

THE FeS-ZnS SYSTEM A GEOLOGICAL THERMOMETER

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A b s t r a c t. In the first part of this paper, the FeS — ZnS equilibrium diagram is presented. Laboratory equipment and methods used for the establishment of the diagram are described. The end members of the system as well as the α and β mix-crystals are studied. The ZnS α - β inversion mechanism has received special attention, and the relationship between inversion temperature and mix-crystal composition is established. The increase in the ZnS lattice dimensions due to the replacement of Zn by Fe is explained by assuming that the mix-crystal bonds acquire a more ionic character as their FeS content

increases. Thermodynamic calculations are applied for determinations of the equilibrium curves below 400° C.

The influence of pressure upon the FeS solubility in the ZnS lattice has been calculated, and the results in part checked by means of laboratory experiments.

The FeS activity was investigated and was found to decrease very little from stoichiometric FeS to FeS₂. However, it drops sharply, when S is added beyond the amount indicated by the FeS₂ formula. Studies were conducted of the unmixing of FeS from mix-crystals. It was also found that small amounts of Mn and Cd have little or no influence on the solubility of FeS in ZnS.

In the second part, chemical, spectrographic and x-ray methods for determination of the composition of sphalerite ore specimens are described. Results of the analyses together with the temperatures deduced from the composition of the samples are presented in tabular form. Some of the localities from which specimens were obtained are described with a view to ascertaining the pressure conditions prevailing during ore deposition. Discussions whether the mix-crystals contain as much FeS as prescribed by the (P,T) conditions of ore formation, are often of little value unless coupled with field work and microscopic studies. While FeS in many cases seems to have been present in ample quantities to satisfy the equilibrium requirements, Mn, Cd, and the trace elements never occurred in sufficient amounts to saturate the ZnS lattice. The only reliable index of temperature of formation is FeS. The distribution of the other elements is not necessarily related to this temperature. Possible applications of the FeS — ZnS system to geological problems are outlined.

PART I.

Introduction.

The temperature-pressure conditions existing in rocks and ore bodies at the time of their formation, have been discussed in a great number of publications. Several methods have been applied for determinations of geologic temperatures. In some instances geological temperatures have been directly measured, for example in lavas, but in most cases the temperatures have been deduced from ascertained facts regarding the effect of heat on various physical properties of minerals. Of such methods may be mentioned high-low inversion of quartz, liquid inclusion methods, etc.

As has been emphasized by a number of authors, the concentrations of elements in mix-crystals under certain conditions may serve as our most reliable geological thermometers, provided enough thermodynamic data of the minerals are known. The general principles underlying such thermometers are clear, but in no case is enough

data available for an accurate and absolute thermometer to be established among the several systems in which mix-crystals occur. Among the ore minerals the importance of mix-crystals as a guide to geologic thermometry has been discussed, but so far nobody has thoroughly investigated any of the mix-crystal series in the laboratory.

The FeS-ZnS Solid Solutions.

Many sulfide minerals can enter into solid solution with one another, and in some instances the solid solutions persist as homogeneous minerals, stable at normal temperatures.

It has long been known that ZnS has the ability to dissolve appreciable amounts of FeS. In nature pure, colorless ZnS is extremely rare. Most sphalerites contain iron and traces of other elements and are no longer colorless, but yellowish to brown, sometimes almost black depending upon the amount of iron dissolved. Provided sufficient iron sulfide was present during the formation of the mix-crystals, the ZnS would dissolve an amount of iron determined by the temperature and pressure conditions existing during the formation of the sulfides.

In numerous ore deposits pyrrhotite occurs intimately connected with sphalerite (marmatite). From geological studies it has been shown that an abundance of iron was often present during the entire process of ore formation. Therefore, in such cases one may safely assume that equilibrium conditions existed between free pyrrhotite and the FeS dissolved in the sphalerite lattice at the time of sphalerite formation. In any sample of sphalerite fulfilling the above-mentioned conditions, the amount of FeS dissolved is related to the temperature of formation of mix-crystals. Hence, the temperature of ore-deposition, disregarding pressure, may be determined from the amount of FeS dissolved in the sphalerite lattice using the FeS-ZnS diagram (fig. 1). The modifying influence of pressure upon the equilibrium is demonstrated in fig. 9.

The FeS-ZnS System.

Very little work has previously been done on the FeS-ZnS system. FRIEDRICH¹ investigated the melting curves and found a eutectic to exist in the system for 5 % ZnS at 1170° C. Later ALLEN and CRENSHAW² investigated the effect of iron on the inversion point of

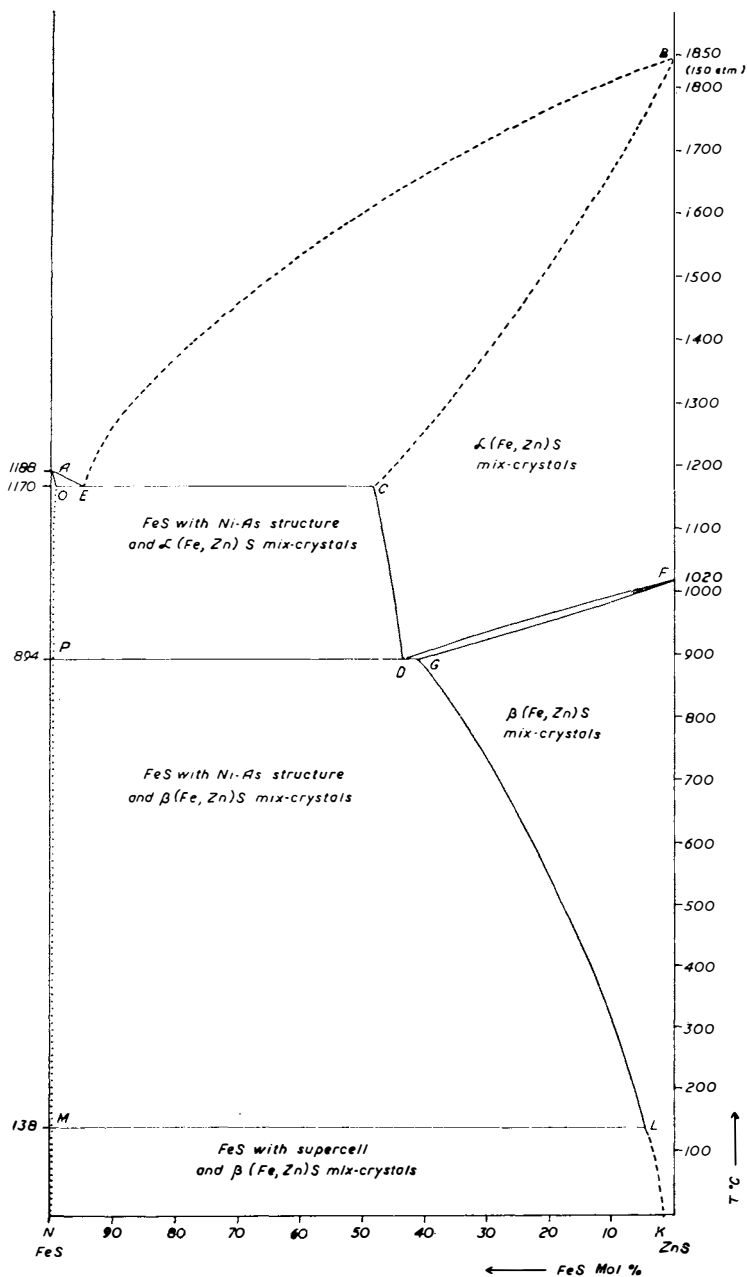


Fig. 1. The FeS-ZnS equilibrium diagram.

sphalerite. They showed that the sphalerite-wurtzite inversion temperature decreases with increasing amount of iron dissolved in the ZnS lattice.

The complete FeS-ZnS phase diagram is shown in figure 1. This diagram was drawn as a result of more than 250 runs with mixtures of FeS and ZnS in varying proportions. The time needed for equilibrium to be established in the system varied from a few hours at 1000° C to nine months at 500° C.

The liquidus curves AE and part of EB were established by FRIEDRICH, his values as well as values for parts of these curves given in the "International Critical Tables" have been used in Fig. 1. Below the eutectic temperature, 1170° C, there are two series of solid solutions. The solubility of ZnS in hexagonal FeS, however, is, even at 1160° C, less than 1/2 % by weight and is of no practical importance for the later application of the diagram. This solid solution series is suggested by a stipled line (OPMN). The solubility of FeS in α and β ZnS is appreciable as seen from the curves CD and GLK.

Zinc sulfide occurs in two enantiotropic modifications. β ZnS (sphalerite) with a cubic face-centered lattice, being the low temperature modification, converts at 1020° C into α ZnS (wurtzite) with a hexagonal, close-packed lattice.

The FG curve was partly determined by ALLEN and CRENSHAW as mentioned above. For their studies these investigators, however, used sphalerite ores containing impurities of Mn and Cd, each of which depresses the inversion point even more than iron does. Therefore, their results were somewhat lower than the ones obtained by the present author in his runs with pure sulfides of iron and zinc.

Pure FeS melts at about 1188° C under atmospheric pressure. The pure α ZnS on the other hand does not melt at normal pressure, but sublimates at 1185° C. It is reported to melt at 1850° C under 150 atm. pressure.¹ Therefore the upper right part of the diagram (fig. 1) falls slightly outside the isobaric section represented by the rest of the diagram.

From fig. 1 it is seen that above the curves AE and EB there exists one melt. In the fields AOE and BEC liquid and solid coexist, the composition of the liquid being determined by AE and BE and

¹ International Critical Tables.

the composition of the solid being determined by the solidus curves AO and BC. In the field AON one finds mix-crystals formed by solution of ZnS in FeS. In the field BCDF α (Fe,Zn) S mix-crystals occur, and in the FGK area β (Fe,Zn) S mix-crystals are stable. The separating FGD field contains both α (Fe,Zn) S and β (Fe,Zn) S mix-crystals.

The End Components of the FeS-ZnS System.

Before going any further in the discussion of the presented diagram and the description of laboratory equipment and methods, it may be appropriate to look into the properties of pyrrhotite as well as the two enantiotropic modifications of zinc sulfide.

1. Pyrrhotite.

The crystal structure of pyrrhotite is of the NiAs type.¹ Crystals of this type are often associated with a super-cell which makes the understanding of these crystals hard.

According to the literature, ferromagnetic pyrrhotite exists in the composition range $\text{Fe}_{48}\text{S}_{52}$ to $\text{Fe}_{466}\text{S}_{534}$ and has the nickel-arsenide type structure (see fig. 2). Paramagnetic pyrrhotite is confined to the composition range $\text{Fe}_{50}\text{S}_{50}$ to $\text{Fe}_{48}\text{S}_{52}$ and has two kinds of structures: nickel-arsenide type in the high sulfur half of the field and a super-cell in the region near ideal com-

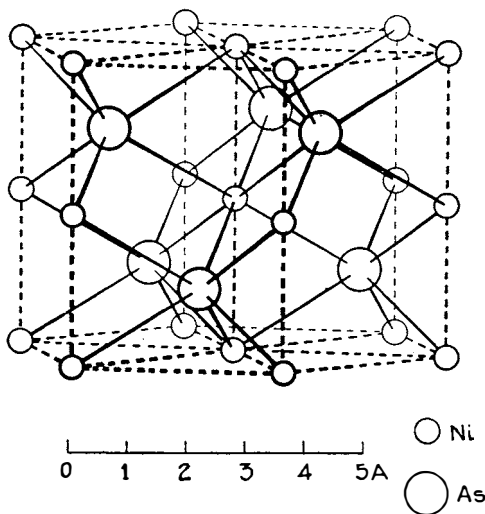


Fig. 2. The NiAs structure. Hexagonal FeS is obtained when Ni is replaced by Fe and As by S. (Strukturbericht).

¹ Whether natural pyrrhotite has true hexagonal crystallographic properties or is of a pseudo-hexagonal character has been discussed by BUEGER³. After having investigated single crystals of pyrrhotite from two localities, Buerger concluded that pyrrhotite either belongs to a low hexagonal or to an orthorhombic or even may be monoclinic symmetry.

position FeS (the border being about $\text{Fe}_{49}\text{S}_{51}$). FeS at room temperature shows the super-cell which has a hexagonal or trigonal symmetry, and contains 12 molecules; and which in volume is six times as large as the normal cell. The a_o ($5.946\text{\AA} \approx 3.453 \cdot \sqrt{3}$) of this lattice is the long diagonal of a_o (3.453\AA) for the simple Ni-As cell; its c_o (11.720\AA) is approximately twice as great as that of the Ni-As cell (c_o 5.860\AA). (FeS_x : $a_o = 3.43\text{\AA}$, $c_o = 5.68\text{\AA}$). Whether this so called super-cell has the characteristics of a super-lattice has to the author's knowledge not so far been investigated.

On heating, the super-cell is transformed to the Ni-As arrangement. The transition point depends upon the composition of the pyrrhotite. Stoichiometric FeS inverts at 138°C while pyrrhotite of composition $\text{FeS}_{1.09}$ passes from the super-lattice to the simple Ni-As grouping at the lower temperature of 74°C . The Ni-As structure in turn suffers another transition at 325°C involving a discontinuous change of spacing but not of atomic arrangement. These transitions have been studied by HARALDSEN^{4, 5, 6, 7, 8, 9} who presented a diagram showing the transition points and variations in lattice parameters for FeS as related to the temperature.

Variation in the sulfur content of the pyrrhotite series of which troilite (FeS) is considered an end member has been shown by ALLEN, CRENSHAW, JOHNSON and LARSEN¹⁰ to be as much as 6.5 %, the equivalent formula being $\text{Fe}_{1.18}\text{S}$. The high sulfur ratio has been shown (LAVES¹¹, HÄGG¹², HÄGG and SUCHSDORFF¹³) to be due not an excess of sulfur, but to iron atoms missing from their structural positions. Recent work by JENSEN¹⁴ shows that if this explanation holds at high temperatures, the lattice has a maximum stability when there are a certain number of vacant iron positions, corresponding to a composition of $\text{FeS}_{1.08}$ or $\text{Fe}_{12}\text{S}_{13}$.

According to JENSEN the solubility of iron in FeS is negligible, though there is a possibility that it may be greater at high temperatures.

A review of the literature by JENSEN shows that the limit of solubility of S in FeS at low temperatures is about 39.1 % (as compared with 36.5 % S in FeS). This limit increases with the increase in temperature to about 40.7 % at 677°C .

The first x-ray examination of a mineral belonging to the nickel-arsenide group was undertaken by AMINOFF¹⁵. In this structure each

atom has six nearest neighbors of the other sort, but the arrangement of the neighboring atom is different for the two kinds of atoms. Thus in pyrrhotite a sulfur atom is surrounded by six Fe atoms at the apices of a trigonal prism. The immediate neighbors of an Fe atom are six S atoms arranged octahedrally, but there are also two Fe atoms sufficiently near to be considered bonded to the first Fe atom (Wells¹⁶).

The minerals with the Ni-As structure often have a metallic character (BRAGG¹⁷) besides the mentioned variation in composition. In the more metallic systems with this structure the eight neighboring atoms are approximately equidistant from the metal atom. As a general rule the closer the atoms approach equidistant positions the more metallic are the bonds. (For instance for CoSb the Co-Sb distance is 2.58Å and the Co-Co distance 2.60Å. The corresponding distances for FeS are 2.45Å and 2.89Å. CoSb which has equidistant atoms is much more metallic than FeS whose atoms are far from being equidistant).

2. The β ZnS (*Sphalerite*).

In sphalerite the zinc atoms are arranged on a face-centered cubic lattice. The sulfur atoms, arranged on a similar lattice, are so located that each is between four zinc atoms. Figure 3 shows only the four sulfur atoms included within the unit cell, but it will be clear that if the pattern is continued they will build up a lattice like

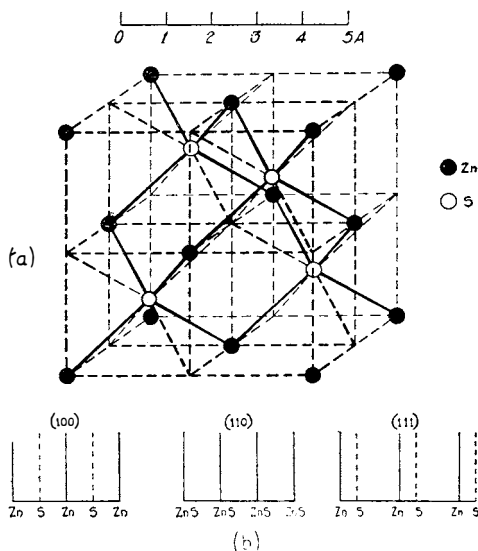


Fig. 3. a. The structure of sphalerite, ZnS. b. The arrangement of planes parallel to (100), (110), and (111), the last illustrating the polar nature of the [111] axis. (BRAGG¹⁷).

that of the zinc atoms. The arrangement is like that of diamond, if one replaces both Zn and S with C. Whereas diamond is holohedral, the distinction between Zn and S causes the present structure to be hemihedral.

Figure 3 shows that the sulfur atoms are surrounded by four zinc atoms at the corners of tetrahedra which are always similarly oriented. Hence the whole structure has the symmetry of a tetrahedron, not that of a cube. This is seen in an alternative way by the arrangement of the $[111]$ planes shown in figure 3b. These planes are alternately Zn and S in pairs, and therefore the direction perpendicular to them ($[111]$ axis) is polar. Opposite faces $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ are not identical in character. The characteristics are in accord with the symmetry of sphalerite crystals displayed on etching.

The number of Zn and S atoms (Z) in the unit cell is $Z = 4$. The length (a_w) of the unit cell has been determined by several workers. The literature gives values varying from $a_w = 5.39$ to 5.42 Å. In crystals with the diamond, sphalerite, or wurtzite arrangement each atom is surrounded tetrahedrally by four other atoms. If the atoms are those of fourth-column elements or of two elements symmetrically arranged relative to the fourth column, the number of valence electrons is right to permit the formation of a tetrahedral covalent bond between each atom and its four neighbors. In ZnS an extremely covalent structure places the formal charges 2^- on zinc and 2^+ on sulfur. It is probable that the bonds have enough ionic character in this crystal and others of similar structure to make the actual charge of the atoms much smaller.¹⁸ Wells¹⁶ also assumes that the ZnS bonds must have appreciable ionic character. The ZnS bonds it may be concluded are intermediate between ionic and covalent bonds.

3. The α ZnS (Wurtzite).

This high temperature form of zinc sulfide is hexagonal, and its structure is related to that of β ZnS in a simple way.¹⁹ The relation resembles that between cubic and hexagonal closest packing. Zinc atoms in blende are on a face-centered cubic lattice, whereas in wurtzite they are nearly in the positions of hexagonal closest packing. This, as pointed out by Bragg, is the alternative of close packing

and produces just as dense a structure as the face centered cubic packing provided the hexagonal axial ratio c/a is 1.633 (which is twice the ratio of the height of a regular tetrahedron to its edge). The wurtzite tetrahedra are practically regular. (That means c/a is almost exactly 1.633. The same is true of CdS). In both structures the sulfur atoms lie between four zinc atoms. The wurtzite structure is shown in figure 4.

If the structure of blende is pictured standing on a tetrahedron face, the relation between blende and wurtzite may be seen without difficulty. The zincblende structure may be produced from the wurtzite structure by a rotation of 60 degrees of alternate pairs of $[0001]$ atomic layers about the threefold axis. The hexagonal axis of wurtzite is polar. The sheets of atoms parallel to the basal plane all have Zn above and S below in each pair (CdS has a similar structure). The distances between the atoms are practically identical with those in zincblende. SHÖJ²⁰ showed that the transformation planes may be the $[111]$ for zincblende and the $[0001]$ for wurtzite. The hexagonal a and c value calculated when using the zincblende $[111]$ as basal plane were only about 0.7 % smaller than the values calculated from x-ray diagrams.

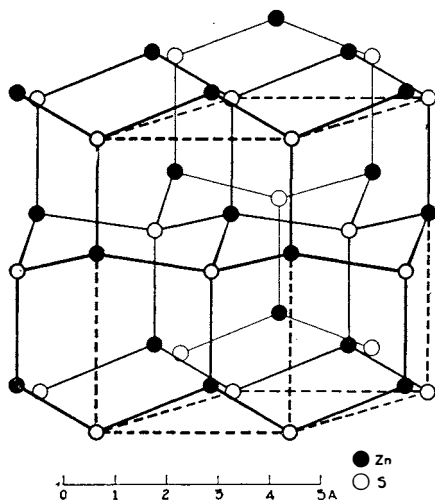


Fig. 4. The structure of wurtzite, ZnS. (Strukturbericht).

Equipment for the Runs.

The essential parts of the furnaces used are the core ($1\frac{1}{4}$ "— $1\frac{1}{2}$ " diameter) of alundum with nichrome wire wound around and cemented to the core, and insulating fire bricks (cut to fit around the core and inside a cylindric mantel 10" diameter). These furnaces could be run at 900—1000° C for long periods and as high as 1100° C

for shorter periods of time. The energy input was controlled with "temcometers". Chromel-Alumel thermocouples were used between 200° and 1000° C. For the same temperature interval a "Brown Electronik" recorder gave temperature readings every 1½ minutes on a continuously moving chart. Platinum-rhodium thermocouples in connection with a Rubicon potentiometer were used for readings of temperatures higher than 1000° C.

With this equipment it was possible to control and record the temperatures within $\pm 5^\circ$ C of the real values.

The Bombs.

Because of the high vapor pressure of sulfur it was necessary to let the sulfide formations take place in closed bombs made of a material that would not react with the enclosed substance. As material for the bombs, transparent quartz glass tubing was chosen.

The bombs had to be evacuated in order to prevent oxides forming and thus stagnate or completely prevent the sulfide formation.

While iron sulfide forms easily from iron and sulfur at a temperature as low as 500° C, it was expected to be necessary to heat the mechanical compound of zinc and sulfur at more elevated temperatures in order to obtain a complete zinc sulfide reaction.

The bombs therefore had to be made of a tubing with thick enough walls to withstand the vapor pressures of sulfur and zinc at such temperatures. It was believed that it would not be necessary to exceed 850° C in order to have the zinc sulfide formation take place. The vapor pressure of sulfur is about 40 atm. at 850° C, while the vapor pressure of zinc at the same temperature is less than 1 atm. (boiling point for Zn is 907° C).

Quartz glass tubing with an internal diameter of 6 mm and a wall thickness of 3 mm was found to withstand this pressure and therefore was used for the runs. For later runs where ready made sulfides were mixed together, tubing with thinner walls was used, and in cases where a very small amount of substance was needed, the bombs were made of tubing with 2 mm inside diameter and 1 mm thick walls.

The procedure of making these bombs was as follows: The quartz glass tubing was fire polished at one end over an acetylene flame so as to form a closed, rounded end. The substance was then inserted in

the tube and the tube again heated about $1\frac{1}{2}$ to 2 inches from the end and drawn out into a capillary. The tube was then connected with a Cenco Hyvac pump which gave a vacuum of about 0.3 Micron Hg. The air in the system had to be pumped out slowly and carefully so that no substance would be drawn out with it. This was done by controlling the rate of air flow with a partially closed stopcock. After a suitable vacuum was obtained the capillary was heated again and the bomb sealed off.

The Formation of FeS and ZnS.

Pyrrhotite, of almost stoichiometric FeS composition, (very slight excess of sulfur) was made from analytically pure iron and sulfur, in a bomb of the type previously described. The bomb was heated at 540°C for 48 hours and then quenched. The resulting hexagonal pyrrhotite crystals were about $1/30$ mm long, paramagnetic and of a medium dark grey color. X-ray powder diagrams of this substance showed the Ni-As arrangement.

Sphalerite was made from analytically pure zinc and sulfur mixed together in the proportion given by the ZnS formula. The formation of this sulfide did not take place as easily as that of pyrrhotite. A very high vacuum in the bomb and heating for 7—8 days at a minimum of 870°C proved to be necessary in order to obtain a complete reaction. In the first few runs the required vacuum was not obtained, consequently ZnO layers were formed on the Zn-crystals preventing ZnS to form.¹ The sphalerite formed was of an almost pure white color and occurred in cubic crystals the size of which was approximately $1/25$ mm. Some of the sphalerite was heated at 1050°C for 8 hours in a closed bomb. The resulting hexagonal wurtzite crystals were of a slightly yellow color.

The Mix-crystals.

Solid solutions were found to form from mixes of the pure sulfides. The mix-crystals readily formed at temperatures above 850°C .

¹ An interesting study of the formation of ZnO films on Zn crystals has recently been done by RAETHER²¹. The oxide film formed on exposure of metallic zinc to the air, was monocrystalline and parallel to the orientation of the Zn crystal lattice. The thickness of the film was 20—40 Å at room temperature, and increased at elevated temperatures.

Below this temperature mix-crystals formed only after prolonged heating. In order to establish the equilibrium curves of the FeS-ZnS diagram, the composition of the mix-crystals, formed at given temperatures, had to be determined. Therefore the optical properties as well as the specific gravities and unit cell dimensions of mix-crystals of known compositions, were studied thoroughly. The refractive index was found to increase with increasing iron content, this being in agreement with results obtained by ALLEN and CRENSHAW² who determined the refractive indices for sphalerite ores with varying amounts of iron. The specific gravity was found to decrease with increasing iron content, a fact also observed previously by the above mentioned workers. Further, an increase in the unit cell dimensions with increasing iron content was observed by means of x-ray powder diagrams. X-ray studies of the variations in the cell dimensions of sphalerites with varying amounts of iron have previously been undertaken by RINNE,²² GOLDSCHMIDT,²³ BRAEKKEN,²⁴ and CHUDOBA.²⁵ The former three authors, with the x-ray equipment available at that time, found no expansion in the lattice caused by the presence of iron. CHUDOBA, who calculated the spacings from x-ray powder diagrams of four sphalerite ores, found different unit cell length values for all four.¹ At the time the present work was started, little information, therefore, existed concerning the influence of iron alone on the spacing of sphalerite.

After comparing the three above mentioned methods for determination of the composition of (Fe, Zn) S mix-crystals, the x-ray method was considered the best suited. [With the refractive index method the iron content could be determined within 1 %. Pure sphalerite has a refractive index $n = 2.36$ and the mix-crystals with maximum iron content go up to $n = 2.525$. As no liquid goes that high, compounds of sulfur and selenium were used for the determinations of these high refractive indices. The sulfur-selenium compounds are not as convenient to use as liquids and are not very desirable for exact determinations.

The specific gravity was determined by the BILTZS'²⁶ pycno-

¹ it may here be mentioned that two of the specimens, used by CHUDOBA for his experiments, also contained a substantial amount of manganese and some cadmium, which both influence the spacing.

meter method and an accuracy of ± 0.003 was obtained. The specific gravity is $d = 4.110$ for pure sphalerite and 3.935 for (Fe, Zn) S with $36\frac{1}{2}\%$ FeS by weight. This method gives fairly accurate determinations of the Fe content of the mix-crystals (about $\frac{1}{2}\%$), but is slow. The x-ray powder diagram method gave by far the best results when a suitable internal standard was used.]

The X-ray Work.

The x-ray powder diagrams were taken in an improved Debye-Scherrer cylindrical camera (diameter $D = 114.6$ mm) designed by the North American Philips Co., Inc. The various factors entering the design of this camera and interrelated in their influence on the properties of the patterns are considered in a paper by W. PARRISH and E. CISNEY.²⁷ This camera has a light-tight cover so that it is not necessary to make the exposures in a dark room or to cover the film with black paper. The primary x-ray beam passes through two conical tubes between which the thin rod-shaped specimen is mounted. After placing the specimen in a slot on the axis of the camera, accurate centering is done by means of a threaded "pusher" perpendicular to the axis. During exposures a cap containing a fluorescent screen is placed on the end of the exit tube. On this screen the primary beam and the shadow of the specimen may be observed. This fluorescent screen is covered on the inside with black paper making the camera light-tight, and on the outside with lead glass absorbing the remainder of the primary beam. The film is placed in the camera according to Straumanis method: the film takes up nearly 360° and two holes of 9 mm diameter are punched in it where the tubes are to be inserted. The film is expanded against the inner wall of the camera by means of a movable finger which pushes one end of the film, the other end being fixed by a stop. While the exposure is being made the specimen is rotated continuously around its axis by a pulley attached to a small electric motor.

The sample was mixed with Duco Household Cement and rolled out between two glass plates to form a cylindrical rod. Much care was taken in giving this rod a true roundness and an even thickness.

In order to investigate what influence the rod thickness has on the sharpness of the lines of the powder diagrams, several rods of

different thicknesses were made from pure sphalerite. It was found increasingly difficult to obtain sharp lines as the rod thickness d , exceeded 0.4 mm. Very good sharpness was achieved for $d = 0.35$ mm. The sharpness obtained for this thickness did not differ noticeably from that obtained for $d = 0.25$ mm. For this reason the rods were made approximately 0.30 mm thick; a tolerance of 0.05 mm was allowed.

The centering of the rods was done with much care to obtain the best possible accuracy.

The films were measured by means of a recorder (Picker) giving readings as exact as ± 0.05 mm.

It was calculated that for the smallest θ used (about 58°) the biggest possible error in spacing, caused by an uncertainty of ± 0.05 mm in reading was $\pm 0.00003A$. In order to compensate for film shrinkage, variations ($d = 0.25$ — 0.35 mm) in rod thickness and a series of systematical errors, about 30 % rock salt was mixed in as internal standard with the samples.

WYCKOFF²⁸ gives for NaCl, $a_0 = 5.62869A$. Fe radiation with Mn filter was used for the powder diagrams. (Cu radiation with Ni filter was tried and found excellent for pure ZnS, but when more than 5 % Fe is present, the background of the film gets almost as dark as the reflections and accurate readings are increasingly harder to obtain.) The wave lengths used were:

$$\text{Fe } K\alpha = 1.9373 A$$

$$\text{Fe } K\alpha_1 = 1.93597 A$$

$$\text{Fe } K\alpha_2 = 1.93991 A$$

The exposure time varied from 20—25 hours. The NaCl [440] and [422] lines were used as standard lines and their θ values were computed from the a_0 value given above and the wave lengths. The β ZnS lines used for the calculations were the [333] and [422] lines. These reflections are located between the above mentioned NaCl lines.

Lattice Dimensions of Pure β ZnS and the β (Fe, Zn) S Mix-crystals.

Several x-ray powder diagrams were made of the pure β ZnS. The calculated unit cell lengths varied from $a_0 = 5.39837$ to $a_0 = 5.39861 A$, the mean value being $a_0 = 5.3985 A$. Out of eight determinations six were inside the limit of error of $5.398_{\pm 1}A$.

The a_0 values of the mix-crystals were determined from a smaller number of powder diagrams (each film was measured twice). Therefore the limit of error is bigger than that given for pure β ZnS. However, when only a couple of x-ray diagrams were made of a given mix-crystal composition and the a_0 values were calculated, the discrepancy in these values never exceeded $\pm 0.0002A$. This value will be given as the limit of error in the a_0 values for the β mix-crystals.

Table I gives the final results of experiments carried out to determine the relationship between mix-crystal composition and unit cell length. In the last two vertical columns are given the molecular volumes and specific gravities calculated from the a_0 values. (The N value used for these calculations is $6.02 \cdot 10^{23}$).

TABLE I.

Number of runs.	FeS content of β mix-crystals		Unit cell length a_0 in A	Calculated molecular volume	Calculated specific gravity
	wt. %	mol. %			
4	0	0	$5.398_{5\pm 1}$	39.3332	4.1150
6	5	6.69	$5.400_{0\pm 2}$	39.3594	4.0921
6	10	11.98	$5.401_{8\pm 2}$	39.4054	4.0675
6	15	17.80	$5.404_{3\pm 2}$	39.4601	4.0417
6	20	23.48	$5.406_{6\pm 2}$	39.5105	4.0163
4	30	34.47	$5.410_{9\pm 2}$	39.6049	3.9669
5	36.5	41.36	$5.413_{4\pm 2}$	39.6598	3.9359

The results of the four runs listed in the upper column of table I have been mentioned already (see above).

In the next five horizontal columns the results from a total of twenty-eight runs are presented. The details of these runs are found in table II.

It is believed that the data given in table II are presented so clearly that individual discussion of each run is not required. In the first vertical column is given the amount of FeS mechanically mixed in with β ZnS. These compounds were then heated for a period of time given in column two, at a temperature given in column three. The a_0 values of the resulting β mix-crystals are presented in column four. In columns five, six and seven are shown the results of a number

TABLE II.

Composition: FeS mixed with ZnS	Duration of runs	T°C	Unit cell length a_0 in Å	Duration of runs	T°C	Unit cell length a_0 in Å
5 wt.% (6.69 mol.%)	1 week	850	5.4001	2 weeks	750	inhomog. substance
	2 weeks	850	5.4000	3 weeks	750	5.3999
	3 weeks	850	5.4001	4 weeks	750	5.4001
10 wt.% (11.98 mol.%)	1 week	860	5.4015	2 weeks	750	inhomog. substance
	2 weeks	860	5.4018	4 weeks	750	5.4017
	3 weeks	860	5.4018	6 weeks	750	5.4017
15 wt.% (17.80 mol.%)	1 week	850	5.4041	2 weeks	750	inhomog. substance
	2 weeks	850	5.4044	4 weeks	750	5.4041
	3 weeks	850	5.4043	6 weeks	750	5.4043
20 wt.% (23.48 mol.%)	1 week	850	5.4064	3 weeks	750	5.4063
	2 weeks	850	5.4065	4 weeks	750	5.4065
	3 weeks	850	5.4066	6 weeks	750	5.4065
30 wt.% (34.47 mol.%)	4 days	890	5.4105			
	10 days	890	5.4108			
	3 weeks	890	5.4109			
	4 weeks	890	5.4109			

of runs carried out with compounds of the same compositions as before but at the lower temperature of 750° C.

It appears (table II) that the time needed for the formation of homogeneous mix-crystals at 750° C is much longer than it takes for such mix-crystals to form in the 850—890° C temperature range. In no instance homogeneous products were formed in the course of two weeks at 750° C, while at 850° C one week was sufficient, and at 890° C only four days were required.

In the last horizontal column of table I is given the maximum amount of FeS that can be dissolved in the β ZnS lattice (at 894° C where the β mix-crystals containing a maximum amount of FeS

invert to the α modification) and the corresponding a_0 value. These data will be further treated when the α - β inversion curves for the mix-crystals are studied.

Runs conducted at 890° C with compounds consisting of 40 wt.% (45.0 mol.%) FeS mixed with β ZnS produced mix-crystals with $a_0 = 5.413_{1\pm 2}\text{\AA}$ which is bigger than the a_0 value obtained from runs containing 30 wt.% (34.47 mol.%) FeS. However, this increase is

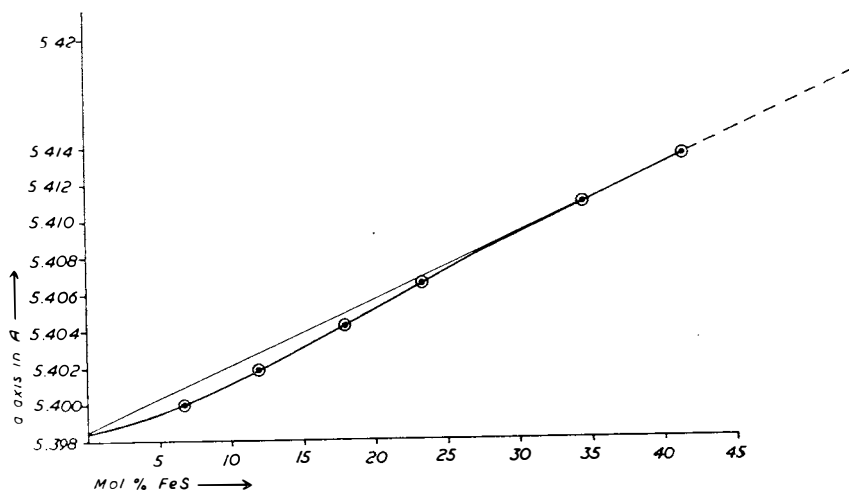


Fig. 5. Curve showing the relationship between the unit cell length and composition of β (Fe, Zn) S mix-crystals.

smaller than that obtained when the FeS content was increased from 20 wt.% (23.48 mol.%) to 30 wt.% (34.47 mol.%).

The a_0 values so far known may be plotted against the FeS content of the mix-crystals. This has been done in figure 5.

The points plotted for mix-crystals containing less than 30 wt.% (34.47 mol.%) FeS are seen to lie below a straight line drawn between the a_0 values for pure β ZnS and for mix-crystals containing 30 wt.% (34.47 mol.%) FeS. The biggest deviation occurs for mix-crystals with around 10 wt.% (11.98 mol.%) FeS. The distance becomes gradually smaller with increasing FeS content and mix-crystals with about 27 mol.% FeS are seen to lie on the straight line.

If one assumes the plot to continue as a straight line, one finds

that the a_0 value of $5.413_{1\pm2}$ Å corresponds to 36 wt.% (40.84 mol.%) FeS. (As will be remembered from above this a_0 value was derived from runs at 890° C containing 40 wt.% (45.0 mol.%) FeS).

In order to check whether the above assumption is correct, two runs were conducted at 890° C. In both cases 36 wt.% (40.84 mol.%) FeS was mixed with ZnS. The runs lasted one and two weeks respectively. The unit cell length values calculated from x-ray diagrams were $a_0 = 5.4130$ and 5.4132 Å. This proved that the a_0 versus composition plot continues as a straight line at least up to this point, and further that the maximum solubility of FeS in β ZnS at 890° C is 36 wt.% (40.84 mol.%).

The α - β Inversion Temperatures of the Mix-crystals.

A run at 900° C with a mixture consisting of 40 wt.% (45.0 mol.%) FeS and β ZnS produced α mix-crystals. From this and from the data obtained earlier, one may conclude that the maximum amount of FeS that can be dissolved in β ZnS is a little more than 36 wt.% (40.84 mol.%) and that the inversion point for mix-crystals of this composition is situated between 890 and 900° C.

A series of eight runs was then started in order to determine this inversion point. The first four runs were made with a mixture of 50 wt.% (55.1 mol.%) FeS and ZnS. This compound was first heated at 920° C (above the inversion point) for four days and later run for two weeks at temperatures and with results as shown in table III. The other four runs were made with 40 wt.% (45.0 mol.%)

TABLE III.

Duration of each run 2 weeks		Duration of each run 2 weeks	
Original α mix-crystals		Original β mix-crystals	
T° C of runs	Resulting modification	T° C of runs	Resulting modification
895	α	896	α
892	β	894	β
893	β	895	α
894	α	893	β

FeS mixed with ZnS. The compounds were first run at 880° C for three weeks so that homogeneous β mix-crystals were formed. Later these mix-crystals were used for runs also shown in table III.

For these runs special temperature controls were used so the uncertainty in the temperature measurements should not under any circumstances exceed $\pm 3^\circ$ C. From table III the inversion point is seen to be $894 \pm 3^\circ$ C. In other words no α (Fe, Zn) S mix-crystal is stable below 894° C.

The β mix-crystals produced in four of the eight tabulated runs, were used for x-ray powder diagrams. The a_o values calculated from these were all inside $a_o = 5.413_{3 \pm 2} \text{Å}$. Assuming the a_o versus composition curve in figure 5 to be a straight line, the obtained a_o value corresponds to a mix-crystal composition of 36.5 wt.% (41.36 mol.%) FeS. As a check on this assumption a mixture containing 36.5 wt.% FeS and ZnS was run at 894° C for seven days. Powder diagrams of the mix-crystal gave: $a_o = 5.413_{4 \pm 2} \text{Å}$. (These data have already been presented in table 1). The a_o versus composition curve is thus a straight line from a composition of about 27 mol.% and through 41.36 mol.% FeS.

Because of the limited solubility it is not possible to find out the further course of this curve. However, if the straight line is extended towards full replacement of ZnS by FeS a ZnS type FeS with $a_o = 5.4345 \text{Å}$ results.

The FG curve in figure 1 gives the temperatures at which β mix-crystals on heating will start to convert to the α modification, and at which α mix-crystals on "cooling" completely will convert to the β phase. In order to determine this curve, α mix-crystals of composition as shown in table IV were run from four to seven days at temperatures close to their inversion points.

The FD curve gives the temperatures at which α mix-crystals on "cooling" will start to convert to the β phase, and at which β mix-crystals on heating completely will change to the α modification. This curve was established by running β mix-crystals as shown in table V.

In table VI a compilation is presented of the inversion temperatures obtained from the twenty-five runs described in tables III through V.

The α - β inversion point for pure ZnS (upper column in table VI) was determined by ALLEN and CRENSHAW.² The limit of error in the

TABLE IV.
Runs with α mix-crystals.

Composition of α mix-crystals	T° C	Duration of runs	Resulting modification
10 wt. % (11.98 mol. %) FeS	995	4 days	α
	985	4 days	$\alpha + \beta$
	980	4 days	β
	982	4 days	$\alpha + \beta$
20 wt. % (23.48 mol. %) FeS	950	5 days	$\alpha + \beta$
	940	5 days	β
	943	5 days	β
	948	5 days	$\alpha + \beta$
30 wt. % (34.47 mol. %) FeS	920	7 days	$\alpha + \beta$
	910	7 days	β
	915	7 days	$\alpha + \beta$
	912	7 days	β

TABLE V.
Runs with β mix-crystals.

Composition of β mix-crystals	T° C	Duration of runs	Resulting modification
10 wt. % (11.98 mol. %) FeS	990	4 days	$\alpha + \beta$
	995	4 days	α
	993	4 days	α
20 wt. % (23.48 mol. %) FeS	965	5 days	α
	960	5 days	α
	955	5 days	$\alpha + \beta$
30 wt. % (34.47 mol. %) FeS	930	6 days	α
	927	6 days	α
	923	6 days	$\alpha + \beta$

other inversion point determinations in the same table does not exceed 4° C.

A modification may be present to a certain amount, depending upon its crystal symmetry, without showing up on the x-ray diagram.

TABLE VI.

Composition of mix-crystals	T° C for points on the FD curve	T° C for points on the FG curve
Pure ZnS	1020 \pm 5	1020 \pm 5
10 wt.% (11.98 mol.%) FeS	992 \pm 4	980 \pm 4
20 wt.% (23.48 mol.%) FeS	958 \pm 4	945 \pm 4
30 wt.% (34.47 mol.%) FeS	925 \pm 4	913 \pm 4
36.5 wt.% (41.36 mol.%) FeS.		894 \pm 3

The phases in question are of a hexagonal and cubic symmetry respectively and thus certainly will be detected in the powder diagrams if they constitute as much as ten per cent of the total sample. It is possible that in some runs one phase has been present to the extent of less than ten per cent and has thus not been detected. Therefore the curve FG theoretically could be lying a little lower and the curve FD a little higher than indicated. The FGD field is rather narrow, meaning the inversion takes place completely over a narrow temperature interval. (maximum 13° C). Therefore, if in certain runs a phase was present to the amount of less than ten percent and thus not detected, the corresponding error in the inversion temperature of any mix-crystal would amount to 1.0 to 1.5° C at the most. This uncertainty is taken into consideration in the limit of error given in the inversion temperatures.

The Mechanism of the α - β Transformation.

In order to shed some light on the α - β transformation mechanism of the mix-crystals an extensive series of experiments were carried out.

The dimensions of the mix-crystals depend to a certain extent upon how long the compounds are heated. Mixtures with varying proportions of FeS and ZnS were heated for one week at temperatures

slightly above the inversion points of the respective compounds. Thus α mix-crystals were produced, all of which seemed to be fairly equal in size, about 0.05 mm long. The crop of crystals produced in each run was then divided, by weighing, in two equal parts. While the one half was set aside for later runs, the other half was in each case sealed into a bomb and heated in vacuum for three more weeks at the same temperature as before the batch was split. The crystals grew in size during these three weeks and measured about 0.2 mm in length after completion of the runs.

The 0.2 mm mix-crystals from each run were then heated for four hours at temperatures of 50–60° C below their inversion points. In all cases it was then found that a complete transformation to modification β had taken place. The 0.05 mm mix-crystals (formed in the course of seven days) showed no signs of transformation after having been heated for four hours at temperatures of 50–60° C below their inversion points. Prolonged runs at the same temperatures showed in no case transformation after twelve more hours, but complete transformation in all cases after a total of twenty-six hours.

One here is comparing equal masses of mix-crystals, but the crystals in the one case are about: $\left(\frac{0.2}{0.05}\right)^3 = 64$ times as big in volume

as in the other case. Consequently there are about 64 times as many “small” crystals to be transformed as there are “big” ones. In comparative runs with small and large numbers of mix-crystals of equal size it was found that a small number always converts much faster than a large number. DEHLINGER²⁹ showed that an Au-Cu single crystal only required a few minutes to transform from the regular to the tetragonal modification, in polycrystalline material the transition process lasted about ten hours. Explaining this phenomenon, DEHLINGER assumed that the transition in one crystal unit takes place immediately when at some point in the crystal a few atoms have arranged themselves in accord with the new symmetry. Under such an assumption the time necessary for the arrangement of the few atoms will be identical with the time of complete transformation. SHÔJI²⁰ showed on a theoretical basis how the transition in zinc sulfide could take place in the easiest way — the symmetry planes before and after transition being in a well defined position to each other. Since

similar orientation relationships are observed in the metal transitions KRÖGER³⁰ expected that DEHLINGER's ideas for the metals should apply also to pure zinc sulfide and showed it to be so.

While DEHLINGER and KRÖGER compared the time needed for transition of one crystal with that of polycrystalline material, one is in this case dealing with crystals that differ in number as well as in size. If all crystals were of the same size one should reasonably expect that the larger number would transform slower than the smaller number. Comparing equal masses, the total surface area of a large number of "small" crystals is many times bigger than that of a small number of "big" crystals. (The ratio being 16 : 1 in the earlier mentioned runs). An increased area of exposure should hasten the inversion at least if this is aided by a fluid phase in which the transforming material is soluble. The studied transformation, however, took place in a dry state, and is believed to proceed as a wave from centers that have already started to transform. Therefore, the fewer crystals present the more readily the transformation proceeds. (The ideal case being a single crystal transformation). In the runs with a great number of small crystals the transformation process was believed to be inhibited for the following two reasons: 1) A new center must arise in each grain of powder. 2) Heat must be transmitted through the intervening space from one crystal to another. This must take place chiefly by radiation from one crystal to its neighbors. Both these factors slow down the transformation. (BUERGER³¹).

Grinding of the wurtzite type mix-crystals was found to influence the intensities of the lines in x-ray powder diagrams. Thus after only two minutes of grinding the wurtzite lines were becoming diffuse, and getting even more so after four and eight minutes. The sphalerite [333] and [422] lines gradually appeared and were intense after thirty-two minutes. After sixty-four minutes of grinding, the pattern seemed to be entirely that of sphalerite. Grinding thus supplies the activation energy required to effect the transformation. The effect produced by grinding may also be produced by pressure and shear as shown by BRIDGMAN³² who by such means irreversibly inverted wurtzite to sphalerite.

Further, a similar change in intensities as produced by grinding was observed on x-ray diagrams made after *a* mix-crystals had been

heated 30–40° C below their inversion point for one, two, three, four, eight, and sixteen hours respectively.¹

The ZnS α - β inversion involves no change in the first coordination of the atoms. The energy change must be accounted for by a change in the coordination of non-nearest neighbors. The transformation is sluggish as seen from the above described experiments. The α - β inversion for sphalerite has by BUERGER³¹ been classified as a reconstructive transformation of a secondary coordination. The experiments carried out by the present author have verified BUERGER's criteria for a transformation of this kind.

A Comparison of the Zn-S α - β Inversion with Liquid-solid Transitions.

Liquid-solid transitions have in recent years been investigated carefully, and some interesting results have been obtained. SCHAEFER³⁴ found for instance that tiny droplets of water (10–15 microns in diameter) might be super-cooled to a temperature of –39° C before inverting to ice. VONNEGUT³⁵ has studied the liquid-solid transition in tin particles. TURNBULL and CEC³⁶ studied the solidification of small metal droplets on a high temperature microscope stage. These investigations revealed that at least from a statistical standpoint the solidification temperature of smaller particles tends to be lower than that of larger ones. It has similarly been shown for solid transformations that large crystals invert at a higher temperature than small crystals, (LENNARD-JONES and DENT³⁷). Undoubtedly not only the droplet size but also the time is of importance in deciding at which temperature solidification takes place. Thus if a small droplet solidifies instantly at a low temperature, it probably would solidify after some seconds, minutes or hours at a temperature somewhat closer to its melting point. In other words, if one has two chambers,

¹ Some of the x-ray powder diagrams made from these mix-crystals indicated a stacking disorder similar to that described by BARRETT³³ to occur in a number of pure metals. A disorder transformation has crystallographic characteristics substantially identical with the reconstructive type of transformation when the inversion is sluggish. It is therefore possible that the ZnS α - β inversion should be classified as a stacking disorder transformation instead of a reconstructive transformation.

the one containing comparatively big droplets and the other small droplets, and keep the droplets in both chambers super-cooled to the same degree, one would find that the larger droplets solidify first and then after some time the small ones. Thus there may be an analogy between liquid-solid inversions and α - β inversions like the one in ZnS.

TURNBULL³⁸ has derived a kinetic expression for the rate of transformation from liquid to solid by homogeneous nucleation as follows:

$$dV/dt = Iv (V_0 - V).$$

Here V is the total volume transformed in the time t , V_0 is the total volume at $t = 0$, I is the rate of nucleation per unit volume, and v is the volume of the droplet. The expression is deduced on the assumption that the nucleation has obtained a steady rate. It is important that the droplet size is uniform and accurately known.

The above equation may be integrated to give:

$$V = V_0 (1 - e^{-Ivt}).$$

As an experiment, one may now apply the last equation on the ZnS α - β transition. There were equivalent volumes (V_0) of 1/25 mm and 1/5 mm long particles. For the volume V_1 of small particles transformed in time t_1 one may write:

$$V_1 = V_0 (1 - e^{-I_1 v_1 t_1}).$$

For the volume V_2 of the larger particles transformed in time t_2 , one may write:

$$V_2 = V_0 (1 - e^{-I_2 v_2 t_2}).$$

When complete transformation of both small and larger particles has taken place, $V_1 = V_2$ and consequently:

$$1 - e^{-I_1 v_1 t_1} = 1 - e^{-I_2 v_2 t_2} \text{ or:}$$

$$I_1 v_1 t_1 = I_2 v_2 t_2$$

The rate of nucleation is proportional to the volume.¹ If I is the nucleation rate in the small particles, then the nucleation rate in

¹ This is an assumption made by TURNBULL for liquid-solid transitions. Nucleation of a new phase in a transformation in the solid state is a complex phenomenon, and as yet no general theory of it exists. The assumption made for liquid-solid transitions by the above mentioned author is here made for a solid-solid transformation as an experiment.

the larger particles will be $I_2 = 64 I$. Remembering that $v_1 = (0.05)^3$ and $v_2 = (0.2)^3$ one obtains:

$$I \cdot (0.05)^3 \cdot t_1 = 64 \cdot I \cdot (0.2)^3 \cdot t_2 \text{ or:}$$

$$t_1 = 4^6 \cdot t_2$$

In other words, the time needed for complete inversion of the small crystals is according to this calculation, 4000 times longer than that required for the large crystals to transform to the β phase. Even if the result of the t_1/t_2 ratio calculation in no respect can claim to be more than approximate, it shows the same trend as the experimental data.

Lattice Dimensions of Pure α ZnS and of the α (Fe, Zn) S Mix-crystals.

From x-ray powder diagrams were calculated the unit cell a_0 and c_0 values for pure α ZnS as well as for the α (Fe, Zn) S mix-crystal series. (The rod thickness was as before $d = 0.30 \pm 0.05$ mm, and the same NaCl lines as earlier served as internal standard).

$$\text{For } \alpha \text{ ZnS was calculated: } a_0 = 3.814_{0 \pm 3} \text{ \AA}$$

$$c_0 = 6.257_{6 \pm 3} \text{ \AA}$$

The introduction of FeS into the α ZnS lattice causes an expansion in the lattice dimensions, very similar to that obtained for β ZnS. Table VII shows the relationship between unit cell dimensions and the composition of the mix-crystals.

TABLE VII.

Number of runs	FeS content of mix-crystals		T° C	a axis in Å	c axis in Å	Calculated molecular volume	Calculated specific gravity
	wt. %	mol. %					
3	0	0	1050	$3.814_{0 \pm 3}$	$6.257_{6 \pm 3}$	39.4160	4.1065
3	4.75	5.77	1020	$3.815_{6 \pm 4}$	$6.260_{7 \pm 4}$	39.4668	4.0821
3	9.30	11.18	990	$3.816_{6 \pm 4}$	$6.263_{8 \pm 4}$	39.5085	4.0595
5	22.00	25.72	980	$3.821_{9 \pm 4}$	$6.275_{3 \pm 4}$	39.6912	3.9902
3	30.00	34.47	960	$3.824_{7 \pm 4}$	$6.281_{6 \pm 4}$	39.7892	3.9485

The time required to obtain homogeneous mix-crystals in the runs tabulated above, appeared to be relatively short. A heating of

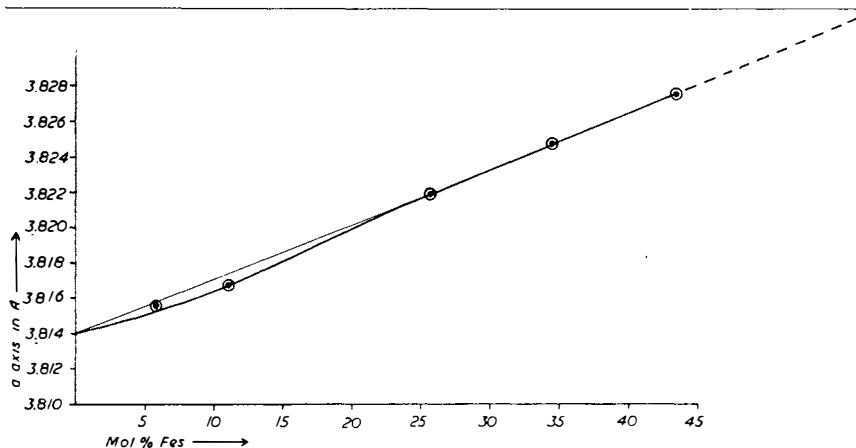


Fig. 6a. Curve showing the relationship between the unit cell a_0 and composition of $a(\text{Fe, Zn})\text{S}$ mix-crystals.

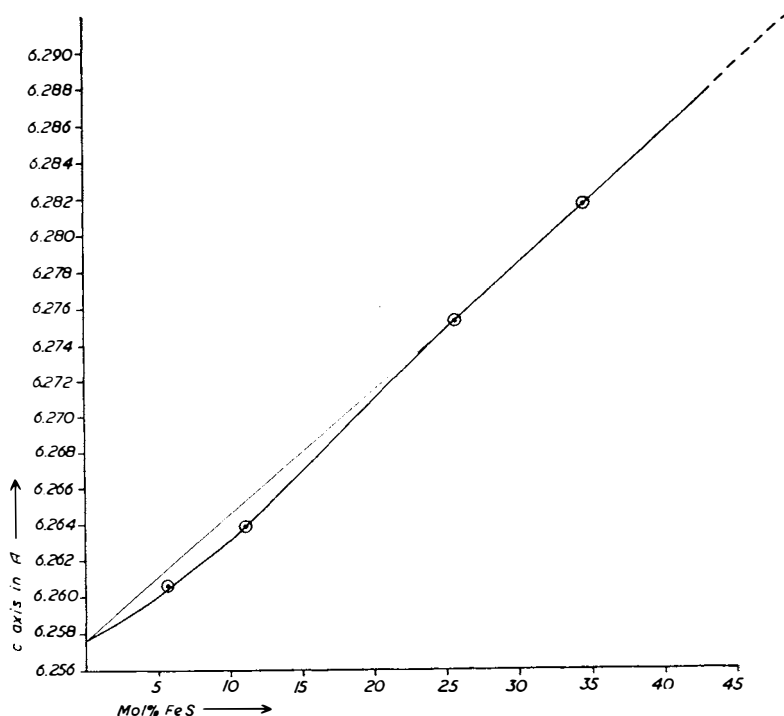


Fig. 6b. Curve showing the relationship between the unit cell c_0 and composition of $a(\text{Fe, Zn})\text{S}$ mix-crystals.

forty-eight hours proved to be ample in all cases. (The same a_0 and c_0 values were obtained from runs lasting two days as from those lasting seven days). The a_0 , c_0 values respectively for the α (FeZn) S mix-crystal series are plotted versus mix-crystal composition in figures 6a and b. These plots show by comparison with figure 5 that the α ZnS behave analogously to the β ZnS when FeS is introduced into the lattice.

The Temperature-composition Relationship of the Equilibrium α Mix-crystals.

The CD curve (see figure 1) gives the equilibrium α (Fe, Zn) S mix-crystal composition.

In order to determine this curve two runs were conducted at 910° C. In the first of these runs 39.75 wt.% (44.74 mol.%) FeS; and in the second 50 wt.% (55.1 mol.%) FeS were mixed with ZnS. The runs lasted seventy-two hours and the following unit cell lengths were calculated from x-ray powder diagrams: $a_0 = 3.827_{7\pm4}\text{\AA}$ and $c_0 = 6.288_{0\pm4}$ for the first run, and $a_0 = 3.827_{6\pm4}$ and $c_0 = 6.288_{2\pm4}$ for the latter run. The curves shown in figure 6a and 6b are seen to be straight lines from a mix-crystal FeS content of 22 wt.% (25.72 mol.%) through 30 wt.% (34.47 mol.%). Assuming the curves to continue in this manner, the above given a_0 and c_0 values point to a mix-crystal composition of 38.5 wt.% (43.45 mol.%) FeS.

A mixture of this composition was run as a check at 910° C for seventy-five hours. The a_0 and c_0 values of the resulting α mix-crystals were well within the limit of error of the values given above. This shows that the curves in figure 6a and 6b continue as straight lines beyond the composition of 30 wt.% (34.47 mol.%) FeS.

In order to determine another point on the CD curve a mixture containing 50 wt.% (55.1 mol.%) FeS was run for forty-eight hours at 950° C. The unit cell dimensions of the mix-crystals thus formed were: $a_0 = 3.828_{0\pm4}\text{\AA}$ and $c_0 = 6.288_{6\pm4}$. This corresponds to α mix-crystals containing 39.2 wt.% (44.17 mol.%) FeS.

If the solid solution were ideal, one now might, on the basis of the already known points on the CD curve, calculate the further course

of the curve.¹ Such computations give for the FeS solubility about 46.0 mol.% at 1050° C and about 48.0 mol.% at 1170° C.

The Properties of the α and β Mix-crystals.

The physical properties of mix-crystals are functions of the properties of the end members of the mix-crystal series. Sometimes these functions are relatively simple. Thus GRIMM and HERZFELD³⁹ from the lattice energy studies by BORN and LANDÉ^{40, 41, 42} derived a formula for the volume relationship existing between mix-crystals in a number of binary series.²

In figure 7 a are plotted unit cell length, molecular volume and specific gravity, each versus β mix-crystal composition. Figure 7b presents the same functions for α mix-crystals. The unit cell length versus mix-crystal composition curves are of such a nature that they cannot be expressed by a mathematical formula of the type derived by BORN and LANDÉ.

When mix-crystals of higher symmetry (as in the present case) are formed without deformation of the anions and without changes in the chemical bonds, the physical properties of the mix-crystals will vary nearly proportionally to the composition.

As will be seen later in this paper, the mix-crystal formation involves a change in the chemical bonds. This, therefore, explains why the BORN and LANDÉ formula is invalid in this case.

The curves presented in figures 7a and b are plotted from the data given in tables I and VII and extended by extrapolation towards complete replacement of ZnS by FeS.

In figure 7a one has on the left side β ZnS and on the right an FeS with the β ZnS structure. This hypothetical cubic FeS has the following characteristics: $a_0 = 5.4345$ Å, molecular volume about 40.125 Å³, and specific gravity $d = 3.63$.

Similarly in figure 7 b one finds on the left side α ZnS and on the

¹ The background for these calculations will be discussed later in this paper.

² This work is well known and a further discussion of it here seems unnecessary. It may only be mentioned that both RETGER'S⁴³ and VEGARD'S⁴⁴ laws are special cases of GRIMM and HERZFELD'S more general formula.

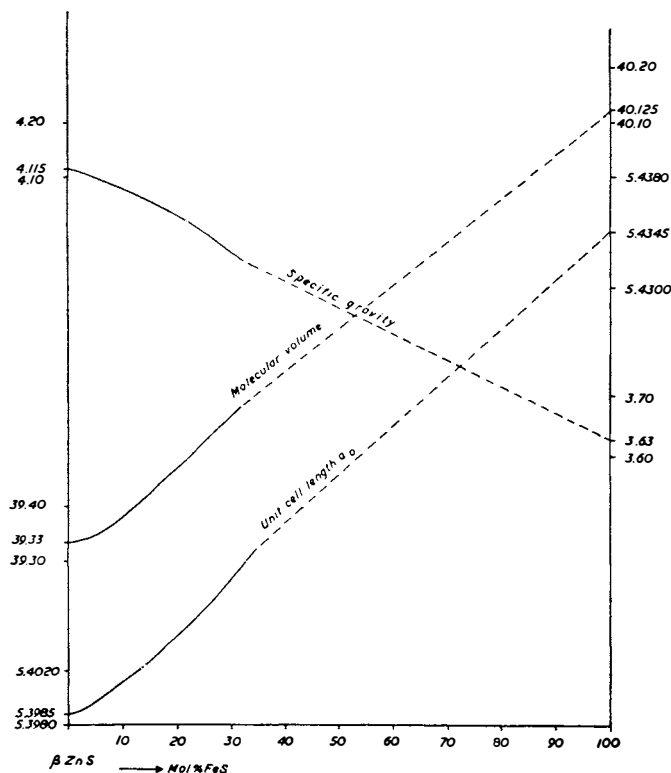


Fig. 7.a. Variations in the physical properties of β (Fe, Zn) S mix-crystals as functions of their composition.

right an FeS with the α ZnS structure. This hypothetical hexagonal FeS is earmarked as follows:

$a_0 = 3.845 \text{ \AA}$, $c_0 = 6.328 \text{ \AA}$, molecular volume about 40.46 \AA^3 and specific gravity $d = 3.60$.

The data given above are, without exception, obtained from rather daring extrapolations and must be regarded as approximations. Nevertheless, they are presented here because some later calculations are based upon them.

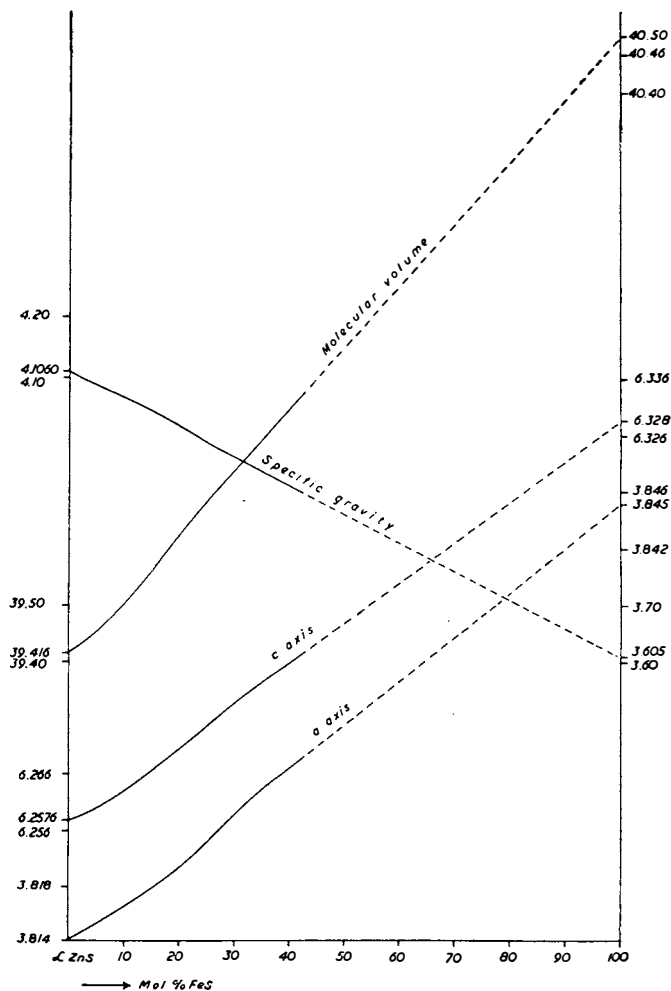


Fig. 7b. Variations in the physical properties of α (Fe, Zn) S mix-crystals as functions of their composition.

The Influence of Pressure upon the ZnS α - β Inversion.

The molecular volumes of β and α ZnS as well as of both types of mix-crystals have been calculated from x-ray data. (See tables I and VII, and figures 7 a and b).

The molecular volume of β ZnS is 39.333 \AA^3 and of α ZnS it is 39.416 \AA^3 . The α - β transformation consequently is accompanied by a change in volume, $\Delta V = 0.083 \text{ \AA}^3$ for each molecule, or $0.083 \cdot 10^{-24} \cdot N = 0.05 \text{ cm}^3$ per mol. (Avogadro's number, $N = 6.02 \cdot 10^{23}$).

The Clapeyron-Clausius equation gives the temperature of transformation T , as a function of the pressure P :

$$dT/dP = T \cdot \Delta V / \Delta H,$$

where ΔH is the heat of transformation. The heat absorbed when β ZnS converts to the α modification is, $\Delta H = 3190 \text{ cal/mol}$.⁴⁵

Thus: $dT/dP = 1293 \cdot 0.05/3190 = 0.0203 \text{ degree/atm}$.

The dT/dP ratio has a positive value, since modification α has a greater molecular volume than modification β and since heat is absorbed.

Thus, under pressure, the β modification increases its stability field. At a pressure of one thousand atm., the inversion will take place around 1040°C . The molecular volumes for mix-crystals of any composition may be found in figures 7 a and b. The difference in the readings gives the wanted ΔV value. As an approximation, ΔH may be assumed constant for the mix-crystal series. Thus, when T as well as ΔV and ΔH are known, the influence of pressure upon the inversion point of mix-crystals of any composition may be calculated.

Magnetic Properties of the Mix-crystals .:

While pure ZnS is diamagnetic, both the α and β mix-crystals are attracted by a magnet. The force of attraction is clearly a function of the mix-crystal iron content, and increasing with the latter. Unfortunately no quantitative measurements could be undertaken of the magnetic properties of the mix-crystals. It is believed, however, that if such measurements were done and the results plotted versus mix-crystal composition, curves very much like the ones presented in figures 5 and 6 would be produced. In other words there would exist a definite relationship between unit cell dimensions and the magnetic properties of the mix-crystals.

Reasons for the Increase in Unit Cell Dimensions due to the Introduction of Iron.

It has in the foregoing been shown that the introduction of iron into the zinc sulfide lattice causes an increase in the unit cell dimensions of both the high and low temperature modifications of ZnS. Such an increase might not be expected because iron both as ion and atom is smaller than zinc. WELLS¹⁶ gives for the radius of Zn^{2+} in 4 coordination: 0.74Å, and for Fe^{2+} in 6 coordination 0.75Å. The approximate radius of Fe^{2+} in 4 coordination may be obtained from the last value by subtraction of about 5 %, which gives 0.71Å. The radius of the Zn atom in 4 coordination is 1.31Å (WELLS¹⁶) and the value given for Fe in 6 coordination is 1.23Å. The atomic size of Fe in 4 coordination is somewhat smaller than the size in 6 coordination. How much smaller is not known, but one will assume its radius 1.20Å. The corresponding values for sulfur in 4 coordination are 1.84Å (ionic) and 1.04Å (atomic).

From the earlier presented β ZnS lattice dimensions the Zn-S distance was calculated to be 2.337Å.¹ When iron is introduced into the lattice the interatomic distance increases and by extrapolation of the curve in figure 5 one finds that when all zinc has been replaced, the distance, now between iron and sulfur is 2.353Å.

From the values given above it is found by addition that the Fe-S distance, if the bonds are 100 % covalent, should be $1.20 + 1.04 = 2.24$ Å, and for 100 % ionic bonds $0.71 + 1.84 = 2.55$ Å. The Fe-S distance found by the extrapolation above is larger than the 100 % covalent distance and smaller than the 100 % ionic distance and suggests that the bonds have appreciable ionic character.

From thermochemical data, PAULING¹⁸ and HAÏSSINSKY^{46, 47} have calculated electronegativity coefficients for many elements. These values are such that the difference $X_A - X_B$ between the electronegativity coefficients for any pair of elements equals the square root of E_r , the ionic resonance energy of the bond A—B expressed in electron-volts. From the values of E_r , only differences $X_A - X_B$ are obtained, and it is necessary to assign an arbitrary value of X to

¹ The Zn-S distances in α ZnS were from the a and c values found to be 2.338 Å and 2.346 Å.

one element. The choice of the absolute value of X was determined by the relation of electronegativity to ionization energy and electron affinity (WELLS¹⁶). Pauling plotted the known percentage ionic character for a number of compounds AB against the difference in electronegativity ($X_A - X_B$) and thus produced a fairly smooth curve showing this relationship.

The electronegativities of the elements in question in this paper are for $S : 2.5$, $Zn : 1.5$. The $X_A - X_B$ value for ZnS thus is: 1.0. Applying this value to Pauling's curve one finds that the ZnS bonds have about 20 % ionic character. This value cannot be taken literally, but will at least give some information about the ionic character of the mineral.

HAÏSSINSKY^{46, 47} has pointed out that the electronegativity X of an element is not a constant under all circumstances. It depends on the valency and is not even constant for a given element in a particular valence state, but varies according to the compound from which it was derived. Thus the X value for Fe derived from pyrrhotite is likely to differ from the X value for Fe in FeS of the sphalerite or wurtzite structure type.

If one imagines a linear relationship between the increase in atomic distance (caused by iron replacing zinc) and the ionic character of the bonds in the $(Fe, Zn) S$ mix crystals,¹ one finds that the bonds of the sphalerite or wurtzite type FeS must have approximately:

$$\frac{(2.353 - 2.24)}{2.55 - 2.24} \cdot 100 = 36 \% \text{ ionic character. In other words, the}$$

expansion in the lattice parameters of ZnS may be explained, if one assumes that the percentage of ionic character of the bonds changes from about 20 % for pure ZnS to about 36 % for pure ZnS type FeS .

Changes in the bond types, as above described, have to the author's knowledge never before been applied to mix-crystals. It is believed that this method may be used successfully on many mix-crystal series for which the volume relationships cannot be mathematically expressed by means of a simple formula.

¹ Since the length of the bonds are not proportional to their strength a linear relationship does not exist, but by making a thought experiment as above indicated, one at least is able to show that the bonds of the ZnS type FeS are of a more ionic character than the ZnS bonds.

Earlier in this paper a relationship between the magnetic properties and the unit cell dimensions of the mix-crystals was mentioned. The unit cell dimensions in turn are functions of the bond types. Consequently there exists a definite relationship between the latter and the magnetic properties of the mix-crystals.

The Temperature-composition Relationship of the Equilibrium β Mix-crystals .

Earlier in this paper it has been established that the maximum amount of FeS that can be dissolved in the β ZnS lattice is 36.5 wt.% (41.36 mol.%). Mix-crystals of such composition were produced at 894° C.

In order to determine a number of points on the GK equilibrium curve (see figure 1), an extensive series of runs was undertaken. Equilibrium mix-crystals were produced by solution as well as by exsolution. For the solution runs 40.0 wt.% (45.0 mol.%) FeS was mixed with ZnS, while for the exsolution runs mix-crystals containing 36.5 wt.% (41.36 mol.%) FeS were used.

The results of all these runs are compiled in table VIII.

The points between 800 and 890° C were obtained in the following way. Four bombs were run simultaneously at each temperature shown in table VIII. Two of these bombs contained a mechanical mixture of FeS and ZnS and the other two contained FeS rich α mix-crystals. (Both these compounds are described above). In the former two bombs mix-crystals were produced by solution, while in the latter two bombs mix-crystals of equilibrium composition were formed by exsolution.

After the four bombs had been heated for a period of time, the length of which depended upon the temperature, one bomb of each kind was taken out of the furnace. The mix-crystal composition was determined by means of x-ray diagrams. If there now in both bombs already were produced mix-crystals of identical composition, equilibrium had been established and the run could be interrupted.

Already the runs conducted at 880° C demonstrated that the exsolution process is more sluggish than the solution process.

While equilibrium at 800° C was reached in less than two weeks by solution and in about three weeks by exsolution, four weeks for

TABLE VIII.
The temperature-composition relationship of the equilibrium β mix-crystals.

T°C of solution and exsolution runs	a_o values in A from solu- tion runs	required time for equilibr. by solution	Number of runs	a_o values in A from exsolu- tion runs	required time for equilibr. by exsolution	Number of runs	FeS content of equibr. mix-crystals	
							wt%	mol%
890	5.413 ₁ ± ₂	48 hours	2	5.413 ₁ ± ₂	48 hours	2	36.0	40.84
880	5.412 ₈ ± ₂	48 hours	2	5.412 ₉ ± ₂	72 hours	2	35.0	39.78
870	5.412 ₆ ± ₂	72 hours	2	5.412 ₅ ± ₂	120 hours	2	34.4	39.15
860	5.412 ₃ ± ₂	105 hours	2	5.412 ₄ ± ₂	7 days	2	33.7	38.40
850	5.412 ₀ ± ₂	7 days	3	5.412 ₀ ± ₂	10 days	2	33.0	37.67
800	5.410 ₉ ± ₂	14 days	2	5.411 ₀ ± ₂	21 days	2	29.8	34.25
750	5.409 ₄ ± ₂	4 weeks	3	5.409 ₃ ± ₂	6 weeks	3	26.7	30.89
700	5.408 ₄ ± ₂	9 weeks	5	5.408 ₅ ± ₂	12 weeks	5	24.0	27.93
600	5.406 ₃ ± ₂	19 weeks	4	5.406 ₄ ± ₂	28 weeks	4	19.0	22.35
500	5.404 ₃ ± ₂	40 weeks	12	ϵ equilibrium not reached	more than 54 weeks	12	14.7	17.48

solution and six weeks for exsolution were required at 750° C. At 700° C the needed time was twice as long as that required at 750° C. This as well as the conditions at 600° C and 500° C are presented in table VIII.

For the runs conducted below 800° C a sufficient number of bombs of each type were prepared so one bomb of either kind could be taken out of the furnace and the material investigated each week, or at temperatures below 700° C each month. The variations in the a_0 values thus were recorded from week to week (respectively from month to month).

At 500° C the solution process was complete after nine and one-half months. The a_0 values obtained by means of x-ray powder diagrams after a total heating of eleven months, showed no increase beyond the values obtained after nine and one-half months. The exsolution runs at this temperature were extended to a total of twelve and one-half months. Certain interesting changes in the x-ray lines were recorded, but equilibrium mix-crystals were not obtained.¹

In order to produce equilibrium β mix-crystals also below 500° C, methods different from those previously used had to be devised. Equilibrium was obtained at 400° C after three weeks by the following procedure. A compound consisting of 80 wt.% Zn and 20 wt.% Fe was heated at 850° C for twenty-four hours. This temperature was high enough to melt the compound. Upon quenching, the Zn-Fe alloy was crushed and ground to a fine powder. This powder was placed in a porcelain container inside a quartz tube, which again was stuck through a horizontal open-end furnace. The porcelain container was situated in the hot spot of the furnace, directly under the thermocouple. Through the quartz tube was then passed a mixture of 1 : 1 H₂S and H₂ gases.²

¹ The material produced in the exsolution runs at 500° C showed, after having been heated for six months, separated double (333) and (511) lines instead of coinciding ones. The same happened to the (422) and (242) lines. If all normally occurring lines behaved in the same way one might have explained this by assuming that about equal amounts of mix-crystals of two different compositions were present. However, this was not so. The more probable solution is that one here is presented with mix-crystals of a deformed cubic structure.

² This ratio has been found by T. ROSENQVIST to be the right one for the formation of nearly stoichiometric FeS at 400° C.

After being heated for seven days at 400° C, x-ray powder diagrams showed that 50—60 % of the alloy had been converted to sulfide. The material was reground and put back into the furnace. After two more weeks of heating at the same temperature, all material was found to have transformed to sulfide. Calculations from x-ray powder diagrams of the unit cell length of the resulting β mix-crystals gave $a_0 = 5.4021$ Å. This corresponds closely to 11.0 % FeS by wt. (13.17 mol.%). Further heating of the substance produced no further increase in the a_0 value.

Efforts to apply this method for the formation of β mix-crystals at 300° C were not successful. This temperature is too low for the sulfides to be formed within a reasonable length of time.

In order to obtain equilibrium mix-crystals in a comparatively short time at temperatures below 750° C a number of fluxes were mixed in with the sulfides. It was, however, experienced that the presence of any of these fluxes greatly influenced the equilibrium. A certain type of flux was found to entirely expel the FeS from the ZnS lattice.¹

Thermodynamic Aspects of the FeS—ZnS System.

In the case of an essentially pure solute being in contact with its saturated solution, the equilibrium condition is that the chemical potential (partial molal free energy \bar{F}) for the solute is the same in the two phases. That is:

$$\Delta\bar{F} = \Delta\bar{H} - \bar{T}\Delta\bar{S} = 0 \quad (1), \text{ or: } \Delta\bar{H} = \bar{T}\Delta\bar{S} \quad (2)$$

where $\Delta\bar{F}$ is the difference in partial molal free energy of the pure and dissolved solute, $\Delta\bar{H}$ is the difference in partial molal heat contents of the pure and dissolved solute, and $\Delta\bar{S}$ is the difference in partial molal entropy of the pure and dissolved solute.

In the case of an ideal solution $\Delta\bar{S}$ is given by the equation:

$$\Delta\bar{S} = -R \cdot \ln(x) \quad (3),$$

where x is the mole fraction of solute. If one introduces (3) into

¹ Further studies of the latter type of reactions are now progressing. The results may have significance for the dressing of iron-rich sphalerite ores and will appear in a later publication.

equation (2), one gets: $\Delta \bar{H} = T \cdot [-R \cdot \ln(x)]$ (4), or: $\ln(x) = -\Delta H/R \cdot 1/T$, or: $x = e^{-\Delta \bar{H}/RT}$ (5).

That means, if one plots the logarithm of x versus $1/T$, one gets a curve, the slope of which is $-\Delta H/R$.

Thus in the FeS—ZnS system where FeS is the solute and ZnS the solvent, one may plot the logarithms of the experimentally found FeS concentrations versus $1/T$. This has been done and the results are shown in figure 8. It will be noticed that the points for the con-

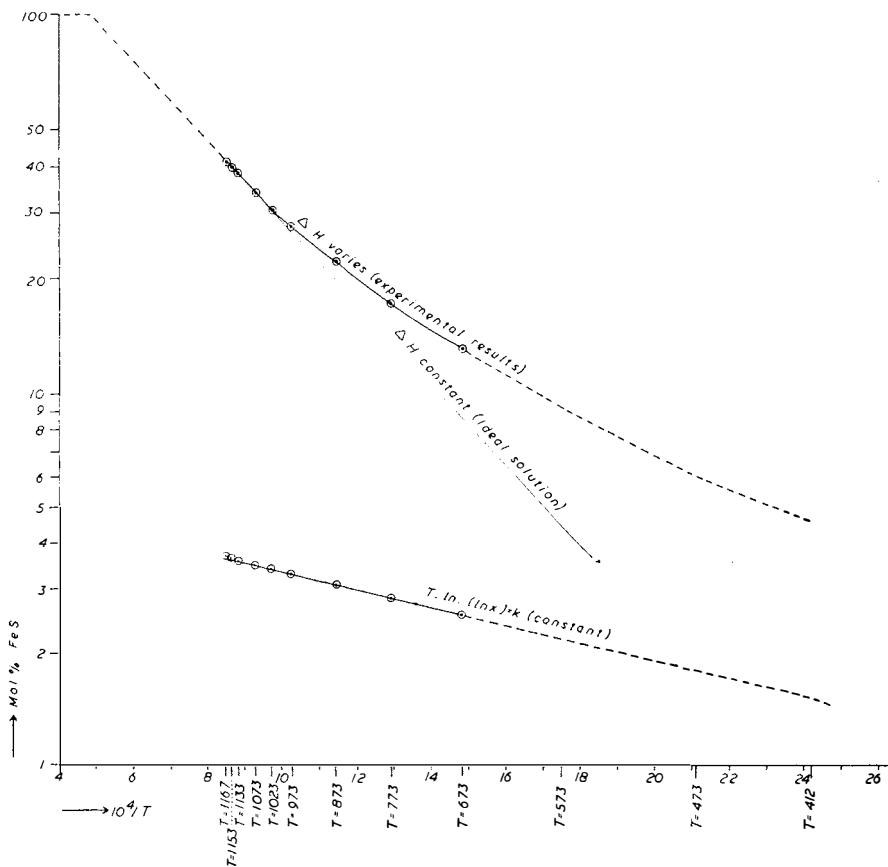


Fig. 8. Upper curve showing the relationship between $1/T$ and $\ln x$. Lower curve showing the relationship between $1/T$ and $\ln(\ln x)$. (In both cases x is the molconcentration of FeS in β mix-crystals.)

centrations between 41.3 mol.% FeS at 1167° K down to 30.89 mol.% at 1023° K lie very nearly on a straight line, in other words the slope of the curve is almost constant = $-\Delta H/R$, and the solution between these temperatures behaves like an ideal one.

Below 1023° K the points are seen to lie above the "ideal solution" values indicated by the straight line in the figure. The distances between this ideal curve and the plotted points increase markedly as the temperature decreases. In other words the solubility of FeS in ZnS is higher at temperatures below 1023° K than one would expect, if the solution were ideal. Ideal behavior at high temperatures and an increasing deviation from ideality at decreasing temperatures has been observed in liquid solutions. In such cases the deviation from ideality often may be expressed by simple equations which usually are of an exponential type. Thus, by plotting the logarithm of the logarithm of the FeS concentration against $1/T$, it is not surprising that all the points may be joined by a straight line. (See lower part of figure 8).

Between 1167° K and 1023° K the $\ln(x)$ versus $1/T$ plot gives a straight line, the slope of which is $-\Delta H/R$. This slope may be expressed by the molconcentrations and temperatures thus:

$$\frac{-\Delta H}{R} = \frac{\ln(x_A) - \ln(x_B)}{1/T_A - 1/T_B} \quad (6) \quad \text{or:} \quad \Delta H = \frac{-R \cdot [\ln(x_A) - \ln(x_B)] \cdot T_A \cdot T_B}{T_B - T_A} \quad (7)$$

where A and B are two points on the straight line.

In (7) one may now insert the values: 41.36 mol.% FeS at 1167° K, and 30.89 mol.% FeS at 1023° K. The result thus obtained is: $\Delta H = -4762.0$ cal/mol. By applying equation (2) one further finds: $\Delta S = -4.08$ cal/mol. degree.

Below point B the slope of the $\ln(x)$ versus $1/T$ curve diverges exponentially away from the constant $-\Delta H/R$ slope. To indicate that the $-\Delta H/R$ ratio is constant no more one may write: $-\Delta H'/R$ for the slope in any given point. In this expression $\Delta H'$ is a variable.

The relationship: $\ln(x) = -\Delta H'/R \cdot 1/T$ (8) may now still be said to exist. By using the $\ln(x)$ and $1/T$ values for points situated close together on the GK curve, and assuming $\Delta H'$ to be constant between each pair of points, one may calculate the respective ΔH and ΔS

values. Table IX shows the variation in ΔH and in ΔS for different temperature intervals.¹

TABLE IX.
Calculated heats and entropies of "mixing".

T°K	— ΔH	— ΔS
1167 — 1023	4762	4.08
1023 — 973	3983	3.89
973 — 873	3748.5	3.85
873 — 773	3297	3.78
773 — 673	2904	3.75
673 — 573	2615.5	3.88
573 — 473	2229	3.89
473 — 411	1737	3.67

It has been shown that the $\ln[\ln(x)]$ values plotted versus the $1/T$ values produced a seemingly straight line. This may be written: $\ln[\ln(x)] = k \cdot 1/T$ (9), or: $\ln(x) = e^{k/T}$. If one inserts this in equation (8), the following formula may be derived: $\Delta H' = e^{k/T} \cdot RT$ (10). The numerical value of k is -577.7 .²

The linear relationship between $\ln[\ln(x)]$ and $1/T$ is useful for the determination of points on the GK curve below 673° K (The lowest temperature at which equilibrium experimentally could be established). When the straight line in this plot is extended towards lower temperatures, one obtains for the solubility of FeS in ZnS the following values:

¹ The formation of mix-crystals involves: 1) pyrrhotite changes its structure to that of ZnS, which implies an energy ΔH_1 , 2) FeS with the ZnS structure enters the ZnS lattice. The energy required for the latter process is the heat of mixing ΔH_2 . The ΔH mentioned above then is really composed of the energy required to transform FeS to the ZnS structure and the energy required for the latter type FeS to enter the ZnS lattice. Similarly the ΔS mentioned above is composed of the FeS transformation entropy and the entropy of mixing.

² By applying equation (9) on six known points on the curve in the lower part of figure 8, three independent determinations of k were done. The results varied from -577.62 to -577.76 , average: -577.7 . In other words k is constant.

at 573° K 9.35 mol.% (7.75 wt.%) and at 473° K 6.17 mol.% (5.08 wt.%).

FeS converts at about 412° K its atomic arrangement from that of the Ni-As symmetry to that of the "supercell", the linear $\ln [x]$ versus $1/T$ relationship cannot be used for determinations of points on the equilibrium curve below this inversion point. The solubility at 412° K is from the plot in figure 8 found to be 4.66 mol.% FeS.

The energy released by this high-low inversion is 1250 cal/mol (KELLY⁴⁸). The difference in energy between the high and low modifications of FeS will at the point L cause a break in the solubility curve as indicated in figure 1. How big the deviation in point L is between the GK and LK curves has not been determined.

Assuming the solubility curve to be ideal above the 894° C inversion point the $\ln x$ and $1/T$ values for the two already known points on the curve CD may be plotted against each other. The extension of the straight line through the two points determines the CD curve. The results of this plot have been mentioned earlier.

The FeS-ZnS diagram and all the results obtained from the numerous runs necessary for its establishment offer a great many possibilities for fascinating thermodynamic calculations. However, in order to keep the size of this paper within reason and not to get astray from the original purpose of providing a geologic thermometer, these will have to be considered at a later date.

Meteoritic FeS.

FeS with a cubic symmetry has been described as occurring in iron meteorites. FEDOROV⁴⁹ even went so far as to report this meteoritic FeS to have the β ZnS atomic arrangement. Thus by replacing all Zn in β ZnS with Fe one obtains FEDOROV's FeS. The physical properties of this FeS are found on the right hand side of figure 7a. Further, by extension of the curves in figure 8 towards full replacement of the Zn, one finds that the heat required would be about 9500 cal/mol at a temperature of around 2300° K. Comparing this temperature with the melting point of the Ni-As type FeS, and further by comparing the specific gravities of the same compounds, one may conclude that FeS of the β ZnS structure type does not exist in meteorites or on earth.

The Influence of Pressure upon the Solubility of FeS in β ZnS.

The mix-crystal composition in the FeS—(Fe,Zn)S assemblage was shown above to be a function of the temperature. In these calculations, however, the influence of pressure on the FeS content of the mix-crystals was not considered.

Equilibrium mix-crystals containing x mol % FeS formed at temperature T and pressure P , will change in composition when the assemblage is exposed to a pressure P_1 . The temperature remains unchanged. The composition x_1 corresponding to the new equilibrium conditions can be shown to be:

$$x_1 = x \cdot e^{\frac{\Delta F - \Delta F_1}{RT}} \quad (11)$$

Here $\Delta F - \Delta F_1$ is the free energy change caused by the change in pressure from P to P_1 . R is the gas constant. (0.082 liter atm./mol degree).

Now: $\Delta F - \Delta F_1 = \Delta V(P - P_1)$, where ΔV is the difference in mol-volume between pyrrhotite and ZnS type FeS.

The equation: $x_1 = x \cdot e^{\frac{\Delta V(P - P_1)}{RT}}$ (12) thus offers an opportunity for calculation of the influence of pressure upon the solubility of FeS in ZnS. It should be remembered that equation (12) has been deduced under the assumption that the solution is ideal. It has previously been stressed that the solution is not ideal. However, the error in the succeeding calculations of the influence of pressure upon the FeS solubility is not significant because the $P - P_1$ value is kept relatively small.

The molecular volume of β ZnS is 39.333 A^3 and that of FeS of the β ZnS structure is about 40.125 A^3 (figure 7a). The molecular volume of pyrrhotite is in the literature given from 29.6 to 29.9 A^3 . Here will be used the mean value of 29.75 A^3 .

Consequently $\Delta V = (40.125 - 29.75) = 10.375 \text{ A}^3$, or:
 $\Delta V = 62.46 \cdot 10^{-4} \text{ liter/mol.}$

In this ΔV is not taken into consideration the compressibility difference between hexagonal FeS and β ZnS structure type FeS. The compressibility of most sulfides is insignificant at pressures of interest to this work. Further the compressibility of hexagonal FeS is likely of the same order of magnitude as that of the β ZnS type FeS. There-

fore in this case the compressibility dependency of ΔV has only theoretical interest and will cause only minute errors in the calculations.

The ΔV value may now be inserted in equation (12) and by application of the T and x values of known points on the GK curve, the solubility-pressure relationships calculated. Table X shows the results of such calculations.

TABLE X.

Calculations of the influence of pressure upon the solubility of FeS in β ZnS

by application of the equation: $x_1 = x \cdot e^{\frac{\Delta V(P - P_1)}{RT}}$ (12)
FeS solubility in mol. %

T°K	Laboratory conditions	1000 atm	2000 atm	3000 atm	4000 atm	5000 atm
412	4.66	3.88	3.22	2.69	2.22	1.84
473	6.17	5.25	4.48	3.79	3.22	2.75
573	9.35	8.17	7.17	6.26	5.47	4.80
673	13.17	11.70	10.49	9.35	8.35	7.45
773	17.48	15.80	14.30	12.95	11.74	10.64
873	22.35	20.49	18.73	17.15	15.73	14.40
973	27.93	25.80	23.82	22.07	20.36	18.84
1073	34.25	31.82	29.70	27.66	25.80	23.95
1167	41.36	38.66	36.23	33.90	31.70	29.76

The data given in table X are presented diagrammatically in figure 9. The influence of pressure upon the solubility is seen by no means to be negligible.¹

¹ The Tuttle apparatus at the Mineralogical-Geological Museum of the University of Oslo was used to check on the data given in table X for equilibrium mix-crystals formed at 500° C. Such mix-crystals were heated at 500° C under a pressure of 1000 atm for four weeks. The a_0 value of the resulting mix-crystals was smaller than that of the original mix-crystals and corresponded as closely as could be determined with the available x-ray powder cameras to about 16.5 mol. % FeS. This must be considered in fair agreement with the value of 15.8 mol. % FeS given in table X. Four weeks might not have been sufficient time for equilibrium mix-crystals to form. However, that unmixing takes place is established beyond doubt.

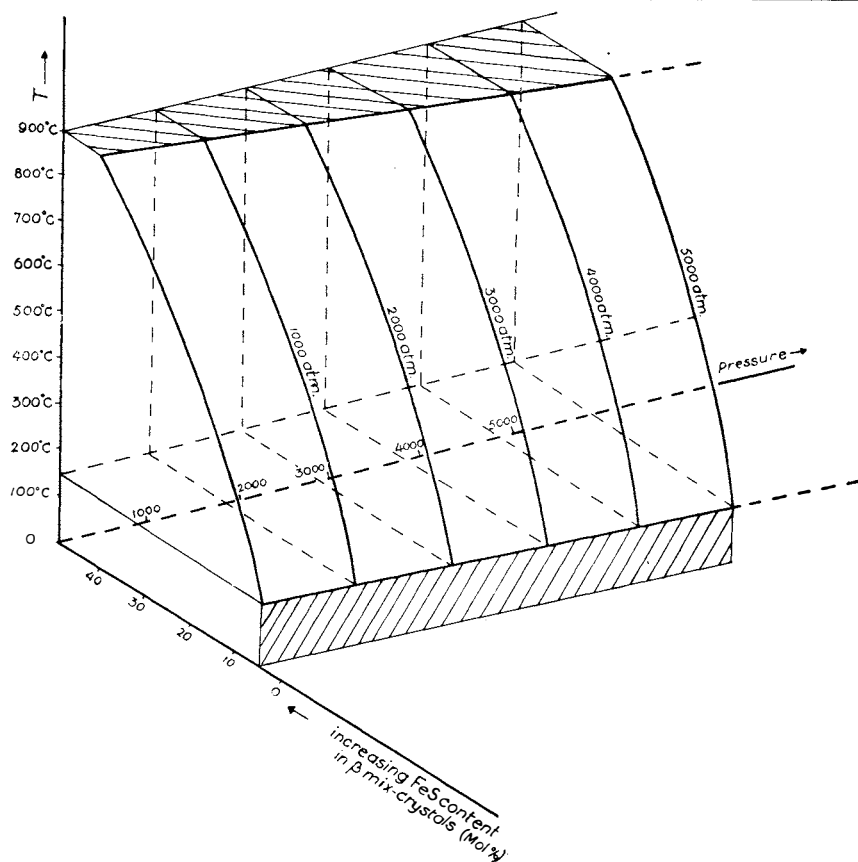


Fig. 9. Block diagram showing the relationship between temperature, pressure and composition of equilibrium β mix-crystals.

The FeS Activity.

The pyrrhotite which in nature forms mix-crystals with zincblende contains more sulfur (or rather, less iron) than indicated by the FeS formula. The FeS activity of pyrrhotite was expected to decrease with an increasing S : Fe ratio. Further information on this subject was obtained from T. ROSENQVIST,¹ who has investigated the FeS activity of iron sulfides over a wide temperature range.²

¹ Institute for the Study of Metals, University of Chicago.

² The results of this research have not been published and the writer is grateful to ROSENQVIST for his kind permission to use them in this paper.

These detailed studies showed that the FeS activity of iron-sulfides of composition ranging from FeS to FeS₂ varies very little. The FeS activity of FeS₂ is less than 5 % smaller than that of stoichiometric FeS. However, when sulfur is added in excess of that indicated by the FeS₂ formula, a sharp drop in the FeS activity is recorded.

ROSENGVIST'S results agreed with those obtained from a number of runs with β ZnS and FeS and where extra S was added. These runs took place at 750, 800 and 850° C and lasted from 4 days to 3 weeks. When equilibrium was established the spacings were calculated from powder diagrams in the usual way.

In the cases where the excess sulfur was less than necessary to form FeS₂, the spacings obtained were nearly the same as those obtained in the previous runs where no extra sulfur had been added. However, when sulfur was added in excess of that necessary to form FeS₂ a sharp decrease in the FeS solubility was recorded. In the table XI the results obtained from a number of runs at 850° C have been compiled. As comparison is given the a_o value and FeS content of mix-crystals formed from ZnS and FeS without added sulfur.

TABLE XI.
Experiments carried out at 850° C.

Amount of excess S	No. of runs	Mix-crystal a_o value in A	Mix-crystal FeS content mol. %
None	5	$5.412_{0\pm 2}$	37.7
Almost enough to form FeS ₂	3	$5.411_{8\pm 2}$	Average: 37.0
More than enough to form FeS ₂	3	$5.407_{8\pm 2}$	26.3

The $a_o = 5.411_{8\pm 2}$ obtained from the runs containing almost sufficient sulfur to satisfy the FeS₂ formula indicates a decrease in the FeS solubility. (Compare with $a_o = 5.412_{0\pm 2}$ obtained when no extra sulfur is added). Although the limit of error in the determinations of the a_o values $5.411_{8\pm 2}$ and $5.412_{0\pm 2}$ is so big that the values overlap, all the a_o values obtained from runs with excess sulfur were

lower than those obtained from runs without extra sulfur. Assuming this difference significant the FeS solubility is seen to be lowered from 37.7 mol.%, when there is no extra sulfur present, to 37.0 mol.% when there is added sulfur to almost satisfy the FeS_2 formula.

This roughly corresponds to a decrease of 2 % in the FeS activity and is seen to be in agreement with ROSENQVIST's results.

When more sulfur is added than necessary to form FeS_2 , the solubility drops to 26.3 mol.%. Corresponding to the sharp drop in the FeS activity as found by ROSENQVIST. It may now be concluded that the FeS solubility in ZnS is not very sensitive to a variation in the S : Fe ratio in pyrrhotites and is only slightly (2 %) decreased when pyrite (FeS_2) forms mix-crystals with ZnS. Consequently the diagram (fig. 1) may be used as a geologic thermometer also where FeS_2 is found in equilibrium with (Fe, Zn) S mix-crystals.

However, if such a situation exists in nature, the diagram presented can not be used where sulfur is present in excess of the amount needed to satisfy the FeS_2 formula.

Exsolution of FeS from the (Fe, Zn) S Mix-crystals.

Earlier in this paper exsolution of FeS was shown to take place fairly rapidly at temperatures above 800° C. Below this temperature the exsolution process requires more time and becomes increasingly sluggish so that at 500° C equilibrium was not established even after 54 weeks. Solution at the same temperature needed 40 weeks to reach equilibrium conditions.

In the runs below 750° C sufficient FeS was unmixed from the mix-crystals formed at 890° C to show up on x-ray powder diagrams. The x-ray lines of this FeS did not coincide with the lines of normal NiAs type FeS. The crystal symmetry of unmixed FeS is much different from that of the NiAs type FeS.¹

¹ Further studies on this unmixing type of FeS are progressing. The unmixing mechanism was discussed orally with M. J. BUEGER who pointed out that this FeS must be expected to show a symmetry different from that of the NiAs type FeS. Determination of this structure may help explain the exsolution mechanism.

The data in the sixth vertical column of table VIII may be plotted on a logarithmic scale versus the temperatures given in the first vertical column of the same table. Thus a rough idea may be obtained of the time required for exsolution at temperatures below those at which equilibrium was experimentally established.

Figure 10 shows this plot. Complete exsolution is by extrapolation of the curve seen at 500° C to take place after 2 years. The corresponding lengths of time at 400, 300 and 200° C are around 5, 17 and 46 years. These values of course may not be taken literally because an extrapolation of the kind presented in figure 10 at best

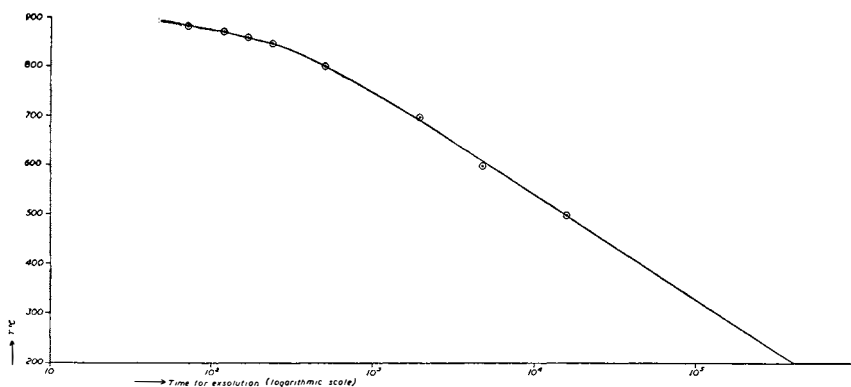


Fig. 10. Curve showing the time required for exsolution of FeS from β mix-crystals as function of temperature. The downward trend of the curve beyond the last point indicated is hypothetical.

only will indicate the order of magnitude of the time periods needed for exsolution. However, even if the above guesswork values be multiplied a thousand times, exsolution will have had ample time to take place in many ore deposits. In large deposits formed at considerable depth the cooling process must have taken thousands of years. Studies of such ores have revealed that exsolution of FeS takes place to a very limited extent. The maximum amount reported does not exceed 2.0 %. The exsolved FeS occurs in lamellae parallel to the crystallographic directions of the sphalerite. STILLWELL⁵⁰ and later EDWARDS⁵¹ studied such minute inclusions in sphalerite from

Broken Hill. The amount of unmixed FeS in this ore was around 1.5 %. In most ores unmixing can not be detected at all.

As will be seen later, the Broken Hill ore was formed at temperatures well above 600° C. Even after the unmixed FeS is subtracted, the composition of the mix-crystals corresponds to a temperature above 600° C. The exsolution process in this ore started, but was arrested before the temperature had dropped to 600° C. This in spite of the fact that the cooling process of this ore must have lasted a great many years. Unmixing of FeS from (Fe, Zn) S mix-crystals in the laboratory was at 600° C completed in 28 weeks. The reason why unmixing takes place in the laboratory and not in nature, may be found when one takes into consideration the impurities frequently found in the mix-crystals in nature. Thus sphalerite whether it is associated with FeS or not, commonly contains manganese and/or cadmium. Both these elements may substitute for zinc in the same manner as iron does. It is possible that the presence of manganese and/or cadmium in the ZnS lattice may inhibit the exsolution of FeS.¹ The Broken Hill ore for instance contains besides iron, an appreciable amount of manganese.

Exsolution in alloys, some of which like the (Fe, Zn) S mix-crystals, occur in two enantiotropic modifications, may in certain cases be speeded up when homogeneous mix-crystals of the high temperature modification are used instead of mix-crystals with the low temperature atomic arrangement. The reason for this is that the inversion process with its rearrangement of atoms to suit the new symmetry, increases the mobility of the atoms and thus offers an opportunity for them to form mix-crystals of equilibrium composition. This principle was tried on the sulfide mix-crystals. α (Fe, Zn) S mix-crystals formed at 910° C and containing 38.5 wt.% (43.45

¹ In an effort to shed some light on the influence of manganese on the FeS exsolution mechanism, a number of closed bombs containing finely ground Broken Hill ore are now being run at 550° C. The mix-crystal composition will be investigated monthly by means of x-ray powder diagrams. The results of these runs will be compared with the rate of unmixing taking place in other bombs being run at 550° C also, containing natural sphalerite rich in iron (as Broken Hill) but free of manganese and cadmium. Similar runs are later to be undertaken with sphalerite ores containing cadmium and no manganese.

mol.%) FeS were used. Five bombs were run at 500° C and five at 400° C. At 500° C the mix-crystals after several weeks inverted to the β phase, but equilibrium mix-crystals were not produced. At 400° the mix-crystals gave beautiful wurtzite x-ray diagrams even after having been heated for four months.

The Influence of Manganese and Cadmium on the Solubility of FeS in β ZnS.

In the foregoing, the FeS-ZnS equilibrium diagram has been presented. For ore deposits which contain only sulfides of FeS and ZnS, the diagram now may conveniently be used for temperature determinations. Most deposits however, contain manganese and cadmium dissolved with iron in the ZnS lattice. In most occurrences manganese is only a trace element, but in certain deposits (for instance Broken Hill) the manganese content may exceed 2 %. The cadmium content of most deposits normally lies between 0.1 and 0.3 %, but in certain cases exceeds 1 %. It was not known whether the presence of Mn and Cd had any measureable effect upon the FeS solubility and it was considered necessary to investigate their possible influence, before the FeS-ZnS equilibrium diagram could be generally used.

The (Mn, Zn) S Mix-crystals.

Manganese sulfide (MnS) occurs in three modifications; one pink MnS has the sphalerite structure, another pink MnS has the wurtzite structure, and a third MnS has the sodium chloride structure. The latter manganese sulfide is of a green color and is always the stable modification into which the two others will convert. The unit cell length of this green MnS is $a_0 = 5.212\text{\AA}$ (KRÖGER).⁵²

When MnS is introduced into the ZnS lattice the sphalerite-wurtzite inversion temperature is lowered. The trend of this inversion curve was found from a number of runs with (Mn, Zn) S mix-crystals. The results of these runs are shown in figure 11. The composition of the mix-crystals as well as the modification obtained from each run are seen from the figure. It is interesting that α mix-crystals containing about 6.0 wt.% (7.6 mol.%) MnS are stable as far down as 765° C.

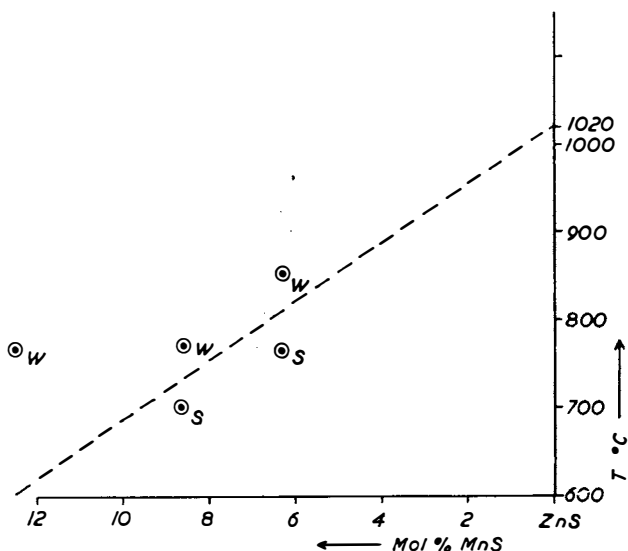


Fig. 11. Mean curve based on points indicated showing approximate relationship between α - β inversion temperature and composition of (Mn, Zn) S mix-crystals.

The (Mn, Zn) S mix-crystals, both of the sphalerite and wurtzite type are orange in color, the color being somewhat deeper for the mix-crystals richer in MnS. The solution of MnS in ZnS takes place much more rapidly than that of FeS in ZnS. Even at 765° C equilibrium (Mn, Zn) S mix-crystals were formed in 96 hours. KRÖGER⁵² studied the solubility of MnS in the α ZnS and found that at 1180° C, 52 mol.% MnS may be dissolved in the α ZnS to form wurtzite type (Mn, Zn) S mix-crystals. KRÖGER⁵² also showed that when mixing ZnS and MnS so the compound contains an excess of MnS, the spacing of this green MnS is not different from other green MnS. Therefore, if the green MnS dissolves ZnS, it can only be in an amount too small to be detected by his method.

In a number of runs green MnS was mixed with ZnS and heated to form β (Mn, Zn) S mix-crystals. The MnS dissolved in the ZnS caused a definite increase in the ZnS unit cell length a_0 as seen from table XII below.

To insure complete solution each compound was run until no

TABLE XII.

MnS content of the mix-crystals		Unit cell length a_0 in Å.
wt %	mol %	
0	0	$5.398_5 \pm 1$
1.25	1.60	$5.399_6 \pm 3$
1.80	2.30	$5.400_2 \pm 3$
2.50	3.20	$5.401_3 \pm 3$
3.50	4.45	$5.403_0 \pm 3$
5.00	6.30	$5.405_9 \pm 3$

further increase in a_0 occurred. In figure 12 the a_0 values are plotted versus the mix-crystal composition.

The (Cd, Zn) S Mix-crystals.

Cadmium sulfide occurs in two modifications. One of these has the sphalerite structure and the other that of wurtzite. The

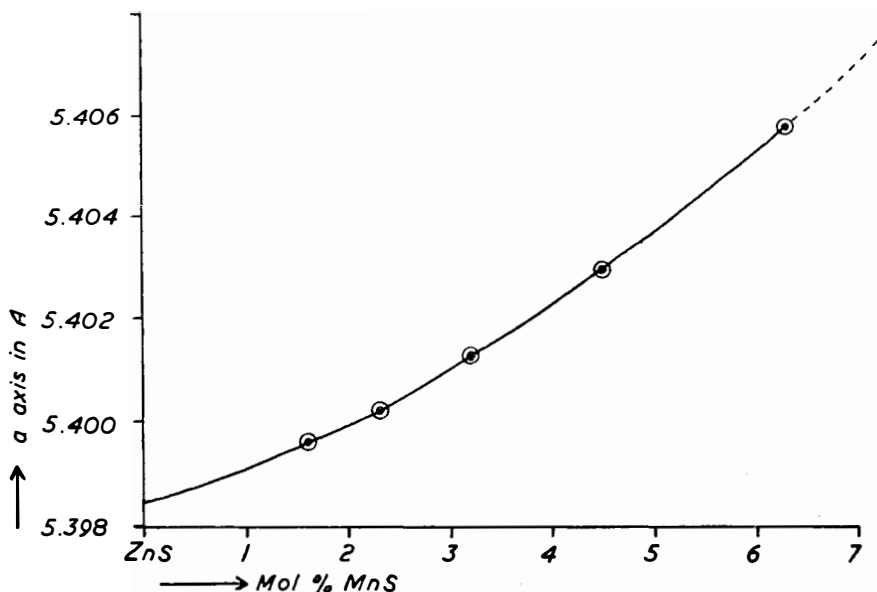


Fig. 12. Curve showing the relationship between the unit cell length and composition of β (Mn, Zn) S mix-crystals.

α ZnS and CdS are completely miscible (KRÖGER⁵³). X-ray powder diagrams of the α (Cd, Zn) S solution series have been made by ROOKSBY.⁵⁴ The solubility of CdS in β ZnS, however, is limited. Mix-crystals containing CdS have a lower α - β inversion point than pure ZnS. In figure 13 is shown the approximate relationship between inversion temperature and mix-crystal composition. The general direction of the inversion curve was found from a number of runs with (Cd, Zn) S mix-crystals containing varying amounts of CdS. The runs were conducted at temperatures ranging from 750 to 1000° C.

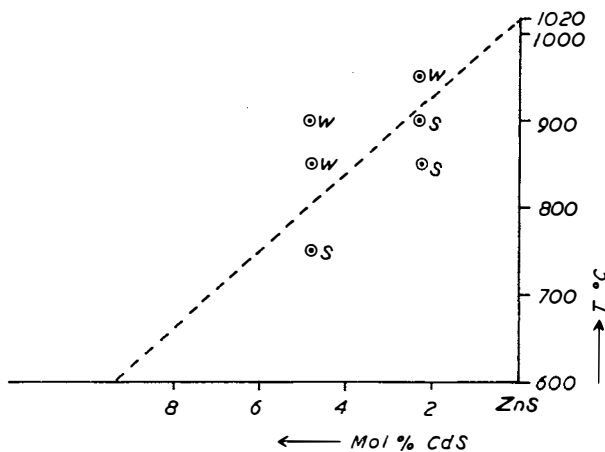


Fig. 13. Mean curve based on points indicated showing approximate relationship between α - β inversion temperature and composition of (Cd, Zn) S mix-crystals.

Mix-crystals containing 10 wt.% (4.8 mol.%) CdS are seen to invert at around 800° C.

Both the α and β type of the (Cd, Zn) S mix-crystals are brightly yellow in color.

Introduction of CdS into the ZnS lattice causes an increase in the unit cell dimensions. A series of runs with mechanical mixtures of ZnS and varying amounts of CdS gave the results shown in table XIII.

Complete solution was insured by the same procedure as applied for the (Mn, Zn) S mix-crystals.

TABLE XIII.

CdS content of the mix-crystals		Unit cell length a_0 in Å.
wt %	mol %	
0	0	$5.398_{5\pm1}$
1.10	0.50	$5.399_{4\pm3}$
1.50	0.70	$5.400_{0\pm3}$
2.50	1.15	$5.403_{0\pm3}$
5.00	2.30	$5.411_{2\pm3}$

The unit cell length versus composition relationship of the mix-crystals is shown in figure 14.

The (Cd, Zn) S mix-crystals, as was earlier experienced with the

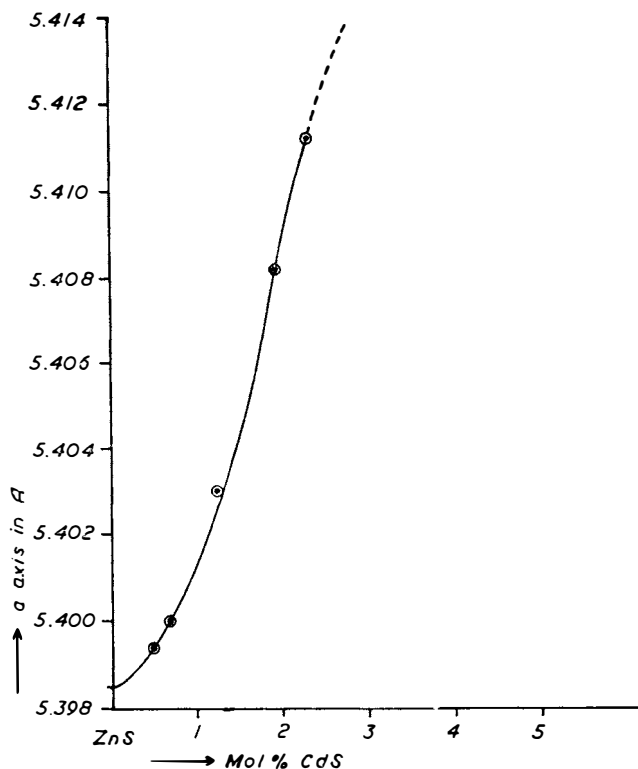


Fig. 14. Curve showing the relationship between the unit cell length and composition of β (Cd, Zn) S mix-crystals.

(Mn, Zn) S mix-crystals, formed at the same temperature in much shorter time than the (Fe, Zn) S mix-crystals.

FeS and MnS as well as CdS, when introduced into the ZnS lattice, all cause an increase in the unit cell dimensions. The increase caused by CdS is much larger than that caused by MnS. The latter increase in turn is much larger than that caused by FeS. Thus the increase obtained when 1.0 mol.% CdS is dissolved in the ZnS lattice is equal to that caused by 3.6 mol.% MnS or to 11.5 mol.% FeS. (See figures 5, 12 and 14). The α - β inversion temperature is similarly much more affected by CdS and MnS than by FeS. (See figures 1, 11 and 13).

The (Mn, Cd, Zn)S Mix-crystals.

Mix-crystals of modification β were formed from a mechanical mixture of CdS, MnS and ZnS. These compounds were heated at temperatures ranging from 750 to 850° C. The increase in the ZnS unit cell dimensions due to both CdS and MnS was calculated from x-ray powder diagrams and found, within the limit of error, to be identical to the sum of increases caused by the same amounts of CdS and MnS when these were independently heated with ZnS. For instance, a solid solution containing 1.8 wt.% (2.3 mol.%) MnS and 1.1 wt.% (0.5 mol.%) CdS in ZnS (heated for seventy-two hours at 800° C) had a unit cell length $a_o = 5.401_{0\pm3}$ Å. Previous runs (see tables XII and XIII) have shown that: 1) 1.8 wt.% (2.3 mol.%) MnS mixed with ZnS and heated below the α - β inversion point, produced mix-crystals with $a_o = 5.400_{2\pm3}$ Å. 2) Similarly formed (Cd, Zn) S mix-crystals containing 1.1 wt.% (0.5 mol.%) CdS had a unit cell length $a_o = 5.399_{4\pm3}$ Å. Thus the increase caused by MnS is: $5.400_{2\pm3} - 5.398_{5\pm1} = 0.001_{7\pm3}$ Å and by CdS: $5.399_{4\pm3} - 5.398_{5\pm1} = 0.000_{9\pm3}$ Å. Under the assumption of additivity the unit cell length of (Mn, Cd, Zn) S mix-crystals containing the above mentioned amounts of MnS and CdS will be: $a_o = 5.398_{5\pm1} + 0.001_{7\pm3} + 0.000_{9\pm3} = 5.401_{1\pm3}$ Å. This a_o value is seen to be well within the limit of error of the $a_o = 5.401_{0\pm3}$ value obtained from x-ray powder diagrams of (Mn, Cd, Zn) S mix-crystals of said composition.

The β (Mn, Cd, Zn) S mix-crystals are of a pinkish-yellow color.

The α (Mn, Cd, Zn) S mix-crystals have been studied by KRÖGER,⁵⁵ who presented the phase diagram for the ZnS-CdS-MnS wurtzite type mix-crystals. The α mix-crystals which contain much CdS and MnS are almost red in color. At 900° C all mixtures containing less than 48 mol.% manganese gave homogeneous products. When more manganese was mixed into the compounds, the runs resulted in red α (Mn, Cd, Zn) S mix-crystals and pure green MnS. Depending on the CdS content the MnS solubility varied from about 48.0 to 52.0 mol.% at 900° C. The presence of CdS therefore influences the MnS solubility very little.

The β (Mn, Cd, Fe, Zn) S Mix-crystals.

A compound consisting of 29.8 wt.% FeS, 1.8 wt.% MnS, 1.1 wt.% CdS and 67.3 wt.% ZnS was run at 800° C for 16 days. The β mix-crystals thus obtained were of a yellowish grey color. The unit cell length was calculated from x-ray powder diagrams and found to be $a_0 = 5.413_{2\pm3}$ Å. In table VIII was shown that equilibrium (Fe, Zn) S mix-crystal contain 29.8 wt.% FeS at 800° C. Such mix-crystals have a unit cell length $a_0 = 5.410_{9\pm2}$ Å. The increase in the cell length caused by the presence of 1.8 wt.% MnS is shown above to be $0.001_{7\pm3}$ Å, and the increase caused by 1.1 wt.% CdS was $0.000_{9\pm3}$ Å. By additivity we find that mix-crystals consisting of 29.8 wt.% FeS, 1.8 wt.% MnS, 1.1 wt.% CdS and 67.3 wt.% ZnS should have a spacing $a_0 = 5.413_{5\pm3}$ Å. The actual value is $5.413_{2\pm3}$ (see above). If now the presence of CdS and MnS have a tendency to decrease the FeS solubility, the x-ray a_0 value should be lower than that found by additivity. Comparing the values it is seen that they are within the limit of error of each other. Therefore, if small amounts of CdS and MnS decrease the FeS solubility, the decrease is too small to be detected by the applied x-ray methods (and will be of the order of, at the most, 0.3 wt.% FeS).

Still the possibility existed that the presence of MnS and CdS might increase the solubility of FeS. In order to investigate this, a mechanical mixture consisting of 31.0 wt.% FeS, 1.8 wt.% MnS, 1.1 wt.% CdS and 66.1 wt.% ZnS was mixed and heated at 800° C for 16 days. The unit cell length of these mix-crystals calculated from x-ray powder diagrams was $5.413_{3\pm3}$ Å.

If now the presence of MnS and CdS increased the FeS solubility to a measurable extent, an a_0 value larger than $5.413_{\pm 3}$ Å should result. Thus, if all the available FeS had gone into the solution a unit cell length of $a_0 = 5.413_{\pm 3}$ Å should have been expected. In a later run about 5 wt.% FeS more was added to the mix-crystals, and the compound was heated again for 15 days at 800° C. No further increase in spacing was observed.

From the above observations, it may be concluded that at least fairly small amounts of MnS and CdS will have no, or at least very little, influence on the solubility of FeS in β ZnS.

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PART II.

Introduction.

In the first part of this paper a geological thermometer based on the solubility of FeS in sphalerite was presented. Provided sufficient amounts of FeS are present to form equilibrium mix-crystals at the prevailing (P,T) conditions, the FeS content of the mix-crystals is a direct function of these conditions. In other words the FeS content of such mix-crystals gives the (P,T) function of formation.

Geological evidence concerning the pressure conditions existing during the mix-crystal deposition, may in natural occurrences often be obtained from other minerals formed simultaneously and under the same conditions as the (Fe, Zn) S mix-crystals.

The order of magnitude of the pressure thus known, the temperature of formation may readily be deduced. (It should here be remarked that an error of ± 1000 atm in the pressure estimate, leads to an uncertainty of about $\pm 25^\circ$ C in the temperature determination).

In part two of this paper methods for determination of mix-crystal composition are described. Applications to geological problems are also considered. For this purpose numerous sphalerite hand specimens from various ore deposits were obtained through the kindness of numerous mining companies, museums, and private individuals. Only a few specimens were collected in the field by the author. Each sample was studied under the binocular lens, and the sphalerite (marmatite) carefully picked. The FeS content was determined chemically by Mr. H. B. WIK, Helsingfors, Finland. The MnS and CdS contents as well as the amounts of a number of trace

elements were determined spectrographically in cooperation with Mr. O. JOENSUU.¹

X-ray powder diagrams were made of all samples.

Determinations of the Composition of the Ore Samples.

1. Chemical Method

The method used by Mr. WIIK for chemical determination of the iron content of the samples was in short as follows: The ground samples were fused by means of potassium pyrosulfate and dissolved in water and sulfuric acid. Thereafter, they were reduced with metallic zinc and sulfuric acid and finally titrated with potassium permanganate ($\frac{1}{20}$ N solution). With this method the average limit of error was ± 1.44 % of the iron content (± 2.27 % FeS).

It was earlier mentioned that a limited amount of FeS sometimes unmixes from the mix-crystals during the cooling process. This unmixed FeS occurs in fine lamellae parallel to the crystallographic directions of the ZnS and too finely distributed to be seen through the binocular lens, much less be separated from the sample.

This FeS thus will be included in the chemical analysis. The temperature of formation deduced from the analytical result in such cases will be higher than that obtained from the x-ray unit cell length, which only tells how much FeS presently is dissolved in the ZnS lattice. Since at the most 2.0 mol.% FeS will unmix (and only from ores formed above 600° C), the difference between these two temperatures does not exceed 35° C. The highest value (the one obtained from chemical analysis) is the temperature of formation of the mix-crystals.

2. Spectrographic Methods.²

Much work was done in an effort to determine the content of FeS, MnS and CdS as well as of a number of trace elements in natural mix-crystals by means of spectrographic methods. The accuracy

¹ The author wishes to stress that Mr. JOENSUU, Department of Geology, University of Chicago, being an expert on spectrographic analyses of this kind, did the major part of this work.

² Spectrographic analyses of trace elements in sphalerites have previously been performed by OFTEDAL¹, STOIBER², GABRIELSEN³ and others.

obtained by these methods was $\pm 5\%$ for the amount of FeS, $\pm 10\%$ for MnS and $\pm 5\%$ for the CdS content. The following description of the spectrographic methods is given by Mr. JOENSUU.

Spectrograph: 21 foot grating instrument by JARRELL ASH, Company.

The dispersion in 1st. order 5 A/mm.

Power Source: Boliden Gruv A. B. Emitator, Sweden. 220 V. D. C.

7 amp. for the major constituents, 5 amp. for the trace analyses.

Electrodes: Anode: Central post. Undercutting type, turned out of

1/4 inch diameter Graphite rod (National Carbon Co. "Special",

Grade) Cathode: 1/8- inch diameter carbon, pointed.

Arc gap: 4 mm.

Slit width: 0.05 mm.

Sector: Five steps with a step ratio of 1 : 2.

Exposure: For trace analyses: 30 seconds, for major constituents: 45 seconds.

Emulsion: Eastman Kodak 103—0 for the trace analyses, Spectrum analysis No. 1 for the major constituents.

Development: 3 minutes at 20° C in Eastman Kodak Developer D-19.

Photometer: Jaco non-recording by Jarrell Ash Company.

a. Determinations from Solids.

For the trace analyses one part of the sample was mixed with three parts of graphite; 20 mg of this mixture was packed in the electrode and arced.

Lines used:

Co	3453.505	5	—	1000 ppm
Ni	3414.765	5	—	1000 ppm
Ag	3382.891	1	—	100 ppm
Cd	3261.057	10	—	10000 ppm
Sn	3175.019	10	—	1000 ppm
Ga	2943.637	20	—	1000 ppm
Pb	2833.069	10	—	1000 ppm
Pb	2663.166	0.1	—	5 %
Ge	2651.178	1	—	1000 ppm

As internal standard was used:

Zn 2712.488

The plate was calibrated using a stepped iron arc spectrum. (PIERCE and NACHTRIEB⁴). For the calculations of the intensity ratios and for the background correction the calculating board was used. This has been described by HONERJÄGER—SOHM and KAISER.⁵

The standards were mixed as oxides with synthetic zinc sulfide. The working curves were linear. The precision of the method for germanium and cadmium is $\pm 5\%$, for the other trace elements $\pm 10\%$ of the amount present.

The zinc sulfide content of the sample ranges from approximately 75 % to 100 %. The analyses were too high because zinc was used as internal standard. The results, therefore, were multiplied by the zinc sulfide percentage. The iron sulfide content was analysed and the zinc sulfide content could be calculated. (SCOTT⁶).

For the iron analyses one part of sphalerite was mixed with one part of cobalt sulfide and eight parts of graphite. Ten mg of this mixture was placed in a central post electrode and arced. The calculations were made as for the trace analyses but no background correction was made. For the construction of the working curves chemically analysed samples were used. The range of iron as sulfide (FeS) was 1—25 %. The precision of the method is about $\pm 5\%$ of the amount present. The lines used:

Fe 3018.982, Co 3013.596.

b. Determination by the Solution Method.

Twenty mg sphalerite was dissolved:

In a small vial 10 drops of the bromine-carbon tetrachloride mixture (2 : 1) were added to the sphalerite. After 5 minutes 2 drops of nitric acid (conc.) were added. After 5 minutes 4 drops of hydrochloric acid (conc.) were added. Bromine and carbon tetrachloride were evaporated at approximately 50° C. Then the acids were evaporated at approximately 90° C. The dry residue was dissolved in 2 cc of 3 % hydrochloric acid. This contained 0.2 mg chromium per ml. to serve as internal standard. For the analyses porous cups were used (FELDMAN⁷). The spectra were excited using a condenser discharge spark from the "Emitator".

Capacitance: 5 μ F

Inductance: 100 μ H

Resistance: 8 Ω

The preparking time was 10 seconds; the exposure time was 2 minutes.

The lines used:

Cu 3273.962	Cr 2751.871
Fe 2753.287	Cr 2751.871
Fe 2739.546	Cr 2751.871
Mn 2933.063	Cr 2751.871
Mn 2576.104	Cr 2751.871

The reproducibility was not good, however. The precision of the method was ± 10 %. The reason for this is probably the tendency of chromium, which was used as internal standard, to form a layer of chromium oxide on the electrode, thus hindering the liquid from getting through the bottom of the cup.

3. *X-ray Method.*

The x-ray technique has been described previously and it should not be necessary to repeat it all here. As will be remembered from this description, the amount of FeS in (Fe, Zn) S mix-crystals may, by use of x-ray powder diagrams, be determined well within the limit of error of ± 0.4 mol.% (corresponding to ± 0.0002 A in the unit cell length a_0). This uncertainty in the FeS determination again corresponds to a limit of error of approximately $\pm 7^\circ$ C in the temperature determinations at temperatures above 400° C, and about $\pm 10^\circ$ C at temperatures below 400° . The temperature determinations of mix-crystals containing only sulfides of iron and zinc, therefore, may well be done by application of the x-ray method. However, whenever manganese and/or cadmium also occur in the mix-crystals, the uncertainty attached to the determinations is increased. The limit of error of ± 0.0003 A in the unit cell length of (Mn, Cd, Fe, Zn) S mix-crystals, implies an uncertainty of about ± 0.6 mol.% in the FeS value. It is seen that when the FeS content of such mix-crystals is known, the x-ray method may serve well for determinations of the sum of the MnS + CdS content. On the other hand whenever the MnS and CdS contents are known, the FeS content may readily be determined from x-ray powder diagrams.

From the foregoing one may conclude that the most practical procedure for determination of the composition of mix-crystals of natural occurrence is:

- 1) Determination of FeS by the described chemical method.
- 2) CdS and MnS may be determined by any of the three methods. (The x-ray method can only be used after analysis on FeS has been performed).

The most convenient way of finding the contents of CdS and MnS is by the spectrographic method.

- 3) The trace elements are determined spectrographically.

The Composition of the Ore Samples.

The ore samples were analyzed in the manner outlined above. The results are shown in table XIV.

The FeS contents are given in column 3 of table XIV. The amounts of MnS and CdS are further found in columns 4 and 5 respectively. Both MnS and CdS replace zinc in the ZnS lattice in the same manner as iron does. It has been found that small amounts of MnS and CdS will not influence the solubility of FeS in ZnS. Table XIV shows that the amounts of CdS and MnS in all the analyzed samples are too small to influence the mentioned solubility. Marmatites often are associated with chalcopyrite. The samples therefore also were analyzed on copper (Cu_2S) as seen from column 6. The copper thus detected was all assumed to occur in chalcopyrite. A correction of the FeS value corresponding to the amount of chalcopyrite was performed. Marmatites are often intimately connected with galena and in the cases where the marmatites are very dark (rich in FeS) it is hard to separate the two minerals quantitatively even with the help of a binocular lens. For this reason analyses on lead were also undertaken. All lead thus detected was assumed to occur in galena. The FeS value then was corrected accordingly. In column 15 are given the temperatures of formation of the mix-crystals obtained from the corrected FeS values. It should be noted that the temperatures listed in this column are not corrected for pressure. The pressure existing during the mix-crystal formation, must be obtained from geological observations. It is clear enough that this is a source of error. As shown earlier an error of ± 1000 atm. in

TABLE XIV.

1	2	3		4	5	6	7	8	9	10	11	12	13	14		15
Specimen no.	Locality	FeS		MnS	CdS	Cu ₂ S	Pb	Ag	Ge	Ga	Ni	Co	Sn	FeS corrected		T°C
		wt %	mol %	wt %	wt %	wt %	ppm	ppm	ppm	ppm	ppm	ppm	ppm	wt %	mol %	
40	*Broken Hill, Australia ^{8,17}	20.10	23.60	1.90	0.14	0.08	10	3	2	10	10	220	10	20.10	23.60	620
30	Mies, Bohemia ²⁰	4.04	4.91	x	0.8	x	280	100	33	10	x	x	95	4.04	4.91	150
43	Long Lake, Ont., Canada.	12.95	15.44	0.03	0.14	x	110	3	x	10	x	5	x	12.95	15.44	455
48	*Tetreault Mine, Quebec, Canada ^{21, 22}	10.82	12.96	0.10	0.19	x	7% high		x	100	x	60	10	11.76	14.06	430
52	*Amulet Mine, Quebec, Canada ^{22,23,24}	13.50	16.08	0.12	0.13	0.5	450	100	9	55	x	160	70	12.95	15.44	455
53	*Calumet Island, Quebec, Canada ^{25,26,27}	12.40	14.80	x	0.19	x	5% high		x	10	35	150	x	13.05	15.55	460
61	Renfrew Prospect, Ont., Canada	5.55	6.72	0.03	0.06	x	230	1	x	x	15	x	x	5.55	6.72	220
60	Buchans, Newfoundland ^{12, 22, 28} ..	5.35	6.48	0.01	0.21	0.40	10% high		x	250	x	x	x	5.44	6.60	205
8	Alston Moor, Cumberland, England ^{29,30}	3.00	3.60	0.03	0.15	0.05	240	17	450	90	x	72	18	3.00	3.60	<138
15	Alston Moor, Cumberland, England ^{29,30}	2.60	3.17	x	0.18	x	150	80	530	x	x	48	x	2.60	3.17	<138
39	Foxdale, Isle of Man, England ^{31,32,33,34}	17.75	20.94	0.02	0.09	x	90	7	60	45	x	50	18	17.75	20.94	570
85	Germoe, Cornwall, Engl. ³⁵	4.60	5.59													180
88	—6—	4.33	5.26													170
89	St. Agnes Mine, Cornwall, England ^{35,36}	9.92	11.91													370

*Localities which have received further attention in text.

1	2	3		4	5	6	7	8	9	10	11	12	13	14		15
Specimen no.	Locality	FeS		MnS wt%	CdS wt%	Cu ₂ S wt%	Pb ppm	Ag ppm	Ge ppm	Ga ppm	Ni ppm	Co ppm	Sn ppm	FeS corrected		T°C
		wt %	mol %											wt %	mol %	
4	Orijärvi, Finland ³⁷	16.60	19.63	0.50	0.16	0.08	3.8%	100	x	50	x	18	27	17.25	20.37	560
64	Kisko Ilijärvi, Finland ³⁷	14.10	16.77	x	0.14	0.25	800	15	x	45	x	100	x	13.83	16.46	480
5	Outokompu, Finland ³⁸	19.38	22.78	1.40	0.13	0.19	310	7	4	95	140	1000	100	19.17	22.54	600
10	Petsamo, Finland	3.85	4.69	x	0.54	x	230	8	32	190	x	48	x	3.85	4.69	145
12	Stansvik, Finland	12.50	14.92	0.79	0.11	x	800	10	x	x	x	x	x	12.50	14.92	440
70	Petsamo, Peuravuono, Finland	8.85	10.65	0.28	0.38	x	170	15	230	130	10	120	x	8.85	10.65	335
72	Karjalohja, Kattelus, Finland	14.75	17.52	0.32	0.14	x	10	1	x	10	10	70	x	14.75	17.52	505
73	Sortavala, Leppäselkä, Finland	1.90	2.32	0.02	0.10	x	500	x	x	x	10	100	x	1.90	2.32	<138
82	* Kimito Island, Finland ^{37, 39, 40}	15.30	18.15	0.84	0.22	0.08	30					200		15.20	18.03	510
38	* St. Christoph, Breitenbrunn, (Erzgebirge), Germany ^{41, 42}															
42	—»—	18.65	21.96	0.30	0.38	x	10	9	x	10	x	50	25	18.65	21.96	595
69	—»—	18.28	21.54	0.60	0.28	x	x	3	x	x	x	55	10	18.28	21.54	585
65	Ivigut Greenland ⁴³	7.17	8.66	0.07	0.41	0.16	14	x	50	15	15	450	x	7.00	8.45	280
66	Marmorilik, Greenland ⁴³	17.55	20.71	0.04	0.18	0.22	1000	40	x	25	x	x	180	17.31	20.44	565
67	Tutup Agtlakofia, Greenland ⁴³	7.30	8.81	0.02		x								7.30	8.81	290
44	Morawicza, Banat, Hungary	4.44	5.40	0.05	0.01	x	210	3	x	x	x	x	x	4.44	5.40	170
18	Grua, Hadeland, Norw. ⁴⁴	5.86	7.09	x	0.27	x	10	22	2	25	x	x	x	5.86	7.09	235
19	—, —	20.40	23.93	0.36	0.24	0.14	170	6	2	21	22	260	45	20.25	23.76	625
		20.10	23.60	0.40	0.25	0.08	x	5	2	15	18	260	18	20.00	23.48	620

TABLE XIV.

1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	
Specimen no.	Locality	FeS		MnS	CdS	Cu ₂ S	Pb	Ag	Ge	Ga	Ni	Co	Sn	FeS corrected	T°C	
		wt %	mol %	wt%	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm			wt %
21	Melkedalen, Ofoten, Norway ⁴⁵	13.10	15.72	0.28	0.13	0.07	10	2	19	160	x	13	x	13.02	15.52	455
23	Sextus, Røros, Norway ^{46,47}	18.90	22.24	0.04	0.19	x	32	20	x	17	40	70	10	18.90	22.24	595
24	Storvarts, Røros, Norway ^{46,47}	12.80	15.28	0.09	0.14	0.05	700	33	x	30	18	26	10	12.75	15.21	450
25	Mofjell, Rana Norway ⁴⁸ ..	7.50	9.05	0.06	0.20	x	3.1%	15	x	90	16	x	x	7.74	9.34	300
57	— ⁴⁹ —	9.40	11.30	0.07	0.17	x	10	x	x	x	x	x	x	9.40	11.30	350
28	Svenningdalen, Helgeland, Norway ⁵⁴	9.70	11.65	x	1.04	0.05	3.2%	100	x	40	10	x	x	9.97	11.97	370
27	Jakobsbakken, Sultjelma, Norway ⁴⁹															480 ¹
86	Bjørkåsen, Ofoten Norway, ⁵⁰	12.32	14.71													440
29	*Kafveltorp, Sweden ⁵¹	16.30	19.29	0.06	0.11	x	5.0%	100	x	90	10	27	90	17.15	20.26	560
31	*Falun, Sweden ⁵¹	20.18	23.68	0.40	0.15	x	5.0%	100	x	80	10	30	160	21.24	24.87	645
58	*Saxberget, Sweden ⁵¹	5.60	6.78	0.02	0.15	x	6.5%	high	x	x	10	70	50	6.05	7.32	245
63	Krigstjärn, Sweden	7.00	8.45	0.41	0.15	x	450	8	x	x	x	x	x	7.00	8.45	275
1	Berg Prospect, Wrangel, Alaska, U.S.A.	16.95	20.03	0.13	0.54	x	470	25	19	x	17	18	46	16.95	20.03	555
3	Sedanka Island, Alaska U.S.A. ⁵²	3.39	4.13	0.01	0.20	x	220	7	x	x	x	200	x	3.39	4.13	<138
7	*Balmat, N.Y., U.S.A. ⁵³ ..	8.30	10.00	0.02		x										320
59	*Edwards Zinc Mine, N.Y., U.S.A. ⁵³	8.90	10.70	0.07	0.06	x	300	10	6	140	x	x	x	8.90	10.70	335
87	— ⁵³ —	8.80	10.60													330
36	Roxbury, Conn., U.S.A.	7.85	9.47	0.01	0.10	x	250	8	73	140	10	130	60	7.85	9.47	305

¹ This temperature was deduced from x-ray powder diagrams only. Corrections for possible occurring MnS and CdS therefore could not be made.

1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	
Specimen no.	Locality	FeS		MnS	CdS	Cu ₂ S	Pb	Ag	Ge	Ga	Ni	Co	Sn	FeS corrected		T _° C
		wt %	mol %	wt%	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	wt %	mol %	
41	Gilman, (Red cliff) Colorado, U.S.A. ⁵⁵	14.70	17.46	0.09	0.23	x	1.8%	75	x	120	x	x	20	15.00	17.80	505
45	Cape Rosler, Mo., U.S.A.	4.95	6.01	0.05	0.18	x	450	8	2	170	x	x	x	4.95	6.01	190
46	Warren, New Hampshire, U.S.A.	8.00	9.64	0.35	0.10	x	5.0%	100	x	150	x	x	x	8.49	10.23	325
54	Austinville, Virginia, U.S.A. ^{56,57,58}	2.45	2.99	0.01	0.18	x	480	7	30	20	x	x	x	2.45	2.99	<138
81	Gray Mine, Illinois, U.S.A. ^{61,62}	2.77	3.38	0.01	0.18	x	580	40	50	40	10	x	x	2.77	3.38	<138
75	Hoskins Mine, Wisconsin, U.S.A. ^{59,60,62}	6.22	7.52	0.01	0.05	x	450	4	110	x	x	x	x	6.22	7.52	245
76	Tiffany Mine, Wisconsin, U.S.A. ^{61,62}	4.70	5.71	0.01	0.08	x	200	14	160	10	x	x	x	4.70	5.71	180
77	Thompson Mine, Wisconsin, U.S.A. ^{61,62}	0.91	1.11	0.01	0.14	x	480	16	40	60	x	33	x	0.91	1.11	<138
78	Rodham Mine, Wisconsin, U.S.A. ^{61,62}	1.62	1.98	0.01	0.10	x	1100	100	x	20	x	54	x	1.62	1.98	<138
79	Shullsburg district, Wisconsin, U.S.A. ^{59,60,61,62}	3.68	4.48	0.01	0.13	x	100	15	70	35	x	20	x	3.68	4.48	~135
80	—>—	5.23	6.34	0.01	0.10	x	450	70	100	30	10	80	x	5.23	6.34	205
56	—>—	4.20	5.10	0.01	0.10	x	5.0%	15	150	x	x	x	x	4.45	5.41	170
83	Joplin, Missouri, U.S.A. ^{60,61,62}	1.54	1.88	x	0.45	x	35	x	120	14	x	x	x	1.54	1.88	<138

the pressure estimate leads to an uncertainty of $\pm 25^\circ \text{C}$ in the final temperature reading. If another system, in addition to the one already completed, was worked out, and mix-crystals of both types were formed under the same (P, T) conditions, one could easily find the exact pressure and temperature of formation.

After having determined the composition of the two types of mix-crystals, one could make a pressure versus temperature plot for each of the two mix-crystal types. (See figure 16 for plot of the Broken Hill ore). Where the curves intersect, one then read off the (P,T) values of formation.

It would of course, be of great value to know both the pressure and temperature existing during the formation of such mix-crystals, and the author hopes in the future to be able to work out another system for this purpose.

Some of the samples did not contain both iron sulfide and sphalerite. Other samples which carried both minerals did not clearly demonstrate that the iron sulfide was present in sufficient amounts during the mix-crystal formation. In all such cases, where equilibrium conditions might not have existed, the values given in column 15 of table XIV must be considered minimum temperatures.

The sequence of deposition, or paragenesis, of the ore minerals in a particular deposit can be determined in part from hand specimens, but a full understanding of the processes involved, can be obtained only from a study of the mineral textures as revealed in polished sections under the microscope.

A detailed description of all the deposits from which the sixty-three samples listed in table XIV originate, would have to be compiled almost entirely from already published accounts and not from the results of the author's own field investigations.

For this reason, and also in order not to increase the volume of this publication unduly, only a few deposits will be briefly described as examples of the applicability of the FeS — ZnS thermometer.

Applications of the FeS—ZnS Thermometer to Geological Problems.

The FeS — ZnS geological thermometer may be used to shed light on a number of problems of geological significance. Many

examples of its applicability for determinations of the temperature of formation of ore bodies are found in table XIV.

Ore bodies are often surrounded by zones of skarn minerals and among the latter marmatite sometimes occurs. In such cases one may determine the temperature of formation of the ore body as well as of the skarn minerals. An example of this is found in table XIV (specimens 38, 42, 69). In many ore bodies more than one generation of marmatite occurs. The samples 25 and 57 as well as 23 and 24 indicate two generations of mix-crystals. Thus assisted by detailed field work and by application of the FeS — ZnS system one may get a good picture of the different stages of metamorphism which ore bodies have undergone.

The temperature of formation of pegmatites has long been a topic of great interest to geologists. In table XIV are found results from determinations of the temperature of formation of mix-crystals in pegmatites.

Geologists have paid great attention to the problems of granitization. In the succeeding paper in this journal KULLERUD and NEUMANN have applied the FeS — ZnS system for determination of the temperature of granitization in an area in Northern Norway.

An important factor in the classification of ore deposits, is the temperature of their formation. Based upon geological information obtained through field work and often coupled with a certain amount of guesswork, an ore body is said to have been deposited within one or other wide temperature range, given names by LINDGREN and others. The FeS — ZnS system offers an opportunity for pinning down the actual temperatures of formation of the ore deposits and thus also sharply defining in degrees the temperature ranges expressed by terms like pyrometasomatic, hypothermal, mesothermal, etc.

These are some of the applications of the FeS — ZnS thermometer. The possibilities for applying the system to other problems are many and fascinating. It is hoped that the thermometer will be a useful tool to geologists in determining geological temperatures.

Examples of Temperature Determinations .

1. Ore Bodies.

a. Broken Hill, New South Wales, Australia. This area is well known to most geologists all over the world, because of the numerous

geological publications issued in connection with its ore deposits. The temperature of formation of the ore bodies has been discussed a number of times among geologists but so far no absolute temperature value has been agreed upon.

It is, therefore, natural that this problem again is discussed in the present paper. The following geological description of the area is compiled from earlier publications.

The ore deposits are confined to the oldest rocks of the region. These rocks, the Willyama series, consist of a shield of ancient sedimentary rocks, basic lavas and intrusive igneous rocks which have suffered erosion. The shield is considered, provisionally, to be Lower pre-Cambrian in age. It is a grand geological complex consisting principally of intensely folded and metamorphosed clays, shales, sandstones and allied types, together with a notable development of acid and basic igneous material (ANDREWS⁸).

A major mountain-building period, associated with igneous intrusions, succeeds the deposition of the sedimentary series. The rocks were folded and intruded by numerous large dikes of dolerite. The peculiar nature and disposition of the intense metamorphism to which the Willyama series has been subjected, suggests that the Broken Hill Shield occupies the site of an area of intense metamorphism produced by great local heating at a considerable depth from the surface and conditions of great pressure. This localized area of intense alteration may be called the Broken Hill Hearth. The main "lode" occurs within the longer axis of this zone of most marked metamorphism. Its trend conforms, definitely, to the local strike of the associated sedimentary and igneous rock exposures, namely, north-east and south-west approximately. These associated rock assemblages comprise a magnificent suite of augen gneiss, platy gneiss, basic lavas (amphibolites), sillimanite-garnet-mica-feldspar gneisses, massive garnetized and granitized sediments. The lodes are massive lead-zinc sulfide replacement ore bodies forming (before erosion) a long continuous, irregularly shaped, flat, curving pencil of ore roughly 2000—3000 feet high and 300 feet thick. In a longitudinal section, the deposit describes a broad arch flat in its middle (highest) portion, and pitching downward at each end. One of the most significant features of the ore is that its boundaries are almost invariably parallel to bedding planes in the ancient metamorphosed sedimentary strata enclosing it.

There is considerable range of opinion regarding the classification of the ore deposit according to its temperature and depth of formation (GUSTAFSON⁹). ANDREWS^{10, 11} took the extreme view that the lodes as well as the igneous rocks of the district were injected under conditions of great temperature, great pressure, and deep burial as "pressure lenses" in "pressure slacks". LINDGREN¹² classed the deposits as hypothermal. GUSTAFSON¹³ believes that folding occurred at great depths characteristic of plastic deformation, perhaps as deep as 20–30 km, whereas ore deposition occurred long after folding, following an interval of uplift and erosion at much shallower depths, and further that the lodes owe their shapes to replacement of folded rocks. The first conspicuous act of ore deposition was the introduction of large amounts of "lode pegmatite" characterized by green microcline and quartz, accompanied by silicification and garnetization of the gneiss. Much, if not all, of the quartz and feldspar of this stage replaced the rock rather than intruded in igneous fashion. In this early stage, the introduction (or recrystallization) of large quantities of rhodonite, johannsenite, pyroxmangite, bustamite, hedenbergite, and garnet, all relatively "high temperature" minerals, occurred. Considerable amounts of pyrrhotite, arsenopyrite and loellingite occur in the ore, often closely associated with hedenbergite. These mineral associations denote relatively high temperature of ore deposition. The large size of the deposit, the general absence of zoning, and the limited extent of wallrock alteration are characteristic of hypothermal deposits as defined by LINDGREN¹² and GRATON.¹⁴

The temperature of formation of the ore deposit has been discussed by MAWSON,¹⁵ who found blue lode quartz from Broken Hill to be the "low" type and believed that ore deposition occurred below 575° C. SCHWARTZ¹⁶ considers that ore deposits containing cubanite-chalcopyrite intergrowths are formed above 400–450° C. STILLWELL¹⁷ described such intergrowths from this deposit. Both these "geological thermometers" mentioned above, are pressure conditioned.

The ore listed first in table XIV is from Broken Hill. In this sample, dark marmatite, some chalcopyrite, and a little pyrrhotite are visible to the naked eye. The sample is believed to be representative, and since free FeS is found with the marmatite, there is reason

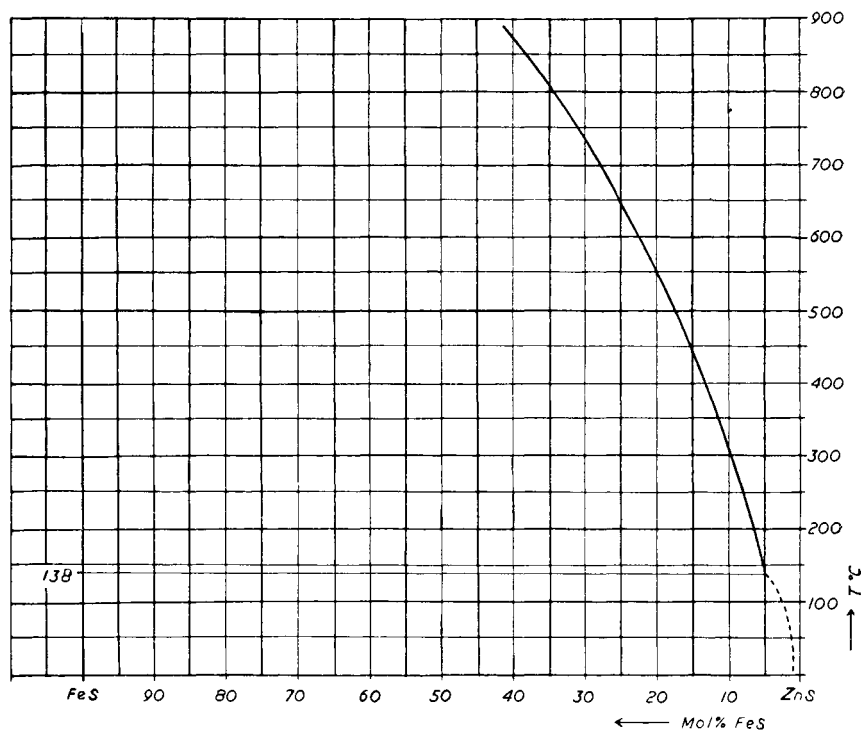


Fig. 15. Graph showing the composition of equilibrium β (Fe, Zn) S mix-crystals as a function of temperature.

to believe that the marmatite contains as much FeS as corresponds to the (P,T) conditions existing during the mix-crystal formation.

Figure 15 shows the part of the FeS — ZnS system (figure 1) of interest for the determinations of the temperatures of formation of natural mix-crystals.

The Broken Hill specimen contains 20.1 wt.% (23.5 mol.%) FeS. This composition corresponds to a temperature of 620° C. This of course is provided the ore formation took place at atmospheric pressure. Figure 9 gives information of the (P,T) relationship for mix-crystals containing any given amount of FeS.

The upper curve in figure 16 shows the pressure versus temperature plot for (Fe, Zn) S mix-crystals containing 23.5 mol.% FeS. The temperature of formation of the Broken Hill marmatite is found somewhere on this curve.

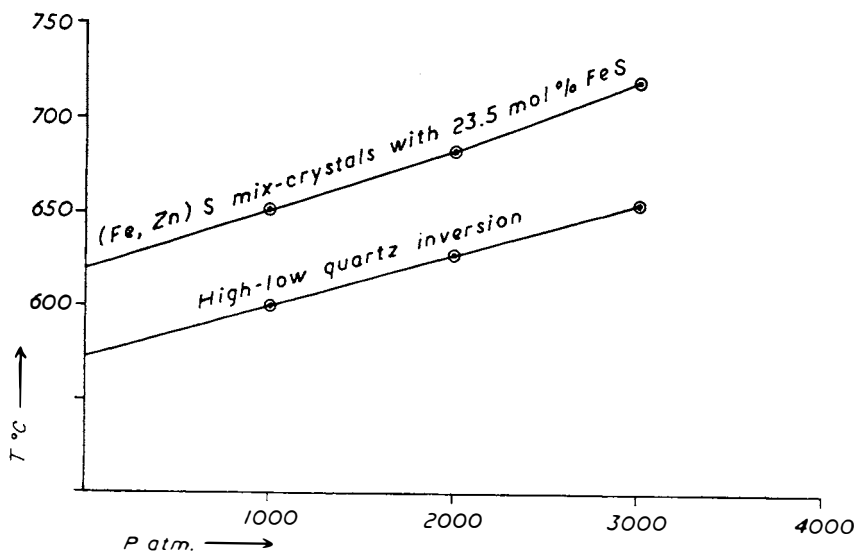


Fig. 16. Comparison between the temperature-pressure relationship for (Fe, Zn) S mix-crystals from Broken Hill (upper curve) and the temperature-pressure relationship for high-low quartz inversion (lower curve).

Geological evidence discussed by GUSTAFSON⁹ indicates that the ore in question may have formed at a depth of about 8 km corresponding to a pressure of about 2500 atm. On this assumption, the marmatite of Broken Hill is seen from figure 16 to have been formed at 700° C.

The lower curve in figure 16 shows the variation in the high-low inversion temperature of quartz as experimentally found by GIBSON¹⁸ and YODER¹⁹. The inversion takes place at about 645° C at a pressure of 2500 atm. As was earlier pointed out, MAWSON¹² found the lode quartz to be of the "low" type. This indicates that the quartz has been formed at a lower temperature than the marmatite.

b. *Amulet Mine, Quebec, Canada.* In the Noranda area, western Quebec, a number of ore deposits are being worked, one of which is Amulet. Here rhyolite, rhyolite flow breccias, and tuffs are intruded by sills and dikes of quartz diorite, all of pre-Cambrian age. These rocks are closely folded and sheared and are intruded by

granite and by great diabase dikes.^{23, 24} The ore carries pyrite, chalcopyrite, pyrrhotite, sphalerite, etc. with very little gangue. (EMMONS²²).

The specimen from this locality contains sphalerite, pyrrhotite, and chalcopyrite. The analysis (see table XIV) indicates a temperature of 455°C before pressure correction. It is hard to make a definite statement concerning the pressure at the time of mix-crystal formation. However, assuming the pressure to have been 2000 ± 1000 atm., the temperature of formation is found (from figure 9) to be $505 \pm 25^{\circ}\text{C}$.

c Balmat — Edwards, New York, U. S. A. At Edwards, and at Balmat,⁵³ N.Y. a garnet gneiss including limestone bodies is found below a thick limestone series above which is a later garnet gneiss. Intruding these are gabbro, amphibolite, syenite, and granite, all probably pre-Cambrian. Great deposits of zinc ore are opened both at Edwards and Balmat. They replace limestone and generally follow the bedding or banding of this. The primary ore minerals are pyrite, sphalerite, galena, chalcopyrite, pyrrhotite and barite. Primary sphalerite is of a dark chocolate-brown color. BROWN⁵³ analyzed primary sphalerite both from Edwards and Balmat Mines. The results of these analyses agree very well with those presented in table XIV of samples 7, 59, and 87.

Assuming that during the ore formation there existed a pressure of 2000 ± 1000 atm., one finds that the temperature of formation of the Balmat marmatite was $375 \pm 25^{\circ}\text{C}$ and for the Edwards marmatites $385 \pm 25^{\circ}\text{C}$.

2. Skarn.

St. Christoph, Erzgebirge, Germany. The ore deposits in Erzgebirge, Germany have been described in detail by REH⁴¹ and KOCH.⁴²

Devonian schists and limestones were intruded by large granitic masses. The main sulfide ores are found on the border between the granite and the country rock. The intrusion of granites resulted in development of skarn minerals. Zinc sulfide is a common constituent of the garnet type of skarn.

Samples 38 and 42 (see table XIV) are taken from two of the main ore bodies in the area, while sample 69 is from the zone of garnet skarn.

The pressure existing during the formation of the ores and the skarn has been appreciable, maybe as high as 2500 atm. If one corrects the temperature readings for a pressure of 2500 ± 1000 atm., one obtains the following temperatures for the formation:

- 1) Main ore bodies: Sample 38: $655 \pm 25^\circ \text{C}$.
Sample 42: $645 \pm 25^\circ \text{C}$.
- 2) Skarn: Sample 69: $345 \pm 25^\circ \text{C}$.

3. Pegmatites.

a. *Tetreault Mine, Quebec, Canada.* The Tetreault Mine,²¹ about 52 miles west of Quebec, lies in an area of quartzites and gneiss intruded by amphibolite and granite pegmatite. A lens of impure dolomitic limestone in gneiss dips 65 degrees east. The ore-bearing member lies near the pegmatite. The limestone is replaced by tremolite rock and by ore composed of sphalerite, galena, pyrite, calcite and micas. (EMMONS²²).

The ore sample from Tetreault Mine is composed of a dark marmatite intimately mixed with galena; a little pyrrhotite and specks of chalcopyrite are also visible to the eye. The analysis of this ore (table XIV) shows that 7.0 wt.% Pb was present in the sample. Assuming all Pb to occur in galena and correcting the analysis accordingly, one finds that the sample contains 11.76 wt% (14.06 mol.%) FeS. Not corrected for pressure, this FeS content corresponds to a temperature of 430°C .

Pegmatites are believed to have formed generally at depths of 1.5 km or more (EMMONS²). This depth corresponds to a pressure of approximately 500 atm. If one assumes a pressure of 1000 ± 500 atm., one finds from figure 9 that the marmatite was deposited at a temperature of $455 \pm 15^\circ \text{C}$.

b. *Calumet Island, Quebec, Canada.* The zinc-lead deposit is located on Calumet Island, Quebec, 53 miles northwest of Ottawa. The complex ores resemble those of Edwards, New York, and Mountauban, Quebec, and other Grenville deposits. They occur in moderately inclined Grenville metasediments, including crystalline limestone, amphibolite, amphibolite-gneisses, quartzite (rustyweathering), gneisses, and various granitized gneisses (migmatites).

The sulfide minerals comprise pyrite, sphalerite, pyrrhotite, galena, tetrahedrite, chalcopyrite, and marcasite, deposited in the order named. The sulfides are leanly disseminated in all the rock types in the ore zones, and lenticular masses largely deposited in carbonate and contact metamorphic rocks. They replace carbonate, quartz, and all silicates except serpentine. The association of the ore minerals with quartz and contact silicates indicates that they accompanied the same agents that produced silicatization and silicification. The association of sulfides with late stage processes in pegmatite like material is evidence that they formed a phase of the pegmatitic or volatile-rich granite magma. This "pegmatitic" material is considered to have been responsible for the contact metamorphism and migmatization as well. (MOORHOUSE,²⁵ ARMSTRONG,²⁶ FITZ.²⁷) Assuming a pressure of 1000 ± 500 atm. to have existed during the formation of this ore, the pressure-corrected temperature of formation is $485 \pm 15^\circ \text{C}$.

c. *Kimito Island, Finland*. The pegmatites from Kimito have been described by ESKOLA³⁷ and PEHRMAN.³⁹ KNORRING⁴⁰ analyzed a sample containing a manganese garnet enclosed in an iron-rich sphalerite from this locality. The result of Knorring's analysis of the sphalerite is found in table XIV. The present author has received a specimen of this sphalerite. Iron-sulfide is not present in this sample. However, PEHRMAN² stresses the occurrence of both pyrrhotite and pyrite with the sphalerite. The temperature of 510°C given in table XIV for this sample, should be corrected for pressure. Assuming a pressure of 1000 ± 500 atm. at the time of formation, one arrives to a temperature of $535 \pm 15^\circ \text{C}$.

4. Sphalerite of More Than One Generation.

Kajveltorp, Falun, Saxberget, Sweden. The ores in these localities are of the so-called Falun type.

The deposits of this type have originated in connection with the metasomatic alteration which has been called "magnesia metasomatism" and is intimately connected with the intrusion of the oldest granites (urgranites) of Central Sweden. These granites intruded

the folded leptite formation (metamorphosed volcanics and sediments). The ore bodies occur mainly in skarn-dolomite zones, or in quartzite. They contain pyrite, chalcopyrite, pyrrhotite, sphalerite etc. (MAGNUSSON⁵¹).

The specimen from Kafveltorp, gave as seen from table XIV, a temperature reading of 560°C . The pressure existing during the ore formation is hard to estimate, but hardly exceeded 2000 atm. Assuming a pressure of 2000 ± 1000 atm., the temperature of formation of this ore is found to be $620 \pm 25^{\circ}\text{C}$.

The specimen from Falun gave a temperature reading of 645°C . Assuming the same pressure as above, one arrives at a temperature of $700 \pm 25^{\circ}\text{C}$ for the formation of this ore.

In Saxberget mine there are two distinctly different types of sulfide deposits. The one type is similar to the ores described from Kafveltorp and Falun, and the other occurs in a straight fissure filled with a fine-grained, compact mass of sphalerite, pyrrhotite, pyrite, chalcopyrite, and galena. The specimen from Saxberget was collected from the latter type of ore. This specimen is, in table XIV, found labelled with a temperature of 245°C . Correction for the influence of pressure (2000 ± 1000 atm.) brings the temperature of formation of this ore up to $295 \pm 25^{\circ}\text{C}$.

Discussion of the Results of the Temperature Determinations.

On studying table XIV, one finds that the FeS content of the analyzed samples varies considerably. The largest amount of FeS (almost 24 mol.%) occurred in the specimens from Grua, Hadeland, Norway and from Broken Hill, Australia. The smallest amount of FeS (about 1.0 mol.%) was found in the specimen from Thompson mine, Wisconsin, U.S.A. The temperature field, within these extremes, ranges from 625°C down to some temperature well below 138°C . The temperatures recorded are not corrected for the influence of pressure. Even if one corrects all temperatures for pressure, the answers obtained will not in all cases give the temperature of formation of the mix-crystals.

Undoubtedly a number of the investigated ores have been formed under non-equilibrium conditions. As previously pointed out, field

work followed by microscopic studies of the individual specimens can alone give definite information about the paragenesis of the ore minerals.

Non-equilibrium conditions seem to have existed during the mix-crystal formation in the Joplin deposit. The amount of FeS dissolved in the ZnS varied in three specimens from less than 1.0 to about 1.9 mol.%. All specimens were composed of a light colored sphalerite and some marcasite. The marcasite, however, is younger than the sphalerite. Consequently mix-crystals of equilibrium composition were not formed.

Because discussions of the conditions existing during ore formation must be based on field work and microscopic study, a further treatment of the specimens one by one is not within the scope of this paper. However, the author is making arrangements of the above mentioned kind for study over a number of Norwegian marmatite ore bodies. The results of this work together with the deduced, pressure corrected, temperatures of formation, will appear in a later issue of this journal.

The Distribution of Minor Elements.

Manganese and cadmium, as earlier discussed, replace zinc in the sphalerite lattice, in the same manner as iron does. The solubility of MnS, CdS respectively in ZnS, of course, is a function of temperature and pressure. The runs conducted with MnS, CdS respectively mixed with ZnS in varying proportions, indicated that both the MnS — ZnS and CdS — ZnS systems are of nearly the same type as the FeS — ZnS system. These runs also supplied evidence as to the maximum solubility of MnS, CdS respectively in ZnS. Without going into details one may conclude, from the above mentioned runs and from the MnS and CdS analyses presented in table XIV, that none of the natural ores analyzed contain nearly as much MnS or CdS as corresponds to equilibrium conditions at the time they were deposited. This of course is not strange because the occurrence of free MnS or CdS formed simultaneously with mix-crystals of ZnS and the mentioned sulfides is, to the author's best knowledge, not on record.

The Mn and Cd distribution in the analyzed samples, therefore,

only reflects the local abundances of these elements and says very little about the temperature of formation of the mix-crystals.

The specimens were analyzed on copper and lead as a check on the purity of the picked samples and as a means of correcting the analyses on FeS. The silver reported in the analyses occurs almost entirely in galena.

The analyses on germanium, gallium, nickel, cobalt, and tin do not supply satisfactory information to allow any conclusions to be made as to their concentration in relation to temperature of formation of the mix-crystals in which they occur.

Like manganese and cadmium, the trace elements are hardly ever present in large enough amounts to saturate the ZnS lattice on their sulfides, at the prevailing (P,T) conditions. The amounts present of any one are, therefore, dictated by their local concentrations at the time of mix-crystal formation and very little by the temperature. At any rate, mix-crystals under-saturated on Mn, Cd, Ge, Ga, Ni, Co, and Sn are formed.

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