Experimental Investigation of Stannite-Sphalerite System in Relation to Ores

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Abstract

The subject of this study deals with phase relations between stannite (Cu_2FeSnS_4) and sphalerite (β-ZnS)/wurtzite (α-ZnS). The phase relations were systematically investigated from liquidus temperature to 400°C under controlled conditions. B-stannite (tetragonal) is stable up to 706±5°C, where it inverts to a high-temperature polymorph α-stannite (cubic) melting congruently at 867±5°C. Sphalerite (cubic, β-ZnS) inverts at 1013±3°C to wurtzite, which is the hexagonal high-temperature polymorph of ZnS. Between α-stannite and sphalerite a complete solid solution series exists above approximately 870°C up to solidus temperature. The melting temperature of α-stannite rises towards sphalerite and reaches a maximum at 1074±3°C, which is the peritectic with the composition of 91 wt. % sphalerite and 9 wt. % α-stannite. At this temperature, wurtzite takes only 5wt. % α-stannite in solid solution which decreases with increasing temperature. The inverson temperature of α/β-stannite is lowered with increasing amounts of sphalerite in solid solution down to 614 ±7°C, which is the eutectoid with the composition of 13 wt. % sphalerite and 87 wt. % α-stnanite. Here, β-stannite contains only 10wt. % sphalerite in solid solution. With decreasing temperature, the ranges of the solid solution on both sides of the system narrow.

The phase relations in the above pure system changed due to the FeS impurities in the sphalerite solid solution. The eutectoid increased from 614±7°C up to 695±5°C (5 wt. % FeS) and 700±5°C (10wt. % FeS), while the peritectic decreased from 1074±3°C down to 1036±3°C (wt. %FeS) and 987±3°C (10wt. %FeS). A most notable change is the appearance of non-binary regions.

An important feature is the combination of this study system with the experimental results reported by Sprinfer (1972). If a stannite-kesterite solid solution is used in the place of stannite as a bulk composition, the inversion temperature is lowered to less than 400°C which belongs to temperatures of the hydrothermal region.

I. INTRODUCTION

Though sulfide minerals have been demonstrated to be useful indicators of geological conditions of ore formation through continuing studies of sulfide system sat many research institutes, sulfosalt systems have undergone little systemetic investigations because sulfosalt minerals themselves have been generally iregarded to serve little or no purpose in the evaluation of ore genesis. However, a number of tin sulfosalts, e. g. stannite and its various species, are much more frequent in nature than the simple tin sulfides. Such minerals often occur only in trace amounts, but in many different types of ore deposits, and their complex nature was first reported in detail by Ramdohr (1944). In nature, the minerals chalcopyrite ($CuFeS_2$), stannite (Cu_2FeSnS_4), and sphalerite (ZnS) are often associated with each other. Furthermore, considerable solid sol-

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ution series exist between stannite and kesterite (Cu_2ZnSnS_4) which modify the complexity of the associated mineral relations. Therefore, these associations may be of some value as potential geological indicators of ore formation. However, the information obtained from the investigation of the natural mineral assemblages are quite limited and the physicochemical conditions can only be better reproduced through laboratory investigation.

Allen, Posnjak, etc. in 1910s began the first synthetic investigation of sulfide minerals at the Geophysical Laboratory of the Carnegie Institution in Washington. The systematic study of Cu-Fe-S system was reported by Merwin and Lombard in 1937. Later the systematic studies of sulfide systems have been continued by Kullerud's reserarch teams in the same laboratory.

As a part of the extensive study of the system chalcopyrite-stannite-kesterite-sphalerite, which is the most important part of the entire system Cu-Fe-Zn-Sn-S, a complete solid solution between stannite and kesterite was first reported by Moh (1960) above 700°C, using salt melts as a flux for the experiments and the pure dry system was investigated by Springer(1972). and the present research work is to investigate the phase relations between stannite and sphalerite under controlled conditions performing experiments in closed, evacuated silica glass tubes. In addition to the pure system, the influence of Fe content and pressure was also investigated, because natural sphalerite often contains iron sulfide in various concentration as a solid solution. This permits a better application to geological problems. However, the geological condition of ore formation is not as simple as in synthetic experiments and contains various factors affecting the phase relations. In the natural process of ore formation water, carbon dioxide and volatiles usually occur, and some components which substitute for the minerals of the system will affect the composition and stabilities of equ-

ilibrium phase assemblages. Therefore, only the investigation of more complex systems under various geological conditions will lead to complete under various geological conditons will lead to complete understanding of the processes of ore formation.

Acknowledgement

II. PREVIOUS INVESTIGATION

The pseudobinary system stannite-sphalerite is part of the chalcoypyrite-stannite-kesterite sphalerite system, which is geologically the most important part of the entire Cu-Fe-Zn-Sn-S system.

It was briefly discussed by Beernhardt (1972) as part of the chalcopyrite-stannite-kesterit esphalerite tetrahedron for better understanding of the entire system Cu-Fe-Zn-Sn-S and was further investigated by Lee(1972).

Stannite-Sphalerite System
Phase equilibria

The pseudobinary system stannite-sphalerite was first reported by Lee (1972). He investigated into phase equilibria from liquidus temperature down to 400°C and according to an available previous information, the inversion point of low temperature stannite (β-Cu_2FeSnS_4) into high temperature

stannite (α-Cu_2FeSnS_4) occurs at about 600°C (Frueh, in Eitel, 1958, p. 25).

Oen(1970) summarized the natural minerals in the system Cu-Fe-Sn-S in hypothetical diagrams, in which the above inversion temperature of α/β-stannite was used as an important reference temperature. Springer (1972) reported that a phase transit i n appeared to take place in stannite at about 680°C and that an endothermal peak was recorded at 878±3°C, its melting point, using differential thermal analysis method. Bernhardt (1972) redetermined the inversion point of of α/β-stannite at 706±5°C and the thermal effect of its melting point between 855°C and 874°C.

Investigations on the inversion temperatures of sphalerite/wurtzite and the melting point of wurtzite have been summarized by Hansen (1958), Elliot (1965) and Shunk (1969).

In Hansen (p. 1171) it is described that Allen determined the transformation point sphalerite$\rightleftarrows$ wurtzite as 1020±5°C and that Tiede investigated the melting point of wurtzite as 1800–1900°C under a pressure of 100-150 atm.

In Elliot (p. 800) it is described that the inversion point of extremely pure crystals is above 1150°C according to Addamiano who noted that ZnS used by Allen contains 0.15% Fe and that the ZnS crystals were contaminated impurities diffusing from the quartz furnace walls. Ammelson (in Elliot, p. 800) reported that pure ZnS was formed from pure ZnS powder at 1050°C under 500mmHg pressure. This is contrary to Addamiano's results, but supports Gobercht'sresults. Addamiano also determined the melting point of wurtzite at 1830±20°C in an atmosphere of Ar under a pressure of 150 psi(about 10 atm.), which is very close to Tiede's results. Therefore, it can be concluded that the melting point is slightly dependent on pressure. Other values, 1049°C by Cussak (in Hansen, p.1171) and 1600-1700°C by Friedich (1908) are too

low. In Shunk (p. 664-665) it is described that Aggarwal and Shalimova reported variations of inversion point over wide limits. The latter found that annealing cubic films in Zn vapor at 640°C caused increasing amounts of hexagonal ZnS to form, whereas annealing in a sulfur vapor caused a return to stoichiometry and cubic structure. Gobercht (in Shunk, p. 664) reported that an endothermal reaction corresponding to the cubic-hexagonal transformation occurred at about 1025°C, which is in good agreement with Allen's results. Buck and Strock (1955) have reported a third modification of ZnS, which was found to occur in the temperature range of approximately 600°C to 1020°C with rhombohedral structure. Vaasuoki (1972) redetermined the inversion temperature of sphalerite/wurtzite as 1013±3°C with synthesized stoichiometric ZnS of high purity.

Crystallographic description

Stannite was earlier tabulated (Beudant, 1826) with the false name of Zinnsulphuret ES^2 1872, 90E=79.01, S^2=20.99 which was a modification of stannite described by Klaproth (1797).

R. Gross and N. Gross (1923) investigated the crystal structure of stannite with the aid of powder photographs and reported a tetragonal unit cell a_0=5.577Å; c_0=5.180Å with atom positions of: Sn at 000; Fe at $\frac{1}{2}\frac{1}{2}0$ 2Cu at $\frac{1}{2}0\frac{1}{2}$ and 4S at undetermined. These values give a unit cell with an axial ratio of a:c=1:0.9287, whereas Spencer (1902) gave a:c=1:0.9827. This discrepancy cannot be ascribed to a topographical error, for Spencer tabulated the measurements made on the angle between the developed faces (001) and (101) on several specimens (this angle being 44°30'), while other investigators reported on the dimension of the cell.

Brockway (1934) investigated the values of the unit cell a_0=5.46Å; c_0=10.725Å with $2Cu_2FeSnS_4$. These dimensions give an axial ratio

for the pseudo-cubic unit of a:c=1:0.282 in agreement with Spencer's value of 0.9827. The density calculated for $2Cu_2FeSnS_4$ in the unit is 4.44 which is very similar to Spencer's observed value of 4.45.

Bragg's analysis of sphalerite was the first example of the determination of the atomic arrangement in a hemihedra crystal (in Bragg, 1955, p.54). It is described in Hansen (1958, p. 1171) that the determination of the parameter, both natural and synthetic, was followed by Gerlach, Lehmann, Renn, Hartwig, Swanson and Kullerud. Sanson determined the most probable value of the parameters of wurtzite a= 3.820Å; c=6.260Å. These values lead to an axial ratio of a:c=1:1.639.

Aswegen (in Elliot, 1965, p.800) redetermined the lattice parameter of FCC β-ZnS to be

a=5.4109Å, and Yu (in Shunk, 1969, p.694) remeasured the lattice parameter of wurtzite to be a=3.823±0.0005Å, and c=6.2631±0.0005Å. Both parameters of sphalerite and wurtzite are in good agreement with the results of Swanson.

Ehrenberg (1931) and Frondel (in Hansen, 1958, p.1171) reported the structure of three modifications of wurtzite.

Buch (1955) reported that rhombohedral γ-ZnS had the parameters of a=3.830Å; c=9.477Å as annealed at 1000°C and a=3.811Å; c=9.348Å as annealed at 850°C. According to Allen (1912), the specific gravity ranges from 3.9-4.1 and decreases with the increase in Fe content, and the calculated value is 4.083.

The crystal forms of stannite and sphalerite/wurtzite are shown in Fig.1.

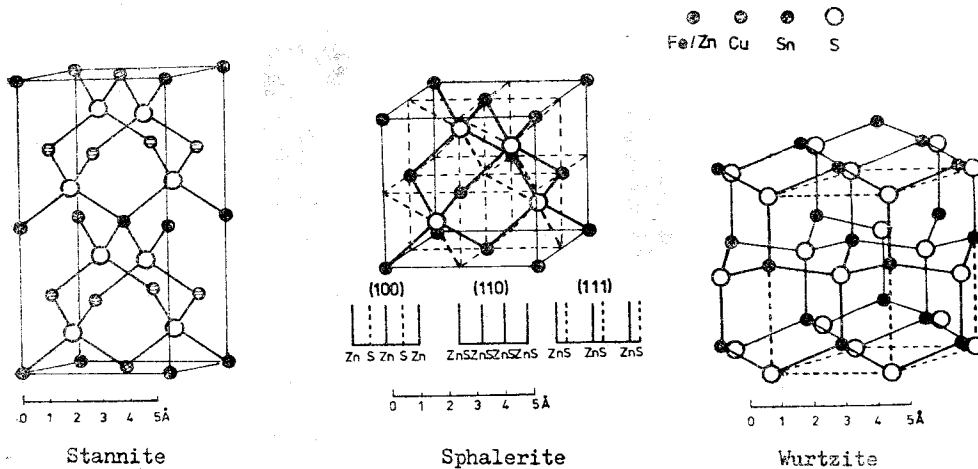Fig.1. Crystal forms of stannite and sphalerite/wurtzite showing arrangement of the atoms in the unit cell. The structural and geometrical-chemical constitution of stannite is related to that of sphalerite. The Zn atoms of the sphalerite are substituted by 2Cu, 1Fe, and 1Sn indicating the superstructure type of stannite. The close structure relations of sphalerite are important for the metasomatic replacement of sphalerite.

The Chalcopyrite-Stannite-Kesterite-Sphalerite-System

This system is the most important part of the entire Cu-Fe-Zn-Sn-S system. Therefore, as a part of the chalcopyrite-stannite-kesterite-sphalerite tetrahedron the study system must be investigated in relation with it. However, only some selected pseudobinary systems and a psedoternary chalcopyrite-stannite-sphalerite system heve baen investigated.

Moh (1960) first reported that a complete solid solution exists at about 700°C between stannite and kesterite using a mixture of NaCl and KCl as a flux with the lowest melting of about 660°C.

Springer (1972) determined the phase relations in the stannite-kesterite system between 300°C and the melting point and the decomposition temperatures, that range from 878 to 1002°C, by quenching and differential thermal analysis experiments. Unlimited solid solution was found to occur above about 680°C, but below that temperature, the two different stannite-kesterite phase are separated by a miscibibility gap. He concluded that natural stannite-kesterite phases are separated by a miscibility gap. He concluded that natural stannite-kesterite exsolutions are explained in the light of experimental results, and zincian stannite can serve as a geological thermometer.

Bernhardt (1972) reported the first phase diagram of the pure chalcopyrite-stannite system in the temperature range between 300 and 850°C. Both inversion points of the end members decrease by taking each other in solid solution down to the corresponding eutectoid temperatures, which are 610 ± 10°C (9wt. % chalcopyrite and 91wt. % stannite) and 460 ± 5°C(61wt. % chalcopyrite and 91wt. % stannite) and 460 ± 5°C (61wt. % chalcopyrite and 39wt. % stannite) respectively.

Vaasjoki (1972) investigated the pseudobinary system a stannite-kesterite from 600°C to about 1100°C. His partly completed diagram shows that the inversion temperature of sphalerite increases to the peritectic temperature (1050 ± 5°C) by taking kesterite. A wide miscibility gap exists between the two endmembers, from low temperature up to about 800°C, and the solubility of kesterite in sphalerite increases with increasing temperature.

Lee (1973) partly investigated the kesterite-chalcopyrite system finding the approximate miscibility limits between the two endmembers. With increasing temperature, the miscibility shows a highly increasing rate up to the solidus at 880 ± 10°C on the chalcopyrite side. Both maximum miscibilities lie at the solidus temperature with the composition of about 10wt. % chalcopyrite and about 90wt. % kesterite on the kesterite side and about 51wt. % chalcopyrite and about 49wt. % kesterite on the chalcopyrite side.

Moh (1973a) found a large miscibility gap at temperatures between 500 and 800°C in the chalcopyrite-sphalerite system, which is now completed in Heidelberg in 1974.

Moh (1974b) described about the pseudoternary chalcopyrite-stannite-sphalerite system in the temperature ranges of 400 to 700°C, according to which α-chalcopyrite shows a relatively large stability field. Less extensive is the α-stannite stability region, whereas the sphalerite solid solution field is extraordinarily narrow. B-stannite and expecially β-chalcopyrite show limited solid solution stability fields which diminish with decreasing temperature.

The Cu-Fe-Zn-Sn-S System

Oen (1970) discussed the paragenetic relatural products occurring in the Cu-Fe-Zn-Sn-S system and plotted his observations in phase diagrams.

Moh (1973b & 1974b) summarized the previous investigations briefly and commented on the importance of its experimental investigation and the present research in Heidelberg.

III. EXPERIMENTAL PROCEDURES

The investigation of phase relation was carried

out by heating well-mixed charges of starting materials in evacuated silica tubes at predetermined temperatures for periods of time necessary to attain equilibrium. Phases present after heating were identified at room temperature by the methods described below, and the results were plotted on equilibrium phase diagrams.

Starting Materials

High-purity elements (all 99.999+%) were used for the preparation of the starting materials: copper and zinc in bars and sulfur in lumps from Asarco; iron powder from Johnson Matthey & Co., tin in bars from the United Mineral and Chemical Corp., New York.

All starting materials were synthesized in evacuated, sealed silica tubes in the manner described by Kullerud(1971).

Stannite was synthesized either directly out of the elements at various temperature or by reaction of binary phases previously prepared. B-stannite is stoichiometric Cu_2FeSnS_4. However, at elevated temperatures, e.g. above 706°C, Cu_2FeSnS_{4-x} is plays a slight sulfur deficiency similar to chalcopyrite $CuFeS_{2-x}$.

Sphalerite (ZnS) was prepared by reacting zinc filings with an equiatomic amount of sulfur. The mixtures were heated at 600~800°C.

The (Zn, Fe)S solid solution bearing 5% Fe and 10% Fe were prepared from carefully weighed portions of FeS and ZnS. The mixtures were heated at 600~800°C for 10~20 days. They were reground once or twice to obtain a homogeneous product.

Experimental Techniques

All runs were prepared in evacuated, sealed silica tubes by mixing predetermined amounts of stannite and sphalerite and also stannite and (Zn, Fe)S solid solution. The runs were heated in horizontal electric furnaces at predetermined temperatures which were measured by a potentiometer (Honeywell), until equilibrium was obtained. The reaction rates depend very much upon the temperature.

At elevated temperatures, they are high, and short periods were required to attain equilibrium; while, at low temperatures, long periods were required owing to slow kinetcs. However, to speed up the reaction rate, most of the probes were reground once or twice and reheated at given temperature to attain equilibrium. In order to reduce vapor space the charge was compressed by inserting a closely fitting silica glass rod into the tube. The runs were quenched quickly in cold water to retain the equilibrium products. Charges for experimental runs weighed 50~100mg, and all weighings were made to a precision of±0.10 mg. Mixing and grinding were carried out under acetone to prevent oxidation.

Identification of Phases

All phases were identified at room temperature (1) visually, (2) with ore microscope, and (3) by X-ray powder diffraction.

(1) Visual identification of phases was often possible through the transparent walls of the silica tube by stereo microscope. The degree of reaction and the phases present could be indicated occasionally. However, for the identification of phases to plot the results on equilibrium phase diagrams only ore microscope and X-ray powder diffraction methods were employed.

(2) Small polished sections of the reaction products were prepared for examination under the ore microscope by using technovit as mounting media. Identification of the phases was aided by using oil immersion.

(3) X-ray powder diffraction patterns were obtained with Philips diffractometer using Ni-filtered CuK_α and also Mn-filtered FeK_α radiations.

IV. THE PURE SYSTEM STANNITE-SPHALERITE

In all aspects discussed below, pure stannite (Cu_2FeSnS_4) and sphalerite (ZnS) were used as starting materials.

The stannite-sphalerite system is an important part of the chalcopyrite-stannite-kesterite-sphalerite tetrahedron, e. g. for its potential possibility in geothermometry. In this study the pure system was investigated under various conditions for better understanding of ore-forming procedures and exsolution textures in nature.

Experimental Results

The condensed T-X diagram (Fig. 2) shows the phase relations of this system above 400°C. Besides a complete solid solution series at elevated temperatures there are two binary regions under the solidus excluding the α-stannite+β-stannite region. Above the solidus, sphalerite or wurtzite or wurtzite solid solutions coexist with liquid. This liquid shows decomposed phases above the liquidus indicating non-binary region. No additional compounds are found between the two endmenbers. Vapor ist present with all phases. All details of the experimental results are given in Table 1.

B-stannite is stable up to 706±5°C, where it inverts into the high temperature polymorph α-stannite, which melts congruently at 867 ±5°C. Between α-stannite and sphalerite a complete solid solution series exists above approximately 870°C up to the solidus. The melting temperature of α-stannite increases with increasing amounts of sphalerite and reaches a maximum at 1074±3°C (91wt % sphalerite and 9wt % stannite), which is the peritectic of this system. At this temperature, wurtzite contains 5 wt. % α-stannite in solid solution, above this temperature the solid solution decreases with increasing temperature, but in this study it was not determined above 1200°C. The inversion temperature of α/β-stannite is lowered by increasing amounts of sphalerite in solid solution down to 614±7°C. Here, α-stannite contains approximately 13wt. % sphalerite, whereas β-stannite contains only 10wt. % sphalerite in solid solution. With decreasing temperature, the
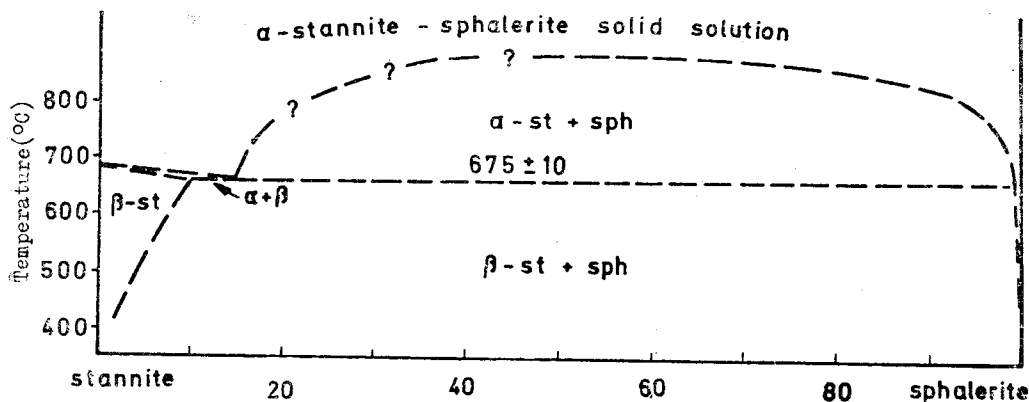

Fig. 10. Phase relations in the system stannite-sphalerite under confining pressure(5kb) and a complete solid solution series exists between stannite and sphalrite.

solid solution of both β-stannite and sphalerite decreases, as illustrated in Fig. 4. For instance, at 400°C β-stannite contains about 9 wt. % ZnS and sphalerite takes only 1.5 wt. % β-stannite in solid solution, respectively.

The inversion point as well as the melting point of stannite was determined by DTA experiments.

The recorded rsults of the inversion point were not clear and its interpretation was difficult. However, at 706±5°C as light endothermal effect was recorded on heating which is a little higher than 680°C reported by Springer (1972). Endothermal effects of the melting point were recorded both on cooling and heating. The melting point
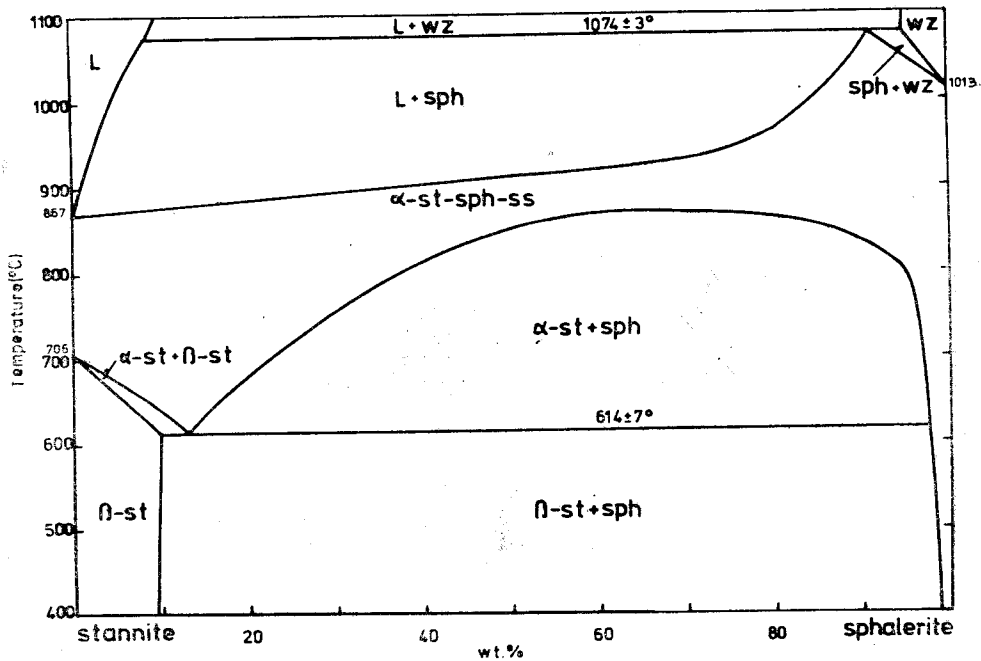
Fig. 2. Phase relations in the stannite-sphalerite sysetm above 400°C. Vapor is present with all phases. A complete solid solution series exists above approximately 870°C up to the solidus between stannite and sphalerite.

was found to be 867±5°C on cooling, which is about 10°C lower than that on heating because of supercooling. The temperature of 867±5°C is in good agreement with the results of the stannite-sphalerite solid solution series determined by the quenching method.

Comparing the inversion point of pure sphalerite with the α/β inversion point of stannite, the former showed a greater effect at 1013°C by endothermal peak, which is a little lower than the 1020±5°C reported by Allen (1921). The melting point was not investigated in the present study.

The stoichiometric runs without excess sulfur yielded melphases in the α-stannite-sphalerite solid solution region towards the sphalerite side at temperatures above 800°C. This is because of the high sulfur vapor pressure coexisting with the charges which then become unstoichiometric

due to loss of sulfur. Therefore, the runs were buffered with a small excess of sulfur to balance the vapor pressure with the solid phases.

In all the experiments which were quenched from temperatures above the solvus one solid phase remained, but when quenched from temperatures early on the solvus most of the runs with a composition of approximately 40 Wt. % to 80wt. % sphalerite and 60wt. % to 20wt. % stannite respectively showed exsolution of the stannite phase in the form of lamella in the stannite-sphalesite solid solution (Figs. 3a and 3b). This exsolution may be explained by slow quenching as well as by an order-disorder relation. However, α-stannite solid solution showed little exsolution textures, and with X-ray powder diffractometer no differences were observed because the separated phase may have very similar X-ray

reflections to the α-stannite solid solution and it is in too small amounts to be detected.

In the stannite + sphalerite region the exsolution of stannite in sphalerite and vice versa was occasionally observed, but they were irregularly granlar and in very small amount (Fig. 4).

In Fig. 2 the region below the solvus is shown as a binary region of α-stannite+sphalerite, but should be marked as a non-binary region. The reason is as follows: Near the solvus, the breakdown products are nearly supersaturated with each other, e. g. α-stannite solid solution and sphalerite solid solution. However, a second reaction takes place proving the pseudobinary character of the sphalerite-rich portion of the α-stannite-sphalerite solid solution region. For example, with decreasing temperature the sphalerite solid solution decreases rapidly and α-stannite should be exsolved. However, sphalerite holds an excess of iron sulfide in solid solution, compared with stoichiometric sphalerite, resulting in a $(Zn, Fe)S$ formula of various compositions. The remaining stannite, which is only stable when it is saturated with a certain of ZnS for FeS, approaches stannite-kesterite mixed crystals. These mixed crystals coexist with shalerite solution. It may be summarized
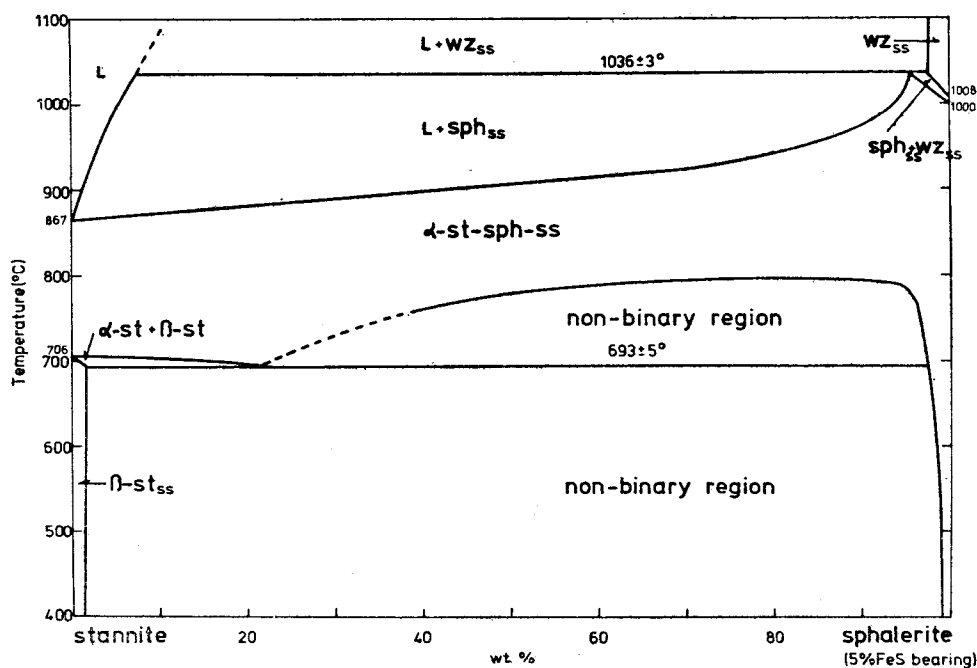
Fig. 6 Phase relations in the system stannite-sphalerite (sphalerite containing 5wt. % FeS in solid solution above 400°C. Vapor is present with all phases, and the pressure of the system is not constant. Two non-binary regions exist between stannite and sphalerite (5wt. % FeS).

with the following simplified formula:

stannite(ss) + sphalerite(ss) →stannite-kestrite (ss) + Fe-containing sphalerite (ss)

$Cu_2FeSnS_4(ss) + ZnS(ss) → Cu_2(Fe, Zn)SnS_4(ss) + (Zn, Fe)S(ss)$

When cooled continuously, the stannite-kesterite mixed crystals may become unstable and break down to β-stannite(ss) and kesterite(ss) coexisting with sphalerite(ss). This reaction becomes clear when compared with the experimental results by Springer (1972) (see Figs. 11).

The peritectic was determined by quenching

experiments. The runs were analysed by the X-ray powder diffraction method at room thmperature.

The runs quenched above the liquidus showed decomposed phases. When runs were cooled slowly, crystallized phases of wurtzite were observed (Fig. 5). The eutectoid was also determined by the quenching method, but it was difficult to distingish the two-phase region (α-stannite+β-stannite) from the one-phase region surrounding it by X-ray powder diffractometer.

Description of Phases

It is obvious that, at elevated temperatures, synthesized stoichiometric stannite and sphalerite of high purity and their solid solutions may have different properties from those observed as natural products. Natural stannites show apparent changes according to mineral associations and impurities. All of the quenched products were examined at room temperature. The optical properties from pure stannite towards sphalerite change continuously along the solid solution series.

Table 1–Experimental Results of the Pure System Stannite-Sphalerite

1) The solvus and eutectoid

wt. % (pure sph.)	T°C	time (hours)	products
11.50	611	250	two-phase (region)
12.50	613	250	two-phase (region)
12.50	615	250	two-phase (region)
15.0	636	250	two-phase (region)
15.0	650	262	one-phase (region)
22.50	703	163	one-phcse (region)
35	800	192	one-phase (region)
40.0	815	72	one-phase (region)
40	790	192	two-phase (region)
50.0	852	72	one-phase (region)
52.50	852	72	two-phase (region)
60.0	870	48	one-phase (region)
70.0	870	48	one-phase (region)
75.0	857	72	two-phase (region)
85.0	852	72	two-phase (region)
85.0	859	72	one-phase (region)
94.50	812	192	one-phase (region)

| 95.0 | 804 | 192 | two-phase (region) |
| 97 | 700 | 160 | two-phase (region) |

2) The solidus and peritectic (ss=α-stannite-sphalerite solid solution)

wt. % (pure sph.)	T°C	time (hours)	products
10.0	887	24	ss+L
30.0	896	24	ss
30.0	904±4	24	ss+L
40.0	900	30	ss+L
50.0	907	30	ss
50.0	910	72	ss+L
70.0	930	24	ss+L(tr)
80.0	962	66	ss+L(tr)
87.50	1040	42	ss+L(tr)
90.0	1060	45	ss
90.0	163	45	ss+L(tr)
91.0	1070	45	ss
92.50	1070	45	ss+wz
92.50	1075	45	wz+L

3) The solubility of stannite in wurtzite

wt. % (pure sph.)	T°C	time (hours)	products
93.5	1075	45	wz+L
95.0	1075	45	wz
95.0	1100	3	wz
95.0	1195	23	wz+L(tr)

4) The solubility of sphalerite/wurtzite in liquid

wt. % (pure sph.)	T°C	time (hours)	products
5.0	1010	24	L
8.0	1070	45	L
9.0	1070	45	L+wz
9.0	1080	45	L
10.0	1103	3	L
15.0	1200	3	L+wz

5) The solubility of β-stannite in sphalerite

wt. % (pure sph.)	T°C	time (ours)	products
98.5	400	1344	sph+β-st(tr)
98.0	512	2952	β-st
97.50	595	250	sph+β-st(tr)

6) The solubility of sphalerite in β-stannite

wt. % (pure sph.)	T°C	time (hours)	products
10.0	400	1344	β—st+sph(tr)
10.0	500	2952	β—st+sph(tr)
10.0	601	250	β—st
10.50	613	250	β—st+sph(tr)

7) The sphalerite and wurtzite region (x-ray powder method)

wt. % (pure sph.)	T°C	time (hours)	products
95	1003	24	sph
95	1025	24	sph
95	1040	24	sph
95	1050	24	sph
95	1060	24	sph+wz
95	1065	24	wz
95	1115	3	wz

V. THE SYSTEM STANNITE-SPHALERITE

(sphalerite containing 5wt. % FeS as impurities)

In all aspects discussed below, besides pure stannite (Cu_2FeSnS_4) a homogeneous sphalerite was used as starting material containing 5wt. % FeS as impurities in solid solution $(Zn, Fe)S$ and is written as sphalerite (5wt. % FeS).

The added FeS content caused changes in the phase relations of the pure system. In addition to two non-binary regions (an upper and a lower) the eutectoid temperature increased from 614±7°C up to 695±5°C with the composition changing from 13wt. % sphalerite and 87wt. % stannite to 22.5wt. % sphalerite (5wt. % FeS) and 77.5wt. % stannite respectively, while the peritectic temperature decreased from 1074±3°C down to 1036±3°C with the composition changing from 91wt. % sphalerite and 9wt. % stannite to 95.5wt. % stannite and 4.5wt. % sphalerite (5wt. % FeS) respectively. Between the two endmembers a stannite-sphalerite (5wt. % FeS) solid solution occurred in a much wider range of temperatures by the decreasing solvus temperatures. The solubilities of

the sphalerite (5wt. % FeS) in β-stannite and of the stannite in wurtzite (5wt. % FeS) showed considerable decreases compared with the pure system.

Experimental Results

The condensed T-X-diagram (Fig. 6) shows the phase relations of this system. At elevated temperature a complete α-stannite-sphalerite (5 wt. % FeS) solid solution series exists. Below the solvus. the two non-binary regions (an upper and a lower) exist. Liquid below the liquidus contains decomposed phases indicating the non-binary. Vapor is present with all phases. All details of the experimental results are given in Table 2. B-stannite inverts into the high-temperature polymorph α-stannite at 706±5°C which melts congruently at 867±5°C which melts congruently at 867±5°C. Between the two endmembers a complete α-stannite-sphalerite (5wt. % FeS) solid solution forms above approximately 795°C in this system. Under the solvus a non-binary region exists. The melting temperature of α-stannite increases with increasing content of sphalerite (5wt. % FeS) along the solid solution and reaches a maximum at the peritectic temperature (1036±3°C) with the composition of 95.5wt. % sphalerite (5wt. % FeS) and 4.5wt. % stannite. At the peritectic temperature, wurtzite (5wt. % FeS) takes only 2.5wt. % stannite in solid solution, above this temperature the wurtzite solid solution diminishes very slowly, but it was not determined above 1200°C in this system. The upper and lower inversion points of sphalerite/ wuritzite (5wt. % FeS) are locacted between 1000 ±4°C and 1008±4°C respectively. The inversion point of α/β-stannite is decreased to the eutectoid temperature (693±5°C) with the composition of 22.5wt. % sphalerite (5wt. % FeS) and 77.5wt. % stannite. At this temperature, β-stannite takes only 1.5wt. % sphalerite (5wt. % FeS) in solid solution. With decreasing temperature, the solid solution decreases on both sidese and between the two endmembers another non-binary region

exists.

The inversion point of sphalerite (5wt. % FeS) was determined from the FeS-ZnS system invest-igated by Kullerud (1953). He determined the inversion point of the sphalerite containing 10, 20, 30, etc. wt. % FeS in solid solution by the X-ray powder diffractometer.

All results were replotted on a graph (Fig. 7) and the inversion temperatures obtained were 1000 ±4°C and 1008±4°C.

In this system considerable non-binary evidences appeared. In the stannite-sphalerite (5wt. % FeS) solid solution region the Zn-poor part (towards the stannite side) was not fully quenchable resu-lting in a gradually unclear solvus towards the eutectoid when quenched above the eutectoid tem-perature. The Zn-rich part towards the sphalerite (5wt. % FeS) also produced amounts of melt-phases in this system. For the determination of the solidus, small amounts of melt-phases occurring in the Zn-rich solid solution part were carefully dis-tinguished from the liquid phases above the solidus. The melt-phases observed by microscopy were distributed irregularly in y-letter forms like fillings between crystals of the solid solution series.

Exsolution textures of lamellae were found in the runs quenched from the solvus temperature. Below the eutectoid temperature in the non-binary region only small amounts of chalcopyrite coexist with a modified kesterite-stannite solid solution in equilibrium with sphalerite. The chalcopyrite was observed in runs containing approximately 15wt. % sphalerite (5wt. % FeS) and 85wt. % β-stan-nite solid solution (Fig. 8).
1) This is a melt-phase of the entire Cu-Fe-Zn-Sn-S system with $Cu_2SnS_{2.5}$ composition, in
   The pritectic was determined in the same method as described in the pure system. The transform-ation temperature of the solid solution near stoic-hiometric stannite could not be determined by the quenching method, and DTA experiments were too sluggish for exact determination of inversion temp-
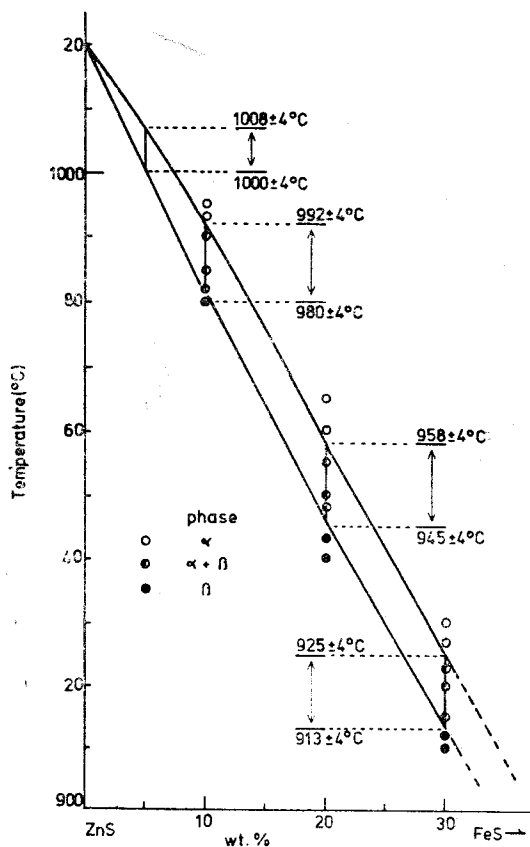
which small amounts of FeS and ZnS are dissolved.

Fig. 7. The upper and lower inversion themperat-ures of sphalerite solid solution with various FeS contents. Data from Kullerud (1953) were replotted on the T-X-diagram.

eratures. However, the limits of the β-stannite and sphalerite (with 5wt. % FeS) solid solution were accurately determined from the nonbinary region by the quenching method.

Description of Phases

The α-stannite-sphalerite (5wt. % FeS) solid solution shows very similar changes of properties to those in the pure system. However, sphalerite containing 5wt. % FeS shows considerable change from the synthesized sphalerite of high purity.

Table 2-Experimental Results of the System
Stannite-Sphalerite (sphalerite containing
5wt. % FeS as impurities; abbr. SS)

ss=α-stannite-sphalerite solid solution

1) The solvus and eutectoid

wt. % (sph. SS)	T°C	time (days)	products
20.0	692	26	non-binary (region)
20.0	700	30	one-phase (region)
21.0	692	26	non-binary (region)
22.0	695	26	non-binary (region)
22.0	703	30	one-phase (region)
25.0	700	30	non-binary (rehion)
35.0	752	8	one-phase (region)
45.0	772	8	non-binary (region)
60.0	793	6	non-binary (region)
70.0	793	6	non-binary (region)
75.0	800	6	one-phase (region)
90.0	800	4	one-phase (region)
95.0	784	6	non-binary (region)
95.0	793	6	one-phase (region)
96.0	695	6	non-binary (region)
96.0	772	30	one-phase (region)
97.5	600	25	non-binary (region)

2) The solidus and peritectic

wt. % (sph. SS)	T°C	time (days)	products
10.0	870	3	L+ss
30.0	885±5	3	ss
30.0	895±5	3	L+ss
50.0	900	2	ss
50.0	910	2	ss+L
70.0	920	2	ss
70.0	930	2	ss+L
90.0	970	3	ss
90.0	980	3	ss+L
95.0	1010	3	ss
95.0	1017	3	ss+L (tr)
95.0	1025	3	ss+L

3) The solubility of stannite in wurtzite solid solution

wt. % (sph. SS)	T°C	time (days)	products
95.0	1100	1	L+wz ss
97.5	1050	1	wz ss+L (tr)
97.5	1145	1	wz ss
98.0	1080	1	wz ss

4) The solubility of sphalerite/wurtzite solid solution in liquid

wt. % (sph. SS)	T°C	time (days)	products
6.0	1025	1	L
7.0	1025	1	L+wz ss
10.0	1070	1	L+wz ss
10.0	1100	1	L
20.0	1200	1	L+wz ss

5) The solubility of β-stannite in sphalerite solid solution

wt. % (sph. SS)	T°C	time (days)	products
97.50	600	25	non-binary
98.0	411	42	non-binary
98.0	497	69	non-binary
99.0	411	42	non-binary
99.0	493	69	one-phase

6) The solubility of sphalerite solid solution in β-stannite

wt. % (sph. SS)	T°C	time (days)	products
1.0	411	42	β-st
1.0	682	26	β-st
2.0	411	42	non-binary
2.0	497	69	non-binary
2.0	585	38	non-binary
2.0	685	26	non-binary

7) The sphalerite and wurtzite solid solution region (x-ray powder method)

wt. % (sph. SS)	T°C	time (hours)	products
95	1000	3	sph ss+L
95	1005	3	sph ss+L
95	1020	3	sph ss+L
95	1027	3	sph ss+L
95	1030	3	sph ss+L
95	1035	3	sph ss+L
95	1038	3	wzss+L
95	1040	3	wzss+L
95	1045	3	wzss+L

VI. THE SYSTEM STANNITE-SPHALERI-
TE (sphalerite containing 10wt. % FeS as impurities)

In all aspects discussed below, besides pure stannite (Cu_2FeSnS_4) a homogeneous sphalerite was used as starting material containing 10wt. % FeS as impurites in solid solution $(Zn, Fe)S$ and is written as sphalerite (10wt% FeS).

The further added FeS content caused the phase relations in the pure system to move a little more into the ternary or quaternary systems. The eutectoid temperature increased from 614 ± 7°C up to 700 ±5°C wich the composition changing from 13wt. % sphalerite and 87wt. % stannite to 22±2wt. % sphalerite (10wt. % FeS) and 78±2 wt. % stannite respectively, which is about 5°C higher than that of the system containing 5wt. % FeS. However, the peritectic temperature of this

system decreased further below from 1074±3°C down to 987±3°C whith the composition changing from 91wt. % sphalerite and to 87.5wt. % sphalerite (10wt. % FeS) and 12.5wt. % stannite. Between the two endmembers the α-stannite-sphalerite (10wt. % FeS) solid solution became more narrow by decreasing melting temperatures of the α-stannite-sphalerite (10wt. % FeS) solid solution. The β-stannite solid solution of this system increased compared with the system containing 5wt. % FeS sphalerite solid solution.

Experimental Results

The condensed T-X diagram (Fig. 9) shows the phase relations of this system above 400°C. Besides the α-stannite-sphalerite (10wt. % FeS) solid solution series at elevated temperatures, there exist two non-binary regions under the solvus. The liquid above liquidus is also non-binary. Vapor is present with all phases. All details of experimental results.
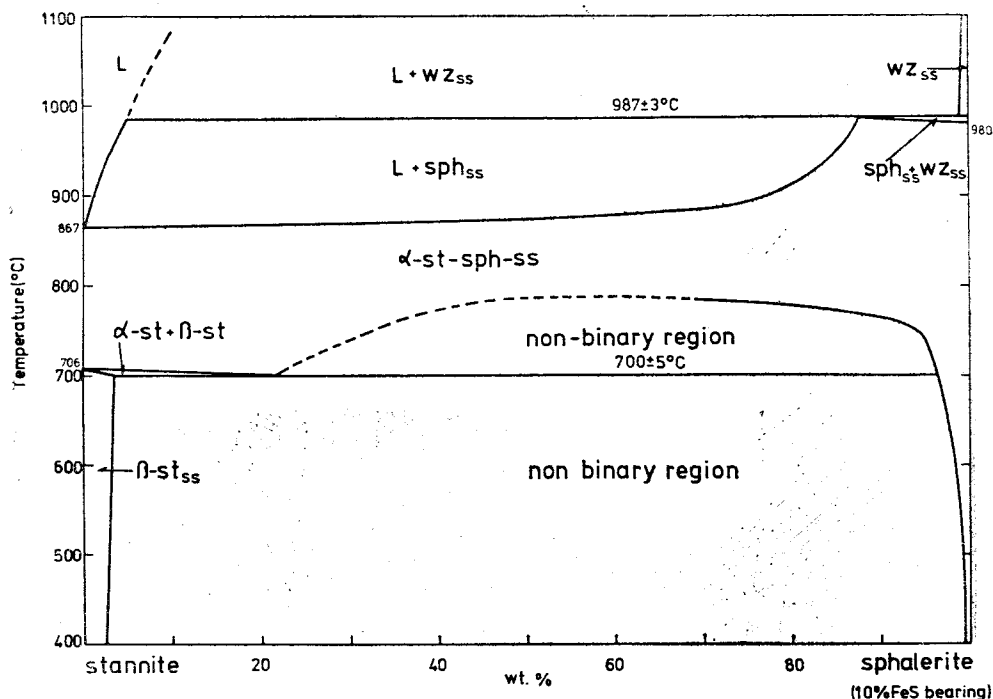

Fig. 9. The phase relations in the system stannite-sphalerite (sphalerite containing 10wt. % FeS) above 400°C. Vapor is present with all phases, and the pressure of the system is not constant. Two non-binary regions exist between stannite and sphalerite (10wt. % FeS).

are given in Table 3. β-stannite is stable up to $706\pm5°C$, where it inverts into high temperature α-stannite and melts congruently at $867\pm5°C$. Between two endmembers a complete α-stannite-sphalerite (10wt. % FeS) solid solution series exist from 780°C up to the solidus. Under the solvus two non-binary regions exist. The melting of α-stannite increases towards the sphalerite (10 wt. % FeS) side and reaches a peritectic at $987\pm3°C$. Here, sphalerite (10wt. % FeS) solid solution contains about 12.5 ± 1 wt. % stannite, whereas the wurtzite(10wt. % FeS) solid solution contain only 1 wt. % stannite in solid solution which decreases with increasing temperature, but was not determined above 1050°C. The upper and lower inversion points of the sphalerite/wurtzite (10wt. % FeS) are located between $980\pm4°C$ and $992\pm4°C$ respectively. The inversion point of α/β-stannite is decreased by sphalerite (10wt. % FeS) down to the eutectoid temperature $(700\pm5°C)$ with the composition of 22 ± 2wt. % sphalerite and 78 ± 2wt. % stannite (10wt. % FeS). At this temperature, β-stannite contains only 3.5 ± 1wt. %sphalerite (10wt. % FeS) in solid solution. Below the eutectoid temperature, there exists another non-binary region. With decreasing temperature the solid solutions of β-stannite and sphalerite will narrow on both sides of this non-binary region.

The observed phenomena are very similar to those in the system containing 5wt. % FeS in sphalerite solid solution. However, the α-stannite-sphalerite (10wt. % FeS) solid solution is less easily quenchable in the Zn-poor part (towards the stannite side) and produced more melt-phases in the Zn-rich part towards the sphalerite (10wt. % FeS) side resulting in an unclear solvus. Along the central part of the solvus, there is no apparent difference between the solid solution region and the upper non-binary region. The quenched solid solution showed two different phases which were very similar to the two phases in the upper non-binary regions. However, as already explained, this system is non-binary and its solvus is a surface within the ternary or quaternary system.

Description of Phases

The α-stannite-sphalerite (10wt. % FeS) solid solution shows very similar changes of properties to those in the α-stannite-sphalerite (5wt. % FeS) solid solution. However, sphalerite (10wt. % FeS) shows still apparent change from the sphalerite (5wt. % FeS).

Table a—Experimental results of the system stannite–sphalerite (sphalerite containing 10wt. % FeS as impurities; abbr. SS) ss=α–stannite–sphalerite solid solution

1) The solvus and eutectoid

wt. % (sph. SS)	T°C	time (days)	products)
20	700	30	one-phase (region)
23	701	30	non-binary (region)
25	701	30	non-binary (region)
30	733	15	non-binary (region) (?)
30	751	15	one-phase (region) (?)
40	751	15	non-binary (region)
40	768	15	non-binary (region)
40	813	6	one-phase (region) (?)
50	771	30	non-binary (region)
50	790	6	non-binary (region)
50	814	6	one-phase (region) (?)
60	783	6	non-binary (region)
60	792	6	non-binary (region) (?)
60	813	6	one-phase (region) (?)
70	768	14	non-binary (region)
70	783	14	non-binary (region)
70	790	6	one-phase+melt (tr)
80	751	14	non-binary (region)
80	773	14	non-binary (region)
90	730	14	non-binary (region)
90	740	14	non-binary (region)
90	751	14	one-phase (region)
95	722	30	non-binary (region)
95	740	14	non-binary (region)
96	722	30	one-phase (region)
97	722	30	one-phase (region)

2) The soildus and peritectic

wt. % (sph. SS)	T°C	time (days)	products
10	870	3	L+ss
20	872	3	L+ss
30	888	3	L+ss
50	870	3	ss
50	880	3	L+ss
50	890	3(hr)	L+ss
70	880	3	ss
70	887	3	L+ss
70	895	3(hr)	L+ss
80	913	3	ss
85	980	3	ss+L
87	980	3	ss+L
88	980	3	ss
89	980	3	ss

3) The solubility of stannite in wurtzite solid
   solution

wt. % (sph. SS)	T°C	time (days)	products
95	1040	3	L+wz ss
98	1020	3	wz+L
99	1020	3	wz+L

4) The solubility of sphalerite and wurtzite solid
   solution in liquid

wt. % (sph. SS)	T°C	time (days)	products
4	982	3	L
5	982	3	L+wz
7	982	3	L+wz

5) The solubility of β-stannite in sphalerite
   solid solution

wt. % (sph. SS)	T°C	time (days)	products
99	412	70	non-binary (region)
99	502	70	non-binary (region)
97	600	25	non-binary (region)
98	600	25	non-binary (region)
99	600	25	one-phase (region)
96	700	30	non-binary (region)
97	700	30	one-phase (region)

6) The solubility of sphalerite solid solution
   in β-stannite

wt. % (sph. SS)	T°C	time (days)	products
1	412	70	β-stannite
2	412	70	β-st
3	412	70	non-binary
1	498	50	β-st
2	498	50	β-st
3	498	50	non-binary
2	593	40	non-binary
3	593	40	non-binary
3	600	40	β-st

7) The sphalerite and wurtzite solid solution region
   (x-ray powder method)

wt. % (sph. SS)	T°C	time (hours)	products
95	952	24	sph ss
95	977	24	sph ss
95	984	24	sph s
95	990	24	wz ss

VII. THE EFFECT OF PRESSURE

The phase relations depend on the vapor pressure
conditions and vary in equilibrium with vapor.
Therefore, the phase relations should be studied
in relation with various pressure conditions, e. g.
confining and partial pressures.

The phase relations of the present study have
been determined only in the presence of vapor.
Strict application of the information derived is,
therefore, limited to occurrences in which vapor
occurred as a phase at the time of ore formation.
Since vapor may not always have been present at
the time of ore formation, the phase relations in
absence of vapor should also be considered.

Only very few experiments were carried out
with collapsible gold capsules under confining
pressure (5kb,) and its detailed study, is not a
part of the present study. However, the effects of
pressure will be investigated in future for the
application of the study system in nature.

According to the above experiments on the pure
system α/β-stannite inversion temperature is
lowered only to 675 10°C which is higher 6147°C

in the pure condensed system. Similarly to the condensed system a complete solid solution series exists between α-stannite and sphalerite at elevated temperature. The phase boundary curve can not determined precisely due to slow quenching, which requires 15 to almost 60 seconds from reaction temperature to room temperature in cold seal bombs(see Fig. 10)

VIII. DISCUSSION AND APPLICATION OF THE STUDY SYSTEM

On the basis of the experimental results of this study a possible geological temperature indicator will be discussed in relation to the investigations by Springer (1972) and Kullerud (1953).

The α/β-Stannite Inversion

Exsolution and inversion textures are very useful to understand ore-forming conditions. It is relatively common in stannite and was recognized early by Reinheimer, Schneimer, Schwartz, Lindgren and Crevelry. A systematic study of tin minerals relating to stannite was carried out by Ramdohr (1944) (all in: Ramdohr, 1969).

1. The pure stannite-sphalerite system

The inversion point of α/β-stannite is lowered with increasing amounts of sphalerite to a minimum of 614±7°C with 13wt. % ZnS in solid solution. This indicates that cubic stannite is a stable phase down to the temperature of about 600°C, where it is in equilibrium with sphalerite in this system (see Fig. 2). Cubic stannite was recognized as high-temperature form by Ramdohr (1944) with the name "Zinnkies? II'". He reported that the α/β transformation was shown by inversion twinning and exsolution phenomena and that the transformation occurred at about 600°C. Later, the name isostannite was proposed by Claringbull (1956) for the cubic stannite (Zinnkies? II) found at Cligga Head, Rerranporth, Cornwall, and he proved that isostannite is a high-temperature form by heating normal tetragonal stannite. Other exsolution textures were observed in ores from high-temperature ore deposits, e. g. Broken Hill (620°C) and Outukumpu (600°C). These observations are more or less in agreement with the experimental results of the study system. The eutectoid is only 14°C higher than the extrapolated inversion point (600°C) by Ramdohr (1944). But there is still some difficulty in applying the experimental results to nature, because these values are too high to explain the exsolution textures observed in ore specimens from low-temperature ore deposits.

2. The stannite-kesterite system

Ramdohr (1944) described with observed evidences that the inversion point of stannite (600°C) is improbably high, typical cubic exsolution textures occurring in complex stannite aggregates must have taken place above 250°C due to recrystallization of a pseudocubic lamellae intergrowth, and isostannite may be stable to room temperature owing to various impurities. Harris and Owen (1972) have found a good example of stannite exsolution in an ore from British Columbia. As a result of this discovery, Springer (1972) heated samples of this ore to 300°C and 350°C for 9 weeks. After treatment at 300°C, only the remains of the stannite exsolution were visible and after annealing at 350°C the samples appeared to be completely homogenized. This result is in good agreement with the phase diagram of the stannite-kesterite system (see Fig. 11) Most exsolution and inversion phenomena observed in natural stannite were supposed to occur at lower temperatures as in examples described above. Springer's proposed phase diagram may shed light upon some of them. However, the inversion points are obviously variable according to geological conditions of ore formation. And for an application of the experimental investigation to a certain stannite ore, it must be considered what is the important factor in ore deposits including stannite. Temperature and pressure, which are the most important parameters of ore formation,

can be controlled systematically 'in certain ranges in laboratories. Therefore, mineral associations and content of elements should be considered.

Springer's diagram shows that the inversion temperature of stannite decreases with increasing amounts of kesterite: approximately 565–600°C (10mol. % stannite and 90mol. % kesterite), 450–510°C (20mol. % stannite and 80mol. % kesterite) and 335–415°C (30ml. % stannite and 70 mol. % kesterite) (see Fig. 11). Therefore, if stannite is added by sphalerite solid solution of various amounts of kesterite, the α/β-stannite inversion temperature can be expected to decrease much lower than in the pure system.
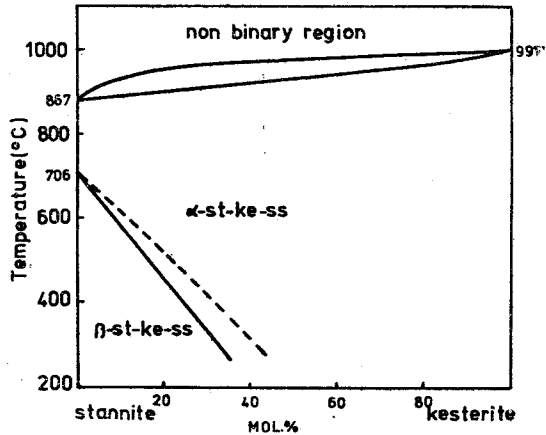
Fig. 11. Phase relations in the pseudobinary system stannite-kesterite (from Springep, 1972), with refined inversion and melting points.
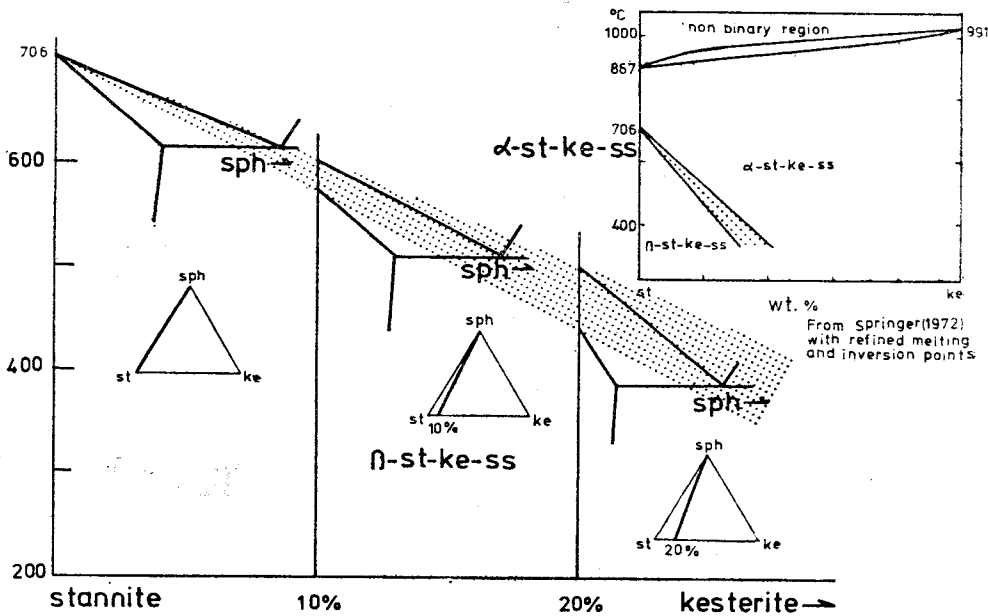
Fig. 12. Stannite-sphalerite system projected on the stannite-kesterite system. Left: stannite-sphalerite; middle: stannite-sphalerite (stannite containing 10wt. % kesterite); right: stannite-sphalerite (stannite containing 20. wt% kesterite)

3. Combination of the pure stannite-kesterite system and additional sphalerite

This can be simplified in a triangle diagram in which the compositional ratio is clearly expressed between stannite, kesterite and sphalerite. However, all triangle diagrams show only isothermal sections. Therefore, in order to understand the problem it is better to project the inversion of the stannite-sphalerite system (with its decreasing temperature of stability of α-stannite by taking sphalerite in solid solution) on the stannite-kesterite system described by Springer (1972).

The inversion point of stannite is 706±5°C at its stoichiometric high purity and lowered by 92°C.

by sphalerite. If similar decrease occurs to the stannite containing various amounts of kesterite in solid solution, the lowered values will be expected to decrease as low as they can be applicable to nature (Fig. 12). In nature, chalcopyrite is closely associated with mineral phases in the stannite kesterite system and will also decrease the inversion temperature. In addition to the associated minerals, certain metal elements were found to be an important factor in nature to decrease or increase the inversion temperatures by substitution of small amounts of Fe for Zn in the sphalerite formula (Zn, Fe) S was found not to decrease the inversion point.

The Sphalerite/Wurtzite Inversion

1. The FeS-ZnS system

This system was investigated by Kullerud (1953) to study its possibility as a geothermometer. According to the results, the inversion point of sphalerite/wurtzite decreases with increasing amounts of FeS from 1020±5°C to 992±4°C till 980±4°C (10wt. % FeS), 958±4°C til 945±4°C

(20. wt. % FeS) 925±4°C till 913±4°C (30wt. % FeS) and 894±3°C (36.5wt. % FeS). He described the possibility that the temperature interval of inversion is rather narrow (maximum 13°C) (see Fig. 7).

2. The pure stannite-sphalerite system

The pure system in the study shows that the inversion point of sphalerite/wurtzite increases with increasing amounts of stannite up to 1074± 3°C.

3. Combination of the pure stannite-sphalerite system and additional FeS in sphalerite solid solution

The peritectic temperature which is the highest transformation temperature of sphalerite/wurtzite was decreased from 1074±3°C to 1036±3°C and 987±3°C by taking sphalerite solid solution of 5 and 10wt. % FeS as an endmember. This may indicate that the peritectic temperature will decrease continuously to certain limits with increasing amounts of FeS (Fig. 13). Various transformation
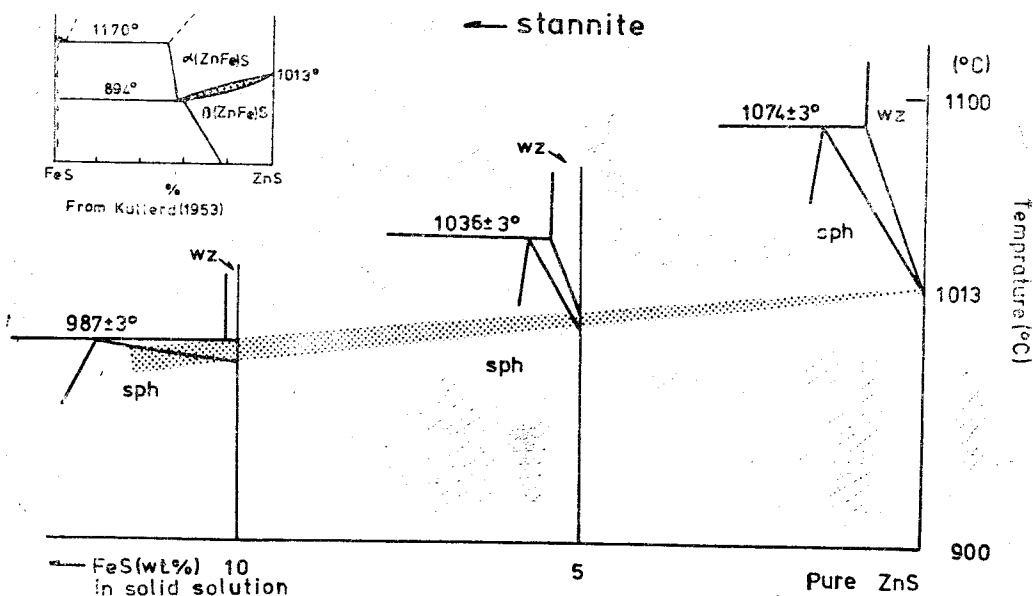

Fig. 13. Stannite-sphalerite system projected on the FeS-ZnS system. Right: stannite-sphalerite: middle: stannite sphalerite (sphalerite containing 5wt. % FeS): left: stannite-sphalerite (sphalerite containing 10wt. % FeS).

temperatures of natural sphalerite/wurtzite may be partly explained in the light of this experimental results. In general, reversible transformation sphalerite wurtzite is supposed to take place at 800 (Fe-rich) up to 1020°C, and Ehrenberg (1931) found that Fe-rich wurtzite remained in Fe-poor sphalerite in nature. Therefore, this indicated a possibility to decrease the transformation point by adding Fe-content to the pure system and to explain one of the reasons why the transformation takes place in wide intervals of temperature.

Also other impurities may cause the decrease of the inversion temperature e.g. Mn (Skinner, 1959), Cd, etc.

Mineral Associations

This study system is not applicable to the initial ore-forming conditions of the hydrothermal ore deposits, but it may be used to shed on other types of ore deposits. In nature, stannite is found in many types of sulfide ore deposits in close association with sphalerite, chalcopyrite, kesterite, pyrite, etc. The sphalerite which occurs in high-tempreature ore deposits in equilibrium with pyrrhotite contains larger amounts of Fe in solid solution.

If a stannite-sphalerite solid solution is cooled very slowly to the two-phase (α-stannite+sphalerite) region, a separation of an iron-rich and a zinc-rich phase can be expected. The compositional and optical difference between the separated phases will be greater with decreasing temperature. This explains the genetic association of both minerals and rich Fe-contents in sphalerite of high-temperature ore deposits.

All experiments were carried out in the presence of vapor. Because of high rock pressure P total >Ps and complexity in ore forming conditions in nature, it is improbable that the natural minerals formed under the same conditions attained in the laboratory. Therefore, the data obtained in this experimental investigation may be not directly

applicable to the determination of conditions under which stannite-sphalerite minerals formed. However, the experimental data may be used for better understanding of the ore-forming conditions.

It may be concluded that the inversion and exsolution temperatures vary according to the geological conditions of ore formation, in which pressure and mineral associations and impurities always take part.

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黃錫石—閃亞鉛石系의 實驗研究와 天然鑛物에의 活用

李　　　在　　　英

　자연계의 硫化鑛物 産出狀態를 보면 Stannite는 Chalcopyrite나 Sphalerite등의 硫化鑛物과 隨伴이 잘 되며 Kesterite와는 넓은 범위에걸친 固溶體를 형성한다. 따라서 이러한 隨伴現象에 따르는 地質學的 관계가 鑛床生成條

件, 特히 그 溫度에 대한 指示物로서 활용가능성이 인정되고 있다. 그러나 자연계의 鑛物隨伴 및 共生關係의 연구자료는 극히 제한되어있으므로 鑛床生成에 대한 物理化學的 條件의 究明은 현대식 장비로 조직적인 실험을 통해서만 가능하다.

본연구에서는 鑛床生成의 온도를 변수로 택하고 순수한 Stannite-Sphalerite系에 대한 相平衡關係를 구명하고 이系에미치는 不純物(자연계에서 가장 흔히 隱伴되는 FeS)과 壓力(5kb)의 영향에대한 실험을 실시하였다. 먼저 두 始作物質(Stannite와 Sphaleite)을 合成하고 이들의 一定한 重量比의 혼합을 石英管속에 넣어 진공밀폐하고 이 것을 實驗試料로서 400°C에서부터 용융온도까지 일정온도로 유지시킨 Horirgontal Furnace에서 加熱反應시켰다. 대부분의 家驗試料는 加熱反應을 촉진시키기위하여 再混合하였다. 平衡에 도달된 實驗試料는 急冷하여 ore-micr-oscope, X-ray diffractometer 및 DTA로 相平衡關係를 검토하였다.

1. 순수한 Stannite-Sphalerite系; Stannite의 結晶은 온도가 상승하면 706±5°C에서 正方型(β-stannite)에서 第軸型(α-stannite)으로 變移하고 867±5°C에서 용융한다. Sphalerite는 온도가 상승하면 等軸型(β-ZnS)에서 六方型(α-ZnS)인 wurtzite로 變移한다. 上記 兩變移는 互變(enantiotropy)이다. 본계는 兩鑛物의 共存區域의임계온도인 약 870±5°C에서 solidus temperature까지 完全固溶體를 형성하며 온도가 더욱 상승하면 固溶體는 용융하기 시작한다. α-stannite는 sphalerite의 함량이 증가할수록 용융온도가 상승하여 stannite 9wt.% sphalerite 91wt%에서 최고, 1074±3°C (peritectic)에 도달한다. 이 온도에서 wurtzite는 α-stannite를 5%만 함유하고 그 함량이 감소되면 용융온도는 상승한다. stannite의 變移溫度는 용융온도와는 반대로 sphalerite의 함량이 固溶體중에서 증가할수록 하강하여 α-stannite 87wt.%, sphalerite 13wt.%에서 614±5°C (eutectoid)로 하강한다. 이 온도에서 β-stannite는 sphalerite를 10% 함유한다. 온도가 계속 하강하면 β-stannite와 sphalerite의 상호(固溶量)은 각각 감소하기 시작한다.

2. 불순물 (FeS)의 영향; 순수한 系의 eutectoid temperature는 FeS가 5%, 10%로 증가함에따라 614±7°C에서 695±5°C, 700±5°C로 상승하고 peritectic temperature는 1074±3°C에서 1036±3°C, 987±3°C로 하강한다. 그리고 순수한 系의 upper binary region(α-stannite+sphalerite)이 non-binary region으로 점차로 변화한다.

3. 순수한 系에대한 壓力 (5kb)의 영향. stannite는 condensed system에서 sphalerite의 함량증가로인하여 變移溫度가 614±5°C까지 하강하나 onfining pressure(5kb)下에서는 이보다 약 600°C 더 높은 675±10°C까지 밖에 하강하지 않는다. 그리고 β-stannite의 sphalerite 固溶量도 eutectoid temperature에서는 condensed system의 경우와 비슷하나 온도가 하강하면 현저한 감소를 보이고 sphalerite에서의 stannite의 固溶量의 극히 적다. 完全固溶體가 stannite와 sphalerte사이에 존재하는 반면 upper binary region의 온도범위가 좁아진다.
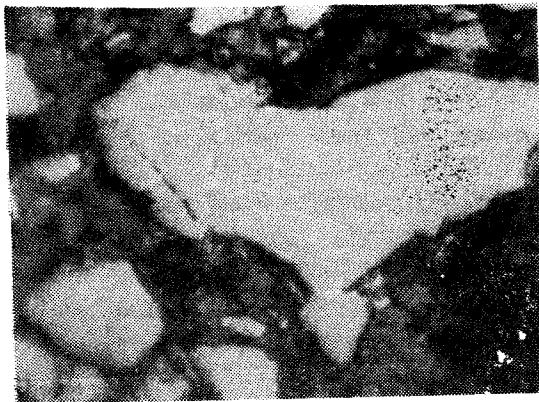
Fig. 3a Exsolved stannite (fine lamellae) in "sphalerite" on quenching at ca. 852°C with the average composition of 52.5wt.% sphalerite and 47.5wt.% stannite. The material, of course, is a stannite-sphalerite solid solution. Section approximately (111). Oil immersion, 650x.
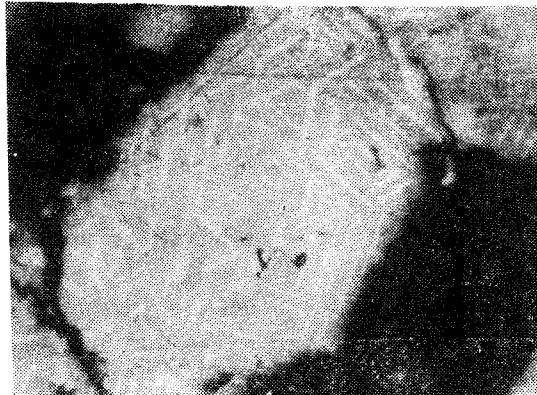
Fig. 3b. Exsolved stanntie (lamellae) in "sphalerite" on quenching at ca. 830°C with the average composition of 45wt.% sphalerite and 55 wt.% stannite. The matrix is a stannite-sphalerite solid solution. Section approximately ll (001). The lamellae cube. Oil immersion, 650x.
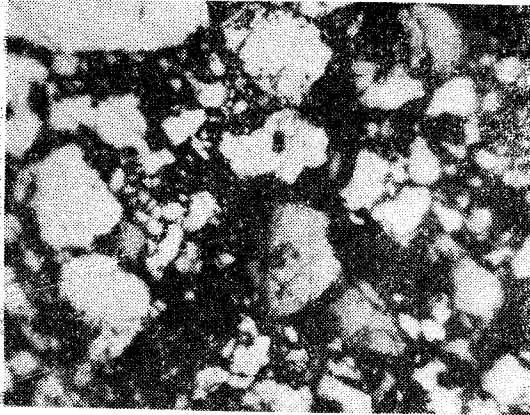
Fig. 4. Exsolved stannite (white) and sphalerite (grey) in one another on quenching at ca. 600°C with the average composition of 30 wt. % sphalerite and 70wt. % stannite. Oil immersion, 650x.
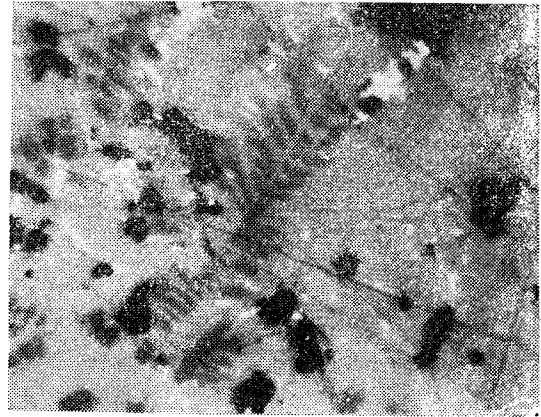

Fig. 5 Crystallized wurtzite (dark grey), quenched at ca. 1200°C with the average composition of 15wt. % sphalerite and 85wt. % stannite. Oil immersion, 650x.
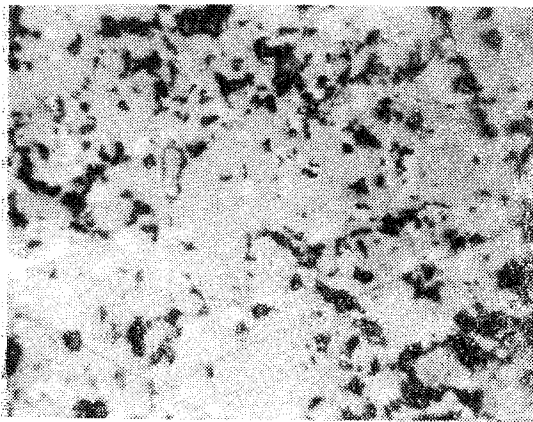

Fig. 8. Chalcopyrite coexisting with the stannite-kesterite solid solution which contains fine-grained chalcopyrite. Quenched at ca. 650°C. Oil immersion, 650x.