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A REINVESTIGATION OF THE STANNITE (Cu_2FeSnS_4) – KESTERITE (Cu_2ZnSnS_4) PSEUDOBINARY SYSTEM

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ABSTRACT

The pseudobinary system stannite (Cu_2FeSnS_4) – kesterite (Cu_2ZnSnS_4) was investigated in the temperature range from 500 to 800°C using synthetic starting materials and molten NaCl–KCl eutectic fluxes in evacuated, sealed silica tubes. A solvus separating stannite and ferrokesterite–kesterite intersects the liquidus, indicating that no solid solution [β-$Cu_2(Fe,Zn)SnS_4$] extends entirely across the system. An inflection in the boundaries of the miscibility gap implies that an unquenchable high-temperature phase, presumably cubic $Cu_2(Fe,Zn)SnS_4$, exists. Below the inflection at *ca.* 700°C, the two-phase region slopes toward the iron end-member composition. Thus, exsolution lamellae of ferrokesterite–kesterite in stannite should exist, and the compositions of coexisting stannite and ferrokesterite–kesterite define a temperature. The phase α-$Cu_2(Fe,Zn)SnS_4$ is shown not to be a pseudobinary phase, and although encountered in this study, it is not likely an equilibrium reaction-product. The experimentally determined subsolidus phase-boundaries do not correspond well to those implied by natural assemblages. The reasons for the lack of agreement are unclear, but at present, a stannite–kesterite geothermometer cannot be considered to be experimentally calibrated.

Keywords: phase relations, stannite, kesterite, ferrokesterite, geothermometer.

SOMMAIRE

Le système pseudobinaire stannite (Cu_2FeSnS_4) – kesterite (Cu_2ZnSnS_4) a fait l'objet d'une étude entre 500 et 800°C de matériaux synthétiques placés dans un bain NaCl–KCl eutectique dans des contenants de silice scellés et évacués. Un solvus entre stannite et ferrokesterite–kesterite recoupe le liquidus, ce qui indique l'absence d'une solution solide continue β-$Cu_2(Fe,Zn)SnS_4$. Une inflection des limites de la lacune de miscibilité serait due à une phase de haute température non-trempable, probablement la forme cubique de $Cu_2(Fe,Zn)SnS_4$. En dessous de l'inflection, à 700°C environ, le champ de stabilité de deux phases coexistantes tend vers le pôle ferrifère. Des lamelles d'exsolution de ferrokesterite–kesterite seraient donc possibles dans la stannite, et la composition des deux phases définirait donc une température. La phase α-$Cu_2(Fe,Zn)SnS_4$ n'est pas pseudobinaire; quoiqu'elle apparaît ici, elle serait un produit métastable. Les champs de stabilité subsolidus indiqués par les expériences ne correspondent pas très bien avec ceux qui sont déduits des assemblages naturels, pour des raisons qui ne sont pas claires. Le géothermomètre fondé sur l'equilibre stannite–kesterite n'est donc toujours pas calibré.

(Traduit par la Rédaction)

Mots-clés: relations de phases, stannite, kesterite, ferrokesterite, géothermomètre.

INTRODUCTION

Phase relations along the pseudobinary join Cu_2FeSnS_4–Cu_2ZnSnS_4 are of interest in relation to the occurrence of stannite and kesterite, the mineralogical counterparts of the end members. Intergrowths of the two minerals exhibit textures suggestive of exsolution (*e.g.*, Harris & Owens 1972), and Springer (1972) proposed that such relationships could serve as a geothermometer.

Moh (1960) reported, without further details, that a complete solid-solution characterizes the system. He later indicated that the solid solution is complete above 700°C (Moh 1975). Franz (1971) reported on syntheses of various structural modifications of the iron end-member. In a study on the system stannite–sphalerite, Bernhardt (1972) inferred that transformation from cubic to tetragonal symmetry in stannite occurs at 706°C, as indicated by DTA experiments, a result confirmed in a high-temperature X-ray-diffraction study by Bente (1974).

The only complete study of the join Cu_2FeSnS_4–Cu_2ZnSnS_4 was attempted by Springer (1972), who employed dry syntheses and molten halide flux experiments in sealed, evacuated silica tubes, as well as DTA experiments. Although both end-members melted congruently, he found that intermediate members melted incongruently to products that depart from binary compositions. At high temperatures, he found that a complete solid-solution extends across the system as a phase he called β-$Cu_2(Fe,Zn)SnS_4$. At 680°C, he found the iron end-member to invert to a different structure, α-$Cu_2(Fe,Zn)SnS_4$. From this temperature a two-phase loop opens with decreasing temperature and increasing zinc content. Moh (1975) accepted Springer's work but offered some modifications. He equated Springer's 680°C α–β transition to the 706° transition of Bernhardt and suggested that the high-temperature form should be designated as α-$Cu_2(Fe,Zn)SnS_4$, and the low-temperature form, as β-$Cu_2(Fe,Zn)SnS_4$.

Work on the system was begun anew because of the obvious disagreement between the α-$Cu_2(Fe,Zn)SnS_4$ form [or the β-form of Moh 1975] and the structure of natural stannite. Also, Kissin & Owens (1979) reported the synthesis of end-member stannite and kesterite at 800°C in molten halide fluxes, a result in disagreement with previous results. Finally, some of Springer's original experimental products preserved in polished section could be re-examined; in addition, nearly all of the Guinier camera films of his run products are on file at CANMET. Re-examination of these revealed some problems of interpretation of results, which are discussed below.

EXPERIMENTAL

Starting materials were synthesized in two steps from elements certified by the manufacturer as 99.999% pure. As a first step, CuS, FeS, ZnS and SnS were synthesized in evacuated silica tubes by standard methods. These components were then mixed in proportions appropriate to the iron and zinc end-members and reacted in evacuated silica tubes at 800°C for periods of up to two weeks. Microscopic examination of the products indicated that equilibrium had not been achieved. The products were reground and reacted in a NaCl–KCl flux at 800°C for 4 days. Homogeneous Cu_2FeSnS_4 and Cu_2ZnSnS_4 were obtained as the products of this procedure. Subsequently, intermediate members on the join were synthesized at intervals of 10 at.% from mixtures of the end members by reacting them in a molten halide flux at 800°C for four days. This procedure resulted in products consisting of stannite, kesterite, or both, which are believed to be at equilibrium.

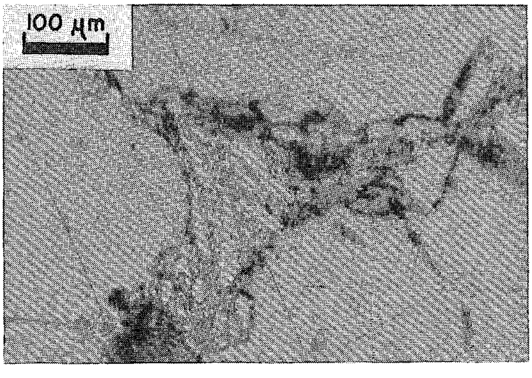

FIG. 1. Photomicrograph of the products of the 50 mole % Cu_2ZnSnS_4 experiment at 800°C, illustrating the presence of a melt phase in synthetic kesterite + stannite mixture.

The materials synthesized at 800°C were used as starting materials for experiments at 700, 600 and 500 ± 2°C. The experiments lasted four days at 600 and 700°C, and eight days at 500°C. In all cases, molten halide fluxes were employed. The products were X-rayed with Co*K*α radiation using a Guinier camera with NaCl as an internal standard. The run products at 800°C also were X-rayed in a Gandolfi camera using Co*K*α radiation. Cell parameters were refined using the PARAM program of Stewart *et al.* (1972).

Electron-microprobe analyses of Springer's (1972) products and natural specimens were carried out on an MAC Model 400 electron-probe microanalyzer at CANMET operated at 25 kV and a specimen current of 0.028 μA. Data were reduced by means of the EMPADR program of Rucklidge & Gasparrini (1969). The products of this study were analyzed on an ETEC Autoprobe at the University of Toronto, operated at 20 kV and a beam current of 75 nA. Data were reduced by means of the PESTRIP program, a University of Toronto modification of Statham's (1976) peak-stripping procedure. The Cu*K*α,Fe*K*α, Sn*L*α and S*K*α lines of a Cu_2FeSnS_4 standard were used for Cu, Fe, Sn and S, and the Zn*K*α line of a synthetic Cu_2ZnSnS_4 standard was used to determine Zn in both cases.

RESULTS

Although a total of 32 experiments were made in the course of this study, a few did not yield interpretable results. As illustrated in Figure 1, a melt phase was encountered at 800°C with most of the bulk compositions having 40 mole % Cu_2ZnSnS_4 or greater. As the materials synthesized at 800°C were used as starting materials for lower-temperature experiments, the melt phase that formed in some of these did not re-equilibrate in some of the lower-temperature experiments, with the result that the bulk compositions of the starting materials were altered.

The overall phase-relationships are illustrated in Figure 2. The results are apparently strikingly different from those of Springer (1972); however, these differences are more apparent than real. As noted above, melt was encountered in experiments containing between 40 and 90 mole % Cu_2ZnSnS_4 at 800°C. This relationship is fitted by the very flat solidus loop. A two-phase region separating stannite containing about 20 mole % Cu_2ZnSnS_4 and ferrokesterite containing about 50 mole % Cu_2ZnSnS_4 is evident at 800°C. This two-phase region narrows at 700°C and displays a sharp inflection at about this temperature. This inflection

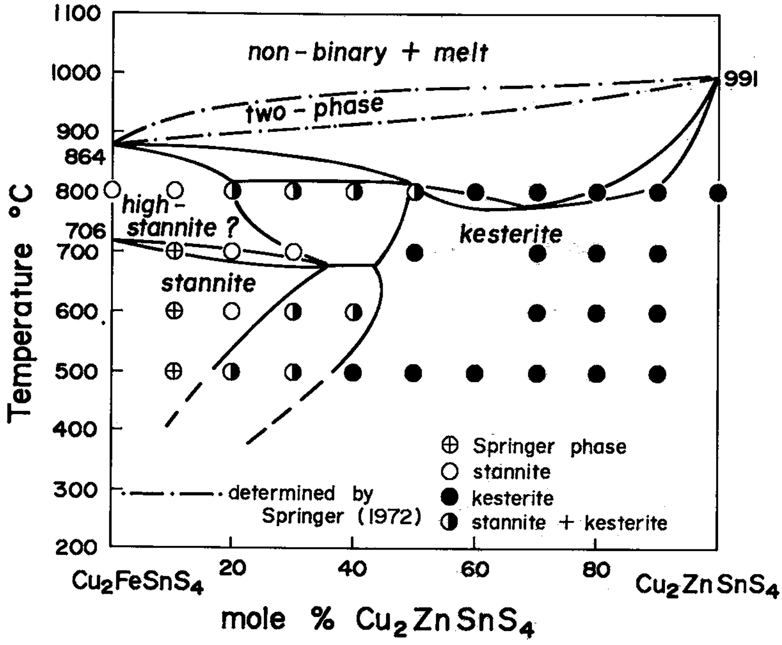

FIG. 2. Phase relations in the pseudobinary system Cu_2FeSnS_4–Cu_2ZnSnS_4, as determined in this study. Experimental points for 60 mole % Cu_2ZnSnS_4 at 700 and 600°C and 40 mole % Cu_2ZnSnS_4 at 700°C are missing owing to the presence of unreacted melt phase in starting material. Insufficient product for analysis was obtained at 600°C for 50 mole % Cu_2ZnSnS_4.

appears to be the result of a phase change in the stannite solid-solution.

The nature of the miscibility gap between stannite and kesterite at 800°C was further investigated by cell-parameter refinements based on Gandolfi camera data for the experimental products (Fig. 3). The parameters of products containing stannite were determined based on a tetragonal cell and plotted in terms of 2*a* and *c* *versus* composition of the (Fe,Zn) site. Parameters of products containing kesterite were obtained based on a pseudocubic cell, as resolution of *a* and *c* was not obtained, as evidenced by the superimpositions of reflections such as 020–004, 220–024, *etc.* The trend of cell parameter *versus* composition of the (Fe,Zn) site in natural stannite and kesterite is indicated by lines on the diagram. Meaningful data were not obtainable for the starting compositions 40 and 50 mole % Cu_2ZnSnS_4 owing to interferences by melt phases. At 10 mole % Cu_2ZnSnS_4, Guinier – de Wolff films show the presence of stannite only, but a stannite pattern could not be obtained on the Gandolfi camera, perhaps because of the small grain-size of the experimental product.

The cell parameter for the synthetic kesterite phase at 800°C differs little from the trend established for natural specimens by Kissin & Owens (1989). The cell parameters of synthetic stannite at 20 mole % Cu_2ZnSnS_4 and the synthetic kesterite at 30 mole % Cu_2ZnSnS_4 show a slight tendency for convergence, in comparison to the trend established by Kissin & Owens (1979). However, both products contain mixtures, and the small tendency toward convergence seems to be most likely attributable to a shift of the center of peaks due to mixtures of the two phases.

No phase change was observed in quenched stannite synthesized above the inferred two-phase loop, extending from 706°C at the Cu_2FeSnS_4 end-member to about 30 mole % Cu_2ZnSnS_4 at a somewhat lower temperature. However, the change to a cubic structure, inferred from DTA experiments by Bernhardt (1972) and observed in high-temperature X-ray studies by Bente (1974), implies that an unquenchable high-temperature cubic phase was present above the inferred two-phase loop.

Below about 700°C, a two-phase region separates iron-rich stannite from ferrokesterite. The slope of the limbs of the solvus indicates that the formation

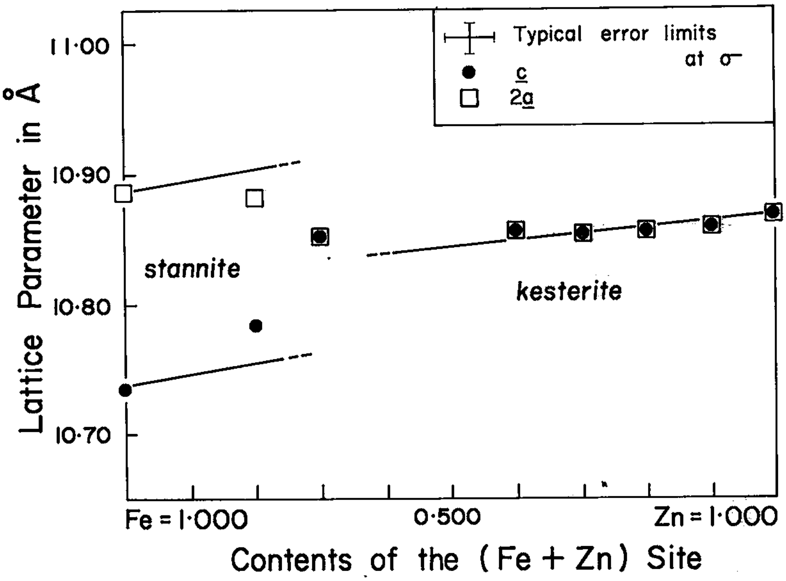

FIG. 3. The presence of a miscibility gap between stannite and kesterite at 800°C, demonstrated by a plot of cell parameter *versus* composition of the (Fe + Zn) site. Points are missing at 10 mole % Cu_2ZnSnS_4 owing to poor results and at 40 and 50 mole % Cu_2ZnSnS_4 owing to interferences from the presence of additional phases in the melt. Lines indicate trends for cell parameters of natural specimens according to Kissin & Owens (1979).

of exsolution lamellae of ferrokesterite within a stannite host is to be anticipated if stannite is cooled into the two-phase region. According to the phase diagram, stannite may be considered to be the high-temperature polymorph of ferrokesterite.

Finally, in experiments containing 10 mole % Cu_2ZnSnS_4, stannite was not formed at 700, 600 and 500°C, but a phase corresponding to that called α-$Cu_2(Fe,Zn)SnS_4$ by Springer (1972) appeared. For reasons to be elaborated on later, the designation "Springer phase" is employed in this study. The Springer phase does not lie along the Cu_2FeSnS_4-Cu_2ZnSnS_4 pseudobinary join and does not have the X-ray-diffraction pattern of stannite, as discussed below. Its occurrence appears to signify a departure from equilibrium pseudobinary behavior that at present cannot be adequately explained.

COMPARISON WITH THE RESULTS OF PREVIOUS STUDIES

The major differences between the results of the present study and those of Springer (1972), as well as those of earlier investigators, merit some attention, especially as it was possible to examine most of Springer's original materials. At the outset, it must be borne in mind that it was subsequent to Springer's (1972) work that the structural difference between stannite and kesterite was demonstrated (Hall *et al.* 1978), and the mineralogical bases for distinguishing the two minerals were clearly established (Kissin & Owens 1979). Springer distinguished α- and β-$Cu_2(Fe,Zn)SnS_4$ on the basis of the apparent extinction of the 011, 013, 121, 123 and 031 reflections in α-$Cu_2(Fe,Zn)SnS_4$, and inferred that the latter was equivalent to stannite, in spite of the unexplained difference in structure.

Re-examination of Springer's film records confirms the phase diagram that he presented, based on his criteria for the differentiation of the two phases. Figure 4 reproduces Springer's phase diagram, with annotations incorporating the results of the present re-examination. Firstly, the occurrence of the α-$Cu_2(Fe,Zn)SnS_4$ phase, here renamed the Springer phase, does indeed correspond to the field of α-$Cu_2(Fe,Zn)SnS_4$ determined by Springer, with only minor discrepancies. The presence of a two-phase loop separating the fields of α- and β-$Cu_2(Fe,Zn)SnS_4$ in Springer's diagram is not supported by examination of his experimental products, a point conceded by Springer himself. The field of β-$Cu_2(Fe,Zn)SnS_4$ contains stannite in iron-rich portions of the diagram and kesterite in zinc-rich portions, which clearly indicates that no solid solution extends across the diagram. In fact, boundaries separating stannite and kesterite in Springer's experi-

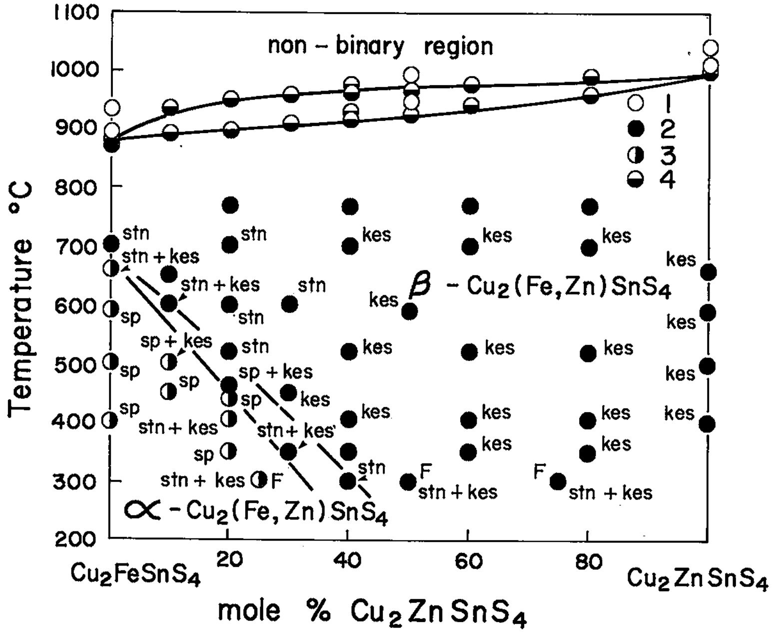

FIG. 4. Springer's (1972) phase diagram for the pseudobinary system Cu_2FeSnS_4–Cu_2ZnSnS_4, incorporating the results of the re-examination of most of his products and Guinier films. Springer's designations: 1 melt, 2 β–$Cu_2(Fe,Zn)SnS_4$, 3 α–$Cu_2(Fe,Zn)SnS_4$, 4 endothermic DTA peaks. Phase boundaries shown are those of Springer. Symbols: stn stannite, kes kesterite, and sp Springer phase.

ments would closely resemble those determined in the present work (*cf.* Fig. 2). A major exception lies in the experiments at 300°C, in which stannite + kesterite coexist across the entire join. Such a result is unlikely to be representative of equilibrium. The structures could be clearly distinguished on the basis of the occurrence of doublets or single reflections for X-ray reflections of the type 020–004, 220–024, *etc.* Doublets indicate $2a$ greater than c by 0.19 Å in stannite, whereas single reflections indicate $2a$ approximately equal to c in kesterite, as elaborated by Kissin & Owens (1979).

Results of electron-microprobe analyses of six of Springer's products are presented in Table 1. The series of experiments labeled PSX 7 and PSX 17 were carried out at 500 and 592°C, respectively, whereas the numbers 20, 21 and 22 refer to Cu_2FeSnS_4, Cu_2ZnSnS_4 and $Cu_2(Fe_{0.5}Zn_{0.5})SnS_4$ starting compositions, respectively. It is evident that the Cu_2ZnSnS_4 and $Cu_2(Fe_{0.5}Zn_{0.5})SnS_4$ compositions produced kesterite, as is seen also from the annotated phase-diagram (Fig. 4). However, the Cu_2FeSnS_4 compositions yielded phases with the structural formula $Cu_{2+x}Fe_{1-x}SnS_4$ or, in more general terms, $(Cu,Fe)_3SnS_4$, indicating that the Springer phase is not a polymorph of $Cu_2(Fe,Zn)SnS_4$ but, in fact, lies off the pseudobinary join. The Springer phase is not equivalent to kuramite, which is reported to possess the structure of stannite (Kovalenker *et al.* 1979).

The X-ray pattern of the Springer phase contains many extinctions of hkl reflections having $l = 2n + 1$. However, the extinction rule does not apply, as other reflections of the same type, *e.g.* 033, are present. However, if tetragonal symmetry is assumed, permitted reflections retain the rule $h + k + l = 2n$, indicating a body-centered cell. The space group would then be of the form $I\bar{4}$**. However, precise designation of the space group would require single-crystal X-ray studies.

The Springer phase, as shown above, departs from the pseudobinary join Cu_2FeSnS_4–Cu_2ZnSnS_4. It appears to form as a result of lack of equilibration of the pseudobinary compositions. In my experiments, I was unable to attain equilibrium in dry silica-tube experiments even at 800°C, although Springer (1972) appears to have been more successful at the highest temperatures in iron-rich materials and down to as low as 350°C in zinc-rich materials. However, it seems that at 680°C and lower, his iron-rich compositions failed to reach equilibrium.

Franz (1971) reported syntheses of cubic

TABLE 1. CHEMICAL COMPOSITION OF SELECTED PRODUCTS OF SPRINGER'S EXPERIMENTS (1972)

							atomic proportions				
Sample	Cu	Fe	Zn	Sn	S	Total	Cu	Fe	Zn	Sn	S
PSX-20 500°C	30.51	11.98	-	27.60	29.98	100.10	2.06	0.92	-	1.00	4.02
PSX7-21 500°C	29.26	-	14.36	27.36	29.00	99.98	2.03	-	0.97	1.02	3.98
PSX7-22 500°C	29.24	6.96	7.03	27.59	29.58	100.40	1.99	0.54	0.47	1.00	4.00
PSX17-20 592°C	30.50	11.89	-	27.72	29.69	99.80	2.07	0.92	-	1.01	4.00
PSX 17-21 592°C	29.35	-	14.42	27.16	29.25	100.18	2.03	-	0.97	1.00	4.00
PSX 17-22 592°C	28.90	7.10	7.63	26.66	29.75	100.04	1.97	0.55	0.51	0.97	4.01

Concentrations reported in wt. %. Atomic proportions are based on eight atoms.

Cu_2FeSnS_4 and tetragonal Cu_2FeSnS_4 with the chalcopyrite structure. Re-examination of his results in the light of the results of Kissin & Owens (1989) and the present study gives rise to quite a different interpretation. The X-ray powder pattern of the cubic phase was indexed on a 10.88 Å cell by Franz. Kissin & Owens (1979) noted that kesterite can be indexed on a cubic cell of the same size. The discovery of ferrokesterite (Kissin & Owens 1989) and the establishment of a solid solution with the kesterite structure at high temperatures (Moh 1960, Springer 1972, this study) lead to the inference that Franz synthesized end-member ferrokesterite. Single-crystal X-ray studies of Franz's material are necessary to resolve the question.

The "tetragonal phase with chalcopyrite structure" synthesized by Franz (1971) does not have that structure according to his data, as it contains the 002 reflection, forbidden in the space group of chalcopyrite ($I\bar{4}2d$; Hall & Stewart 1973). Comparison of the patterns of the Springer phase and the "tetragonal phase" reveals that they are very likely of the same material. The extra reflections reported by Franz are clearly those of SnS, and Wang (1982) indicated that other weak doublets attributed by Franz to an admixture of the cubic phase are in fact due to splitting of some reflections, notably 002. Similar splitting was observed in patterns of the Springer phase, indicating that its true symmetry is very likely lower than tetragonal.

Pietzsch & Fritzsch (1984) studied a phase synthesized at 440°C using Mössbauer spectroscopy, X-ray diffraction and density measurements. On the basis of the last technique, they concluded that the formula of the phase is $Cu_2FeSnS_{3.95}$, based on a kesterite structure ($I\bar{4}$). The density experiments are not highly convincing, given the presence of some unexplained discrepancies and the failure to consider some model structures that are also possibilities. As well, although the space group $I\bar{4}$ is given by Pietzsch & Fritzsch, many possible reflections of the type *hkl* with $l = 2n+1$ are absent, although 013, 035, 039, 251 and 631 are observed. It seems more likely that they synthesized the Springer phase, as it would be anticipated at 440°C based on the results of Springer (1972) and this study.

The complete characterization of the Springer phase requires single-crystal X-ray work, as powder-diffraction studies have so far been based on the possibly incorrect assumption that its structure is that of stannite or kesterite. The mineralogical significance of the Springer phase also is unclear, although it may be related to kuramite. More study is required in order to resolve these questions.

The Springer phase, as indicated previously, does not lie on the pseudobinary join and does not correspond to any known stannite kindred nor does it bear on the high-temperature phase relations of stannite. However, in view of the discovery of petrukite (Kissin & Owens 1989), which lies off the pseudobinary join, the possible significance of the phase may be in an as yet undiscovered stannite kindred.

The existence of the sharp discontinuity in the plot of cell parameter *versus* composition of the (Fe,Zn) site in stannite and kesterite, as noted by Kissin & Owens (1979) for natural specimens and from this study in the synthetic system at 800°C, has been disputed by Corazza *et al.* (1986) and Bernardini *et al.* (in press). Corazza *et al.* reported that $2a$ and c converge with increasing Zn-content in a study of a suite of natural specimens. However, the cell parameters of seven of eight stannite specimens lie on the trends established by Kissin & Owens (1979). The apparent convergence is highly dependent on the eighth specimen from Cligga Head, Cornwall. Kissin & Owens (1989) found that stannite and kesterite or ferrokesterite are intimately intergrown in complex textures in specimens from this locality and that study of very small, carefully selected grains with the Gandolfi camera is necessary in order to obtain an accurate X-ray-diffraction record. As Corazza *et al.* (1986) employed a diffractometer, requiring a larger amount of sample, their result is consistent with that obtainable from a stannite–kesterite mixture. However, this possibility is detectable and can be distinguished if solitary reflections such as 002, 011, 112 and 121 are doubled or broadened.

Bernardini *et al.* (in press) obtained a similar result for a series of compositions synthesized at 750°C. Convergence of 2*a* and *c* occurs at about 60 mole % Cu_2ZnSnS_4 in their study. According to my results, stannite and kesterite coexist between 20 and 50 mole % Cu_2ZnSnS_4 at 750°C. Therefore, the apparent convergence reported by them is explicable as the result of a mixture of stannite and kesterite. In both the Italian studies, however, the authors have given 2*a* and *c* of kesterite, showing a slight divergence of the two parameters. However, reflections such as 020–004 and 220–024 are not resolved, indicating that 2*a* and *c* cannot be distinguished, at least in the low range of diffraction angles they employed. The divergence of 2*a* and *c* in kesterite samples is therefore an artifact of the method of calculation. Mössbauer spectra obtained by Bernardini *et al.* (in press), apparently at 25°C, are not conclusive.

TABLE 2. COMPOSITIONS OF INTERGROWN STANNITE AND KESTERITE

Snowflake mine and Stannex prospect, near Revelstoke, British Columbia, Canada		
UT 218 (Kissin & Owens 1979)		
kesterite host:	Fe35	Zn65
stannite lamellae:	Fe63	Zn37
Stannex (Harris & Owens 1972; reanalyzed)		
kesterite host:	Fe33	Zn67
stannite lamellae:	Fe64	Zn36
Snowflake mine (UT)		
kesterite host:	Fe33	Zn67
not possible to analyze stannite lamellae.	-	-
Cligga mine, Perranzabuloe, Cornwall, England		
GSC 14147 (Kissin & Owens 1989)		
section B, area 1		
stannite host:	Fe62	Zn38
kesterite lamellae:	Fe37	Zn63
section B, area 2		
stannite host:	Fe65	Zn35
kesterite lamellae:	Fe36	Zn64

Fe and Zn: percentage of Cu_2FeSnS_4 and Cu_2ZnSnS_4 components normalized to 100%. GSC: National Reference Collection, Geological Survey of Canada. UT: University of Toronto, Department of Geology Collection.

APPLICATION TO STANNITE–KESTERITE OCCURRENCES

Springer (1972) proposed that intergrowths of stannite and kesterite, which presumably define equilibrium pairs, might serve as a geothermometer, based on compositions of the two minerals on either limb of the miscibility gap. Attempts to apply such a geothermometer were made by Springer (1972). He utilized the data of Harris & Owens (1972) on a stannite–kesterite intergrowth from the Stannex prospect near Revelstoke, British Columbia and by Petruk (1973) for an intergrowth identified as consisting of stannite–kesterite from the Mount Pleasant mine, Charlotte County, New Brunswick. These specimens, as well as others, were reanalyzed using improved standards, and the results are given in Table 2 in terms of mole percentage of the Cu_2FeSnS_4 and Cu_2ZnSnS_4 end members. The Mount Pleasant specimen does not contain a stannite–kesterite intergrowth, but petrukite (*cf.* Kissin & Owens 1989) intergrown with a mineral of similar composition. All of the specimens are lamellar intergrowths apparently representing exsolution of one phase from the other and, presumably, an equilibrium assemblage at some temperature. The specimens from the Snowflake mine and Stannex prospect all consist of stannite lamellae in a kesterite host. The compositions of the stannite are very similar, as are the compositions of the kesterite. The specimens from the Cligga mine consist of kesterite lamellae in a stannite host, and, again, the compositions of stannite are similar, as are the compositions of the kesterite. As well, the compositions of the minerals from British Columbia are very similar to those from Cligga mine.

Comparison of the data of Table 2 with the phase diagram (Fig. 2) reveals several discrepancies. The compositions of stannite and kesterite do not lie on the solvus of the stannite and kesterite–ferrokesterite solid solutions, nor any reasonable extrapolation thereof. Both limbs of the solvus would have to lie in much more zinc-rich regions of the diagram, and the gap would have to be wider. Finally, the slope of the two-phase loop separating stannite and kesterite–ferrokesterite implies that an iron-rich stannite cooling into the two-phase region should exsolve kesterite–ferrokesterite, as seen in the Cligga mine specimens (Table 2). However, exsolved lamellae of stannite in a kesterite host, as seen in the specimen from Snowflake mine and Stannex prospect, are not possible in a phase diagram with the configuration as shown in Figure 2.

The discrepancies indicate that the condensed phase-relations (Fig. 2) cannot apply to natural specimens. Although the effect of geologically realistic pressures on phase boundaries is unknown, the molar volumes of stannite and kesterite–ferrokesterite do not differ by much, and, as noted by Springer (1972), phase boundaries are unlikely to be shifted significantly by increased pressure.

The existence of both types of intergrowth relationships implies that the miscibility gap between stannite and kesterite–ferrokesterite must both widen and shift to more zinc-rich compositions at temperatures below those of the present study. As well, the limbs of the solvus between stannite and kesterite must slope toward the end-member compositions in order to account for the formation of kesterite lamellae in stannite in iron-rich bulk compositions and stannite lamellae in kesterite in zinc-rich bulk compositions.

DISCUSSION

The appearance of the Springer phase in both this study and that of Springer (1972) implies that equilibrium was not achieved for iron-rich compositions below about 700°C. As discussed previously, lack of equilibrium is evidenced by the non-pseudobinary composition of the Springer phase and the absence of a two-phase region separating stannite from the field of the Springer phase (*cf.* Figs. 2, 3). The most likely cause for the appearance of the Springer phase appears to be the inability of the most iron-rich compositions to attain equilibrium with decreasing temperatures due to increasing sluggishness of reaction. Oxidation of Fe^{2+} to Fe^{3+} or of Cu^{+} to Cu^{2+} (or both) also is a possibility but seems less likely, as the problem should be increasingly serious with increasing temperature rather than the converse.

An even more serious problem is the lack of agreement in phase relations from either this study or from that of Springer (1972) with stannite–kesterite compositions in two-phase lamellar intergrowths. It may be that the stannite–kesterite miscibility gap also is affected by the same lack of equilibrium evidenced by the appearance of the Springer phase. In any event, in view of the clear problems present in attaining equilibrium even using molten halide fluxes, an experimental resolution of this problem does not seem to be available.

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