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SKUTTERUDITES (Co, Ni, Fe)As_{3-x}: COMPOSITION AND CELL DIMENSIONS[1]

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ABSTRACT

Skutterudites were synthesized by heating mixtures of Co, Ni, Fe and As at 600° to 800° C. in sealed evacuated silica tubes. The resulting phases were identified by powder *x*-ray diffraction methods and by ore microscopy.

Analyses of natural skutterudites by numerous workers have indicated nonstoichiometric compositions with a deficiency of As. It has been suggested that the As deficiency may be due to the presence of other phases as impurities. In the present study, synthetic cobalt skutterudite was found to have a small but real As deficiency, even in the presence of crystalline As, but this deficiency is of insufficient magnitude to account for the large deficiencies indicated in many analyses of natural skutterudites.

Natural skutterudites are known to vary widely in their Co, Ni, and Fe content, but pure Ni and Fe members are unknown. The same is true for synthetic skutterudites. The limits of solid solution vary little with temperature between 600° and 800° C., and most natural skutterudites fall within the limits of solid solution observed for the synthetic phases.

The cell edges of 26 synthetic skutterudites with nickel content equal to or greater than iron content are related to composition by the function,

$$a = 0.1240X - 0.0246Y + 8.2060$$

where a is the cell edge in Å, X is the mole ratio Ni/(Co+Ni+Fe), and Y is the mole ratio Fe/(Co+Ni+Fe). The function describes the measurements to a standard deviation of 0.00086 Å. The cell edges of 13 analyzed natural skutterudites of other workers show fair agreement with the synthetic ones, and are described by the above function to a standard deviation of 0.0097 Å. The deviations of the measured cell edges of natural skutterudites from cell edges computed using the function are not demonstrably due to either differences in (As+S)/(Co+Ni+Fe) ratios or total sulfur content.

INTRODUCTION

Natural skutterudites suitable for chemical analysis are relatively rare. They usually occur in intimate intergrowths with other arsenides or sulfosalts, and single crystals are commonly zoned or partially replaced by other minerals. Analyzed natural materials have seldom been adequately examined to ensure homogeneity. Consequently the arsenic deficiencies indicated by most chemical analyses of skutterudites may in reality be the result of analyzing inhomogeneous material. In addition, variations in cell edge have been related to variations in composition in a very general way.

As part of a larger investigation of part of the system Co-Ni-Fe-As, the range in composition of skutterudites synthesized between 600° and

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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 Institution of Washington.

800° C. was studied and the cell edges for various compositions determined.

Nomenclature of the arsenides. Following the classification of Holmes (1947), the higher arsenides of Co, Ni, and Fe fall into two general groups: the skutterudite series and the so-called "orthorhombic" diarsenides.

Members of the skutterudite series are isometric triarsenides approaching the ideal composition (Co, Ni, Fe)As_3, but usually are deficient in arsenic content. The approximate range of Co, Ni, and Fe contents of natural and synthetic skutterudites is shown in Fig. 1(A). The Ni and Fe end members have not been synthetized nor found as minerals.

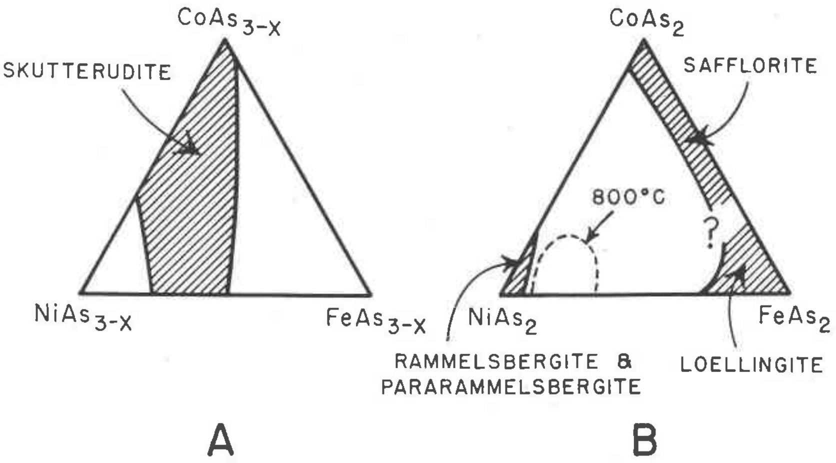

FIG. 1(A). The extent of Co, Ni, and Fe substitution in synthetic skutterudite at 800° C. Skutterudite solid solution is shown by the shaded area. It will be shown below that the extent of such substitution in natural skutterudite is probably about the same. The compositions $NiAs_{3-x}$ and $FeAs_{3-x}$ are neither compounds nor minerals.

FIG. 1(B). The approximate extent of Co, Ni, and Fe substitutions among the natural diarsenides. The natural solid solutions are shown by shading. At 800° C. the solid solutions cover all of the triangle except for the area within the dashed lines.

The so-called "orthorhombic" diarsenides include the truly orthorhombic minerals, loellingite, $FeAs_2$, rammelsbergite and pararammelsbergite, $NiAs_2$, and the monoclinic mineral, safflorite, (Co, Fe)As_2. Judging from the chemical analyses summarized by Holmes (1947) the probable extent of solid solution among these minerals is as shown in Fig. 1(B). The extent of solid solution at 800° C. among the synthetic diarsenide phases is much greater than that reported for natural diarsenides. At 800° C. there is nearly continuous solid solution with a small miscibility gap between rammelsbergite and loellingite.

The writer has followed Holmes' (1947) general scheme of nomenclature but for simplicity has not used his modifiers, cobaltian, ferrian, or nickelian which refer to arbitrary subdivisions of the skutterudite field corresponding to either Co, Fe, or Ni predominance. In fact the field of ferrian skutterudite appears to be so small that it is of doubtful value. In the present work the name, "cobalt skutterudite" will be used when discussing the pure cobalt end member.

Prior to Holmes' classification, the nomenclature of the Co, Ni, and Fe arsenides was complicated by the acceptance of arsenide minerals of cobalt and nickel which appeared to have isometric symmetry but whose chemical analyses indicated that they were more nearly diarsenides than triarsenides. "Isometric diarsenides" rich in nickel were called chloanthite and those rich in cobalt were called smaltite. However, the *x*-ray patterns of various specimens of cholanthite and smaltite were found to correspond to those of skutterudite, loellingite, rammelsbergite, safflorite or a mixture of these. Consequently, Holmes (1947) recommended dropping the names chloanthite and smaltite and these names have now largely been abandoned in favor of the name skutterudite.

EXPERIMENTAL WORK

Materials. The iron used in the present work was N.B.S. standard sample 55d. The nickel was Driver Harris H.P. remelted electrolytic nickel (99.8 per cent Ni and 99.9 per cent Ni+Co). The cobalt was obtained from the National Bureau of Standards, and a qualitative spectrographic examination indicated Ni+Fe to be less than 0.1 per cent and no other impurities in significant quantities. The arsenic was c.p. grade from the Amend Drug and Chemical Co.

Arsenic oxidizes very readily, particularly if finely ground. Consequently, the arsenic crystals were cleaned just before weighing by holding them in a Bunsen burner flame until the oxide coating sublimated and the crystal faces were shiny. Material treated in this manner and ground to fragments with a maximum size of about 1 mm gained weight in air at about 0.1 per cent per hour. Hence, coarse grains were used and the fines discarded. Samples of cobalt and nickel, which had been reduced in a hydrogen atmosphere at 600° C., gained weight much more slowly. A sample of cobalt powder left exposed to the air showed an increase in weight of only 0.01 per cent after one month.

Method of synthesis. The skutterudites were made in sealed silica tubes. These were either simple sealed tubes or "tube-in-tube" arrangements where the metal was placed in an open tube inside a larger tube containing arsenic. In the first type, mixtures of iron, cobalt, nickel, and arsenic, or of end-member phases were used. The tubes were evacuated to less than 1 mm mercury before sealing. The amount of oxygen left in the largest tubes at this pressure would be about 0.04 mg. The weight of the samples ranged from 100 mg to over 1 g.

The "tube-in-tube" type was used to determine the maximum ratio of arsenic to cobalt in skutterudite. Approximately 100 mg of cobalt was placed in a small open tube of known weight and the total weight determined. The increase in weight was equal to the weight of the cobalt. This tube was placed in a larger tube containing ample arsenic to maintain a saturated vapor. The larger tube was then evacuated and sealed. After the sample was annealed for periods ranging from 5 to 37 days, it was quenched. The outer tube was carefully broken open and the inner one removed and weighed. The gain in weight indicated the amount of arsenic that had combined with the cobalt. The samples were then reground and the procedure repeated. It was sometimes necessary to repeat this cycle several times to obtain constant weight and a single homogeneous phase. After the final heating a polished section of the sample was examined under the microscope. It was assumed that the small amount of material lost during grinding was of the same composition as the rest of the sample.

Making the Co-Ni-Fe skutterudite solid solutions required higher temperatures than necessary for making cobalt skutterudite. Although arsenic reacted with mixtures of cobalt and nickel in a few days at 600° C. to form a nickel-free cobalt skutterudite plus rammelsbergite, it was necessary to heat the charges at 800° C. to form the Co-Ni skutterudite solid solutions. Even at 800° C., Co-Fe and Ni-Fe skutterudites did not become homogeneous without regrinding and reheating. When some of these solid solutions were annealed for three months at 600°, they did not break down, indicating that the nickel-free cobalt skutterudite, which first formed, was probably metastable. Mixtures of Co-Ni monarsenide solid solution plus arsenic heated at 600° C. also failed to produce Co-Ni skutterudite solid solutions.

X-ray measurement. The cell edges of skutterudites were determined with a Norelco *x*-ray diffractometer using copper radiation ($CuK\alpha_1 = 1.54050$ Å) and either thoria (ThO_2) or silicon as an internal standard. The thoria was the same material used by Frondel (1955) in his accurate determination of the cell size of thoria and by Skinner (1957) in his measurement of the thermal expansion of thoria. Skinner's value for the unit cell was 5.59525 ± 0.0001 Å at 25° C. and his conversion of Frondel's previous value from kX units to Ångstrom units and from 31.6°

to 25° C. gave 5.59520 ± 0.00005 Å. The silicon was provided by H. S. Yoder of the Geophysical Laboratory. The value used for its cell edge was 5.43077 Å at 25°. When silicon was used as an internal standard, the (932), (763) line of the cubic skutterudite was measured. When thoria was used, this same line was measured for skutterudites smaller than 8.235 Å, and the (831), (750), (743) line and the (822), (660) line for the larger unit cells. At least four measurements were made on a single mount of each specimen, two with the diffractometer running toward the larger 2θ angles, and two running toward the smaller. The goniometer speed was one-fourth or one-half degree per minute and the chart speed was one-half inch per minute. In most cases the same line was measured all four times, but for some runs two different lines were each measured twice.

ARSENIC CONTENT

Synthetic skutterudite. The maximum and minimum arsenic contents of skutterudite were determined only for the cobalt end member. The maximum arsenic content was determined by the "tube-in-tube" method for pure cobalt skutterudite, and was found to be $CoAs_{2.960\pm0.09}$ at 800° C. The minimum arsenic content was determined by heating mixtures of cobalt and arsenic metals with known total compositions and examining polished sections of the samples for the next lower arsenide. The minimum arsenic content lies between $CoAs_{2.940\pm0.002}$ and $CoAs_{2.950\pm0.002}$. The limits of error in this work are estimated from the accuracy with which the samples were weighed. Three runs by the "tube-in-tube" method gave two compositions equal to $CoAs_{2.960\pm0.001}$ and one of $CoAs_{2.961\pm0.001}$ after heating for 7, 12, and 37 days, respectively. Examination of polished sections of all three samples revealed only skutterudite. The 7- and 12-day runs were reground and reheated for 10 days and 5 days, respectively. The inner tube of the former run became contaminated with solid arsenic and was discarded; the latter gave a composition of $CoAs_{2.954\pm0.001}$ which indicated a slight loss of material from the inner tube. A simple sealed tube run of a composition equal to $CoAs_{2.950\pm0.002}$ gave a homogeneous skutterudite while runs of $CoAs_{2.940\pm0.002}$ and lower in arsenic gave skutterudite plus cobalt diarsenide. Thus the range of compositions of cobalt skutterudite is at least from $CoAs_{2.950\pm0.002}$ to $CoAs_{2.960\pm0.001}$ at 800° C.

The lack of any detectable difference in unit-cell edge between cobalt skutterudite made in the presence of excess solid arsenic and that made in equilibrium with cobalt diarsenide also indicates a limited range of arsenic content. Cell-edge measurements made on four separate mounts of a pure cobalt skutterudite made at 800° C. in equilibrium with cobalt diarsenide (Table 1, no. 206) gave 8.2055 ± 0.0002 Å (standard error of

Table 1. Cell Dimensions of Skutterudites (Unless Otherwise Stated, Skutterudites were Synthesized at 800° C. in the Presence of Excess As)

Run No.	Co:Ni:Fe	Meas. a (Å)	Calc. a (Å)	Internal standard	Remarks
204	100:0:0	8.2056		Si	15 days; measurements made on 8 different diffractometer mounts, standard deviation = 0.00026 Å.
		8.2055		Si	
		8.2051		Si	
		8.2058		Si	
		8.2056		Si	
		8.2057		Si	
		8.2059		Si	
		8.2053		Si	
		Avg 8.2056	8.2060		
206	100:0:0	8.2057		Si	15 days; $Co_{26}:As_{74}$, contained some $CoAs_2$. Measured 4 different diffractometer mounts, standard deviation = 0.0003 Å.
		8.2053		Si	
		8.2059		Si	
		8.2053		Si	
		Avg 8.2055	8.2060		
282b	95:0:5	8.2087		Si	7 days, reground, 4 days more.
282c	95:0:5	8.2091		Si	Reground and heated 3 days more.
282d	95:0:5	8.2087		Si	Added As (total As = 88 percent of sample), heated 4 days more.
285b	92.5:0:7.5	8.2112		Si	2 days, reground, 3 days more.
18c	90:10:0	8.2191	8.2184	ThO_2	20 days at 600° C., 63 hrs at 800° C.
281b	90:0:10	8.2144		Si	24 hrs, reground, 6 days more.
281c	90:0:10	8.2145		Si	Reground, 4 days more.
187	87.5:6.25:6.25	8.2111	8.2122	ThO_2	69 hrs.
19b	80:20:0	8.2303	8.2308	ThO_2	10 days.
283b	80:10:10	8.2170	8.2159	Si	7 days, reground, 4 days more.
283c	80:10:10	8.2163	8.2159	Si	Reground, 3 days more.
286b	80:7.5:12.5	8.2166		Si	4 days, reground, 3 days more.
188	80:5:15	8.2168		ThO_2	69 hrs.
273b	80:5:15	8.2178		Si	17 days, reground, 3 days more.
273c	80:5:15	8.2177		Si	Reground, 4 days more.
90c	75:25:0	8.2380	8.2370	ThO_2	4 days at 700° C., 63 hrs at 800° C.
130	75:12.5:12.5	8.2182	8.2184	ThO_2	65 hrs.
276b	75:8:17	8.2203		Si	17 days, reground, 3 days more.
276c	75:8:17	8.2208		Si	Reground, 4 days more.
287	68.75:12.5:18.75	8.2228		Si	1 day, reground, 4 days more.
156	62.5:25:12.5	8.2356	8.2339	ThO_2	3 days.
189	62.5:18.75:18.75	8.2241	8.2246	ThO_2	69 hrs.
154	62.5:12.5:25	8.2236		ThO_2	3 days.
295b	60:40:0	8.2553	8.2556	ThO_2	3 days, reground, 3 days more.
86c	50:50:0	8.2693	8.2680	ThO_2	96 hrs at 600° C. + 63 hrs at 800° C.
86d	50:50:0	8.2691	8.2680	ThO_2	After 61 more hrs.
198	50:35:15	8.2464	8.2457	ThO_2	10 days.
148	50:25:25	8.2312	8.2309	ThO_2	66 hrs.
177	40:60:0	8.2798	8.2804	ThO_2	4 days.
293b	37.5:31.25:31.25	8.2373	8.2371	ThO_2	3 days, reground, 4 days more.
293c	37.5:31.25:31.25	8.2374	8.2371	ThO_2	Added As (total As of sample = 91 per cent), 3 days.
197	35:50:15	8.2653	8.2643	ThO_2	10 days.
180	25:62.5:12.5	8.2813	8.2804	ThO_2	9 days.
105	25:50:25	8.2629	8.2619	ThO_2	65 hrs.
292b	25:37.5:37.5	8.2447	8.2433	ThO_2	3 days, reground, 4 days more.

TABLE 1. (*continued*)

Run No.	Co:Ni:Fe	Meas. a (Å)	Calc. a (Å)	Internal standard	Remarks
195	15:65:20	8.2804	8:2817	ThO_2	10 days.
196	15:50:35	8.2603	8.2594	ThO_2	10 days.
98	0:75:25	8.2910	8.2928	ThO_2	63 hrs.
289b	0:70:30	8.2842	8.2854	Si	26 days, reground, 15 days.
290	0:65:35	8.2775	8.2780	Si	26 days, reground, 15 days.
291	0:60:40	8.2694	8.2706	Si	26 days, reground, 15 days.
288b	0:55:45	8.2629	8.2631	Si	1 day, reground, 26 days.
288c	0:55:45	8.2631	8.2631	Si	Reground, 15 days.

the mean). The measurements on eight separate mounts of a cobalt skutterudite made in the presence of excess solid arsenic (no. 204) at 800° C. gave 8.2056±0.0001 Å. In addition some measurements were made on cobalt skutterudites prepared at 600° C. in the presence of cobalt diarsenide and also on cobalt skutterudites prepared with solid arsenic present in excess. No significant difference was observed from the above values.

Difficulties were experienced in tube-in-tube runs with iron and nickel present and the runs burst before equilibrium could be attained. A run with equal amounts of Co, Ni, and Fe gained arsenic equivalent to an arsenic to metal ratio of 2.92 before it burst. A run with equal amounts of Ni and Fe reached a ratio of 2.88. In this case, however, the composition lay outside the limit of solid solution of skutterudite, and loellingite was observed to be present. Therefore, the arsenic-to-metal ratio of the skutterudite would have to be higher than that observed.

Natural skutterudites. Holmes (1947) compiled 195 analyses of diarsenide minerals and skutterudites made between 1810 and 1945. He critically reviewed the evidence bearing on the symmetry and homogeneity of the minerals, calculated the metal-to-arsenic ratios, and plotted them on triangular diagrams with Co, Fe, and Ni at the corners. His attempt to make cobalt skutterudite with an arsenic deficiency failed to produce any skutterudite with a cell dimension different from skutterudite made with the composition $CoAs_{2.95-3.00}$. Consequently Holmes concluded that the arsenic deficiencies indicated in chemical analyses of isometric arsenides were probably due to the almost universal inhomogeneity of the specimens rather than substitution of cobalt, nickel, or iron atoms for arsenic atoms or omission of arsenic atoms from the skutterudite structure. He pointed out (p. 333) that "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 . . . had been examined by *x*-ray diffraction methods."

It should be noted in considering analyses of natural material that

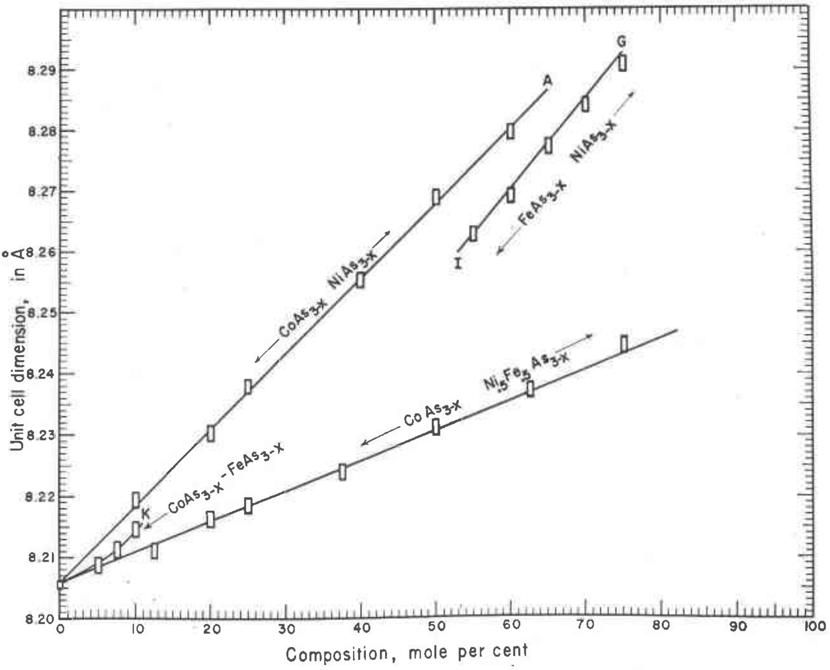

Fig. 2. Relationship between cell edges and Co, Ni, and Fe content for some solid solutions of synthetic skutterudites made in the presence of crystalline arsenic and vapor at 800° C. Formulas indicate theoretical end members for each series and arrows indicate whether the associated end member lies on the right or left edge of the diagram. Thus, the three series with $CoAs_{3-x}$ as an end member all converge at 8.2060 Å and zero per cent of the other end members. The measured values are indicated by rectangles. The letters A, G, and I refer to compositions indicated by the same letters in Fig. 3.

skutterudite, loellingite, safflorite, and rammelsbergite, when massive, are nearly indistinguishable in hand specimen. In polished sections all these minerals are very similar in color and hardness. However, skutterudite can be distinguished because of its isotropism. The most certain means of identification is by x-ray diffraction, but generally the sample taken for a powder mount is too small to be representative if one is trying to detect small amounts of other phases present as impurities. The writer made up mixtures of skutterudite and rammelsbergite and found that as much as 7 per cent by weight of rammelsbergite present with skutterudite could not be detected by x-ray diffraction methods. In this case, detection should have been relatively easy as the identity of the impurity was known and its strongest lines are not masked by skutterudite lines. In natural minerals the problem of detecting unknown phases is more difficult.

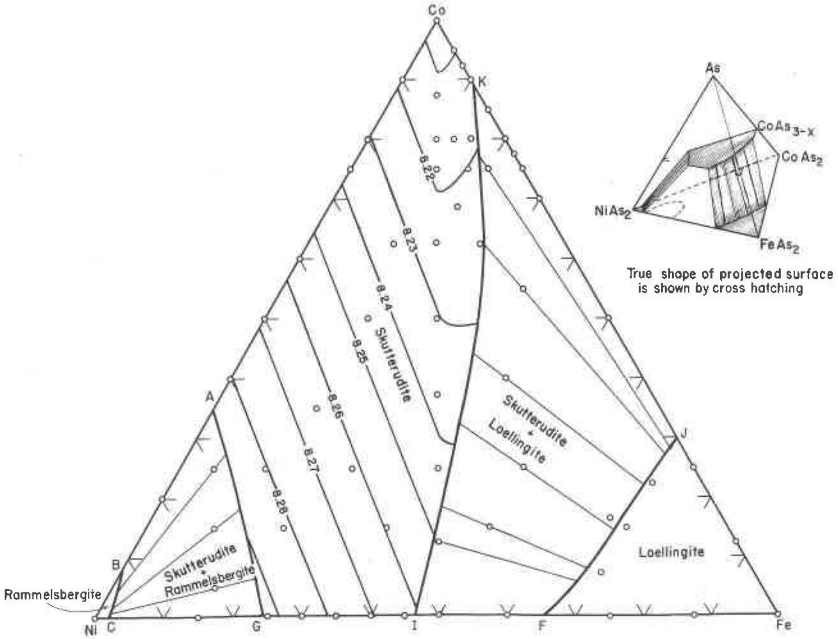

FIG. 3. Co, Ni, and Fe substitution in phases stable at 800° C. in the presence of vapor (approximately 25 atmos. of vapor pressure) and crystalline arsenic. The diagram can be viewed as a projection from the arsenic corner of the tetrahedron (see inset) onto the $CoAs_2$-$NiAs_2$-$FeAs_2$ base. The fields of loellingite, FJFe, and rammelsbergite, BCNi, lie on the base and the other three fields are projected on to the base. The numbered contours in the field of skutterudite, AGIKCo, are lines of equal cell edge. In the field of skutterudite plus loellingite, KIFJ, and skutterudite plus rammelsbergite, ABCG, tie lines connect pairs of coexisting phases. Circles indicate total compositions of samples. Compositions are in mol per cent of Co+Ni+Fe. Note that of the very extensive diarsenide solid solution at 800° C. shown in figure 1(B), only the nickel-rich and iron-rich compositions are stable with crystalline arsenic.

The present investigation indicates that the isometric arsenides can have a small, but real, arsenic deficiency, but that it is not enough to account for the large deficiencies indicated by many analyses. The work on cobalt skutterudite at 800° C. indicates that the arsenic/cobalt ratio ranges between about 2.94 and 2.96. Cobalt skutterudite made at 600° C. had about the same cell dimension as that made at 800° C. The data on the maximum arsenic content of skutterudites of mixed cobalt, iron, and nickel composition indicate arsenic/cobalt ratios of at least 2.92. The plots of cell dimensions against compositions (Figs. 2 and 3) are linear for skutterudites whose Fe content is less than the Ni content, suggesting that there is no great variation in arsenic content for such skutterudites stable in the presence of crystalline arsenic. With respect to the minimum arsenic content, it seems to the author unlikely that the mixed cobalt, iron, and nickel skutterudites have arsenic contents much lower than that of pure cobalt skutterudite but there is no direct experimental evidence.

The arsenic deficiency found in this study for synthetic skutterudites is of the same magnitude as that reported by Jouravsky (1948) for five analyses of parts of unusually large (5 cm) crystals of skutterudites from Bou Azzer. The ratios of (As+S)/(Co+Ni+Fe) for the five samples were 2.90, 2.92, 2.93, 2.94, and 2.97. Jouravsky concluded that a small but real arsenic deficiency existed in the natural skutterudites.

In summary, the large arsenic deficiencies previously reported for natural skutterudites are probably due to inhomogeneous materials. However, there is a small but real arsenic deficiency in synthetic skutterudite which probably also exists in natural skutterudite.

Co:Ni:Fe Ratios and Cell Edges

Synthetic skutterudites. In addition to compiling chemical analyses and reviewing previous work on synthesis of arsenides, Holmes (1947) synthesized skutterudites of various compositions. He made a number of attempts, but failed to produce pure nickel and iron skutterudites. He heated 15 samples with arsenic present in excess of that required to make skutterudite and with differing proportions of two or all three of the metals, iron, cobalt, and nickel. Six of these samples produced apparently homogeneous skutterudites and the rest produced mixtures of skutterudites and diarsenide phases. For these runs, "various temperatures between 550° and 1050° C. were employed" (p. 320).

Holmes compared the cell dimensions of his synthetic skutterudites with those of seven natural skutterudites of known compositions. As one of the natural and eight of the 15 synthetic skutterudites were inhomogeneous, they could be assigned only approximate compositions. Holmes concluded that the cobalt end member had the smallest cell dimension, and that "increasing amounts of nickel, iron, or nickel and iron result in an increase in the length of the cell edge" (p. 329). The present work shows general agreement with Holmes' conclusions.

Figure 2 shows the relationship between cell edge and composition for the Co-Ni, Ni-Fe, and Fe-Co skutterudites and for the series between cobalt skutterudite and the 50 per cent Ni, 50 per cent Fe skutterudite. This diagram is based on values given in Table 1. Within the limits of accuracy, the changes in cell edges with composition are linear, except for the limited solid solution in the Fe-Co skutterudites.

Figure 3 shows the cell edges of skutterudites as contour lines on a

Co-Ni-Fe composition triangle. These contours were based on 34 skutterudites with different ratios of Co, Fe, and Ni. Each ratio produced a homogeneous skutterudite. The cell edges of these skutterudites are given in table 1. Figure 3 also shows the limits of skutterudite solid solutions at 800° C.

The contour lines in Fig. 3 are straight for skutterudites in which the Ni/Fe ratio is more than 1. At ratios slightly less than 1, the contours change their direction by more than 90°. Thus for a fixed content of Co, substituting Fe for Ni first causes the cell dimension to decrease, then pass through a minimum value, and finally to increase again. There was no indication of a change in symmetry. At present the cause of this peculiar "trough" in the cell dimensions is unknown. Two possibilities might be a changing As/(Co+Ni+Fe) ratio or an increased ordering of the Ni and Fe atoms near a Ni/Fe ratio of 1.

The hypothesis that the skutterudite cell edges are a linear function of Co, Ni, and Fe content for Ni/Fe ratios equal to or larger than 1 was tested in the following way: Thirty-seven measurements of cell edges for 26 samples of skutterudites in the above composition range were analyzed by the method of least squares and a plane was fitted to them. The following expression describes the relationship between cell edges in Å and Co:Ni:Fe ratio for Ni/Fe ratios of 1 or larger.

$$a = 0.1240X - 0.0246Y + 8.2060$$

where X is the molecular ratio Ni/(Co+Ni+Fe) and Y is the molecular ratio Fe/(Co+Ni+Fe). The standard deviation of the fit was ±0.00086 Å.

An estimate of the standard deviation of the cell edge for a single composition was made from a number of other samples where Co-Fe skutterudite coexisted with loellingite and arsenic at 800° C. These skutterudites should all have the same composition even though the samples have different bulk compositions. Twelve such skutterudites had an average cell dimension of 8.2150 Å with a standard deviation of 0.0006 Å. As this standard deviation is not significantly smaller than the value obtained by the least squares analysis, the assumption of cell edge being a linear function of the Co, Ni, and Fe content (where Ni/Fe is equal to or greater than 1) appears to be valid for the degree of accuracy obtained. The lines in Fig. 2 and the contours in Fig. 3 were calculated from the above expression.

All the skutterudites in Figs. 2 and 3 were made in the presence of excess crystalline arsenic in order to assure that they were saturated with arsenic. A sample with a particular Co:Ni:Fe ratio and excess arsenic will produce the same skutterudite regardless of the amount of arsenic added. The reason is that practically all the cobalt, nickel, and iron are in the skutterudite phase and adding more arsenic will not affect this Co:Ni:Fe ratio. This was verified experimentally by adding large quantities of arsenic to skutterudites already in equilibrium with crystalline arsenic. No change in cell edges was observed (Table 1, nos. 282 and 293).

The limits of solid solution of skutterudite (lines A–G and I–K of Fig. 3) were most easily determined along the sides of the triangle. For example, in the Co-Ni series, a run with a composition between A and B consisted of arsenic, arsenic-rich vapor, skutterudite and rammelsbergite. Because there are four phases in a three component system, the system is univariant. Fixing the temperature makes the system invariant. This means that all four coexisting phases are fixed in composition, regardless of the bulk composition. Changes in bulk composition between A and B will change the proportion of skutterudite present in the sample but not its composition at the point, A. Therefore, the cell dimension of a skutterudite coexisting with rammelsbergite, arsenic, and vapor along the line A–B can be compared with the appropriate a versus composition plot of Fig. 2 and the composition of the skutterudite at A determined. Points G, K, and I were determined in a similar manner and are probably accurate to about ±1 mol per cent.

Three points between A and G were determined in a similar way. The same phases are involved. As very little Co, Ni, or Fe is involved in the solid arsenic or the vapor phase, these phases need not be plotted. The line between the coexisting rammelsbergite and skutterudite must pass through the point corresponding to the Co:Ni:Fe ratio of the sample. Such a line would have to radiate from the small rammelsbergite field, B-C-Ni. Therefore, these lines could vary but little from the lines shown in Fig. 3. These lines intersect the contours of skutterudite cell dimensions. The intersection with the contour representing the cell dimension of the skutterudite found in the sample marks the limit, A–G.

The iron-rich limit (I-K) of skutterudite was determined partly by the above method and partly by the presence or absence of loellingite. Its accuracy is probably ±3 per cent near the middle of curve I-K.

In order to see how these limits of solid solution change with temperature, some portions of samples in which skutterudite coexisted with arsenic and loellingite or rammelsbergite were reheated for three months, some at 700° C. and some at 600° C. The changes in cell dimensions indicated changes in the limits as shown in Table 2. However, equilibrium was approached from only one direction and may not have been attained.

Natural skutterudites. As the work at 600° and 700° C. suggests changes in the limits of the Co, Ni, and Fe content of skutterudite of only a few

TABLE 2. CHANGE IN LIMITS OF SKUTTERUDITE SOLID SOLUTION WITH TEMPERATURE

A, G, I, and K refer to points shown in Fig. 3

Temp., °C.	A Co-Ni, Mole per cent Ni	G Ni-Fe, Mole per cent Ni	I Fe-Ni, Mole per cent Ni	K Fe-Co, Mole per cent Fe
800	65	75	53	10
700	62	74	52	8
600	62	74	49	6

per cent from the limits observed at 800° C., this field is probably not much different in shape or extent at temperatures below 600° C. The analyses of natural specimens tend to confirm this.

The majority of analyses of natural skutterudites compiled by Holmes (1947) fall within the limits established for the synthetic skutterudites. In detail, about two-thirds of these analyses fall within the limits shown in Fig. 3 for the skutterudite field at 800° C., and most of the remainder are no further than 5 per cent outside the limits. As the field of artificial skutterudites only occupies about half of the area of the triangle, this would seem to be a significant proportion of the analyses. The three analyses that fall well outside the field (nos. 29–32, 43, and 136) and three of the four which are no further than 5 per cent outside the field (nos. 20–21, 47, 185) were made between 1856 and 1886 and hence the materials were not examined by reflecting microscope or by *x*-rays to establish their homogeneity. The fourth analysis (no. 154), dated 1924, was made on a mixture of loellingite and skutterudite.

More recently, Jouravsky (1948) analyzed cores and rims of two crystals plus the whole of a third crystal of skutterudite. These five analyses all fall well within the limits of skutterudite shown in Fig. 3.

The 15 skutterudite analyses reported by Godovikov (1960) (which include four specimens leached in various reagents) all fall within the limits shown in Fig. 3. However one specimen (no. 29) and its leached counterpart (no. 25) fall approximately on the line A–G of Fig. 3.

The only analyzed skutterudites for which cell edges have been determined are seven reported by Holmes (1947) and eleven reported by Godovikov (1960). The Co:Ni:Fe ratios, (As+S)/(Co+Ni+Fe) ratios, and cell edges of these skutterudites are summarized in Table 3. In addition, the calculated cell edges for synthetic skutterudites of the same Co:Ni:Fe ratio have been listed along with the difference in cell edge between the natural and the synthetic. Most natural skutterudites have a cell edge that falls within 0.01 Å of that of the synthetic skutterudites. The largest differences are those of nos. H-19 and H-20. Both of these specimens (particularly no. H-19) have very low arsenic-to-metal ratios and the cell dimensions are 0.02 Å and 0.03 Å larger than the maximum cell size observed for any skutterudite at 800° C. One would expect that an arsenic deficiency of the magnitude indicated by the analyses would produce a skutterudite with a cell size smaller than that of the synthetic skutterudite with the same Co:Ni:Fe ratio. The analyses for nos. H-19 and H-20 are those reported by Short (1930) who established the homogeneity of these specimens from polished sections. Holmes (1947, p. 370) examined Short's section of H-19 and found it to be only slightly inhomogeneous. The remainder of the original specimen could not be located. Specimen G-29 which was used by Godovikov in leaching experiments is zoned. The four samples of this specimen which were leached lost nickel by amounts ranging from 2 to 8 mole per cent $NiAs_{3-x}$. However the differences between measured cell edges and calculated cell edges of the leached samples remained approximately the same as that of G-29.

TABLE 3. CELL DIMENSION OF ANALYZED VERSUS SYNTHETIC SKUTTERUDITES

(Specimen numbers beginning with G refer to Godovikov (1960), those beginning with H to Holmes (1947). The cell edges of natural skutterudites have been converted from the kX units of the original papers to Ångstrom units. Equation (1) was used to determine a(Calc.).)

Spec. No.	Co:Ni:Fe	$\frac{(As+S)}{(Co+Ni+Fe)}$	a(Å) (meas.)	a(Å) (calc.)	Diff.
H-16	~100-0-0		8.204	8.206	−0.002
H-17	90.8-.5-8.7	2.83	8.207	8.213[1]	− .006
H-18	49.3-23.2-27.5	2.66	8.239	8.230[1]	+ .009
H-19	45.4-43.4-11.2	1.43	8.320	8.257	+ .063
H-20	19.2-65.1-15.7	2.46	8.311	8.283	+ .028
H-21	26.9-58.5-14.6	2.78	8.274	8.275	− .001
H-22	74.7-18.6-6.7	2.81	8.211	8.227	− .016
G-15	60.4-31.6-8.0	2.79	8.224	8.243	− .019
G-16	47.2-39.4-13.4	2.82	8.245	8.252	− .007
G-17	50.2-38.2-11.6	3.02	8.253	8.250	+ .003
G-18	46.4-48.4-5.2	3.03	8.259	8.265	− .006
G-19	49.6-42.5-7.9	2.93	8.261	8.257	+ .004
G-20	35.2-54.1-10.7	2.86	8.269	8.270	− .001
G-21	42.6-48.6-8.8	2.92	8.271	8.264	+ .007
G-22	37.0-54.9-8.1	2.85	8.277	8.272	+ .005
G-23	42.8-52.1-5.0	3.06	8.282	8.270	+ .012
G-24	36.8-56.1-7.1	3.02	8.288	8.274	+ .014
G-29	26.6-67.1-6.3	2.95	8.311	8.288	+ .023

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[1] Estimated from Fig. 3.

One would expect a zoned skutterudite to give a different cell edge than an unzoned one with the same total composition. On an *x*-ray powder pattern, either film or diffractometer tracing, the measured lines would be the integrated total of the diffraction energy due to each component of different composition. However, phases of different compositions diffract with different intensities. The effect of the unequal intensities is to produce apparent offset or asymmetry of the measured lines in the direction of the stronger intensities. For instance, with copper radiation the zones rich in nickel give lines of stronger intensity than those rich in cobalt. This would offset the lines on powder photographs and diffractometer charts toward larger cell dimensions.

If one omits the three skutterudites discussed above, H-19, H-20, and G-29, thirteen skutterudites remain with Ni content greater than Fe content. The expression for the cell edge as a function of composition fits these 13 skutterudites with a standard deviation of 0.0097 Å. This is much larger than the standard deviation of 0.00086 Å for the natural skutterudites.

One factor partially accounting for the larger standard deviation of the natural samples is that these measurements were made by several different individuals in different ways. They are all reported only to the nearest 0.001 Å with no estimate of the accuracy. This basic uncertainty in the accuracy of the data makes any further effort to correlate the deviations with other factors such as As/(Co+Ni+Fe) ratios or sulfur content very difficult.

There are two other fundamental uncertainties which cannot be evaluated. Many skutterudites are strongly zoned with the cores relatively rich in nickel. The only skutterudite in Table 3 where the description mentioned zoning was G-29, but others may be zoned. Also, the skutterudites with (As+S)/(Co+Ni+Fe) much below 2.90 probably contain some diarsenides or niccolite as an impurity. As these impurities would usually have a very different Co:Ni:Fe ratio from the skutterudite, the ratio obtained by chemical analysis would not be that of the skutterudite but of skutterudite plus impurity.

Both Holmes and Godovikov included sulfur with arsenic in their (As+S)/(Co+Ni+Fe) ratios. The substitution of sulfur for arsenic occurs in loellingite and it seems reasonable that a similar substitution might occur in skutterudite. However, there is no information other than the chemical analyses of natural skutterudites.

Godovikov (1960) attempted to relate the cell edge to the arsenic and cobalt content. He first plotted the cell edges versus the mol per cent of cobalt for the skutterudites shown in Table 3 plus the synthetic skutterudites of Holmes (1947). He then superimposed three straight line contours of equal (As+S)/(Co+Ni+Fe) ratio on this diagram. Critical examination of his data reveals little real correspondence between these contours and the analyses. While it is possible to contour the points, the straight lines of Godovikov are highly idealized and seven of the 22 points are at least one contour interval out of place. In addition, his choice of cobalt content as an ordinate was unfortunate. As shown in Fig. 3, the contours of equal cell edge cross the lines of equal cobalt content at about 70 degrees over most of the skutterudite field. Hence a change in the Co:Ni:Fe ratio of 7 mol per cent iron will change the cell edge of a skutterudite with a fixed cobalt content by 0.01 Å. The three points on Godovikov's diagram (Fig. 1) labeled 3, 5, and 6 owe their positions to their relatively high iron content. When the cell edge is plotted against the mol per cent of nickel, these three points are completely changed in their positions relative to the other points.

If the cell edge of the natural skutterudites varied with (As+S)/(Co+Ni+Fe), the most sensitive test should be to eliminate the effect of Co, Ni, and Fe on the cell edge and plot the difference in cell edge between the measured value and the calculated value for the same Co:Ni:Fe ratio against the (As+S)/(Co+Ni+Fe) of the natural skutterudite. When the writer made such a plot using the data in Table 3, he could see no significant pattern or trend. The writer also tried plotting the differences in cell edges against sulfur content of the natural skutterudites but again there was no apparent relationship.

The only other element that was reported in these skutterudites in appreciable amounts is antimony. The largest amount listed was 0.41 weight per cent for H-21. Rosenqvist (1953) gives the cell edge of $CoSb_3$ as 9.036 Å. Assuming that the cell edge is a linear function of the antimony content, 0.41 per cent Sb would increase the cell edge by only 0.003 Å. Thus applying corrections in the cell edges for antimony content would not appreciably alter the data.

The writer also fails to see clear evidence in the data summarized by Godovikov for his conclusion that Co, Ni, and Fe substitute extensively for As and S in the skutterudite structure. If one plots the (As+S)/(Co+Ni+Fe) ratios against the specific gravities given in his Table 6 entitled "Dependence of specific weight on the value of (As+S)/me", one obtains a wide scatter of points with a vague trend toward higher specific gravity at lower ratios which Godovikov interprets as evidence of the above substitution. Unfortunately many of the ratios are below about 2.9 and probably these skutterudites contain some other arsenides of lower arsenic content. Thus it should be recognized that a trend toward higher specific gravity with lower As content would also occur if the specimens were not truly homogeneous but consisted of mixtures of skutterudite (G. 6.5) and diarsenides (G. 7.1 to 7.5) or niccolite (G. 7.8). The writer feels that the existing data on natural skutterudites are not yet adequate for a conclusion as to the type of substitution involved.

In conclusion, the cell edges of most of the analyzed natural skutterudites are in good agreement with the cell edges of synthetic skutterudites with the same Co:Ni:Fe ratio. The differences between the two show no relationship to the reported (As+S)/(Co+Ni+Fe) ratios or the total sulfur content of the natural skutterudite. With the exception of some old analyses which probably represent inhomogeneous material, the natural skutterudites fall within the limits of solid solution shown in Fig. 3.

CONCLUSIONS

Skutterudites exhibit a small but real departure from stoichiometric proportions, even in the presence of crystalline arsenic. However, ratios of (As+S)/(Co+Ni+Fe) smaller than about 2.90 reported in chemical analyses of skutterudites are probably due to admixed phases of lower arsenic content.

The limits of solid solution with respect to Co, Ni, and Fe have been determined for synthetic skutterudites at 800° C. These limits appear to change very little between 800° and 600° C. The 18 natural skutterudites for which both chemical analyses and cell edges are available all fall within these limits, as do most other analyzed skutterudites.

The relationship between cell edge and cobalt, nickel, and iron content is linear for skutterudites in which the Ni/Fe ratio is larger than 1. The differences between observed and calculated cell edges for skutterudites show no particular relation to either (As+S)/(Co+Ni+Fe) or to sulfur content.

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