[AMERICAN JOURNAL OF SCIENCE, VOL. 260, DECEMBER 1962, P. 761-782]

THE SYSTEM Ni–As–S: PHASE RELATIONS AND MINERALOGICAL SIGNIFICANCE

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ABSTRACT. Phase relations in the ternary system Ni–As–S were determined in rigid silica-glass tubes between 700° and 450°C, with some additional data at lower temperatures.

The only ternary phase in the system, corresponding to the mineral gersdorffite for which the accepted formula is NiAsS, has a large variation in its As/S ratio. It is homogeneous from $NiAs_{1.77}S_{0.23}$ to $NiAs_{0.77}S_{1.23}$ at 700°C. Gersdorffite in equilibrium with $NiAs_2$ (rammelsbergite or parammelsbergite) has the composition $NiAs_{1.80}S_{0.20}$ and $NiAs_{1.72}S_{0.28}$ at 660° and 450°C, respectively. This is a difference of only 2 weight percent arsenic. The unit cell edge of gersdorffite between stoichiometric NiAsS and $NiAs_{1.80}S_{0.20}$ is given by the equation

$$a = 5.6939 + 0.000470X,$$

where a is the unit cell edge of gersdorffite (in Å) containing X weight percent $NiAs_2$. Gersdorffite analyses from the literature are reviewed and several new specimens examined to demonstrate that natural gersdorffite also has a large variation in its As/S ratio.

Complete solid solution exists between niccolite ($Ni_{1\pm x}As$) and $\alpha Ni_{1-x}S$ (the high-temperature modification of millerite) above 595° ± 5°C. The solvus was determined from 595° to 400°C along the join from NiAs to NiS.

Approximately 1 weight percent sulfur substituting for arsenic lowers the polymorphic inversion of rammelsbergite to pararammelsbergite from 590° ± 10°C to 475° ± 25°C.

Stable assemblages in the synthetic system correspond closely to the associations found in nature.

INTRODUCTION

Thirteen minerals are composed essentially of the elements nickel, arsenic, and sulfur. They are: native arsenic, rammelsbergite, pararammelsbergite, niccolite, maucherite, native sulfur, vaesite, polydymite, millerite, heazlewoodite, realgar, orpiment, and the ternary phase gersdorffite. The compositional relations of these thirteen minerals are shown in figure 1. Heazlewoodite is found almost exclusively in serpentinized periodotites, whereas sulfur, orpiment, and realgar commonly occur in low-temperature deposits such as fumaroles and hot springs. The remaining nine minerals are either characteristic or common in the nickel-cobalt-native silver ore deposits (Bastin, 1939), which are exemplified by the Erzgebirge of Germany, and the Great Bear Lake and Cobalt-South Lorraine districts of Canada.

A knowledge of the phase relations in synthetic systems furnishes information on the stability ranges of minerals and mineral assemblages, as well as information on the compositional limits of minerals in different assemblages as a function of total pressure and temperature.

Abbreviations and chemical formulae of minerals used in tables and illustrations are shown in figure 1. In addition, the following formulae are used for synthetic phases which are not known as minerals: (a) $Ni_{5-x}As_2$, (b) $Ni_{3\pm x}S_2$ for the high-temperature polymorph of heazlewoodite (Ni_3S_2), (c) $\alpha Ni_{1-x}S$ for the high-temperature modification of millerite ($\beta Ni_{1-x}S$), and (d) αNi_7S_6. $Ni_{5-x}As_2$ and $Ni_{3\pm x}S_2$ are used as empirical formulae and it is not known whether they are correct structurally.

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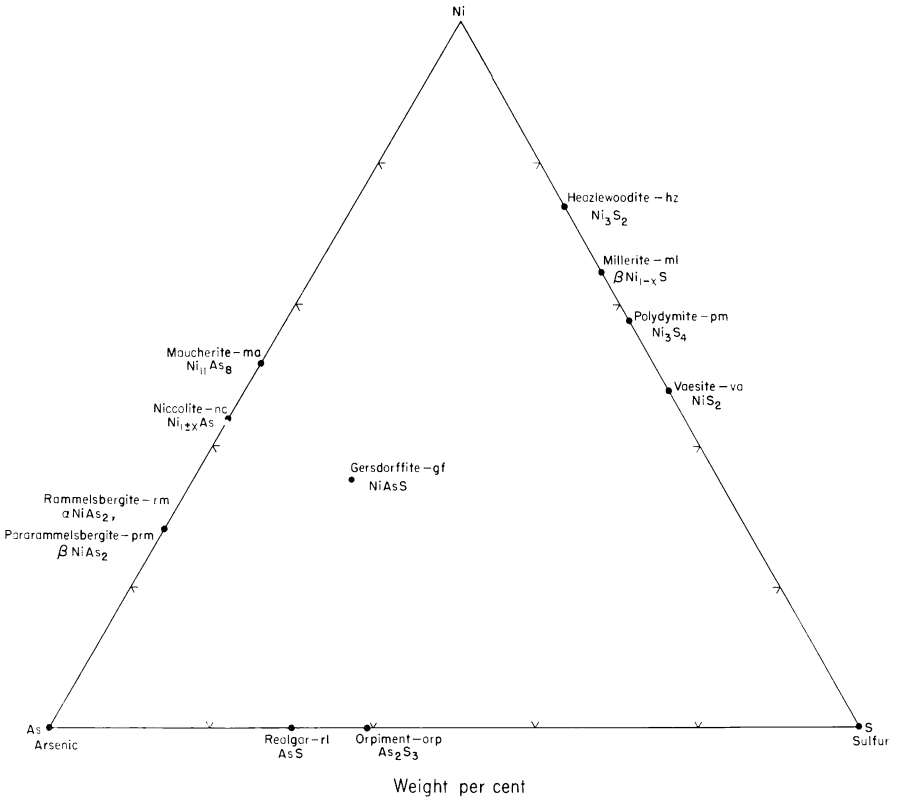

Fig. 1. Minerals in the system Ni–As–S, their abbreviations and chemical formulae. Only the ideal stoichiometric compositions are shown.

PREVIOUS STUDIES

The phase relations and crystallography of the phases in the binary systems Ni–S and Ni–As are described elsewhere by Kullerud and Yund (1962) and Yund (1962), respectively. These studies were preliminary to the investigation of the ternary system Ni–As–S; they will not be reviewed here.

The arsenic sulfides realgar (AsS) and orpiment (As_2S_3) melt at 321° and 310°C, respectively (Jonker, 1909). Thus between 321° and 814°C, the triple point of arsenic, the only condensed phases in the system As–S are metallic arsenic and an arsenic-sulfur liquid. The composition of this liquid in equilibrium with metallic arsenic at 600°C is 77.2 ± 0.1 weight percent arsenic, according to Clark (1960). He also found that less than 0.1 weight percent sulfur is soluble in crystalline arsenic at 600°C and estimated the solubility to be $\leqslant$0.5 weight percent at 350°C. The phase relations in the system As–S below the melting point of realgar are not pertinent to the present study.

Synthesis of the ternary phase gersdorffite has not been previously reported, to the author's knowledge. Ramsdell (1925) investigated the structure

of gersdorffite and found it to be similar to pyrite except for an ordering of the arsenic and sulfur atoms. Peacock and Henry (1948) reported that arsenic and sulfur are actually statistically distributed in the S_2 sites of the pyrite structure. They therefore assigned gersdorffite to the same space group as pyrite ($Pa3$) rather than to $P2_13$. The cell edge reported for natural gersdorffite varies from 5.604 ± 0.05 Å (Peacock and Berry, 1940) to 5.731 Å (Olshausen, 1925).[1]

EXPERIMENTAL METHODS

The temperature-composition relations in the system Ni–As–S were studied by quenching experiments in rigid silica-glass tubes. Pressure-temperature relations in a very limited portion of the system were investigated by collapsible gold tube experiments. These techniques and the apparatus, chemicals, and X-ray standards used in this study are identical with those described by Kullerud and Yund (1962) and Yund (1962).

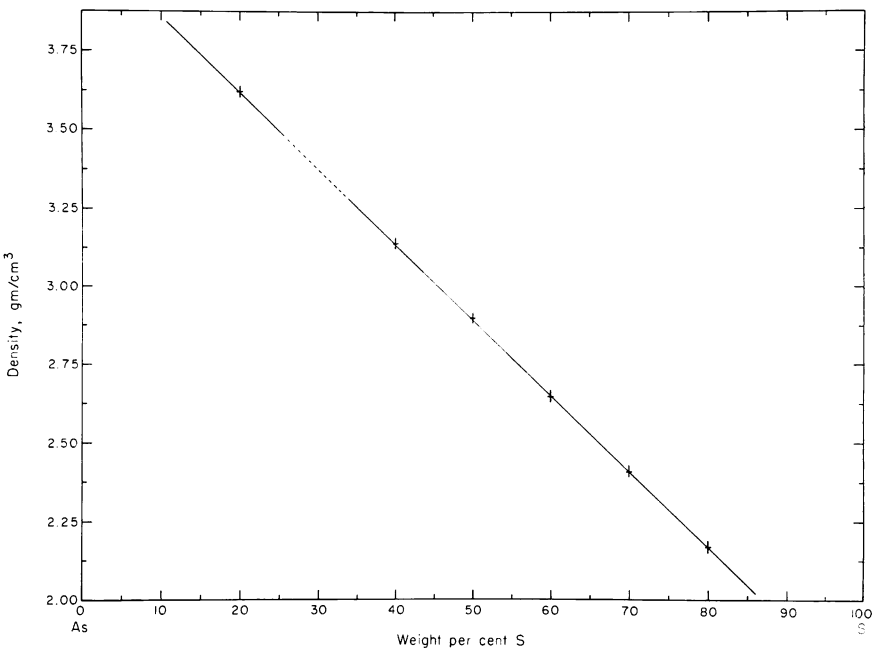

Fig. 2. Density as a function of the composition of arsenic-sulfur glasses. The dashed portion of the curve near 30 weight percent sulfur represents the approximate compositional interval in which the liquids cannot be quenched to a homogeneous glass.

EXPERIMENTAL RESULTS

Arsenic-Sulfur Glasses

Early in the study of the ternary system Ni–As–S it was found desirable to have a convenient and rapid method for determining the composition of arsenic-sulfur liquids. These liquids can be readily supercooled to homogeneous glasses whose densities may be measured on a Berman balance. The X-ray

[1] Units originally given in kX (1 Å = 1.00202 kX).

TABLE 1

Density of arsenic-sulfur glasses

Wt % S	Heating period, hours	T,°C	Density,* gm/cm³
80.00	8	660	2.17
70.00	8	700	2.41
60.00	8	660	2.65
50.00	5	725	2.90
40.00	10	700	3.14
30.00	10	700	†
20.00	10	700	3.62

* Standard deviation of these measurements is 0.02 gm/cm³.

† Contained crystalline AsS.

powder patterns of seven glasses of different composition indicate that the sample of 30 weight percent sulfur alone contained crystalline material of AsS composition (table 1). The straight line shown in figure 2 is the least squares fit to the data in table 1 and has the equation

$$D = 4.11 - 0.0242X,$$

where D is the density of an arsenic-sulfur glass containing X weight percent sulfur. The standard deviation of this line from the data is less than 0.01 gm/cm³, as compared with the standard deviation of 0.02 gm/cm³ of the individual measurements, and supports the hypothesis that the relation is linear. The dashed portion of the curve on either side of 30 weight percent sulfur represents the approximate compositional interval in which the liquids cannot be quenched to homogeneous glasses.

All the glasses that were used to establish the relation of density to composition were quenched to room temperature from temperatures between 660° and 725°C (table 1). Several glasses were also prepared by quenching liquids from below 600°C. These glasses had a lower density than glasses of corresponding compositions that were quenched from a higher temperature.[2] Therefore the density versus composition relation shown in figure 2 is valid only for glasses quenched from above 600°C.

Clark (1960) reports that approximately 0.12 weight percent iron is soluble in an arsenic-sulfur liquid at 600°C. Although the solubility of nickel has not been measured, it is reasonable to expect that its solubility would be similar to that of iron. Even if several tenths of 1 weight percent nickel dissolves in these liquids, the change in density would be insignificant compared to the experimental error in the density measurements. Therefore, figure 2 can be used to determine the composition of arsenic-sulfur liquids synthesized be-

[2] There was no indication of crystalline material in the X-ray powder patterns of the glasses quenched from below 600°C, but incipient crystallization that was not sufficiently developed to be observed by X-ray diffraction might account for their anomalous densities. Another possible explanation for this change in density is that the liquids undergo structural changes below 600°C, which are quenched into the glasses. Several molecular species are known in liquid sulfur, and possibly more than one species exist in liquid arsenic (Moller, 1952).

tween 600° and 700°C in experiments whose bulk compositions lie in the ternary system Ni–As–S.

The System Ni–As–S

Pressure and composition of the vapor in silica-glass tube experiments.— The results of silica-glass tube experiments are shown in a series of isothermal sections. Although the composition of the vapor is not shown in these diagrams, vapor is a stable phase in all assemblages. The vapor pressure in a four-phase univariant assemblage (three condensed phases plus vapor) in a ternary system is fixed for a given temperature, as the only degree of freedom is the concentration of the components. Similarly in an assemblage of less than four phases, which has two or more degrees of freedom, the vapor pressure is not fixed for a given temperature except along a tie-line in a three-phase field. Vapor pressures over the different assemblages could not be measured in silica-glass tubes. The vapor volume in these experiments was carefully restricted with a glass rod, and a correction for loss of material to the vapor was not necessary.

The only information available on the composition of the vapor is from Jonker's (1909) study of the arsenic-sulfur system. At 1 atmosphere pressure he found that the vapor is arsenic-rich compared to the coexisting liquid for compositions of greater than 61 weight percent arsenic, and the reverse relation holds for compositions from 0 to 61 weight percent arsenic. This was confirmed by Clark (1960) for a composition of 77 weight percent arsenic heated in a silica-glass tube at 663°C.

TABLE 2

Equilibrium assemblages in the system Ni–As–S at 700°C as determined in silica-glass tubes

Starting material*	Wt % As†	Wt % S	Heating period, days	Condensed phases
Ni + AsS	14.00	6.00	27	L
Ni_5As_2 + hz	20.00	11.00	22	Ni_5As_2 + $Ni_{3\pm x}S_2$‡
Ni + AsS	25.20	10.80	27	Ni_5As_2 + ma + $Ni_{3\pm x}S_2$
hz + As	15.00	22.69	11	Ni(As,S) + $Ni_{3\pm x}S_2$‡
hz + ma	5.00	24.00	15	$Ni_{3\pm x}S_2$ + ma (~5%)
ma + αNiS	44.17	3.00	150	ma + Ni(As,S)
ma + αNiS	42.77	4.00	150	ma + $NiAs_{0.56}S_{0.44}$ + $Ni_{3\pm x}S_2$
hz + rm	63.78	3.00	22	nc + rm + gf
rm + AsS	71.55	5.00	13	rm + gf + As
rm + S	67.50	6.00	22	gf + As + L
αNiS + L_{70}	5.00	41.00	56	$\alpha Ni_{1-x}S$ + gf + va
nc + S	22.43	60.00	19	gf + va + L
Ni + AsS	38.51	16.49	28	Ni(As,S) + gf
nc + AsS	61.50	11.70	31	gf + L
nc + S	33.64	40.00	19	gf + L
As + S	86.00	14.00	2	$L_{17.3}$§ + As

* L_{70} denotes an arsenic-sulfur glass of 70 weight percent sulfur.

† Wt % Ni = 100 − (As+S).

‡ The stable phases at 700°C were deduced from textural relations (see text).

§ The sulfur content (17.3 weight percent) of this liquid was determined from its density.

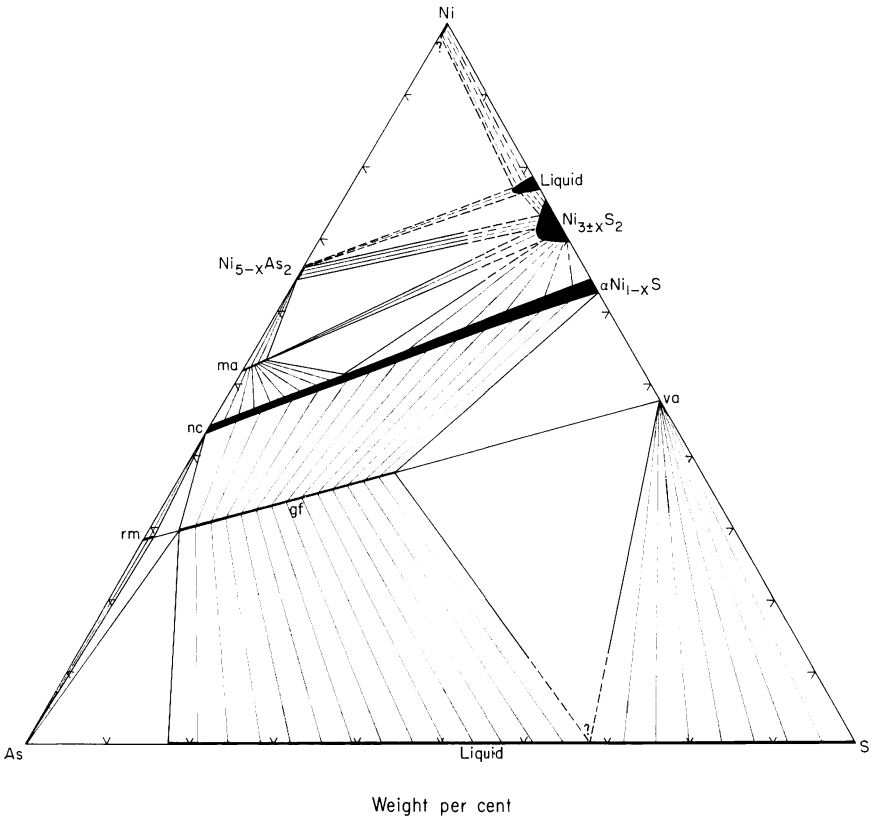

Fig. 3. Phase relations in the system Ni–As–S at 700°C. Vapor is a stable phase in all assemblages. The boundaries of the upper liquid field and of $Ni_{3\pm x}S_2$ into the ternary are only approximate.

Equilibrium assemblages at 700°C.—The stable assemblages in the system Ni–As–S were first determined at 700°C in silica-glass tubes. These experiments are listed in table 2 and the phase relations are shown in figure 3. The nine univariant four-phase assemblages (three condensed phases plus vapor) at 700°C are shown as clear areas in figure 3. There are thirteen bivariant three-phase assemblages (two condensed phases plus vapor) shown by closely spaced, parallel, or radiating lines (tie-lines). The composition of niccolite and gersdorffite in these assemblages will be discussed later. It will suffice for now to note that complete solid solution exists between niccolite and $\alpha Ni_{1-x}S$, and that there is extensive solid solution of arsenic and sulfur in gersdorffite. These solid solutions are shown in figure 3 by the black area and the heavy dark line, respectively. The maximum arsenic content of the arsenic-sulfur liquid at 700°C was determined from its density and figure 2 to be 82.7 ± 0.8 weight percent.

The boundary of the upper liquid field in figure 3, and the bivariant assemblages associated with it, were not accurately determined because the phase

TABLE 3

NiAs-αNiS solid solution series at 700°C

Wt % NiS	Heating period, days	Condensed phases	d_{110}, Å*
0.00	10	NiAs	1.8096
8.49	25	Ni(*As*,S)	1.8021
19.00	31	Ni(*As*,S)	1.7911
28.30	25	Ni(*As*,S)	1.7818
42.00	31	Ni(*S*,As)	1.7685
53.78	22	Ni(*S*,As)	1.7579
64.00	31	Ni(*S*,As)	1.7476
73.59	24	Ni(*S*,As)	1.7405
83.00	31	Ni(*S*,As)	1.7318
91.08	25	Ni(*S*,As)	1.7257
100.00	10	NiS	1.7192

* Standard error of the mean of eight measurements for each sample is 0.0003 Å.

relations above the tie-line from $Ni_{5-x}As_2$ to $Ni_{3\pm x}S_2$ were not considered important to the present study. In addition, the boundary of the phase $Ni_{3\pm x}S_2$ was not studied in detail.

Niccolite-$\alpha Ni_{1-x}S$ solid solution.—Bulk compositions between NiAs and NiS were prepared with finely ground NiAs and αNiS as reactants (table 3). A homogeneous phase, which can be represented by the general formula

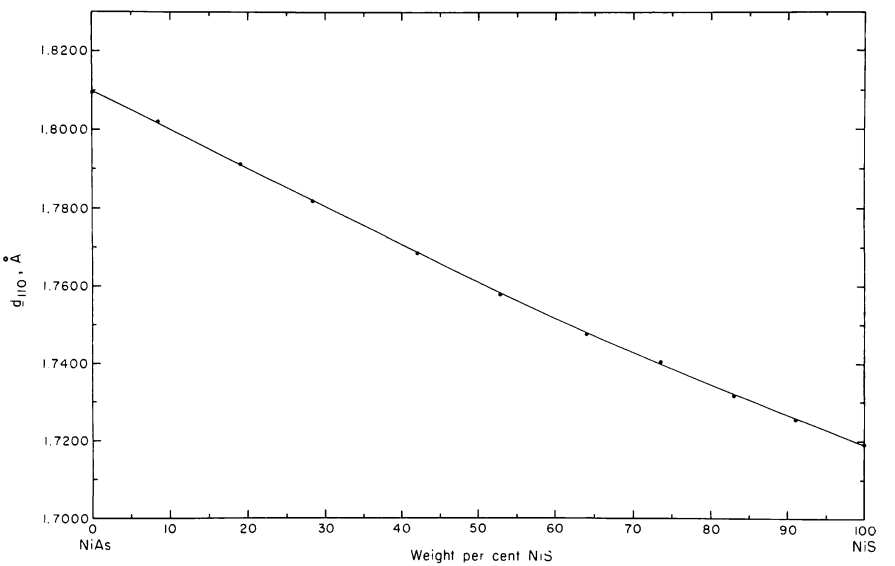

Fig. 4. d_{110} as a function of the composition of Ni(As,S).

TABLE 4

Variation in the Ni/(As+S) ratio of $Ni_{1-x}(As,S)$ at 700°C

Starting material	Wt % As	Wt % S	Heating period, days	Condensed phases
ma + AsS	51.00	3.92	24	$Ni_{>0.959}(As,S)$ + gf
Ni_5As_2 + AsS	44.00	8.44	19	$Ni_{>0.953}(As,S)$ + gf
hz + As	27.87	19.27	19	$Ni_{>0.926}(As,S)$ + gf
hz + As	26.33	19.67	77	$Ni_{0.954}(As,S)$
hz + AsS	15.00	27.40	20	$Ni_{>0.931}(As,S)$ + gf
hz + AsS	14.00	27.37	20	$Ni_{0.960}(As,S)$

Ni(As,S), was formed in all experiments after 20 days at 700°C.[3] Thus complete solid solution between NiAs and NiS was established. The variation in d_{110} as a function of Ni(As,S) composition is shown in figure 4.

Niccolite ($Ni_{1\pm x}As$) and $\alpha Ni_{1-x}S$ are not stoichiometric compounds; their metal-to-nonmetal ratio is not restricted to a 1:1 ratio. Intermediate members of the niccolite-$\alpha Ni_{1-x}S$ solid solution series would also be expected to have a variable metal-to-nonmetal ratio. This variation is manifested in the width (as seen on an isothermal section) of the trivariant field $Ni_{1\pm x}(As,S)$-vapor. The metal-to-nonmetal ratio was investigated at several points between the end members at 700°C (table 4). As shown in figure 3, the boundary of the niccolite-$\alpha Ni_{1-x}S$-vapor field is slightly concave inward on the side toward gersdorffite. The boundary on the other side of this area, $Ni_{1+x}(As,S)$ in equilibrium with maucherite or $Ni_{3\pm x}S_2$, is essentially a straight line, as the maximum value x in the formula $Ni_{1+x}As$ is only 0.025 at 700°C (Yund, 1962), and solid solution does not occur on the nickel-rich side of αNiS (Kullerud and Yund, 1962).

The solvus between NiAs and NiS was investigated by means of a series of exsolution experiments, using a homogeneous phase of Ni(*As,S*) composition as starting material (table 5). Exsolution of Ni(*As*,S) and αNi(*S*,As) from Ni(*As,S*) was complete after 21 days at 500°C (see table 5). The compositions of the exsolved phases were not measurably changed after heating for an additional 42 days, which is accepted as proof that the phases had essentially reached chemical equilibrium. Compositions of the exsolved phases were obtained from their d_{110} values and figure 4. Similar time versus composition studies at lower temperature (table 5) were used to determine points on the solvus, which is shown in figure 5.

There was no measurable difference in the values of d_{110}, and hence in the composition, of the exsolved phases when maucherite was added to the starting material (table 5). Thus the join between stoichiometric NiAs and

[3] If two elements are in solid solution, the one present in the largest atomic percentage will be italicized. If the atomic percentages of the elements in solid solution are approximately equal, then both elements will be italicized. This will distinguish the formula Ni(*As,S*) from the general formula Ni(As,S) which applies to the complete solid solution series regardless of the arsenic-to-sulfur ratio.

TABLE 5

NiAs-NiS solvus*

Heating period, days	T,°C	Ni(*As*,S)		αNi(*S*,As)	
		d_{110}, Å	Comp., wt % NiS†	d_{110}, Å	Comp., wt % NiS†
63	600	No change, still homogeneous Ni(As,S)			
31	590	1.7808	29.3	1.7423	70.6
31	585	1.7830	27.1	1.7392	74.3
28	550	1.7924	17.5	1.7326	82.5
21	500	1.7991	10.8	1.7261	90.7
63	500	1.7994	10.5	1.7266	90.2
30	400	1.7974	12.5	1.7220	96.2
109	400	1.7995	10.4	1.7218	96.5
213	400	1.8004	9.3	1.7216	96.7
650	400	1.8028	7.2	1.7216	96.7
190	300	1.782	~26	1.724	~85
570	300	1.800	~9	[βNi(*S*,As)]	
79	550	1.7918	10.8	1.7325	82.5
79	550	1.779	[Ni_{1-x}(*As*,S)]	1.744	[αNi_{1-x}(*S*,As)]

* Starting material was homogeneous Ni(*As*,S) of 53.78 weight percent NiS, 46.22 weight percent NiAs. The second to last experiment also contained some $Ni_{11}As_8$, and the last experiment contained some NiAsS.

† Values are correct to within ± 0.5 weight percent except for approximate compositions. Compositions of exsolved phases were determined from figure 4.

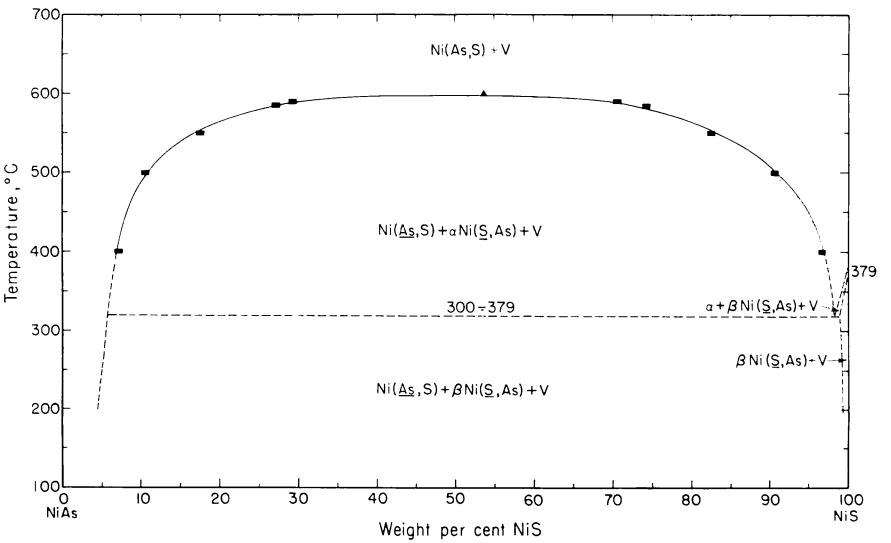

Fig. 5. NiAs–NiS solvus. The triangle represents a homogeneous phase of 53.78 weight percent NiS which did not break down. Compositions of phases which formed by exsolution from a homogeneous phase of 53.78 weight percent NiS are shown by rectangles. Dashed lines represent relations that were not accurately determined.

stoichiometric NiS appears to be truly binary. However, when gersdorffite (of NiAsS composition) was added, the d_{100} values of the exsolved phases were not identical with those established earlier. Thus niccolite and $\alpha Ni_{1-x}S$ in equilibrium with gersdorffite are nickel deficient; the spacing curve shown in figure 4 cannot therefore be used to determine their compositions.

Composition of gersdorffite.—Gersdorffite is the only ternary phase in the system Ni–As–S. Samples were prepared at 700°C with bulk compositions along a line between $NiAs_2$ and NiS_2 (table 6). Compositions between $NiAs_2$ and stoichiometric NiAsS reacted readily to form a homogeneous phase. $Ni(As,S)_2$; but compositions between NiS_2 and stoichiometric NiAsS reacted very slowly to form $Ni(S,As)_2$.[4] Consequently the latter compositions were heated for a very long period to ensure complete reaction (see table 6). The

TABLE 6

Variation in the cell edge of gersdorffite solid solution*

Wt % NiS_2†	Heating period, days	Condensed phases	a of gf, Å‡
4.74	115	gf + rm	5.7318
11.12	22	gf	5.7262
13.41	22	gf	5.7245
17.05	36	gf	5.7195
24.90	22	gf	5.7093
30.33	22	gf	5.7023
37.07	10	gf	5.6940
37.07	26	gf	5.6940
40.72	750	gf	5.6923
44.41	750	gf	5.6893
47.74	750	gf	5.6867
50.91	750	gf + va	5.6864

* All samples were prepared at and quenched from 700°C.

† Composition expressed as weight percent of NiS_2 and $NiAs_2$.

‡ Standard error of the mean of eight measurements for each sample is 0.0008 Å.

unit cell edges of gersdorffite in these runs were calculated from measured values of d_{311}. The straight lines shown in figure 6 are the least squares fit to the data in table 6, and the line through $Ni(As,S)_2$ compositions has the equation

$$a = 5.6939 + 0.000470X,$$

and the line through $Ni(S,As)_2$ compositions has the equation

$$a = 5.6943 - 0.000438X,$$

where a is the unit cell edge of gersdorffite (in Å) containing X weight percent $NiAs_2$ in the first equation and X weight percent NiS_2 in the second equation. The standard deviation of these lines from the data is less than half the standard deviation of the individual measurements, which indicates that the relations are truly linear and that the abrupt change in slope at stoichiometric NiAsS is real.

[4] See previous footnote. The formulae given here are convenient to represent gersdorffite compositions on either side of stoichiomtric NiAsS. These formulae should not be interpreted as representing solid solution of sulfur in rammelsbergite ($NiAs_2$) or of arsenic in vaesite (NiS_2).

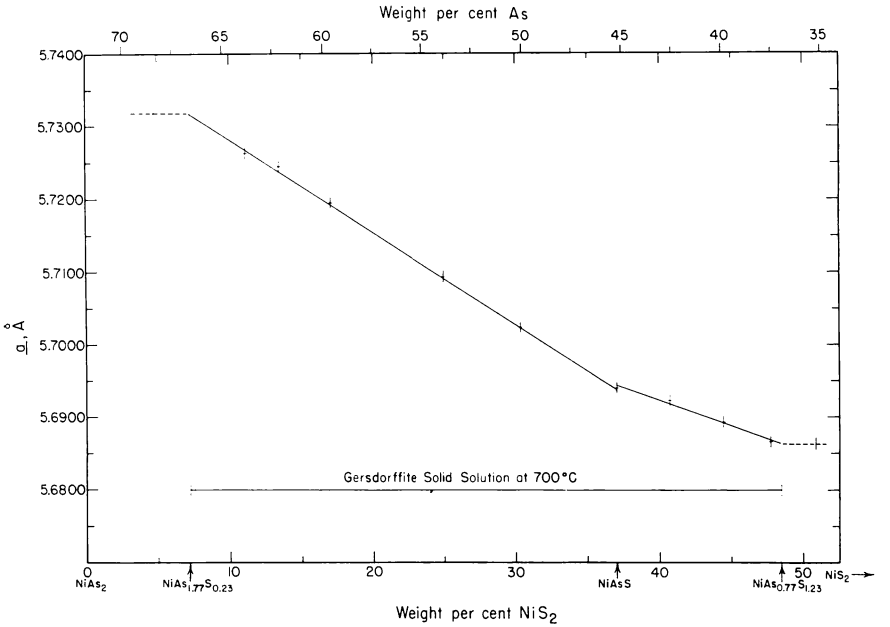

Fig. 6. Variation in the unit cell edge, *a*, as function of gersdorffite composition.

The maximum arsenic content at 700°C corresponds to the formula $NiAs_{1.77}S_{0.23}$, and the maximum sulfur content at that temperature corresponds to the formula $NiAs_{0.77}S_{1.23}$. Thus gersdorffite solid solution extends along a line from rammelsbergite to vaesite, with the largest amount of solid solution on the $NiAs_2$ side of stoichiometric NiAsS. The difference in the arsenic content between the ends of this solid solution is approximately 30 weight percent.

X-ray powder patterns of gersdorffite and vaesite are not identical. The powder patterns of natural gersdorffite, synthetic NiAsS, natural vaesite, and synthetic NiS_2 are shown in figure 7. The presence of the (110) reflection in the patterns of gersdorffite rules out the space group $Pa3$ proposed by Peacock and Henry (1948). This reflection is consistent with the space group $P2_13$ and supports the structure proposed for gersdorffite by Ramsdell (1925). NiS_2 belongs to the same space group ($Pa3$) as pyrite (de Jong and Willems, 1927), and the lower symmetry of gersdorffite apparently results from an ordering of arsenic and sulfur in the S_2 sites of the pyrite structure (Ramsdell, 1925).

The (110) reflection was not observed in powder patterns (film or diffractometer trace) of $Ni(As,S)_2$ mix-crystals on either side of stoichiometric NiAsS. Apparently the intensity of (110) is too low for it to be recorded on powder patterns except for compositions very close to NiAsS. Presumably this reflection would be recorded on single-crystal photographs.

The reason for the apparently abrupt change in slope of the curve in figure 6 is not clear. It may be due to a phase change, but a single-crystal X-ray study is required before a solution to this problem can be given.

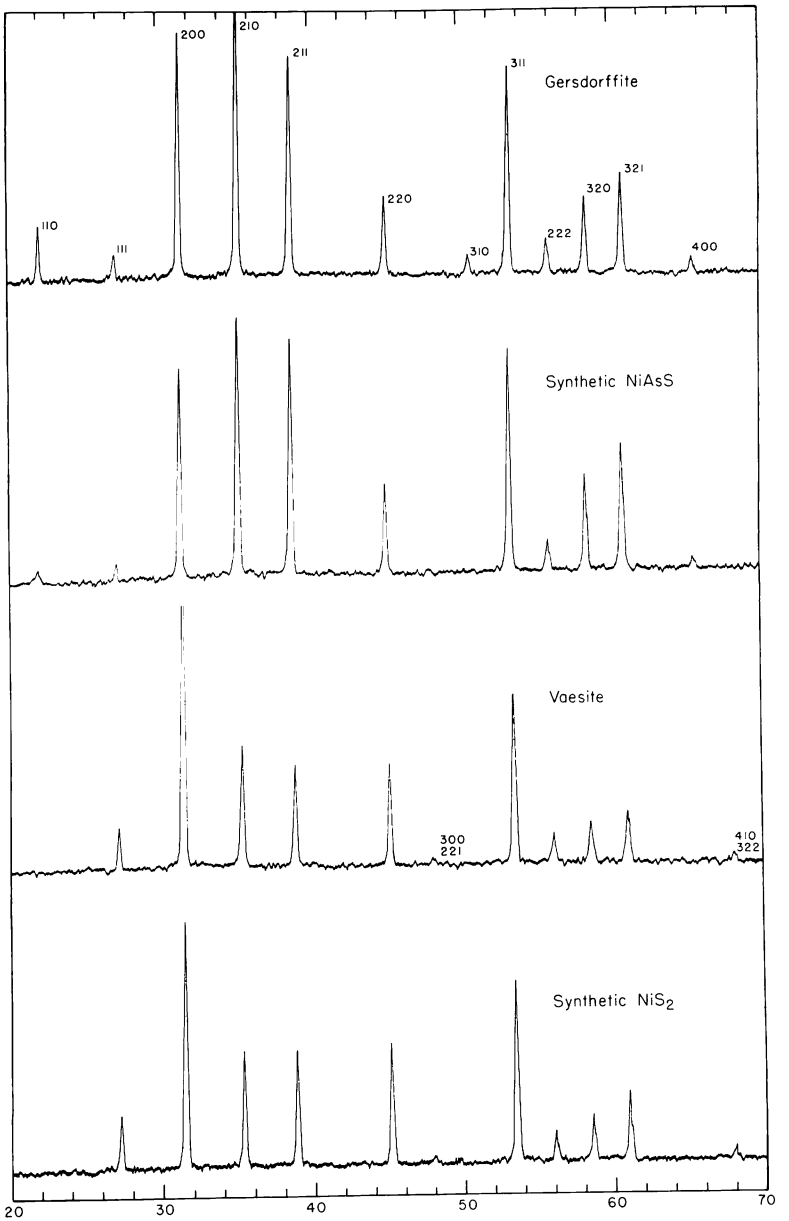

Fig. 7. X-ray powder patterns of gersdorffite, synthetic NiAsS, vaesite, and synthetic NiS_2. All patterns were obtained on a Norelco diffractometer with CuKα radiation. The intensity scale is linear. Gersdorffite from Mitterberg, Salzburg, Germany; vaesite from near Katanga, South Africa.

TABLE 7

Variation in the maximum arsenic content of gersdorffite as a function of temperature and pressure*

Heating days period,	T, °C	Condensed phases	*a* of gf, Å
115	700	gf + rm + As	5.7318
14	700	gf + rm + nc	5.7318†
50	660	gf + rm + As	5.7295
125	660	gf + rm + As	5.7331
250	660	gf + rm + As	5.7331
75	600	gf + rm + As	5.7315
205	600	gf + rm + As	5.7315
50	550	gf + prm + As‡	5.7298
125	550	gf + prm + rm + As‡	5.7305
250	550	gf + rm + As	5.7305
50	500	gf + prm + nc + As‡	5.7301
125	500	gf + rm + As	5.7305
250	500	gf + rm + As	5.7305
75	450	gf + rm + prm + nc + As‡	5.7295
210	450	gf + prm + As	5.7295

* Starting materials for the first heating at each temperature were nc + As + S. In the second and third heating the starting materials were the products from the first and second heating, respectively.

† This was a gold-tube experiment at 2000 bars total pressure using the products from the preceding experiment as starting materials. Some arsenic was lost as a result of diffusion through the gold tube, and the bulk composition moved from the gf-rm-As to the gf-rm-nc assemblage.

‡ Not equilibrium assemblages.

If the substitution of arsenic and sulfur for each other is the only type of solid solution possible in gersdorffite, then the Ni/(As+S) atomic ratio should be constant and equal to one half. Bulk compositions lying slightly above and below a line from $NiAs_2$ to NiS_2 were prepared at 700°C with NiAs plus sulfur as the reactants (fig. 3). Even samples with bulk compositions within 0.5 weight percent nickel of this line contained a third condensed phase, either niccolite or liquid. Therefore, the Ni/(As+S) atomic ratio of gersdorffite is within the limits of 0.500 ± 0.009.

The variation in the maximum arsenic content of gersdorffite as a function of temperature was investigated between 450° and 700°C (table 7). Changes in the cell edge of gersdorffite as a function of time were studied at various temperatures to determine when equilibrium had been attained. The maximum arsenic content of gersdorffite, which occurs at approximately 660°C, corresponds to the formula $NiAs_{1.80}S_{0.20}$.[5] Gersdorffite in equilibrium with $NiAs_2$ at 450°C has the formula $NiAs_{1.72}S_{0.28}$. Thus the arsenic-rich limits of

[5] The maximum at 660°C does not correspond to any known phase change in gersdorffite or rammelsbergite, or to a melting phenomenon.

TABLE 8

Substitution of sulfur for arsenic in rammelsbergite and of arsenic for sulfur in vaesite at 700°C

Composition, wt %	Heating period, days	Condensed phases	Unit cell dimensions,* Å		
			a	*b*	*c*
99.00 $NiAs_2$ 1.00 S	48	rm + As	4.739	5.781	3.558
98.00 $NiAs_2$ 2.00 S	30	rm + As + gf	4.739	5.781	3.557
99.00 NiS_2 1.00 As	49	va + gf(?) + L	5.6883		
98.00 NiS_2 2.00 As	49	va + gf + L	5.6890		

* Standard error of the mean for eight measurements of rammelsbergite: $a = 0.004$ Å, $b = 0.002$ Å, $c = 0.001$ Å. For a of vaesite, 0.0008 Å.

$Ni(As,S)_2$ at 660° and 450°C correspond to a difference of only 3 weight percent $NiAs_2$; the solvus is therefore nearly vertical in this temperature interval.

The effect of a total pressure of 2000 bars on the maximum arsenic content of gersdorffite was studied at 700°C (see table 7). There was no difference in the value of the cell edge, or consequently the composition, after 2 weeks. Although it was not proved that the charge had reached equilibrium in this length of time, the experiment does indicate that a large confining pressure has very little effect on the position of the solvus.

Solubility of NiS_2 in rammelsbergite and of $NiAs_2$ in vaesite.—The substitutions of sulfur for arsenic in rammelsbergite and of arsenic for sulfur in vaesite were studied at 700°C (table 8). Arsenic was a stable phase in experiments using $NiAs_2$ plus sulfur as reactants. The composition of rammelsbergite in each run was determined by drawing a tie-line from arsenic through the bulk composition to the $NiAs_2$-$Ni(As,S)_2$ join. The maximum sulfur content of rammelsbergite was found to be 1.1 ± 0.1 weight percent at 700°C. No attempt was made to measure the sulfur content at lower temperature since it is undoubtedly less than 1.1 weight percent. Cell dimensions of pure rammelsbergite are $a = 4.756$ Å, $b = 5.793$ Å, and $c = 3.544$ Å (Yund, 1962). A comparison of these values with the cell dimensions given in table 8 shows that a and b decrease, whereas c increases when sulfur enters the rammelsbergite structure.

The unit cell edge of vaesite coexisting with gersdorffite and liquid was studied by heating mixtures of NiS_2 and arsenic at 700°C (table 8). There is no measurable difference in the cell edge of vaesite in these preparations and that of pure NiS_2 (5.6890 Å) reported by Kullerud and Yund (1962). Gersdorffite was not positively identified in the sample containing 1 weight percent arsenic; however, vaesite and sulfur-rich gersdorffite are very similar in reflected light, and positive identification of a trace amount of one with the other is not always possible. Assuming that equilibrium was attained, less than 1 weight percent arsenic can substitute for sulfur in vaesite at 700°C.

TABLE 9

Phase relations in the system Ni–As–S below 700°C

Reactants	Wt % As	Wt % S	Heating period, days	T, °C	Condensed phases
hz + As	15.00	22.70	114	660	ma + $Ni_{3\pm x}S_2$ + αNi(*S*,As)*
As + S	85.00	15.00	2	660	$L_{19.9}$† + As
hz + AsS	8.89	27.11	31	640	ma + $Ni_{3\pm x}S_2$ + αNi(*S*,As)‡
Ni_5As_2 + AsS	39.48	4.70	43	600	ma + $Ni_{3\pm x}S_2$
hz + As	15.00	22.70	19	600	ma + αNiS + $Ni_{3\pm x}S_2$
Ni_5As_2 + AsS	41.57	6.43	57	600	ma + Ni(*As*,S)
Ni_5As_2 + L_{70}	32.53	23.47	25	600	αNi_{1-x}(*S*,As) + gf
NiS + L_{70}	5.41	41.59	40	600	$\alpha Ni_{1-x}S$ + gf + va
$NiAs_2$ + AsS	71.55	5.00	18	600	rm + gf + As
As + S	85.00	15.00	2	600	$L_{22.9}$§ + As
hz + As	15.00	22.70	37	500	ma + αNi_7S_6 + αNiS
ma + Ni(*As*,S)	41.57	6.43	46	500	ma + nc + αNi(*S*,As)
Ni(*S*,As) + AsS	34.90	21.10	36	500	nc + αNi_{1-x}(*S*,As) + gf
ma + As + S	81.60	8.00	49	450	prm + gf + As
NiS + AsS	13.00	34.34	50	280	gf + ml + pm

* Contains 71 weight percent NiS, 29 weight percent NiAs.

† An arsenic-sulfur liquid of 19.9 weight percent S.

‡ Contains 78 weight percent NiS, 22 weight percent NiAs.

§ An arsenic-sulfur liquid of 22.9 weight percent S.

Substitution of sulfur for arsenic in maucherite.—$Ni_{11}As_8$ and αNiS were used as reactants to determine approximately the amount of sulfur that can substitute for arsenic in maucherite (table 2). Assuming that none of the sulfur substitutes for nickel, the maximum sulfur content of maucherite at 700°C is 2.0 ± 0.4 weight percent. Cell parameters (tetragonal) of pure $Ni_{11}As_8$ are a = 6.867 Å, c = 21.80 Å (Yund, 1962); those for maucherite with approximately 2 weight percent sulfur are a = 6.840 ± 0.002 Å, c = 21.76 ± 0.01 Å. Thus the substitution of sulfur for arsenic causes a decrease in the unit cell volume of maucherite.

$Ni_{5-x}As_2$, αNi_7S_6, and $Ni_{3\pm x}S_2$.—The substitutions of sulfur for arsenic in $Ni_{5-x}As_2$ and of arsenic for sulfur in αNi_7S_6 were not studied in detail. Their d values appear unchanged regardless of the assemblage in which they are synthesized; solid solution of the third component in these phases is therefore probably less than 1 weight percent.

Limited solid solution of arsenic in $Ni_{3\pm x}S_2$ was observed but not carefully studied. This phase is not preserved in "quenching" experiments unless it contains nearly the maximum amount of arsenic in solution (2 to 4 weight percent). Hence its composition in the different assemblages is unknown, and the bivariant fields between $Ni_{3\pm x}S_2$ and the other phases in figure 3 can only be shown schematically.

Phase relations below 700°C.—Phase relations in the system at lower temperature were determined with relatively few experiments (table 9) after the 700°C isothermal section and details of the various solid solution series had been established. Isothermal sections at 600° and 450°C are shown in figures 8 and 9, respectively.

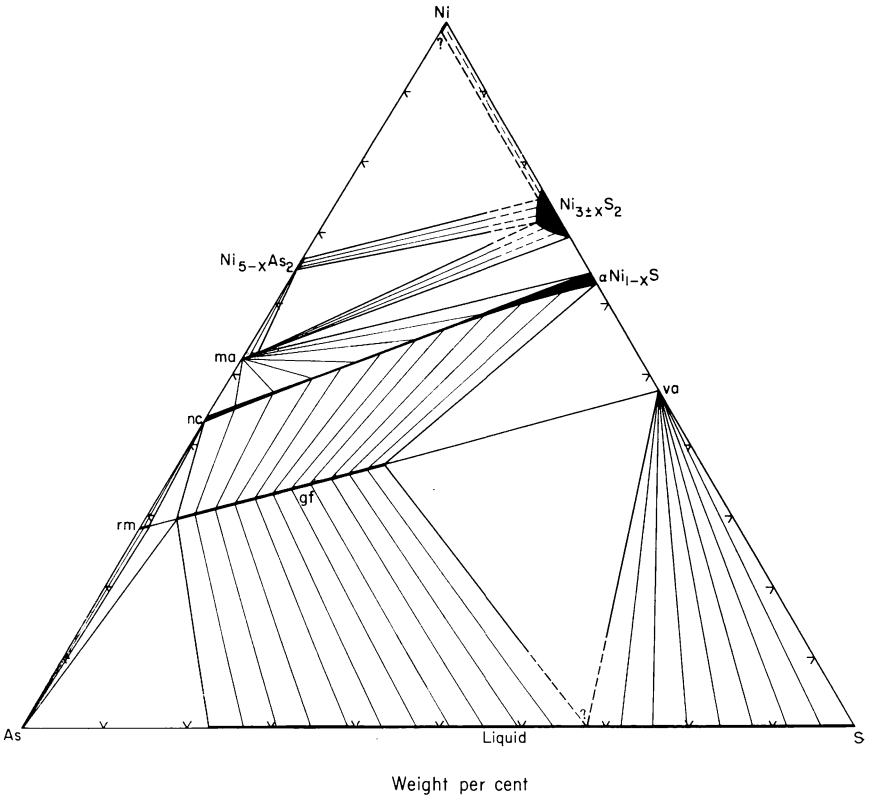

Fig. 8. 600°C isothermal section of the system Ni–As–S. Boundary of the phase $Ni_{3\pm x}S_2$ is approximate except along binary.

Between 700° and 600°C the principal change in the phase relations is in the composition of Ni(As,S) in the assemblage Ni(As,S)-maucherite-$Ni_{3\pm x}S_2$-vapor (fig. 3). The composition of Ni(As,S) mix-crystals in this assemblage corresponds to the formula $NiAs_{0.56}S_{0.44}$ at 700°C, whereas at 660°C the composition of Ni(As,S) in the same assemblage is $NiAs_{0.22}S_{0.78}$. With decreasing temperature the composition of Ni(As,S) in this assemblage continues to move towards NiS, and at 600°C essentially pure NiS is the stable phase in equilibrium with maucherite, $Ni_{3\pm x}S_2$, and vapor (fig. 8).

Below 595° ± 5°C the solid solution between niccolite and αNiS_{1-x} is no longer complete and the univariant assemblages niccolite-gersdorffite-αNi_{1-x}(S,As)-vapor and niccolite-maucherite-αNi(S,As)-vapor become stable. The only additional changes in these assemblages at lower temperature are a decrease in the solid solution of sulfur in niccolite and maucherite and of arsenic in Ni_{1-x}(S,As). The unit cell edge of gersdorffite in the above assemblage at 500°C is 5.6927 Å. which corresponds within the experimental errors to the composition of stoichiometric NiAs (fig. 9).

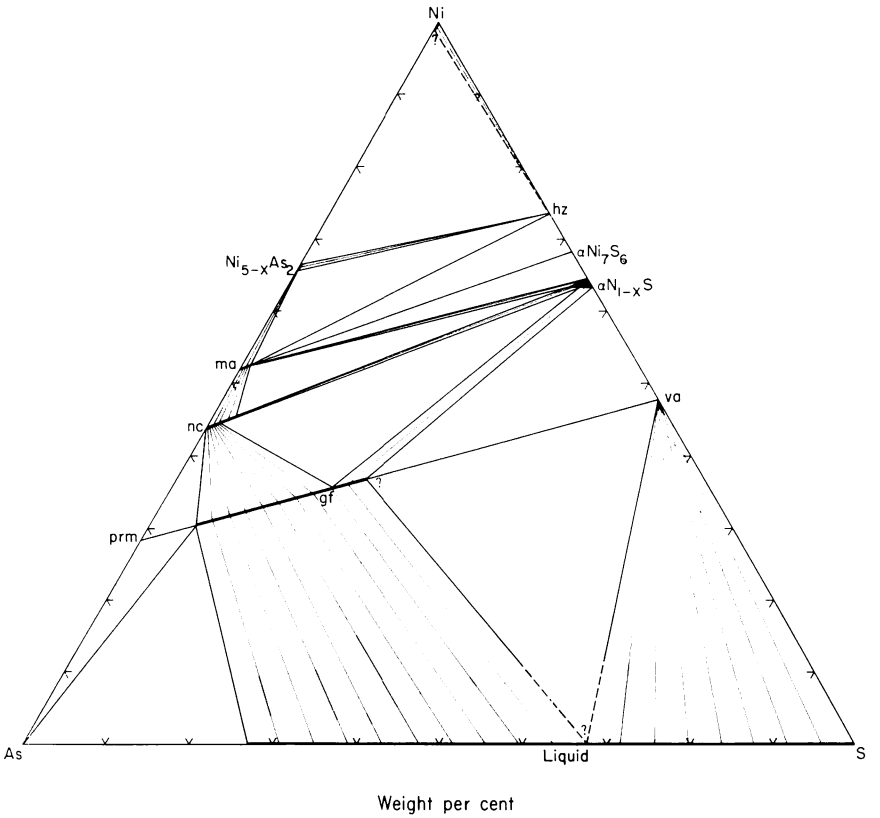

Fig. 9. 450°C isothermal section of the system Ni–As–S.

αNi_7S_6 is stable below 573°C (Kullerud and Yund, 1962) and gives rise to the new univariant assemblages consisting of $Ni_{3\pm x}S_2$-maucherite-αNi_7S_6-vapor and αNiS-maucherite-αNi_7S_6-vapor shown in figure 9. The polymorphic inversion of the high-temperature phase $Ni_{3\pm x}S_2$, where x equals 0, to heazlewoodite occurs at 556°C (Kullerud and Yund, 1962). The effect of arsenic on this inversion has not been studied in detail, but heazlewoodite appears to be the stable polymorph in all assemblages at 450°C (fig. 9).

The inversion of rammelsbergite to pararammelsbergite occurs between 500° and 450°C when it is in equilibrium with gersdorffite and arsenic (table 7). Therefore, pararammelsbergite is the stable polymorph at 450°C (fig. 9), but its sulfur content is too small (<1.0 percent) to be shown on the phase diagram.

Polydymite is stable below 356°C (Kullerud and Yund, 1962) and occurs in the assemblages gersdorffite-millerite-polydymite-vapor and gersdorffite-vaesite-polydymite-vapor (table 9). Phase relations below the melting point of realgar (321°C, Jonker, 1909) and orpiment (310°C, Jonker, 1909) were not investigated.

MINERALOGICAL CONSIDERATIONS

Rammelsbergite and Pararammelsbergite

Synthetic $NiAs_2$ can contain approximately 1 weight percent sulfur at 700°C; this is probably the maximum sulfur content of natural rammelsbergite. The maximum sulfur content of pararammelsbergite was not studied, but it is undoubtedly less than 1 weight percent. Analyses of both rammelsbergite and pararammelsbergite (Palache, Berman, and Frondel, 1944, p. 309, 311) commonly contain 2 to 3 weight percent sulfur, indicating that the analyzed material was not a single phase.

The pararammelsbergite-rammelsbergite inversion occurs at 590°C for pure $NiAs_2$ in equilibrium with niccolite and under the vapor pressure of the assemblage (Yund, 1962). Substitution of sulfur for arsenic lowers the inversion to 475° ± 25°C, and, as cobalt and iron probably lower the inversion at least as much as sulfur does, a minimum temperature for the formation of rammelsbergite in nature cannot be given. Although pararammelsbergite is stable with niccolite to 590°C under the vapor pressure of the assemblage, most natural pararammelsbergite contains iron, cobalt, or sulfur and must have formed at lower temperature.

Niccolite and Millerite

The high-temperature form of NiS is metastable at room temperature and inverts to the low-temperature polymorph, corresponding to the mineral millerite, in a few months at room temperature and atmospheric pressure.[6] Some millerite probably originally crystallized as the high-temperature polymorph (Kullerud and Yund, 1962), but only the low-temperature modification is found in nature. Arsenic substituting for sulfur lowers the inversion of stoichiometric NiS less than 80°C (fig. 5). Although NiS containing approximately 1 weight percent arsenic did not invert to millerite after 10 months at room temperature and atmospheric pressure, arsenic apparently does not decrease the inversion rate sufficiently for NiS to remain as the high-temperature polymorph in nature.

The composition of niccolite occurring in equilibrium with maucherite and millerite (originally αNiS) could be used to determine the temperature of formation of niccolite (fig. 5). Niccolite almost invariably contains some sulfur in solid solution (Dana, 1892, p. 72; Palache, Berman, and Frondel, 1944, p. 237), but it is rarely found associated with millerite in nature.

Vaesite

X-ray powder patterns and optical properties of vaesite and gersdorffite are very similar, making positive identification of these minerals extremely difficult. The (110) reflection is not observed in X-ray powder patterns of all natural gersdorffite specimens, and its absence cannot be used as a criterion for distinguishing gersdorffite from vaesite (fig. 7). Powder patterns of all gersdorffite specimens examined did contain a weak peak corresponding to (400), and this reflection was not observed in powder patterns of vaesite (fig.

[6] Stoichiometric NiS inverts at 379°C, and the most nickel-deficient composition ($Ni_{1-x}S$) inverts at 282°C (Kullerud and Yund, 1962).

7). The relative intensity of (200) compared to (210) or (211) is also useful for distinguishing gersdorffite from vaesite as the intensities of these reflections do not change appreciably with gersdorffite composition. Because of the similarity of vaesite and gersdorffite, it is possible that vaesite is more common than the number of reported occurrences would indicate.

Gersdorffite

Synthetic gersdorffite is homogeneous over a large compositional interval, which extends from 66.7 to 37.0 weight percent arsenic at 700°C, and the arsenic-rich limit changes only slightly as a function of temperature. Analyses of gersdorffite from the literature were studied to determine whether a corresponding compositional variation occurs in natural specimens. Several criteria were used to select what are believed to be the best available analyses. Only those that contained a relatively small percentage of antimony were considered, because the substitution of another anion complicates the problem of the As/S ratio. A small amount of antimony (less than 3 weight percent) in an analysis was grouped with arsenic because it is more closely related to that element than to sulfur. Some iron or cobalt can substitute for nickel; therefore, these three elements were grouped together and the constituents (*Ni*,Co,Fe), (*As*,Sb). and S recalculated to 100 percent. Several analyses were rejected simply because they could not possibly represent a homogeneous phase; i.e., their compositions plotted closer to niccolite than to gersdorffite. The original analyses of the six which were chosen are listed in table 10, and their recalculated compositions are shown in figure 10. The deviation of these analyses from

TABLE 10

Selected analyses of gersdorffite

No.	Ni	Fe	Co	Cu	As	Sb	S	Insoluble	Total	Wt % As+Sb recalculated
1	35.43	—	—	—	45.22	—	19.35	—	100.00	45.22
2	28.13	—	0.56	—	38.41	0.97	16.69	15.58	100.34	46.65
3	27.82	—	0.56	—	36.75	0.95	15.00	18.26	99.34	46.50
4	26.97	8.22	—	—	45.35	—	18.98	0.61	100.13	45.57
5	24.14	9.86	0.94	—	50.04	1.24	13.61	—	99.83	51.37
6	19.82	3.69	8.82	—	57.54	2.99	7.55	—	100.41	60.29
7	31.7	3.1	—	trace	44.5	trace	19.8	—	99.1	44.9

1. Stoichiometric gersdorffite (NiAsS), calculated.
2. Lightfoot (1931). Rhodesia Chrome Mine Limited, Selukwe Peak, Southern Rhodesia. With pyrite and chromite. Much gangue in analysis, but apparently no other sulfide or arsenide admixed with the analyzed material.
3. Lightfoot (1931). Another analysis of material from the same locality as 2.
4. Olshausen (1925). Locality and association unknown.
5. Thomson (1921). Cream Hill Mine, Sudbury, Ontario. With niccolite.
6. Goll (1937) in Palache, Berman, and Frondel (1944). Jacobi drift, Dobschau, Hungary. With "chloanthite" (possibly rammelsbergite?), niccolite, and cobaltite. Outer zone of a zoned crystal. Analysis of inner zone indicates it was not a single phase—see text.
7. Mendelson (1944). East Geduld Mine, Far East Rand, South Africa. A large (1 cm) crystal from a quartz vug, associated with chalcopyrite and pyrite.

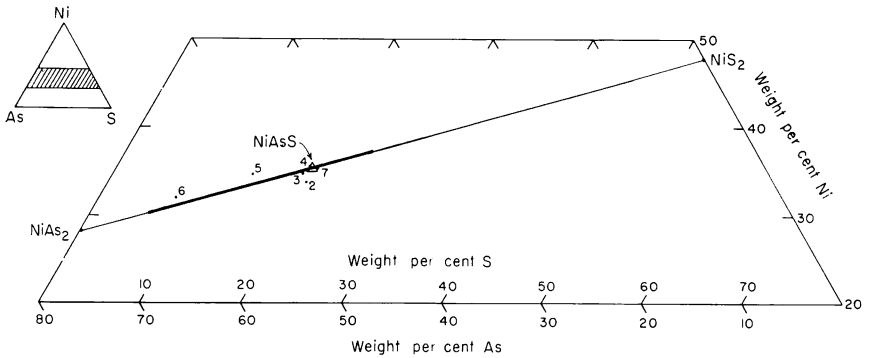

Fig. 10. Variation in the composition of natural gersdorffite (numbers) compared with solid solution in synthetic gersdorffite (heavy line). Numbers correspond to the analyzed specimens listed in table 10.

the line joining $NiAs_2$ and NiAsS does not appear to be real, and it is believed that all six compositions lie on this line within the errors of the analyses. Certainly any proof of a deviation in the Ni/(As+S) atomic ratio from 0.500 would have to be substantiated by more careful analyses of definitely homogeneous material.

The compositional variation of natural gersdorffite has been discussed by various investigators who considered that zoned crystals reflected variations in the content of iron, cobalt, or antimony. Goll (1937) was one of the first to recognize that the compositional variation of some zoned gersdorffite crystals was due to a difference in the As/S ratio. His analyses of an inner and outer zone of a crystal do not necessarily support this conclusion, although they do indicate that natural gersdorffite deviates greatly from stoichiometric NiAsS. Evidently the inner zone was not a single phase, inasmuch as the analysis is closer to niccolite composition than to the line between $NiAs_2$ and NiAsS. The analysis of the outer zone is shown in figure 10 (no. 6) and can be seen to lie near the arsenic-rich limit of synthetic gersdorffite.

A similar observation of the As/S ratio of gersdorffite from the Baldwin Ores, Burma, was made in the same year by Dunn (1937). He identified two varieties of gersdorffite, which he designates as α and β. His comments on the two varieties are as follows (p. 344):

"From the microchemical tests it became obvious, however, that α has a considerable excess of sulfur as compared with arsenic, whilst in β arsenic is in decided excess as compared with sulfur. . . . Like normal gersdorffite, β conforms in all respects with the properties of chloanthite, but the decided and consistent presence of sulfur cannot permit its diagnosis with chloanthite, although I would be in agreement with any view which regarded it as a chloanthite in which sulfur partially replaced arsenic."

Undoubtedly the β variety was gersdorffite with a maximum or near maximum arsenic content. The alleged cubic diarsenide mineral chloanthite is in most instances nickeliferous skutterudite (Holmes, 1947); however, from Dunn's description one is aware of the possibility that arsenic-rich gersdorffite may have been misidentified as chloanthite in at least a few instances.

Dunn describes the α variety as having more sulfur than arsenic and he suggests a possible transition between gersdorffite and bravoite, $(Ni.Fe)S_2$. (The mineral vaesite was not known at the time of his writing.) This is the only known suggestion of a sulfur-rich gersdorffite in nature. It is unfortunate that accurate chemical analyses are not available for the two varieties of gersdorffite that Dunn describes.

The As/S atomic ratio of gersdorffite from the Far East Rand, South Africa (Mendelson, 1944), is 0.96, but this corresponds to stoichiometric NiAsS within the limit of error of the analysis (fig. 10). Probably only one of the gersdorffites listed in table 10 is associated with rammelsbergite (no. 6); therefore, it is not surprising that most of the analyses lie nearer stoichiometric NiAsS than to the maximum arsenic-rich gersdorffite composition.

Niccolite-rammelsbergite (or pararammelsbergite)-gersdorffite is a common assemblage in deposits of the nickel-cobalt-native silver ore-type, and gersdorffite in this assemblage should have an As/S atomic ratio greater than 1. The unit cell edge of gersdorffite in a specimen from Schladming, Styria, Germany, containing the assemblage niccolite-pararammelsbergite-gersdorffite, is 5.7238 $\pm$ 0.0010 Å. A microchemical test for antimony in gersdorffite (Short, 1948, p. 212-218) was positive, but the test indicated that the amount was small. If only a small amount of antimony is present, a cell edge greater than 5.6940 Å (stoichiometric NiAsS) would indicate an As/S ratio greater than 1 because other elements commonly in solid solution (iron and cobalt) cause a decrease in the cell edge of gersdorffite. The cell edge corresponds to an arsenic content of 62.1 weight percent (fig. 6). This is near the maximum arsenic content of synthetic gersdorffite. The powder pattern of this specimen did not contain a peak corresponding to (110), which is also absent in synthetic prepartions except for compositions very close to stoichiometric NiAsS.

A specimen of gersdorffite with chalcopyrite from Mitterberg, Salzburg, Germany, has a cell edge of 5.6910 $\pm$ 0.0010 Å, which is nearly the same as the cell edge of stoichiometric NiAsS. Additional evidence of a composition close to NiAsS is afforded by the presence of the (110) reflection in X-ray powder pattern of this specimen (fig. 7).

Gersdorffite associated with millerite, polydymite, and chalcopyrite was examined from Timagami, Ontario. Microchemical tests indicated the presence of iron in the gersdorffite; therefore, it is not known if the small unit cell size (5.6827 $\pm$ 0.0010 Å) is due to an As/S atomic ratio of less than 1, or if it is caused by the substitution of iron for nickel. However, the (110) reflection was observed in the powder pattern of this specimen, indicating that the As/S atomic ratio is probably close to 1.

Mineral Assemblages

Natural assemblages of nickel sulfide and arsenide minerals correspond closely to the stable assemblages shown in the isothermal section at 450°C (fig. 9) or to the two new assemblages which are formed by a tie-line from polydymite to gersdorffite below 356°C. Descriptions in the literature of coexisting mineral pairs such as maucherite and gersdorffite probably indicate

disequilibrium assemblages rather than changes in the stable assemblages at lower temperature.

ACKNOWLEDGMENTS

This study is part of a dissertation presented to the faculty of the University of Illinois in candidacy for the degree of Doctor of Philosophy. The work was done at the Geophysical Laboratory, Carnegie Institution of Washington, using the laboratory facilities of Dr. Gunnar Kullerud. Drs. G. Kullerud and L. A. Clark, now at McGill University, gave freely of their time for discussions during all phases of the study and their assistance is gratefully acknowledged.

Dr. E. H. Roseboom, U. S. Geological Survey, and Mr. P. R. Brett, Geophysical Laboratory, critically read the manuscript and made many suggestions for its improvement. Specimens were obtained through the cooperation of Professor F. Machatschki, Universität Wien, and Professor Paul F. Kerr, Columbia University.

Financial support was provided by National Science Foundation fellowships.

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