THE SAFFLORITE–LOELLINGITE SOLID SOLUTION SERIES

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Abstract

Electron microprobe analyses of transition metal diarsenide minerals show that there is complete solid solution between $CoAs_2$-$FeAs_2$, limited solution of Co in $NiAs_2$ and no solid solution between $FeAs_2$-$NiAs_2$. The only ternary Co-Fe-Ni diarsenide compositions are in the more cobalt-rich range (safflorite).

The variations of a, b and c of the marcasite-like lattice with composition follow smooth curves in synthetic $(Co, Fe)As_2$ and fall close to these curves for natural $(Co, Fe, Ni)As_2$ minerals.

X-ray diffraction data are given for synthetic and natural Co-Fe diarsenides and the effect of Ni is described. The X-ray data for Berry and Thompson's (1962) safflorite I, II, III, IV, V, and loellingite, are correlated with chemical composition. Synthetic $CoAs_2$ and two natural specimens of high-cobalt safflorite have a measurable monoclinic lattice. The name safflorite is retained for natural $(Co, Fe, Ni)As_2$ compositions from 3–100 mole percent $CoAs_2$, with nickel from zero in low Co minerals to about 30 percent in low Fe minerals. Safflorite is dimensionally orthorhombic in the range from 97 to about 20 mole percent Fe and often measurably monoclinic in compositions lower in iron. The exact composition at which safflorite becomes monoclinic has not been established.

Studies of the stoichiometry of safflorite-loellingite show that the minerals are characterized by vacant arsenic lattice positions which in most cases are fully occupied by metals in excess of a 1:2 metal-arsenic ratio.

Introduction

Various workers have attempted to determine the exact chemical characteristics of the safflorite-loellingite solid solution series ($CoAs_2$-$FeAs_2$). Noteworthy are Roseboom (1963) for his studies in the synthetic system and Holmes (1947) for his work on natural phases. Holmes pointed out the heterogeneity of natural phases and their close association with $NiAs_2$ and $CoAs_3$. Thus many early analyses are probably incorrect. Until recently it was not possible to analyze the exact range of compositions existing in nature. Electron microprobe studies have been conducted (Radcliffe, 1966) on 80 natural samples obtained from most known localities, through the courtesy of Queen's University, Royal Ontario Museum, University of Toronto, and the United States National Museum.

Berry and Thompson (1962) published six different X-ray diffraction patterns for safflorite-loellingite and named these types safflorite I, II,

III, IV, V and loellingite. These determinations were made on minute single crystals and small scratch samples and it was not possible then to correlate these types with chemical composition. By use of electron microprobe, X-ray diffraction, and density measurements on small fragments (20 mg on average), the chemical, stoichiometric, and physical parameters of this solid solution series have been correlated.

ANALYTICAL TECHNIQUES

Eighty polished sections of transition metal arsenides were measured at various points for Co, Ni, Fe, As, and S. Of these, 39 were selected for more detailed study involving complimentary X-ray diffraction analysis and density measurements. Studies were made in the following order: monophase areas of about 2–3 mm in diameter were delineated by drilling a circle on the polished surface of the sample. The encircled areas were then re-checked for homogeneity in the microprobe. Some of the samples were seen to be multiphase or heterogeneous and thus unsuitable for density measurements. Following microprobe analysis, the delineated area was extracted by means of a percussion drill. The density of the solid fragment was measured, prior to crushing and analysis by X-ray diffraction.

As an aid in X-ray diffraction analysis and in the establishing of conversion parameters for microprobe output into chemical composition, six standards were synthesized for the $CoAs_2$-$FeAs_2$ series.

Synthesis of cobalt-iron diarsenides. The compounds were prepared by a subsolidus diffusion technique at 800°C and 10^{-4} mm Hg in the anhydrous system with a low vapor volume. The exact weights of reduced metal sponges were mixed in the stoichiometric ratio of 1:2. Pure $CoAs_2$ (DR-1) and $FeAs_2$ (DR-6) were prepared together with 4 intermediate compositions of $(Co,Fe)As_2$ at intervals of 20 mole percent. Four separate annealing processes, each of one week duration, were necessary to produce a homogeneous diarsenide reaction product.

Electron microprobe analysis. An Applied Research laboratories AMX microprobe was employed in this study. An electron beam of approximately 1 micron diameter, accelerated to 20 KV, impinging on the sample surface, generates a sample current of about 0.020 microamps and a $K\alpha$ X-ray counting rate below 5000 cps which is within the linearity range of the detection system. Correction was made to the integrated 40-second count for instrumental dead time and for the small differences of emission wavelengths of sample and standards (Radcliffe 1966).

Pure metal standards were mounted directly into the polished sections and an intensity ratio obtained. This ratio was converted into weight percentage using Duncumb and Shield's backscatter correction, Nelm's ionization efficiency correction, Philibert's absorption correction and Castaing's fluorescence correction[1].

The method is satisfactory for alloyed phases but not for phases with ionic and covalent bonding unless the absorption correction is modified to allow for the differences of interatomic spacings of pure metal standards, and chemically combined phases. A modification of Philibert's absorption correction was made and basic mass-absorption data were obtained from Kelly (1966) for $K\alpha$ radiation as follows.

[1] Unpublished manual for electron probe microanalyzer, M.I.T., 1965.

Emitter	Co Absorber	Fe Absorber	As Absorber
Co	58	61	110
Fe	68	76	135
As	160	175	38

The mean mass absorption for the alloyed phase was computed equivalent to $CoAs_2$ and $FeAs_2$. This was multiplied by the mean density of each composition which was extrapolated from the pure metal end members after their densities had been measured on a Berman Balance. The resulting linear absorption coefficient was subsequently divided by the mean density of the minerals to give the new mass absorption coefficient.

A series of natural samples were analyzed independently by X-ray fluorescence but due to the difficulty of measuring Co, Fe, Ni, and As, in high concentrations, and to sample heterogeneity, calibration curves utilizing these data have a poor correlation. However their conversion parameters of X-ray intensity ratio (I/I_0) into weight percent are close to the calculated parameters. The mean of the measured conversion parameters, a constant derived by a least squares straight line on the same data, and the calculated theoretical proportionality constants (*i.e.* $I/I_0 \times K$) are given below:

Parameter	$K(Co)$	$K(Fe)$	$K(As)$
means of measured	0.945	0.924	1.035
least squares	0.997	0.921	1.035
calculated	0.940	0.926	1.037

The mean analytical total of 100 analyses after correction was 100.2 percent with a standard deviation of ±1.4 percent.

Density measurements. The density of samples averaging 20 mg was determined by a weight loss procedure on a Berman Balance. Carbon tetrachloride was used as a liquid medium as it has a low surface tension (26.95 dynes/cm at 20°C) and a higher density (1.595) than toluene. The precision error, obtained with Herkimer quartz and pure galena is ±0.39 percent. The density of transition metal arsenides approach 7.0 and the acceptable measuring precision on three successive measurements was thus ±0.03.

X-ray diffraction analysis. The mineral fragments were ground to a fine powder and mixed with Herkimer quartz as an internal standard. Smear mounts were scanned at $\frac{1}{2}$° per minute on a Norelco diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) and a LiF monochromater. No beta filter is necessary but the increase in intensity of the X-ray beam is balanced by the inefficiency of the LiF diffraction monochromater. The method gives sharp peaks, and permits operation at very high sensitivities with a low even background.

The only well-defined peaks which can be readily indexed are 210, 101, 120, and 111. Consequently all samples were scanned 10 times through the interval 33°-40°2θ. The unit-cell dimensions were then determined simultaneously by least-squares calculations on all four diffraction peaks.

The values obtained for the cell constants (Tables 4 and 5) compare favorably to ±0.01 Å with earlier results on synthetic and natural material.

CHEMICAL COMPOSITION

Nomenclature. The terminology of the safflorite-loellingite compositions is not well defined. Safflorite and loellingite have been considered as

distinct mineral species. Peacock (1944) reported that safflorite is monoclinic[1] with rectangular axes for a Nordmarken specimen (Sweden) and loellingite is orthorhombic with a composition close to $FeAs_2$. Holmes (1947) noted a concentration of analyses along the mid-region of the $CoAs_2$-$FeAs_2$ join, and close to $FeAs_2$, and proposed a cut-off between safflorite and loellingite at 70 mole percent $FeAs_2$. Roseboom (1963) cited the previously reported coexistence of safflorite and loellingite. He also described the symmetry of synthetic $CoAs_2$ as monoclinic. For these reasons safflorite and loellingite have been considered to be distinct mineral species, loellingite being nearly pure orthorhombic $FeAs_2$ and safflorite monoclinic $(Co, Fe)As_2$ with a beta angle close to 90°.

Further study of Nordmarken safflorite (safflorite I) and of safflorite III by Weissenberg methods reveals no evidence of monoclinic symmetry. The composition reported for Nordmarken safflorite by Peacock (1944), based on previous analyses on material from the same locality, is suspect. Microprobe analyses of Berry's sample (M4035) and Peacock's sample (M4035 pk) gave similar results which are significantly different from that quoted by Peacock (Palache, *et al.* 1944, p. 308):

Mole %	Peacock	M4035 pk	M4035
$CoAs_2$	44.3	16.3	17.5
$FeAs_2$	55.0	84.7	82.5
$NiAs_2$	0.7	—	—

The present investigators have found a complete range of compositions from $CoAs_2$ to $FeAs_2$ (Fig. 3) and, with only two exceptions, the lattice of these compositions is dimensionally orthorhombic with a marcasite-like structure. Of the natural samples examined, 25 percent lie in the field of loellingite with less than 2 mole percent metals other than iron. The remaining 75 percent are distributed fairly evenly along the $CoAs_2$-$FeAs_2$ join. It is now recommended that loellingite be used for $FeAs_2$ with less than 3 mole percent $CoAs_2$[2] in solid solution and safflorite for the $CoAs_2$-$FeAs_2$ series. This terminology is in keeping with that used by Berry and Thompson (1962), and with previous usage.

Range of natural compositions. Roseboom (1963) studied the synthetic Co-Fe-Ni diarsenide system and showed complete miscibility of Co-Fe-Ni in a diarsenide structure at 800°C except for a small region close to Ni on the Ni-Fe join (Fig. 1). Further work on the extent of this region at higher and lower temperatures led him to conclude that the immiscibility gap probably constitutes a solvus dome. The complete

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[1] Based on asymmetric intensities at high 2θ values on Weissenberg films.

[2] Nickel was not found in iron diarsenide.

DENNIS RADCLIFFE AND L. G. BERRY
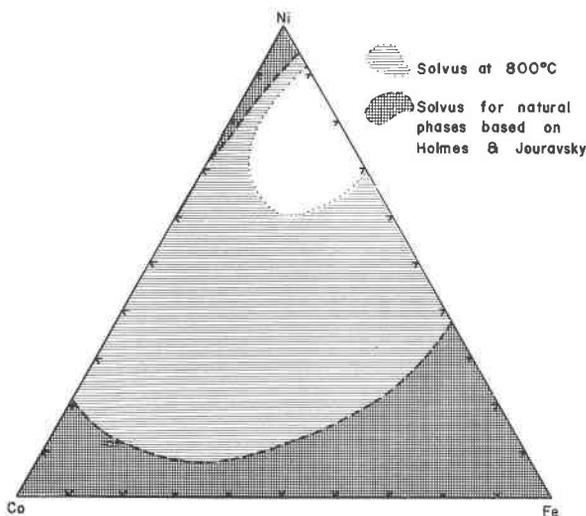
FIG. 1. Solvus for synthetic (800°C) and natural (<800°C) phases,
according to Roseboom (1963).

solubility along the Co-Fe join in the synthetic system was substantiated
by Radcliffe (1966) at 800°C. Roseboom also compiled analyses from
Holmes (1947) and Jouravsky (1959) and sketched the extent of the
solvus for natural phases at temperatures much lower than 800°C
(Fig. 1).

Holmes (1947) compiled all available analyses of natural diarsenides
(about 50) published in the period 1810–1945 and obtained the extent
of the composition limits of natural phases (Fig. 2).

Chemical analyses obtained in this study (Radcliffe 1966) are plotted
on Figure 3. This shows the extent of natural compositions determined by
microprobe techniques. Some representative samples are listed in
Table 1. This limit represents the approximate extent of the solvus at
low temperatures (200–300°C). It is pointed out that coexisting nickel-
rich (generally niccolite) and nickel-poor phases were frequently ob-
served during this study (Table 2). Of the 88 analyses plotted on Figure
3, only three lie outside the limits indicated. These phases are quite
abnormal, of very limited extent in the sample, and are only detectable
with a microprobe e.g. one of the phases occurred only at one point in
sample 1B62 in a 5 micron zone enveloping a core of native silver.
Further away from the silver a more normal composition was measured
with less than 5 mole percent $NiAs_2$.

No cobalt-free Fe-Ni diarsenides were found; this is in accord with
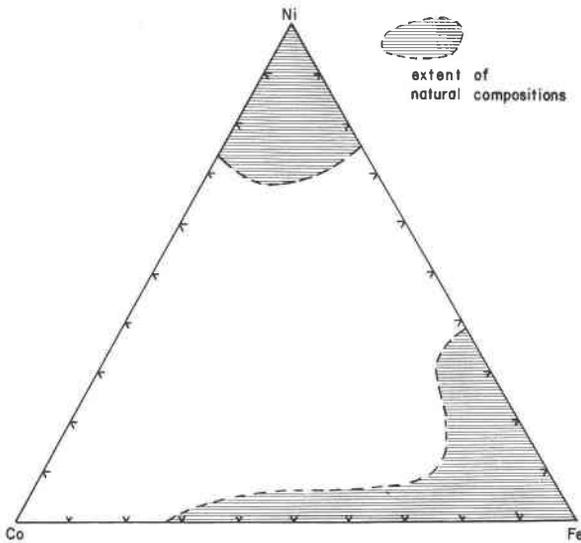
Fig. 2. Extent of natural phases, according to Holmes (1947).

Mikheev's observations (1951). In addition, no ternary compounds exist in Fe-Ni diarsenides unless the cobalt content is in excess of about 25 mole percent. These observations are almost completely contrary to the relationships given by Holmes (1947) and reproduced here in Figure 2. However examination of Holmes' paper shows that the existence of compositions in the nickeliferous loellingite field is based on only three analyses, numbers 80, 81, and 129. Analysis 80 is by Kobell (1868) who notes the presence of arsenopyrite. Analysis 81 was performed by Rammelsberg (1873) who described the sample as loellingite surrounded by breithauptite. Sample 129 was analyzed by Duerr (1907) who notes admixed pyrite and rammelsbergite. Thus in all cases the analyses were probably done on impure material, the impurity probably having a nickel content. The validity of these analyses must be seriously questioned and the existence of a nickeliferous loellingite is unlikely. The existence of ferriferous rammelsbergite is also suspect for similar reasons.

The complete absence of any natural compositions along the Fe-Ni join is in sharp contrast with the complete range of compositions along the Co-Fe join. There is an indication of a weak diffuse maximum near the mid-region, which is a little more Ni-rich than previously described. This is due to the type of sample analyzed as these more Ni-rich members (5-10 mole percent $NiAs_2$) commonly occur as thin veneers (aver-
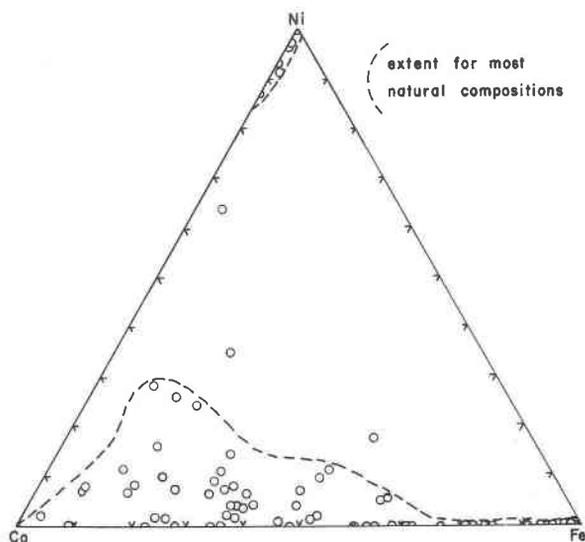
Fig. 3. Extent of natural phases analyzed in this study.

aging 1 mm) surrounding native silver. Such samples are easily analyzed with a microprobe, but not by other, more conventional techniques.

The existence of nearly pure cobalt end-member compositions in minerals has not been previously reported. These samples are intimately intergrown with skutterudite (Radcliffe, 1966) on a fine scale (0.05 mm lenses) and thus are only amenable to analysis by microprobe.

The range of compositions along the Co-Ni join is somewhat peculiar

TABLE 1. SAFFLORITE: SELECTED MICROPROBE ANALYSES FROM RADCLIFFE (1966)

Number	1C03	1B16	1B50	1B35	1B75	1B52	1B63	1B31
Co	2.7	10.8	12.8	16.8	16.2	20.9	22.2	21.2
Fe	25.9	20.7	12.7	9.7	5.6	6.9	5.0	7.6
Ni	—	—	1.9	2.1	6.9	0.3	2.3	—
As	71.2	67.7	72.6	71.7	71.2	69.3	68.4	70.4
S	0.4	1.1	0.6	0.5	0.5	2.6	1.9	1.5
Total	100.2	100.3	100.6	100.8	100.4	100.0	99.8	100.7
Mole % Co	9.0	32.6	45.5	57.7	55.6	73.4	74.5	72.4
Fe	91.0	67.4	47.6	35.0	20.4	25.6	17.7	27.6
Ni	—	—	6.8	7.3	23.9	1.1	7.8	—

TABLE 2. OBSERVED COEXISTING PHASES

Phases	Ag	Sa	Sk	Lo	Ra	Ni	Ge	Ar	Po
Ag	−								
Sa	+	−							
Sk	+	+	−						
Lo	+	−	−	−					
Ra	−	+	−	−	−				
Ni	−	+	+	−	+	−			
Ge	−	+	−	−	+	−	−		
Ar	−	+	−	+	−	−	−	−	
Po	+	+	−	+	−	−	−	−	−

Ag = native silver   Ni = niccolite
Sa = safflorite   Ge = gersdorffite
Sk = skutterudite   Ar = arsenopyrite
Lo = loellingite   Po = pyrrhotite
Ra = rammelsbergite
+ = coexisting discrete phases; − = coexisting phases not observed.

as there is apparently a limited solubility of Co in $NiAs_2$ but no solubility of Ni in $CoAs_2$. Synthetic studies (Roseboom, 1963) along this join show that some Ni could be expected in $CoAs_2$. Possibly the reason for this discrepancy lies in the composition of the geochemical liquids from which these phases crystallized. The processes of geochemical differentiation of Co-Fe-Ni towards an arsenic-rich liquid are such that iron-free Co-Ni liquids do not separate, nor do cobalt-poor (less than 25 mole percent) Fe-Ni liquids. This explanation is supported to some extent by the compositions of observed coexisting phases (Table 2). For example loellingite ($FeAs_2$) was not found in coexistence with a nickel-rich phase, whereas safflorite $(Co, Fe)As_2$ and niccolite are often intimately associated.

Zoning in natural phases. Safflorite associated with a polyminerallic assemblage is invariably zoned or shows definite heterogeneity with regard to the distribution of the Co-Fe-Ni content. Table 3 gives some data for samples associated with native silver and those Co-rich mem-members associated with skutterudite. The width of the zones is quite variable but is often 5-10 μ wide in contact with the other phases but may be up to 50–100 μ.

A diagnostic feature of samples from the Cobalt-Gowganda region, Ontario, is the occurrence of cores of native silver which forms a rectilinear pseudodendritic pattern. Safflorite forms a thin veneer (average

TABLE 3. COMPOSITIONS (MOLE %) OF ZONED ARSENIDES (FIG. 4)

Cat. #	Metallic Cores & Calcite Margins	Co	Fe	Ni
1B34	Ag core	51.2	48.8	—
	massive	51.9	20.3	27.9
1B35	Ag core	68.5	24.7	6.9
	massive	54.5	31.9	13.6
1B52	Ag core	90.1	10.0	—
	massive	74.6	24.4	1.0
1B60	Ag core	40.0	49.7	9.3
	massive	47.1	51.6	1.3
	margin	52.3	47.0	0.7
1B62	Ag core	27.8	55.2	17.0
	massive	31.0	64.2	4.7
1B76	Niccolite core	95.8	3.1	1.1
	massive	84.5	8.5	7.1
1C01	Ag core	42.5	57.5	—
	massive	36.6	63.4	—
	margin	28.6	71.4	—
	Two Phase Zoning			
1B75	Skutterudite	78.7	8.2	13.0
	Safflorite	55.6	20.4	23.9
1B83	Skutterudite	81.1	13.1	5.8
	Safflorite	69.6	21.3	9.1

1 mm) around the silver, and both phases apprently replace calcite. Microprobe analyses of these samples show strong asymmetry with regard to the nickel distribution. Nickel is either concentrated next to silver, or alternatively towards the marginal phase in contact with calcite. Figure 4 shows that safflorite with a Ni-poor core tends to be more cobalt-rich, and that with a Ni-rich core tends to be more iron-rich. This implies that the nickel content is dependent on the Co/Fe ratio (Fig. 5).

It is pointed out that the direction of migration of the composition of the safflorite from the core phase outwards is towards a field in which there is a greater frequency of samples with similar compositions (*cf.*
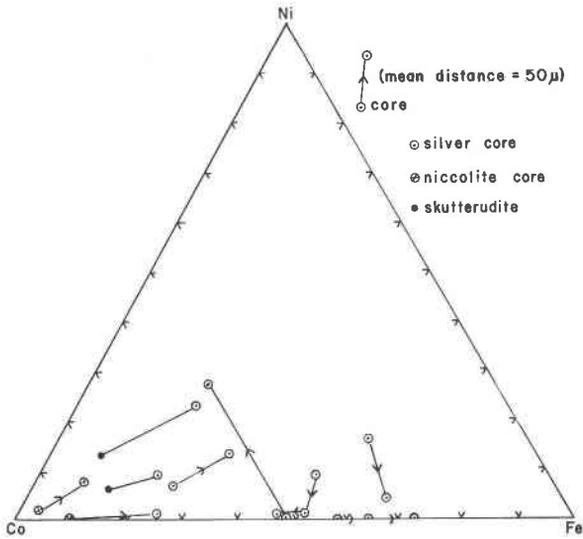
Fig. 4. Compositions of zoned safflorites. Lines with arrows represent the first seven samples of Table 3, lines without arrows the lower two samples in which safflorite and skutterudite coexist.
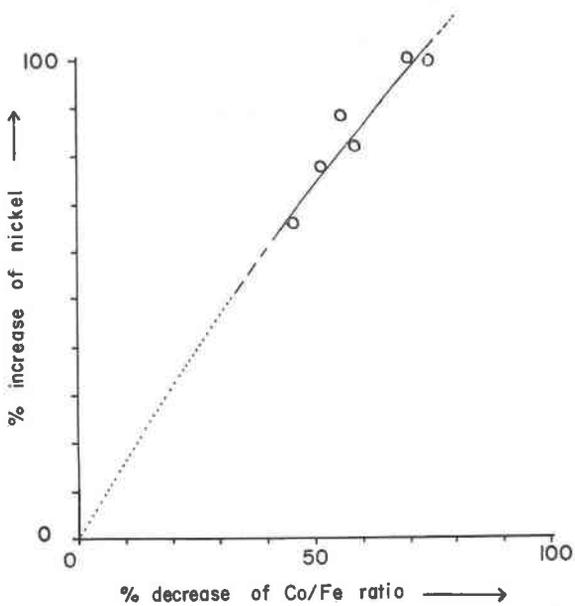
Fig. 5. Nickel content of zoned safflorites.

Fig. 3). In most cases the safflorite phases in immediate contact with native silver have abnormal compositions.

Figures 6 and 7 illustrate the types of zoning found in safflorite-loellingite. Figure 6 is of a loellingite with an average 1.4 mole percent $CoAs_2$ in solid solution. Halos of safflorite which vary from 50 to 100
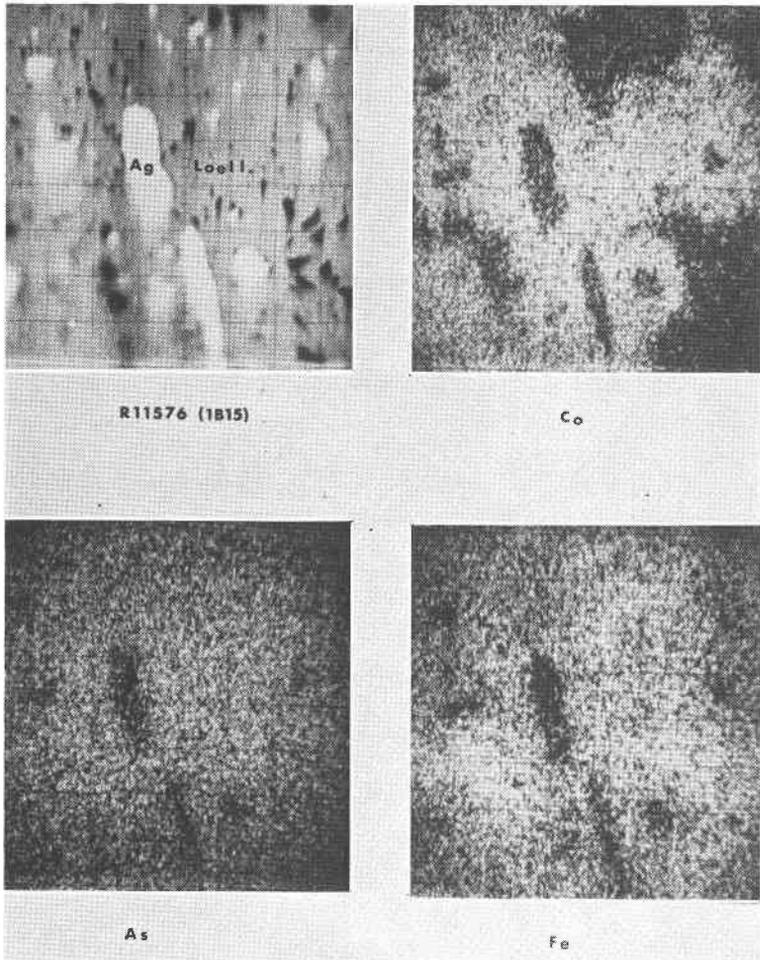
FIG. 6. Top left: Electron backscatter image of loellingite with discrete grains of native silver. Top right: X-ray scanning image showing a concentration of Co in halos surrounding native silver. Bottom left: X-ray image showing homogeneous distribution of As in loellingite. Bottom right: X-ray image showing a more heterogeneous distribution of Fe in loellingite. Grid scale = 0.03 mm.
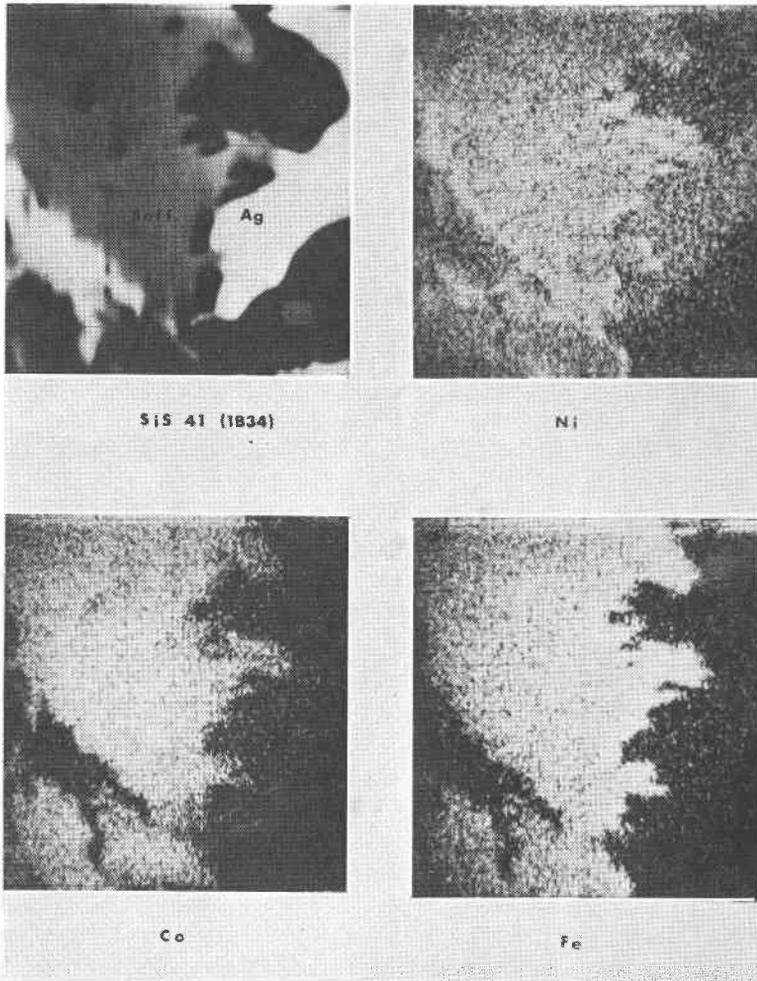
FIG. 7. Top left: Electron image of safflorite and native silver which replaces calcite (black). Top right: X-ray image showing the distribution of Ni in safflorite. Nickel is concentrated at the margins of safflorite in contact with both silver and calcite. Note the presence of some Ni in native silver. A spot check gave 0.3% Ni in this silver. Bottom: X-ray images of Co and Fe. The Co/Fe ratio decreases from left to right across both photographs and the zoning is thus different from that of Ni. Grid scale 0.03 mm.

microns in width occur immediately in contact with native silver. Two types of zoning are shown in Figure 7, in which two areas of native silver, separated by calcite, are all in contact with safflorite. Nickel is concentrated at the margins of the safflorite in contact with silver and

calcite, whereas the Co/Fe ratio of the safflorite varies across the section without apparent regard for the phases with which it is in contact. A puzzling feature is the small content of Ni in native silver, a spot check gave 0.3 percent nickel.

X-Ray Crystallography

The six X-ray patterns of Berry and Thompson (1962) which characterize the safflorite-loellingite series, index on the following orthorhombic cell dimensions:[1]

	a Å	b Å	c Å
Loellingite	5.29	5.98	2.88
Safflorite I	5.26	5.98	2.94
Safflorite II	5.11	5.91	3.11
Safflorite III	5.175	5.950	3.015
Safflorite IV	5.16	5.93	2.99
Safflorite V	5.06	5.89	3.11

This variation of the elementary lattice constants gives rise to a complicated series of diffraction peaks which overlap and interchange position. These reversals are most apparent in the following pairs of peaks; 120-101, 210-111, 220-121, 211-130, and these give the patterns their characteristic appearance. In addition a group of four peaks at higher 2θ positions (310, 031, 221, 131) show more complicated interchanges.

The relative positions of these peaks for Berry and Thompson's six types are plotted on Figure 8 as bar graphs, in the order of increasing cobalt content.

The safflorite I powder pattern differs only slightly from loellingite with a decrease in $\Delta 2\theta$ in the line pairs 120-101, 210-111, 220-121, and 130-211. In safflorite III and IV, which are quite similar, the lines in each pair noted above have interchanged position. This arrangement covers the range from about 30 to 70 atom percent cobalt with very low nickel. In safflorite II and V the order of peaks remains the same as in III and IV but $\Delta\theta$ within each pair increases, apparently with increase in Co/Fe or (Co+Ni)/Fe ratio, approaching pure $CoAs_2$ in V. The change between safflorite I and III and between IV and II seems abrupt but results from a continuous increase in c and decrease in a and b, as expressed in the shift of 011, 101, 111, 121 and 211 to larger d values, accompanied by a shift of 120, 210, 220 and 130 to smaller d values. In the present study safflorite from IB20 and IB85 (both inter-

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[1] Appelations Safflorite I–V refer to X-ray patterns only, and are not strictly mineral or varietal names, although they are characterized by distinct chemical compositions.
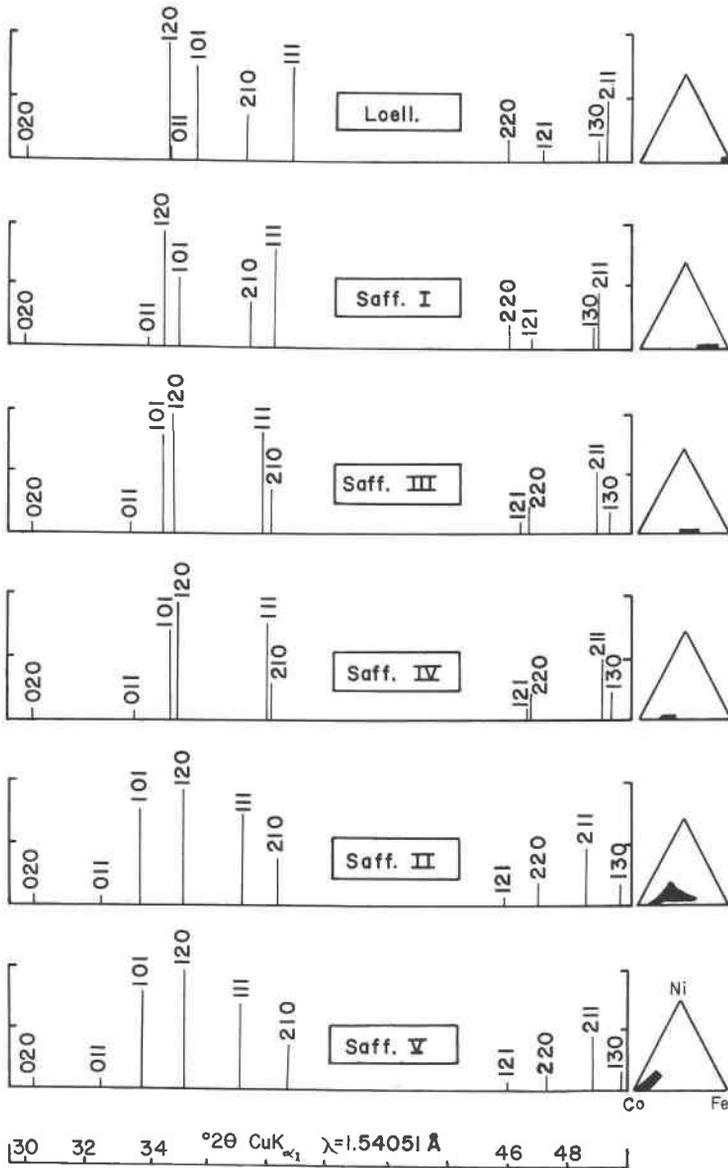
Fɪɢ. 8. 2θ versus intensity (ordinate) for natural safflorites.

grown with skutterudite) gave powder patterns in which $h0l$ and hkl peaks are split or broadened, these require monoclinic indexing. All other natural specimens gave patterns which could be indexed as orthorhombic. Weissenberg study of several natural safflorite fragments (including one of safflorite V) has revealed no divergence from orthorhombic symmetry. Peacock (1944) recorded monoclinic symmetry with $\beta = 90°$ from one set of Weissenberg films, but this has not been observed again.

A similar bar graph (Fig. 9) has been prepared for synthetic safflorite. The cell constants are given in Table 4. DR-1 ($CoAs_2$) shows a splitting of $h0l$ and hkl peaks but no change in $hk0$ and $0kl$. This is distinct evidence for monoclinic symmetry. DR-2 is dimensionally orthorhombic although the hkl and $h0l$ peaks are somewhat broader than similar peaks for less cobalt-rich compositions. Apparently 80 mole percent $CoAs_2$ is close to a measurable transition from orthorhombic to monoclinic symmetry. For ease of comparison, the mean $\bar{h}0l$ and $h0l$, and $\bar{h}kl$ and hkl, were obtained and cell constants calculated as though for orthorhombic symmetry. This is a reasonable procedure as β of monoclinic $CoAs_2$ is very close to 90°.

The X-ray diffraction patterns for synthetic safflorite show very regular trends which are analogous to those found in natural material. DR-6 ($FeAs_2$) is identical to loellingite, DR-5(($Fe_{0.8}Co_{0.2}$)As_2) is very similar to safflorite I and DR-1 ($CoAs_2$) is very similar to safflorite V except for the splitting of hkl and $h0l$ reflections in the former.

Comparison of safflorite I to V with the synthetic data and microprobe analyses of samples previously classified by Berry and Thompson (1962) into a safflorite type gives a distribution of types shown chemically in Figure 10; boundaries are arbitrary.

Only safflorite II and V contain any appreciable nickel in the structure and this has a strong effect on the X-ray patterns. The effect is to 'normalize' the pattern to that of pure $CoAs_2$. This may be explained in terms of the available valency electrons of $Ni(4)$, $Co(3)$, and $Fe(2)$. The effect of Ni and Fe in a safflorite structure is to produce a mean of 3 valency electrons, $i.e.$ the same as cobalt, and the effective covalent radii and electronic structure of Co, and Ni plus Fe, are thus very similar. As a consequence, the lattice dimensions of $CoAs_2$ and safflorite with some Ni and Fe, are quite similar.

Clear evidence of the monoclinic character of synthetic $CoAs_2$ to $Co_{0.8}Fe_{0.2}As_2$, seen in the doubling of several $h0l$ and hkl peaks, is available in this study, in the powder work of several earlier authors, and in the single crystal study by Darmon and Wintenberger (1966). Roseboom (1963) also recorded a monoclinic cell for a synthetic sample
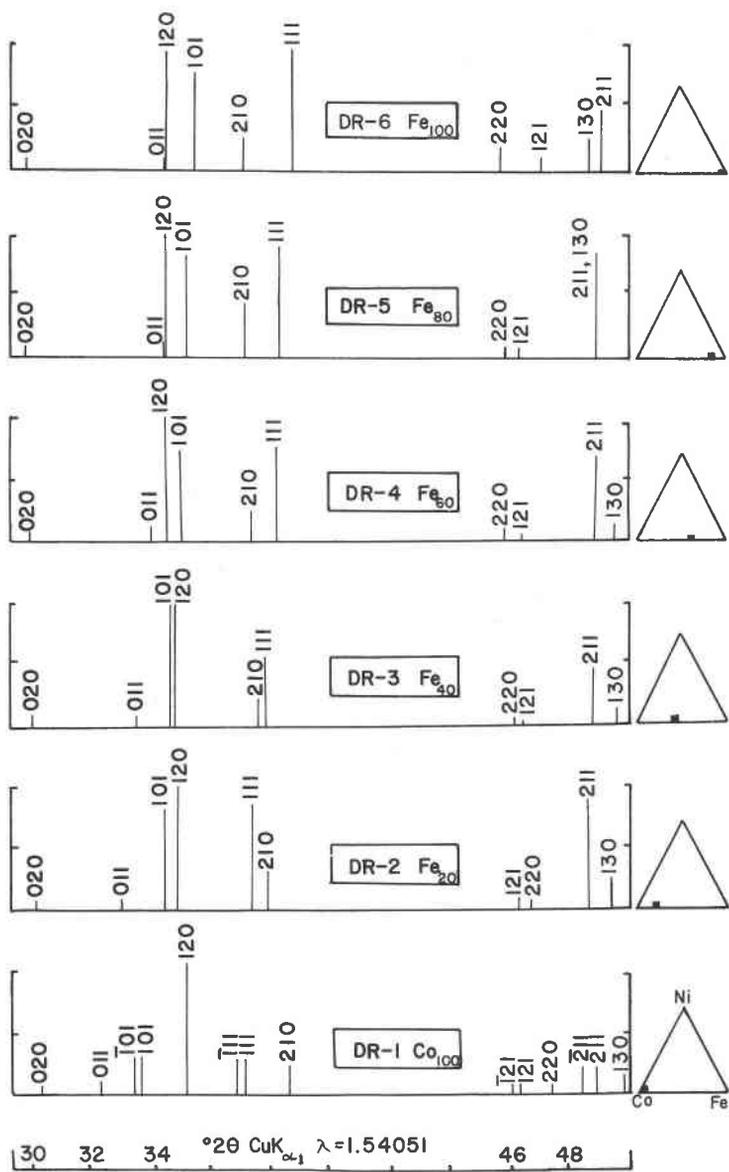
Fig. 9. 2θ versus intensity (ordinate) for synthetic safflorites.
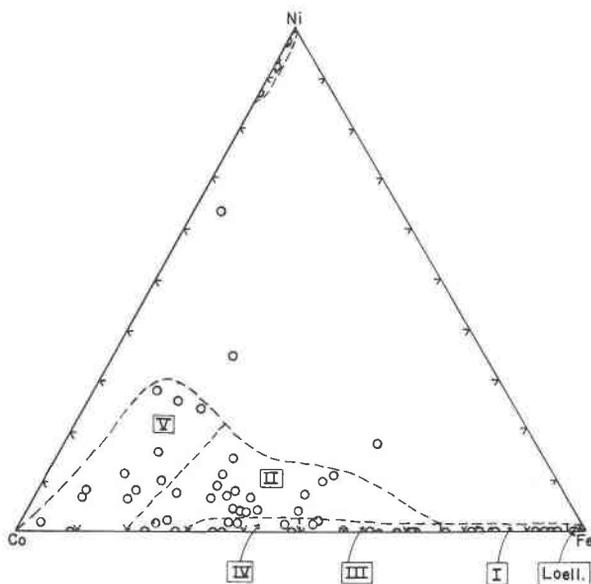
FIG. 10. Compositions of safflorite I to V.

with $Co:Ni = 7:1$. All other compositions yield patterns which can be indexed on orthogonal axes. In addition a few weak lines require the doubling of a and c, as noted below.

CRYSTAL STRUCTURE

Buerger (1932) established that loellingite has the marcasite structure with space group *Pnnm*. Peacock (1941) confirmed this space group; Peacock and Dadson (1940) reported the same space group for rammelsbergite (NiAs$_2$) and Kaiman (1947) confirmed that rammelsbergite also has the marcasite structure. Roseboom (1963) showed that complete solid solution occurs in synthetic phases at 800°C in NiAs$_2$-CoAs$_2$ and in FeAs$_2$-CoAs$_2$. Studies of natural specimens show a complete solid solution in FeAs$_2$-CoAs$_2$, but synthetic CoAs$_2$ and some of the cobalt-rich natural phases show a splitting and/or broadening of hkl and $h0l$ reflections indicating a change to monoclinic symmetry.

Quesnel and Heyding (1962), Roseboom (1963) and Swanson *et al.* (1962, 1966) have all indexed powder diffractometer patterns of CoAs$_2$ using a monoclinic lattice with a B centered cell in which $\beta \approx 90°30'$, $a = 10.1$ and $c = 6.24$ Å are double the values found for the loellingite-like cell. The lattice can be described by a P cell with $a = 5.916$, $b = 5.872$.

$c = 5.960$ Å, $\beta = 116°27'$ (Swanson *et al.*, 1966). Darmon and Winten-
berger (1966) have now confirmed this lattice geometry with single
crystal measurements on synthetic $CoAs_2$, and have deduced the crystal
structure of monoclinic $CoAs_2$.

The variations of cell dimensions of $CoAs_2$-$FeAs_2$ solid solution series
are shown in Figures 11, 12, and 13. With increasing cobalt content there
is an increase in c and cell volume, and a decrease in a and b. Hulliger
and Mooser (1965) have explained these distortions in terms of "Jahn-
Teller" stabilities with respect to octahedral symmetry of the metal-
arsenic atoms. They show that hybridization of the electronic con-
figuration of the metal atoms, which favors the stability of compressed
arsenic octahedra, can occur. Hulliger and Mooser think that the
existence of phases with the marcasite structure is most readily ex-
plained in terms of "Jahn-Teller" distortions. However they do point
out that phases can exist (including marcasite and rammelsbergite) in
which no "Jahn-Teller" distortions can occur. These are called "anom-
alous" marcasites. They also point out that the properties of phases
within each group are variable and the only classifying parameters are
the ratios of the cell edges. Thus:

	c/a	c/b
"anomalous" marcasites (marcasite, rammelsbergite)	$= 0.73$–0.74	0.61–0.63
$CoAs_2$	$= \quad 0.62$	0.53
"Jahn-Teller" marcasites (loellingite)	$= 0.54$–0.56	0.48–0.49

$CoAs_2$ (Fig. 13) falls midway between the two main groups, and the
ratios c/a and c/b vary along smooth curves with increasing iron content
to those of loellingite. The marcasite structure is characterized by
chains of metal-sulfur octahedra whose shared edges are perpendicular
to c. In marcasite and rammelsbergite the metal-metal distance along c
is 3.39 and 3.54. In loellingite this distance is reduced to 2.88, which
increases with cobalt substitution to 3.13 (for pseudo-orthorhombic
subcell) in safflorite.

Darmon and Wintenberger (1966) in their structural study of $CoAs_2$
find Co-Co distances of 2.77 and 3.47 approximately parallel to c. The
sum of these two is equal to the c length of the B centred monoclinic
lattice of $CoAs_2$. These two distances alternate along the c axis. The
structure of $CoAs_2$ is similar to arsenopyrite in which Fe-Fe distances
are 2.89 and 3.53 alternating along the c axis of the B centred monoclinic
lattice. The interatomic distances of 2.9, or less, indicate the existence
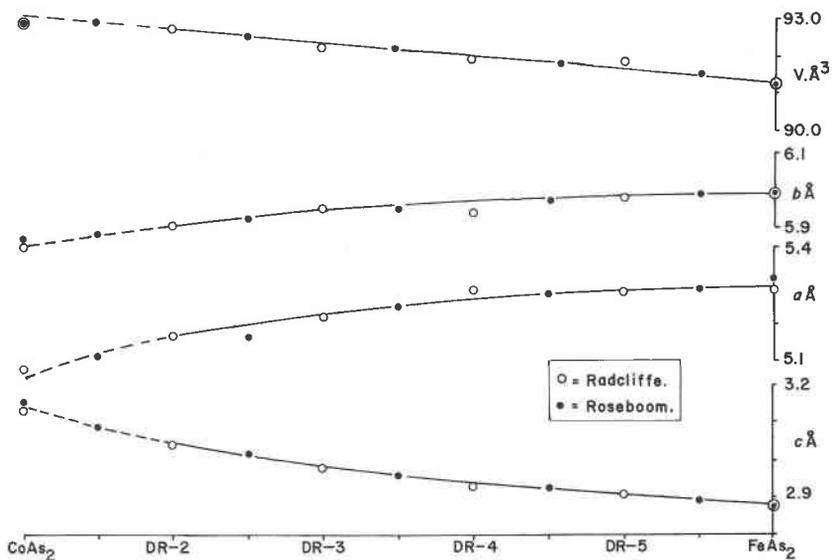
FIG. 11. Synthetic safflorites. Composition versus lattice parameters.
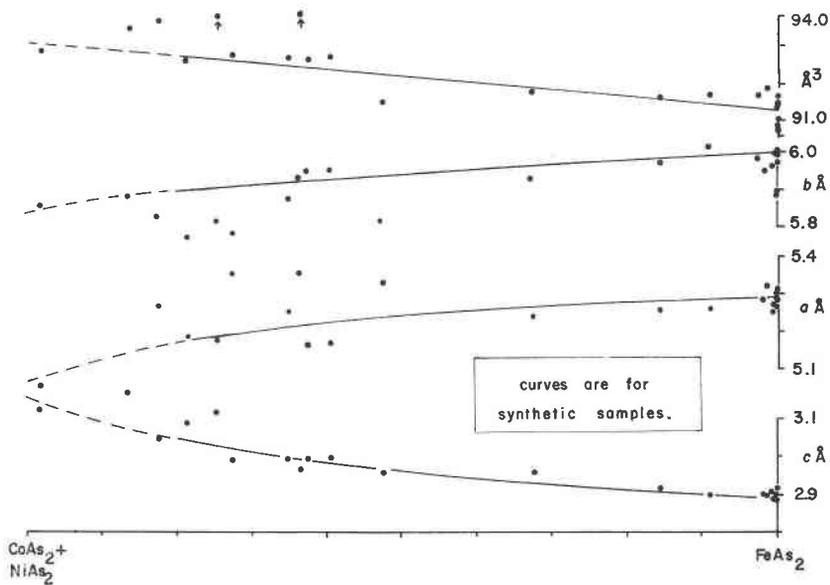
FIG. 12. Natural safflorites. Composition versus lattice parameters.
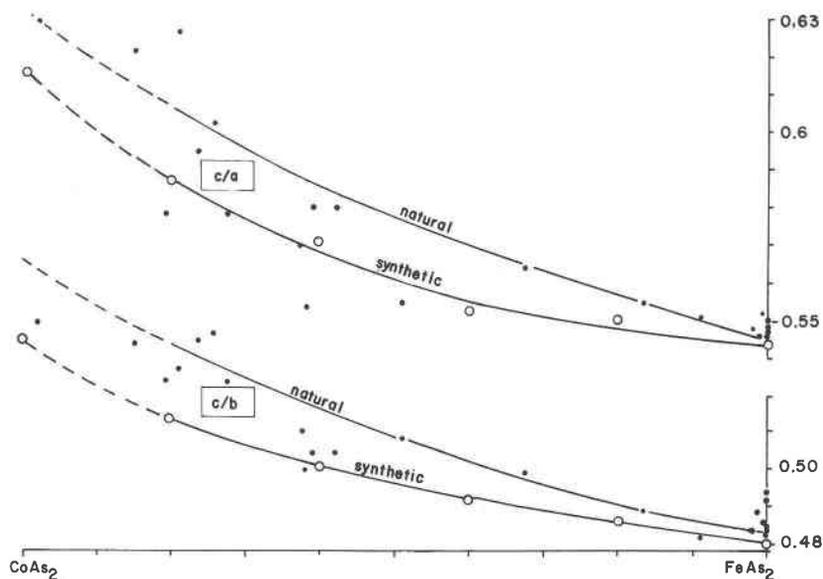
Fɪɢ. 13. Natural and synthetic safflorite. Co/Fe ratio versus c/a and c/b
(loellingite-type cell).

of polycation bonds (Hulliger and Mooser 1965). Nickel (1968) has
recently offered an explanation of this phenomena in terms of ligand
field theory and the number of nonbonded d-electrons. He points out
that substances with 6 nonbonding d-electrons are stable as marcasite
and rammelsbergite or as cobaltite, while those with 5 form arsenopyrite
or safflorite ($CoAs_2$) and one with 4 occurs as loellingite ($FeAs_2$). In
marcasite iron atoms repel each other across the shared octahedral
edge, in loellingite they attract, and in safflorite they alternately attract
and repel. The safflorites, in general, are intermediate between loel-
lingite and $CoAs_2$ in composition, must develop an increasing number
of longer intermetallic bonds with increasing Co content until an
ordered arrangement of alternate long and short bonds is possible in
high Co compositions. The increasing c from loellingite through in-
creasing Co-bearing safflorites is a measure of the average metal-metal
distance across the shared octahedral edge. The number of nonbonded
d-electrons also increases from 4 in loellingite to 5 in $CoAs_2$. The presence
of nickel in high Co safflorites tends to increase the number of non-
bonded d-electrons towards the 5 found in $CoAs_2$, nickel is not found
in iron-free safflorite.

CRYSTAL CHEMISTRY

Properties of safflorite. The cell dimensions of $CoAs_2$-$FeAs_2$ are given in Tables 4 and 5. The variation of cell dimensions along the $CoAs_2$-$FeAs_2$ solid solution series has been determined for the synthetic system by Roseboom (1963) and by the present authors. Both sets of data are plotted on Figure 11 and good agreement was obtained. The value of c decreases with increasing iron content, while a and b increase. The only linear relation of composition is with molar volume and the equation of this line is:

$$\text{mole percent } FeAs_2 = 5629.280 - (60.547 \times \text{molar volume Å}^3)$$

The calculated densities of all the synthetic compositions was 7.47 ± 0.01. Thus the decrease in the cell weight due to increasing iron is balanced by a concomitant decrease in molar volume, probably due to smaller effective covalent radius of iron.

In the natural system (Fig. 12) there is reasonably good agreement of similar plots for nickel-free compositions (*i.e.* compositions with greater than 50 mole percent $FeAs_2$). For compositions $CoAs_2$-$(Co_{0.5}Fe_{0.5})As_2$ there is a wide scatter of points and this is probably related to the effect of nickel on the structure. The plot showing least scatter involved the chemical ratio of $(Co+Ni)/Fe$ (Fig. 12).

Since c is the least variable parameter the data can be somewhat normalized by comparing the c/a and c/b ratio with the Co/Fe ratio. Figure 13 shows that the values for the natural material are consistently higher than those of the synthetic samples.

The reason for the scatter of points in the more cobalt-rich samples is imperfectly understood but is most probably related to variable nickel and sulphur contents, variable temperature of formation, and variable stoichiometry.

The stoichiometry of six safflorites of various compositions and six nearly pure loellingites are given in Table 6. This was determined by considering only the simplest models (*e.g.* Frenkel or Schottky defects) and matching the calculated density of these simple models with the measured density.

The composition of the six safflorites varied from $(Co_{0.75}Fe_{0.25})As_2$ to $(Co_{0.1}Fe_{0.9})As_2$. The stoichiometry is quite variable and no regular trends have been established. However a tendency appears in natural safflorite for part of the anion lattice positions to be occupied by the metals in excess of a 1:2 metal-arsenic ratio. The metal-arsenic solubility limits for synthetic $CoAs_2$ were established by Roseboom (1963) as $CoAs_{1.98}$-$CoAs_{1.99}$. Natural samples apparently show much wider solubility limits, *i.e.*, $(Co,Fe,Ni)As_{1.89}$-$(Co,Fe,Ni)As_2$.

TABLE 4. CELL CONSTANTS AND COMPOSITIONS IN THE SOLID SOLUTION
SERIES $CoAs_2$–$FeAs_2$

Specimen Number	a	b	c	Co	Fe	Ni	As	S
DR–1[a]	5.072	5.878	3.130	100	0	0	100	0
2	5.164	5.913	3.037	80	20	0	100	0
3	5.207	5.946	2.979	60	40	0	100	0
4	5.262	5.979	2.940	40	60	0	100	0
5	5.282	5.975	2.911	20	80	0	100	0
6	5.291	5.987	2.880	0	100	0	100	0
1B20[b]	5.048	5.886	3.144	75.7	13.7	10.6	91.5	8.5
1B52	5.179	5.820	3.122	73.4	25.6	1.1	91.9	8.1
1B32	5.005	5.962	3.142	58.7	15.7	25.6	94.8	5.2
1B44–2	5.173	5.946	3.002	59.0	37.5	3.5	92.2	7.8
1B50	5.327	5.815	2.955	45.5	47.6	6.8	99.8	0.2
1B16	5.237	5.926	2.958	32.6	67.4	0	100.0	0
1B77	5.259	5.970	2.919	16.3	84.7	—	96.5	3.5
1C03	5.259	6.008	2.903	9.0	91.0	—	98.7	1.3
1B15	5.315	5.949	2.906	1.4	98.6	—	98.4	1.6
1B05	5.281	6.000	2.888	—	100	—	100	—

[a] Monoclinic, β not determined, Swanson *et al.* (1966) give $90°28\frac{1}{2}'$.
[b] Monoclinic with $\beta = 90°10'$.

TABLE 5. CELL DIMENSIONS OF PURE $CoAs_2$ AND $FeAs_2$

	Author	a Å	b Å	c Å	β	Material
$CoAs_2$	A. M. Rosenqvist (in T. R. Rosenqvist, 1953)	5.08	5.89	3.10	—	synthetic
	Heyding & Calvert (1960)	5.005[a]	5.87	3.11[a]	—	synthetic
	Quesnel & Heyding (1962)	4.893[a]	5.885	3.167[a]	90°31 1/2'	synethite
	Swanson et al (1960)	5.047[a]	5.872	3.127[a]	90°51'	synthetic
	Swanson et al (1966)	5.048[a]	5.872	3.127[a]	90°28 1/2'	synthetic
	Roseboom (1963)	5.051[a]	5.873	3.127[a]	90°27'	synthetic
	Darmon & Wintenberger (1966)	5.06[a]	5.86	3.12[a]	90°36'	synthetic
	Radcliffe (DR-1)	5.056	5.878	3.130	?	synthetic
	Berry & Thompson (1962)	5.06	5.89	3.11	—	natural (safflorite V)
	Radcliffe (1B20, impure)	5.048	5.886	3.144	90°10'	natural
$FeAs_2$	Buerger (1932)	5.26	5.93	2.85	—	natural
	Peacock (1941)	5.29	5.98	2.88	—	natural
	Heyding & Clavert (1960)	5.300	5.982	2.882	—	synthetic
	Swanson et al (1960)	5.300	5.983	2.882	—	synthetic
	Berry & Thompson (1962)	5.3023	5.9818	2.8802	—	natural
	Roseboom (1963)	5.301	5.979	2.882	—	synthetic
	Radcliffe (DR-6)	5.291	5.981	2.880	—	synthetic
	Radcliffe (extrapolated)	5.285	5.998	2.887	—	natural

[a] Pseudo-cell values—true cell lengths of B lattice are double.

TABLE 6. STOICHIOMETRY OF NATURAL ARSENIDES

	Sample #	Composition	Stoichiometry	Dm	A/B ratio
Safflorite					
	1C03	high iron	$A_1(A_{.04}B_{1.96})_2$	7.34	1:1.89
	1B77		$A_{1.02}B_{2.00}$	7.42	1:1.95
	1B16		$A_1(A_{.03}B_{1.97})_2$	7.32	1:1.92
	1B44-1		$A_1(A_{.01}B_{1.99})_2$	6.99	1:1.97
	1B63		$A_1(A_{.02}B_{1.98})_2$	7.22	1:1.93
	1B20	high cobalt	A_1B_2	7.12	1:2
Loellingite		Co^a S^a			
	1B05	— —	$A_1(A_{.06}B_{1.94})_2$	7.40	1:1.83
	1C16	— 2.3	$A_1(A_{.04}B_{1.96})_2$	7.33	1:1.92
	1B71	— 2.6	$A_1(A_{.03}B_{1.89})_{1.92}$	7.21	1:1.84
	1C14	— 4.1	$A_1(A_{.01}B_{1.98})_{1.99}$	7.29	1:1.93
	1B65	— 5.3	$(A_{.98}B_{.02})B_2$	7.28	1:2.08
	1B15	1.4 1.6	$(A_{.99}B_{.01})B_2$	6.97	1:2.04

[a] compositions in mole % Dm = measured density; A = Co, Fe, Ni; B = As, S.

Properties of loellingite. The cell dimensions, compositions, and stoichiometry of natural and synthetic loellingite are given in Tables 4, 5, and 6.

The stoichiometry of loellingite has been investigated and shows defect structures similar to that of safflorite. In $Fe(AsS)_2$, the sulphur content apparently controls the stoichiometry, *i.e.* with increasing sulphur, the amount of iron occupying the vacant arsenic lattice positions tends to decrease (Table 8). This trend is also accompanied by a general increase of the metal-arsenic ratio. These solubility limits vary from $FeAs_{1.83}$ to $FeAs_{2.08}$ and may be compared with synthetic $Fe(Fe_{0.04}As_{1.96})_2$ which has a metal-arsenic ratio of 1:1.93 (Heyding and Calvert, 1960).

The variation of sulphur with other physical and chemical properties is shown in Figure 14. Samples 1B71 and 1C14 both fall below the correlation lines of a and b. These are from Edenville, New York, and are distinctive in that their stoichiometries show overall anion deficiency despite some of the metals occupying the vacant arsenic lattice positions. It is pointed out that 1B71 may not be quite so highly defective as indicated in Table 6, as the density (Fig. 14) may be in slight error.

Samples from specific localities and thus environments may be characterized by a distinctive stoichiometry *e.g.*, Edenville loellingite discussed above and loellingite from Franklin, New Jersey. In this latter case, Buerger (1932) and Peacock (1944) independently reported $Fe(Fe_{0.08}As_{1.92})_2$ which compares with the present determination (1B05) of $Fe(Fe_{0.06}As_{1.94})_2$.
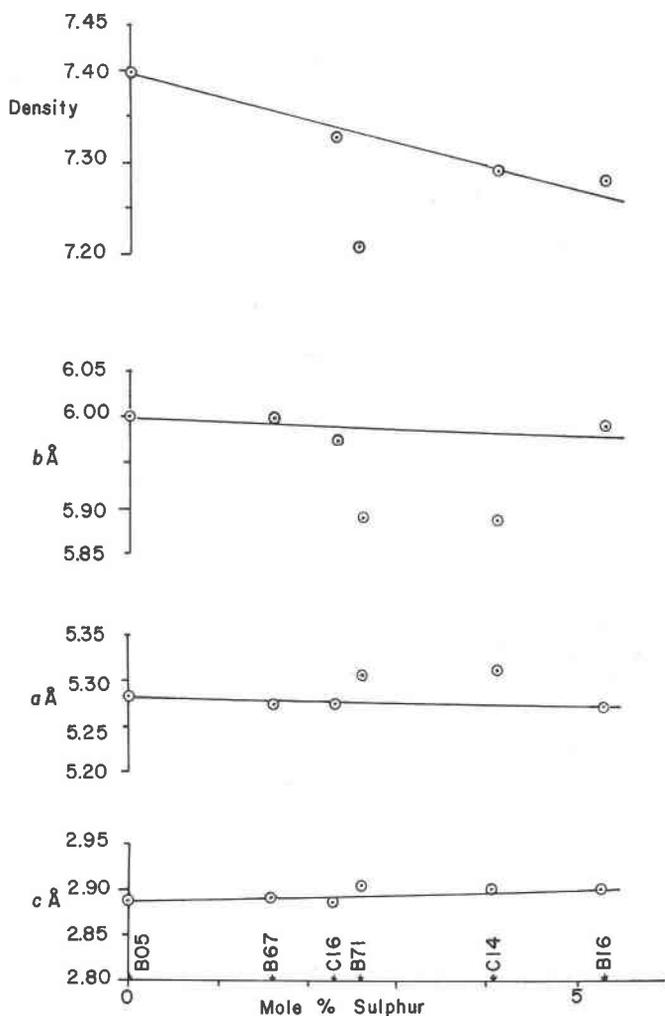
FIG. 14. Loellingite. Sulphur versus lattice parameters and density.

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