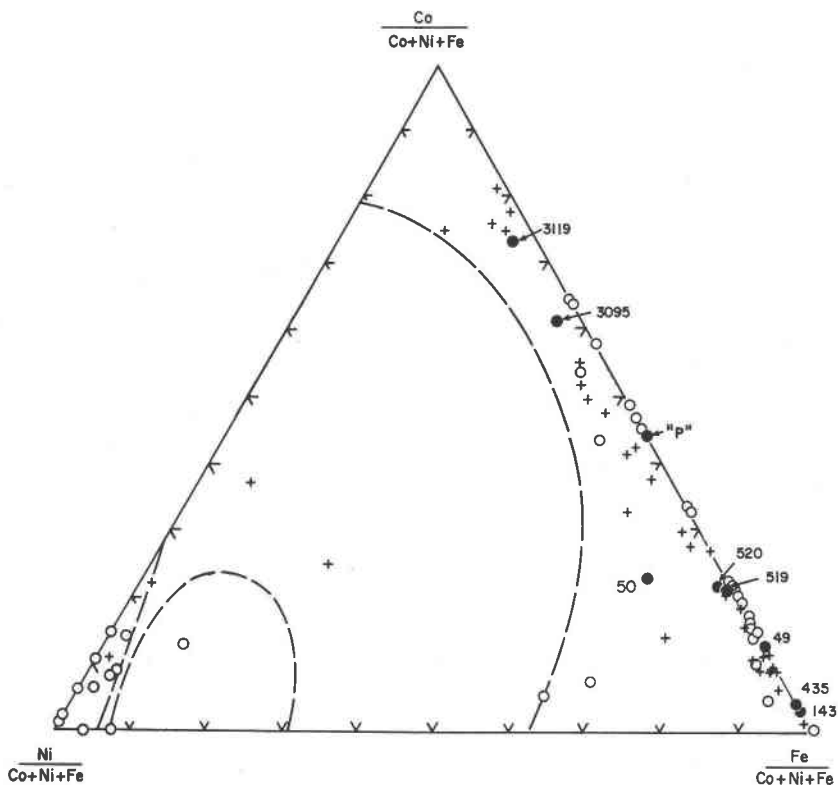


FIG. 5. Co·Ni·Fe atomic ratios of analysed natural diarsenides. Black circles with numbers are after Godovikov (1960). Black circle labeled "P" is from Peacock (1944). Open circles are from Holmes' (1947) compilation. Crosses are Jouravsky's (1959) analyses. Short dashes show approximate extent of solvus observed at 800°C . Long dashes suggest the extent of the solvus at a much lower temperature as a possible explanation for the concentration of analyses near the Ni corner and near the Co-Fe side.

ity of the stable phase, pararammelsbergite, in the loellingite solid solution would have to be less than the solubility of metastable rammelsbergite. The solvus would not only expand along the NiAs_2 - FeAs_2 sideline but would also extend farther into ternary compositions at lower temperatures. From the position of the solvus at 800° , suggested by the short dashes in Fig. 5, intersection of the solvus with the CoAs_2 - NiAs_2 side at some lower temperature would be a logical development. In Fig. 5, the longer dashes suggest how the solvus might appear at some temperature well below 800° C. As most natural diarsenides probably formed well below 800° , their range of solid solution should be much less than that at 800° C. Three homogeneous diarsenides which had been made at 800° C. with Co:Ni ratios of 1:1, 3:5, and 1:3 (samples Nos. 46, 119, and 108 of Fig. 2) were annealed at 600° C. for three and one-half months to see if the solvus reached the CoAs_2 - NiAs_2 side at this temperature. No indication of a miscibility gap was found as the x-ray diffraction patterns were unchanged by the annealing. Three samples (Nos. 95, 58 and 116 of Fig. 2) in the CoAs_2 - FeAs_2 series were similarly annealed but again no changes were observed.

Some of the analyses appear to conflict with this explanation of the distribution. The rammelsbergite in the middle of the 800° C. solvus represents an analysis made in 1856 and Holmes (1947) reported only that it was massive. It could represent a mixture of rammelsbergite and safflorite or even niccolite and skutterudite. Two analyses by Jouravsky (1959) at about 51% and 55% NiAs_2 are more reasonable but do not fit the pattern set by the other analyses. All of Jouravsky's analysed rammelsbergite were checked in polished section and, with the exception of the 51% NiAs_2 sample, are corrected for niccolite (NiAs) which occurred with the rammelsbergites. These two analyses could represent high temperature solid solutions which may or may not have unmixed, or they could be intimate mixtures of rammelsbergite and safflorite.

Some observations in the literature of coexisting loellingite and safflorite indicate a possible break in the series between these two minerals. A number of workers have reported safflorite and loellingite in actual physical contact. These include Orcel and Jouravsky (1935), Dadson (1935, 1937, 1938), and Warren and Thompson (1945). Todd (1926) examined some specimens of ores from Gowganda, Ontario, on which partial chemical analyses had been made. On Todd's specimens 1, 4, and 6, the total chemical composition indicated that the sum of the Co-Fe diarsenides present should have a Co:Fe ratio near 1:2, after accounting for the other observed minerals. In each case Todd observed both safflorite and loellingite. The very low nickel content of specimens 4 and 6 make it unlikely that rammelsbergite could have been present and mistaken for

safflorite or loellingite. Ellsworth (1916) made a similar observation on ore from the Kerr Lake Mine, Ontario. His etched specimen showed three minerals and the chemical analyses (after subtracting arseno-pyrite) indicated a diarsenide composition near 21 per cent CoAs_2 , 79 per cent FeAs_2 for the remaining two minerals. No nickel was present.

Todd's analyses and observations on his specimens 5 and 11 indicate a possible second break in the series near 60 per cent CoAs_2 and 40 per cent FeAs_2 . Both specimens consist predominantly of safflorite and loellingite according to Todd. Thompson (1930) re-examined specimen 5 and stated that he "was able to confirm his (Todd's) impression that the cobalt mineral was orthorhombic and that the other predominant mineral was loellingite." After subtracting the chemical compositions of the other observed minerals, one is left with a total composition near 61 per cent CoAs_2 , 39 per cent FeAs_2 for the safflorite and loellingite. This can be explained by the presence of one mineral richer in cobalt and another poorer in cobalt than the total given.

X-ray data on natural safflorite and loellingite. Samples of analyzed safflorite and loellingite for which the cell edges have been determined are rare. Eight such samples have been described by Godovikov (1960) and one by Peacock (1944). The measured cell edges and some atomic ratios for these samples are given in table 4.

In Fig. 6, the cell edges of the minerals and the synthetic phases have been plotted as a function of $100 \cdot \text{Co}/(\text{Co} + \text{Fe})$. The cell edges of the minerals are shown as crosses and the cell edges of the synthetic phases are open circles connected by a solid line. The solid circles are the cell edges of numbers 3095 and 3119 as determined by Godovikov. These specimens appear to have been incorrectly indexed and the revised cell edges derived from Godovikov's d -values are shown as crosses for the same composition.

The a and b cell edges of the natural diarsenides, with the exception of Peacock's specimen, are smaller than the cell edges of synthetic phases of equivalent $\text{Co}/(\text{Co} + \text{Fe})$ ratios. Similarly, the c edges of the natural diarsenides, with the same exception, are larger than those of the equivalent synthetic phases. In addition to the major constituents, the elements, Ni, S, Sb, Bi, Cu and Au are reported in some of the analyses. We will attempt to evaluate the relative effect of the first four of these elements on the cell edges. Cu is present in only one analysis (3119). Au is present in three (486, 519, 520), but the maximum amount is only 0.2 weight per cent.

The effect of nickel on the cell edges of safflorite and loellingite can be determined from the data of Fig. 4 and Table 2. If one plots these cell edges on a CoAs_2 - NiAs_2 - FeAs_2 mol per cent triangle one can draw lines of

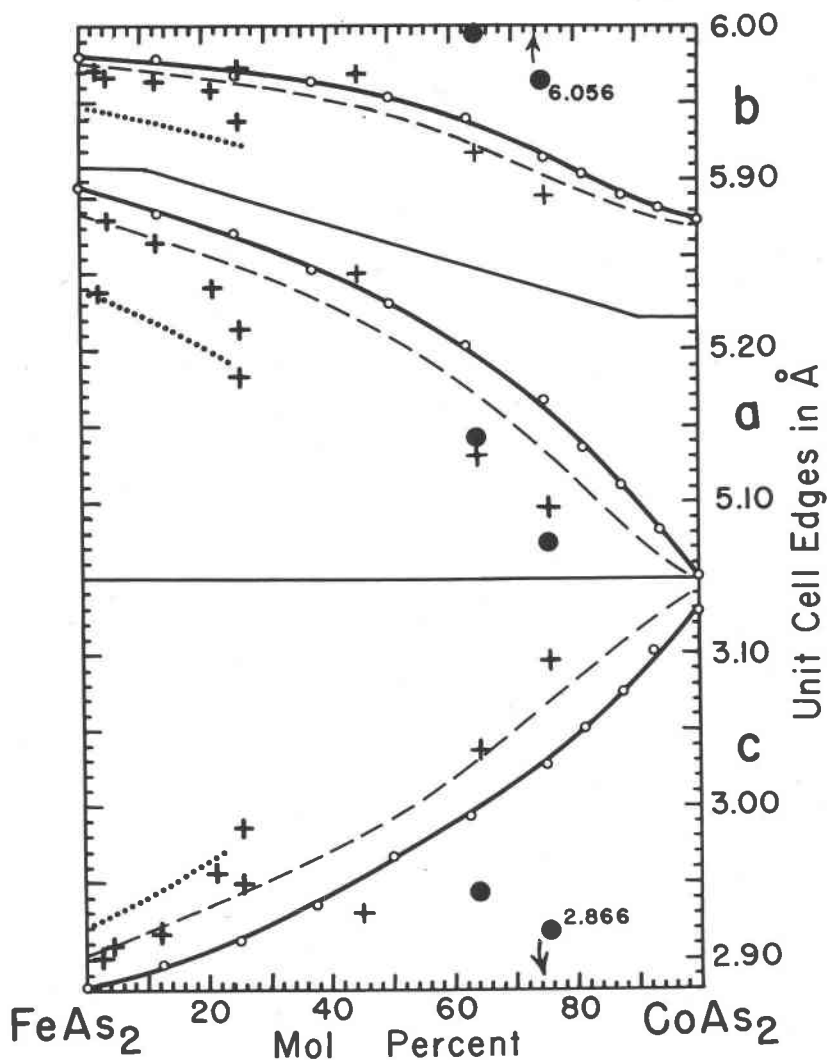


FIG. 6. The cell edges of analysed loellingites and safflorites compared with the cell edges of synthetic diarsenides. The composition axis is in terms of 100 Co/(Co+Fe). The solid lines show the synthetic diarsenides of Co and Fe, as given in Table 2. The dashed lines show synthetic diarsenides with 8 per cent of the Co and Fe atoms replaced by Ni atoms. The dotted lines show synthetic diarsenides with 8 per cent of the As atoms replaced by S atoms. Crosses indicate the analysed natural specimens with 100 Co/(Co+Fe) calculated from the first two rows of table 4: No. 143, 2.82%; No. 486, 4.35%; No. 49, 12.2%; No. 519, 21.3%; No. 50, 25.66%; No. 520, 25.66%; No. "P," 44.8%; No. 3095, 64.03%; No. 3119, 75.40%.

equal cell edge that within the limits of accuracy are straight lines. These lines are essentially parallel but are more closely spaced as one moves away from the FeAs_2 corner. As a consequence, the effect of a given percentage of NiAs_2 on a cell edge is not constant but depends on the $\text{Co}/(\text{Co}+\text{Fe})$ ratio. This can be seen in Fig. 6 where the dashed lines indicate the cell edges of loellingite and safflorites, with eight per cent of the Co and Fe atoms replaced by atoms of Ni. On the CoAs_2 - NiAs_2 - FeAs_2 triangle, the slope of the lines of equal a dimension is such that the change in cell edge due to an increase in nickel content of one per cent is equivalent to an increase in the cobalt content of 1.6 per cent. For the b and c dimensions, the change of one per cent in nickel content is equivalent to changes of 1.5 and 2.0 per cent cobalt respectively. Thus one can make a correction for each cell edge by multiplying the molecular amount of NiAs_2 by the appropriate factor and adding it to the value of $100\text{Co}/(\text{Co}+\text{Ni}+\text{Fe})$ determined from the chemical analysis. The resulting value of "equivalent CoAs_2 " is the content of CoAs_2 which, in a Ni-free Co-Fe diarsenide, would result in the same cell edge as that of the Ni-bearing diarsenide. Thus values of "equivalent cobalt," determined separately for each of the three cell edges, can be applied to the curves of Fig. 4 or 6.

The effect on the cell edges of sulfur substituting for arsenic can be handled in a similar way. Neumann *et al.* (1955) observed that sulfur content affected the d -values of loellingite. Clark (1960) determined the effect of sulfur and cobalt on the (101), (111), (120), and (210) d -values of synthetic loellingite. Using cobalt content as one axis and sulfur content as the other, Clark contoured the d -values for the four spacings above. He found that the contours were straight lines. If one converts Clark's data from d -values into cell edges, one finds that contours drawn on the a (or b or c) edges are also nearly straight lines. These contours are not parallel, however, but tend to converge. If the contours for each cell edge are extended beyond the limits of the diagram, one can locate an approximate focal point. Hence one can closely approximate any contour by a straight line passing through the focal point. Therefore, given a particular Co and S content, one can draw a line through it and the focal point along which the cell edge is approximately constant. If one takes the composition at which this line intersects the Co axis and uses it as an "equivalent CoAs_2 " value, one can then determine the value of the cell edge from Fig. 3 or Fig. 5. Thus the value of the "equivalent CoAs_2 " (C_s) corrected for S can be expressed as follows:

$$(6) \quad C_s = \frac{az - bx}{z - b}$$

The letters a and b are the coordinates of the focal point in terms of Co and S contents respectively, whereas x and z represent the ratios $100 \text{ Co}/(\text{Co}+\text{Ni}+\text{Fe})$ and $100 \text{ S}/(\text{As}+\text{S})$ respectively.

One can correct for both Ni and S by replacing x of the equation (6) by expressions for the "equivalent CoAs_2 " content for Ni bearing diarsenides. For each cell edge, these expressions are simply:

$$(7) \quad C_{\text{Ni}} = mY$$

where Y is equal to $100 \text{ Ni}/(\text{Co}+\text{Ni}+\text{Fe})$ and m is 1.6, 1.5, and 2.0 for the a , b and c edges respectively. Thus equating x of equation (6) with C_{Ni} of (7) and replacing a and b with the appropriate constants, one obtains the following equations:

(8) a edge:

$$C_a = \frac{32.5x + 52y + 232z}{32.5 + z}$$

(9) b edge:

$$C_b = \frac{14x + 21y + 148z}{14 + z}$$

(10) c edge:

$$C_c = \frac{65x + 130y + 200z}{65 - z}$$

In these equations, x is the mol ratio, $100 \text{ Co}/(\text{Co}+\text{Ni}+\text{Fe})$, y is the mol ratio, $100 \text{ Ni}/(\text{Co}+\text{Ni}+\text{Fe})$, and z is the mol ratio, $100 \text{ S}/(\text{As}+\text{S})$. The values of "equivalent CoAs_2 " (C_a , C_b and C_c) which one obtains are then used on the appropriate curves of figure 4 or Fig. 6.

One may visualize these corrections geometrically by considering a triangular prism resting on its base as shown in Fig. 7. Co, Ni and Fe diarsenides lie at the corners of the triangular base and CoAsS , NiAsS and FeAsS at the corners of the top. Within this prism, one may visualize families of surfaces, each composed of all compositions that have the same value for the a (or b or c) edge. The intersection of such a surface and the $\text{CoAs}_2\text{-FeAs}_2\text{-CoAsS-FeAsS}$ side of the prism is a straight line as shown from Clark's data. Similarly the intersection of the surface and the base is a straight line as can be shown from the data in Table 2. These two lines intersect at some point along the $\text{CoAs}_2\text{-FeAs}_2$ edge. Thus it seems reasonable, lacking any information to the contrary, to assume that the surface approximates a plane near the $\text{CoAs}_2\text{-FeAs}_2$ edge and is defined by the two intersecting straight lines. This is the only assumption involved in equations (8), (9) and (10). Given the composition coordinates of any point on any plane of constant cell edge, one can determine by means of these equations where that plane intersects the $\text{CoAs}_2\text{-FeAs}_2$ edge of the prism. With this information (*i.e.*, the "equivalent CoAs_2 ") one can obtain a

numerical value for the cell edge from the data on the series, CoAs_2 - FeAs_2 .

In Table 4, the cell dimensions labeled "calc." were calculated by means of equations (8), (9) and (10) from the chemical analyses. The differences between the measured values and the calculated values are still relatively large in many cases. Furthermore, there is no obvious relation between the differences and the Co, Ni or S content. Similarly, if one contours these differences against any pair of these three elements, one finds no clear relation.

It remained to be seen whether Bi or Sb substituting for As would explain the differences. One can crudely estimate the effect of Sb on the dif-

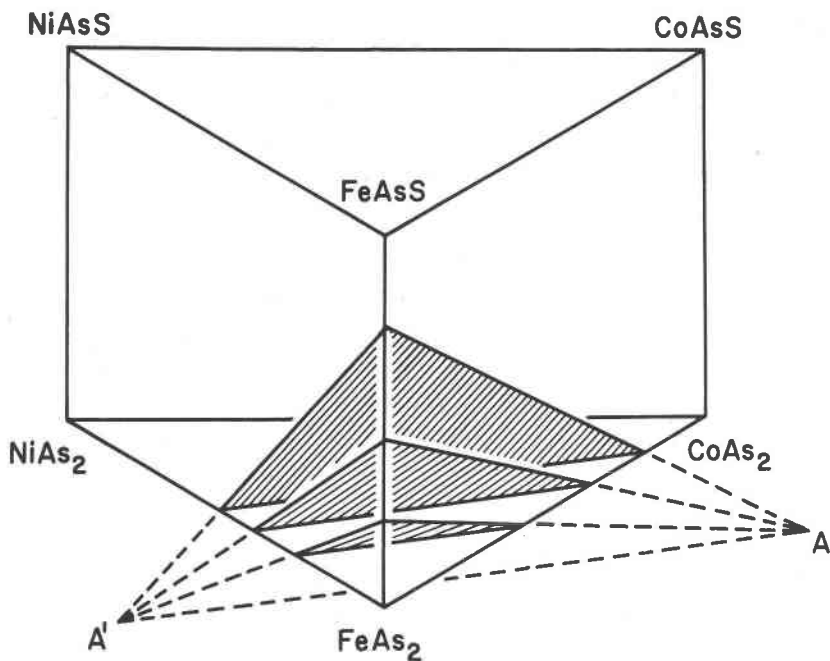


Fig. 7. Illustration of method used to calculate cell edges for safflorites and loellingites containing some Ni and S in solid solution. The shaded planes represent typical surfaces of constant cell edge within the solid figure. The intersections of the planes with the CoAs_2 - NiAs_2 - FeAs_2 base are parallel straight lines. The intersections with the CoAs_2 - FeAs_2 - FeAsS - CoAsS side are straight lines that converge at point A as based on calculations of cell edges from the data of Clark (1960). If the surfaces are planes, they should all converge along a line A-A', parallel to the lines on the base. If one knows the composition of the diarsenide, he can calculate by means of equations (8), (9) and (10) the intersection of the plane containing that composition with the CoAs_2 - FeAs_2 edge. The value of this intersection, called here "equivalent CoAs_2 ," is applied to the solid curves of Fig. 6 to obtain the cell edge.

TABLE 4. CELL EDGES AND SELECTED ATOMIC RATIOS OF ANALYSED NATURAL SAFFLORITES AND LOELLINGITES

Specimen No.	143	486	49	520	519	50	P	3095	3119
100 Co									
Co+Ni+Fe	2.82	4.35	12.2	20.90	20.95	22.93	44.8	61.50	72.66
100 Ni									
Co+Ni+Fe	?	0.06	?	2.35	1.92	10.65	?	3.96	3.64
100 S									
As+S	8.84	3.15	6.54	7.75	2.94	2.01	?	4.44	6.71
100 Sb									
As+S+Sb+Bi	?	—	?	—	—	—	?	0.42	0.84
100 Bi									
As+S+Sb+Bi	?	0.002	?	0.34	0.19	0.41	?	0.07	0.07
100 (As+S)									
Co+Ni+Fe	1.82	1.85	2.01	2.08	1.78	1.88	1.96	1.84	2.07
Cell edges (in Å)									
<i>a</i> meas.	5.238 ± 0.004	5.285 ± 0.004	5.271 ± 0.007	5.214 ± 0.013	5.241 ± 0.008	5.183 ± 0.007	5.25	5.131	5.097
<i>a</i> calc.	5.228	5.274	5.233	5.196	5.247	5.229	5.242	5.113	~5.022
Diff.	+ .010	+ .011	+ .038	+ .018	-.006	-.046	+ .008	+ .018	+ .075
<i>b</i> meas.	5.971 ± 0.008	5.967 ± 0.005	5.964 ± 0.008	5.938 ± 0.009	5.959 ± 0.008	5.972 ± 0.006	5.97	5.919	5.889
<i>b</i> calc.	5.942	5.967	5.946	5.927	5.955	5.950	5.957	5.893	~5.872
Diff.	+ .029	-.000	+ .018	+ .011	+ .004	+ .022	+ .013	+ .026	+ .017
<i>c</i> meas.	2.900 ± 0.004	2.909 ± 0.002	2.916 ± 0.004	2.949 ± 0.003	2.956 ± 0.006	2.986 ± 0.003	2.93	3.036	3.094
<i>c</i> calc.	2.931	2.898	2.933	2.978	2.934	2.968	2.953	3.080	~3.137
Diff.	-.031	+ .011	-.017	-.029	+ .022	+ .018	-.023	-.044	-.043

All cell edges except those of "P" have been converted from kX units to Angstroms. Specimens Nos. 143, 486, 49, 520, 519 and 50 are from Mikheyev (1952) as reported in Godovikov (1960). "P" is from Peacock (1944). Nos. 3095 and 3119 are from Godovikov (1960). The cell edges of 3095 and 3119 are not those of the original paper but have been calculated after reindexing Godovikov's *d*-values. For specimens 143 and 49, the above ratios were calculated from the atomic ratios (Co+Ni)/Fe, (As+S)/(Co+Ni+Fe), and S/As, which were the only chemical data available. Only the ratio, Co/Fe/As, was given for specimen "P."

ferent cell edges by assuming that the cell edges are a linear function of composition between CoAs₂ and CoSb₂, and between FeAs₂ and FeSb₂ as these phases all have the marcasite structure. From this one finds that Sb increases all three cell edges. For a safflorite near the middle of the CoAs₂-FeAs₂ series, substituting one per cent of the As by Sb would increase each cell edge by about 0.005 Å. In Table 4, two analyses, 3095 and 3119, report about 0.4 and 0.8 mol per cent Sb respectively. However, the differences between calculated and observed *a* and *b* cell edges are several times the magnitude one would expect from the amount of Sb present. Furthermore, the *c* edges are much *smaller* than the calculated values.

As there are no phases in the systems Co-Bi, Ni-Bi, or Fe-Bi in which the Co:Bi, Ni:Bi, or Fe:Bi ratio is 1:2, one cannot evaluate the effect of Bi substitution for arsenic in the way used for Sb. However, the effect should be similar to that of antimony in increasing all three cell dimensions, but perhaps somewhat greater in magnitude. The maximum amounts of bismuth substituting for arsenic reported in the analyses for Table 4 are 0.41 (no. 50) and 0.34 (no. 520) mol per cent. However, the measured values for the a edge of no. 50 and the c edge of no. 520 are 0.46 and 0.29 Å *smaller* than the calculated values while all of the other measured edges of these two samples are larger than the calculated values.

As the relatively large differences between calculated and measured values cannot be appreciably diminished by correcting for Sb or Bi content, one must conclude that either the x -ray or chemical data on the natural safflorites and loellingites is at fault or that the relation between cell edges and composition expressed in equations (6), (7) and (8), although adequate for *either* Ni or S substitution, is too simple for the combinations of the two substitutions. Thus additional work should be done on synthetic diarsenides containing both nickel and sulfur.

An error in Godovikov's (1960) indexing of specimens 3095 and 3119 was suspected when it was observed that the b and c edges of these specimens (shown by black circles on Fig. 6) were well over on the opposite side of the curves of cell edges for pure CoAs_2 - FeAs_2 solid solutions, as compared with the other specimens. Thus none of the substitutions discussed above could account for these cell edges. In discussing the changes in d -values with Co content in the loellingite-safflorite series, Godovikov noted that in certain cases pairs of lines in the Fe-rich specimens apparently converged in 3095 and 3119, with a *concurrent change in indices*. In addition he stated that some converging pairs separated again with a change in indices. The writer decided to consider an alternative possibility that the converging lines did not change their indices but crossed as in Fig. 3. A plot of d -values versus composition was constructed using the indexing of Swanson *et al.* (1960) for CoAs_2 , CoFeAs_4 , and FeAs_2 plus two additional sets of d -values calculated from the cell edges in Fig. 2. This diagram revealed that a large number of lines which are clearly separated in the Fe-rich diarsenides cross each other in the vicinity of the compositions of 3095 and 3119. Thus a number of Godovikov's lines actually represent two closely spaced lines. However, among the lines of smaller d -value, the 221, 321, 312, and 341 were unambiguous. From these lines, the cell edges given in Table 4 were calculated.

One might suppose that if equations (6), (7) and (8) can be shown to be valid when both S and Ni are present, then one could determine the composition of safflorites and loellingites by measuring the cell edges, deter-

mining C_a , C_b and C_c from Fig. 2 or Fig. 4, and solving the three simultaneous equations in three unknowns. Unfortunately, unique solutions cannot be found for x , y and z when C_a , C_b and C_c take on certain values which are described by equation (11):

$$(11) \quad C_a - 1.859 C_b + 0.1001 C_c = - 62.76$$

When equation (11) is satisfied, the three equations, (6), (7) and (8) are not independent and an infinite number of solutions exist. For example, this occurs when $C_a=70$, $C_b=76$, and $C_c=85$. Unfortunately, as this situation described by equation (11) is approached, very large errors in the Co, Ni, and S content result from small errors in measurement of the cell edges. For this reason, the method is unsatisfactory for determination of composition over the whole composition range of safflorite and loellingite, the errors being especially large in the Co and Ni content. On the other hand, if one of the three composition variables, cobalt, nickel, or sulfur content is determined by some other method, equations (6), (7) and (8) could be used to determine the other two composition variables.

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