Canadian Mineralogist
Vol. 14, pp. 172-181 (1976)

REACTIONS IN CUBANITE AND CHALCOPYRITE

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ABSTRACT

The temperatures and enthalpies of the solidus and liquidus reactions in cubanite and chalcopyrite have been determined by DTA methods. The heat of the solid-state transition in cubanite was 5.6 kcal/mole; it occurred at 250-300°C when the cubanite was heated at 5°C/min. This compound fuses incongruently at 902°C; the liquidus temperature is about 1015°C. Phase reactions were detected in $CuFeS_2$ (chalcopyrite) at 560 and 650°C. $CuFeS_2$ melts at 880°C and the fusion appears to occur over a narrow but finite temperature range. The addition of $CuFe_2S_3$ to $CuFeS_2$ slightly elevates the incongruent melting point and also depresses the tetragonal-cubic reaction in $CuFeS_2$. Solidus and liquidus data are also reported for the FeS-$CuFeS_2$ pseudobinary system.

SOMMAIRE

La température et l'enthalpie des réactions au solidus et au liquidus de la cubanite et de la chalcopyrite ont été déterminées par les méthodes d'analyse thermique différentielle. La chaleur de transition à l'état solide de la cubanite est 5.6 kcal/mole; cette transition se produit à 250°C-300°C lorsque la cubanite est chauffée à 5°C/min. Ce composé fond incongruentement à 902°C; la température au liquidus est approximativement 1015°C. Les réactions ont été décelées dans le $CuFeS_2$ (chalcopyrite) à 560°C et 650°C. Le $CuFeS_2$ fond à 880°C, et la fusion se produit dans un domaine restreint de température. L'addition de $CuFe_2S_3$ au $CuFeS_2$ élève légèrement le point de fusion incongruente et abaisse la température de la transformation quadratique-cubique dans le $CuFeS_2$. Les données pour le solidus et le liquidus sont aussi présentées pour le système pseudo-binaire FeS-$CuFeS_2$.

INTRODUCTION

Phase relationships in the Cu-Fe-S system are of great importance to process metallurgists involved with copper sulfide ores and concentrates in order to predict and to optimize the flotation, leaching and thermal processing of these commercially significant sulfides. A knowledge of this system is also important to ore mineralogists and geologists in that it bears directly on the origin and history of commercially valuable ore deposits. During the past quarter of a century, many authors have studied this complicated system and have succeeded, at least in part, in elucidating some of the reactions which occur in it. The important contributions in this area have been discussed recently by Barton (1973) and by Cabri (1973) and will not be repeated here. Both authors commented on the extreme complexity of this system, the study of which is rendered difficult by numerous phase transitions, by phases with nearly identical chemical compositions, crystal structures and optical properties and by irreversible reactions and unquenchable phases. Because of these experimental difficulties, many details of this phase system remain uncertain.

Chalcopyrite, $CuFeS_2$, and cubanite, $CuFe_2S_3$, are prominent phases in the central portion of the Cu-Fe-S phase system; both compounds, especially chalcopyrite, are important ores of copper. $CuFeS_2$ is tetragonal at low temperatures (chalcopyrite) but during heating it reacts first to cubic intermediate solid solution (*iss*) and pyrite (Barton 1973) at about 557°C (Pankratz & King 1970; Conard *et al.* 1975) and subsequently it fuses in the temperature range 865-895°C (Kullerud *et al.* 1965). $CuFe_2S_3$ is orthorhombic at low temperatures (cubanite) but at 200-210°C it undergoes a sluggish and seemingly irreversible transformation to cubic *iss* of composition $CuFe_2S_3$ (Cabri *et al.* 1973). The crystallographic changes involved in the $CuFe_2S_3$ transformations are well-documented, largely as a result of the work of Fleet (1970), of Cabri *et al.* (1973) and of Szymanski's (1974) recent refinement of the crystal structure of cubanite and high-temperature $CuFe_2S_3$. Schlegel & Schuller (1952) measured liquidus and solidus temperatures along the $CuFeS_2$-$FeS_{1.08}$ pseudobinary which essentially encompasses the composition $CuFe_2S_3$. A eutectic-type relationship was noted with a eutectic temperature of 896°C; $CuFeS_2$ was observed to melt at 950°C, a temperature substantially higher than that noted by later workers. According to the data of Schlegel & Schuller the liquidus temperature for the com-

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position $CuFe_2S_3$ is about 1040°C. Significantly, these investigators did not indicate either the intermediate solid-solution *(iss)* region or the composition $CuFe_2S_3$ on their phase diagram. In the present study the temperatures and heats of the various reactions occurring in the $CuFeS_2$-$CuFe_2S_3$ system were investigated by DTA methods and the results are discussed with reference to previous work in the Cu-Fe-S system. Some data are also presented for the solidus and liquidus reactions occurring along the pseudobinary join $CuFeS_2$-FeS.

EXPERIMENTAL

Chalcopyrite from Messina, Transvaal was used for the bulk of the experimental work. This material was ground, sized and subjected to magnetic and heavy-media treatment to produce a high-grade chalcopyrite concentrate. Examination of the concentrate by X-ray diffraction analysis using a Guinier-de Wolff camera showed it to consist of chalcopyrite with a faint trace of some unknown impurity. Cubanite ore from the Frood-Stobie mine, Sudbury, Ontario was the starting material for the preparation of a cubanite concentrate. The ore was crushed, sized to –270 +325 mesh and then magnetically upgraded. The concentrates were kept in sealed bottles in a desiccator to minimize oxidation during storage. Point-counting techniques indicated that the concentrate contained 92% cubanite with pyrrhotite, chalcopyrite and pentlandite being the principal impurities. For some experiments a cubanite concentrate made by Dr. L. J. Cabri from the Frood-Stobie ore was also used; this material was prepared by the same general procedure described previously and also contained about 92% cubanite. Synthetic bornite, Cu_5FeS_4, was used as a DTA calibrating material, and synthetic FeS, $CuFeS_2$ and $CuFe_2S_3$ were employed in some of the test work. The synthesis and purities of these synthetic phases have been described by Dutrizac & MacDonald (1973).

For the DTA experiments, the sulfides were mixed in appropriate proportions and then sealed under vacuum in silica tubes to prevent oxidation and the escape of sulfur vapor during heating. The free volume of the cells was approximately four times that of the melted sulfides. The tubes were 6 mm O.D. and 4 mm I.D.; they contained a small well at the bottom for the placement of the thermocouple. Sample weights varied from 10 to 100 mg depending on the experiment; the exact weight was determined by crushing the tube, dissolving the sulfide in aqua regia and then calculating the sample weight by difference. All loaded tubes were centrifuged prior to heating in order to produce a constant degree of sulfide compaction. Samples were run on a Stone Model GS-2 DTA apparatus using either an Inconel or palladium support and Pt-Pt:10%Rh thermocouples. Calcined aluminum oxide, also vacuum sealed in a silica tube, served as an inert reference material. The DTA was calibrated for temperature transitions using the 557°C solid-solid transformation in chalcopyrite and the fusion points of gold, silver and sodium chloride. The measured temperatures were those of the support and any differences between the support and cell temperatures were assumed to be compensated for by the calibration procedure. Programmed heating and cooling rates of 5°C/min were used for all experiments and with such programming rates all the evolved sulfur vapors reacted with the condensed phases during cooling. Condensed sulfur was not observed on the walls of the silica tubes. The differential thermocouple signal was amplified and then passed to one channel of a two-pen strip-chart recorder. The temperature of the sample was passed to the other channel of the recorder; temperatures of the various reactions are presumed to be reliable to ±10°C.

The samples used for some of the experiments were examined microscopically after having been mounted in plastic and polished. Various samples were also subjected to X-ray diffraction and microprobe analyses to try to determine the products formed when the sulfides were heated.

RESULTS AND DISCUSSION

Figure 1 shows the type of DTA trace obtained on heating for natural cubanite and for synthetic $CuFe_2S_3$. Heating of natural cubanite at 5°C/min. yields an endothermic transformation between 250 and 300°C. The peak observed at this temperature was sharp and symmetrical. Cabri *et al.* (1973) showed this transformation to be associated with the transition of orthorhombic cubanite to cubic *iss* of composition $CuFe_2S_3$. This transition is very sluggish and is, accordingly, highly dependent on the heating rate. Cabri *et al.* (1973) were able to detect this reaction by holding natural cubanite at 210°C for 99 days and, consequently, the equilibrium transition temperature must be at least as low as this value. It is not known if the reaction proceeds at even slower rates at still lower temperatures. No additional transformations were observed in natural $CuFe_2S_3$ until about 900-905°C when the sulfide melted incongruently. A shoulder on the cubanite fusion peak suggests that the incongruent melting of the concentrate

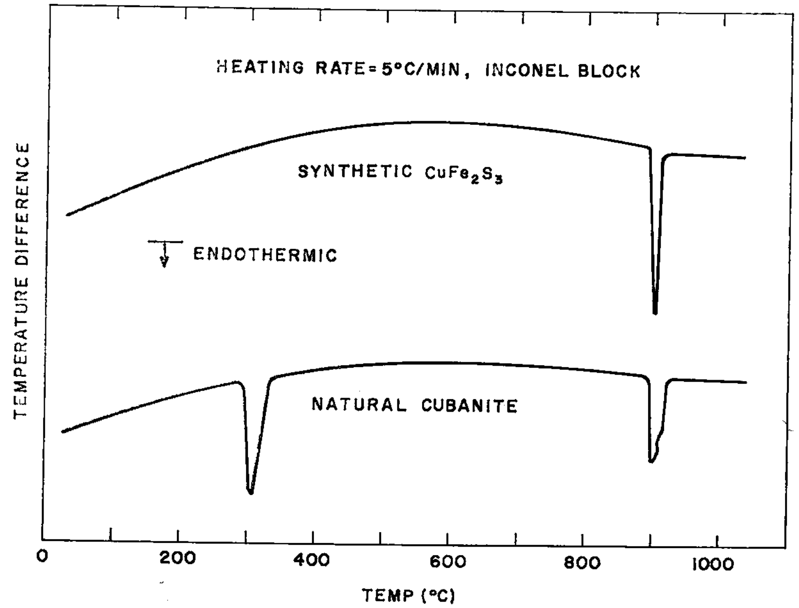

FIG. 1. — DTA curves for cubanite and synthetic $CuFe_2S_3$.

occurs over a narrow temperature range. The cubanite concentrate supplied by Cabri showed a more-pronounced shoulder than the other concentrate although both were of similar purity. No additional peaks were observed, on heating, between 900°C and 1300°C.

Figure 2 shows the type of DTA trace produced when natural $CuFe_2S_3$ was heated and

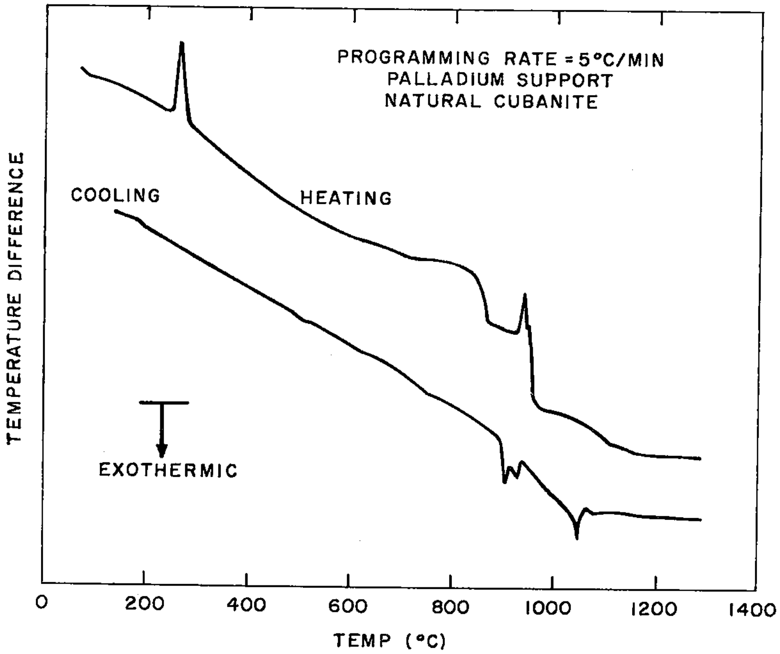

FIG. 2. — DTA curves obtained on heating and cooling for natural $CuFe_2S_3$ (cubanite).

cooled at 5°C/min. These curves were produced using a palladium support without a metallic block and, consequently, considerably more baseline drift was noted than when the Inconel block was employed. The heating cycle shows the cubanite transition at about 260°C as well as the incongruent melting reaction at about 900°C. Further heating produced no additional peaks. During the cooling cycle, however, a small but sharp peak appeared at about 1010-1020°C; presumably this indicates the liquidus temperature. The incongruent melting reaction is also quite apparent at about 900°C but, on cooling, this peak has been nearly resolved into a doublet. A similar situation prevailed for the synthetic $CuFe_2S_3$. Further cooling revealed no additional peaks; that is, the transition at about 260°C is not reversed on cooling at 5°C/min. It is fairly well established that the low-temperature transition is, for practical purposes, irreversible on cooling and this was certainly true in the present study.

Microscopic examination of fused cubanite or synthetic $CuFe_2S_3$ revealed that both materials consisted principally of a "chalcopyrite-like phase" finely exsolved from the *iss* matrix; small quantities of pyrrhotite were also evident. *X*-ray diffraction analysis using a Guinier-de Wolff camera showed that the phases were apparently "chalcopyrite" and cubic *iss* of composition $CuFe_2S_3$.

Figure 3 shows a photomicrograph of synthetic $CuFe_2S_3$ which was heated above the orthorhombic-cubic transition (800°C) and subsequently cooled at 0.5°C/min. The darker matrix material is believed to be cubic *iss* of composition near $CuFe_2S_3$ although the particle size is too fine to permit this to be determined by microprobe analysis. The lighter exsolved phase is optically similar to chalcopyrite; the exsolution laths are about two microns long and one-half micron in width. Since the total composition of the material shown in Figure 3 is $CuFe_2S_3$ and because roughly equal amounts of the two phases appear to be present, it follows from a mass balance consideration that the dark and light phases cannot have the compositions $CuFe_2S_3$ and $CuFeS_2$, respectively. If the *iss* has a composition near $CuFe_2S_3$, then the "chalcopyrite" must have a similar composition, its tetragonal structure notwithstanding. If the "chalcopyrite" approaches $CuFeS_2$ in composition, then the *iss* composition must be well beyond the composition range normally attributed to it (Cabri 1973). Although MacLean *et al.* (1972) and Cabri (1973) have clarified the compositions of phases produced by cooling *iss* of low-iron concentration, the compositions produced during exsolution of more iron-rich *iss* are still largely unknown. This problem arises because the mean exsolution-lamella size decreases drastically as the composition approaches $CuFe_2S_3$. Accordingly, the exsolution features shown in Figure 3 have not been reported previously for heated cubanite although such features have been noted for less iron-rich *iss* by MacLean *et al.* (1972).

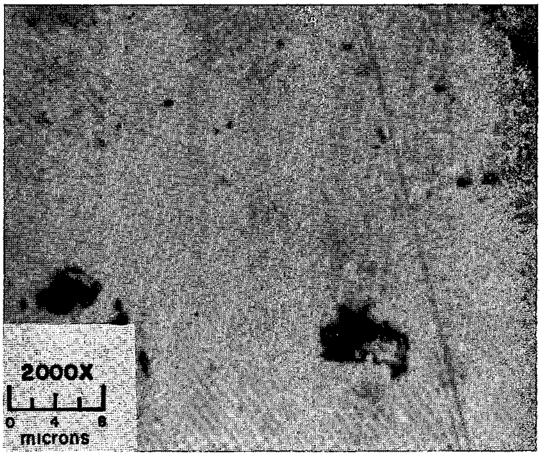

FIG. 3. — Photomicrograph of synthetic $CuFe_2S_3$ heated to 800°C and then slowly cooled. Dark phase is retained *iss* and light phase is "chalcopyrite".

The heat of the orthorhombic-cubic transition in cubanite is not known. Although the irreversible nature of this reaction precludes its determination by conventional drop calorimetry, the heat effect can be estimated by DTA methods. Ingraham & Marier (1965) have shown that the area under a DTA peak is proportional to the heat exchanged during the transition and that heats of crystallographic transitions can be estimated with fair accuracy by this method with the use of suitable calibration curves. Bornite, chalcopyrite and cubanite are all iron-copper sulfides with similar densities and thermal conductivities; they should, therefore, exchange heat in a similar fashion. For these reasons, bornite and chalcopyrite were selected as the calibrating materials in the present study. Pankratz & King (1970) reported a heat of 1.430 kcal/mole for the bornite transition at 212°C and a heat of 2.405 kcal/mole for the chalcopyrite reaction at 557°C; Conard *et al.* (1975) obtained an enthalpy of 2.28 kcal/mole for the chalcopyrite reaction.

Figure 4 shows the calibration curve obtained for bornite and chalcopyrite; evidently, the same curve can describe the heat effects in both sul-

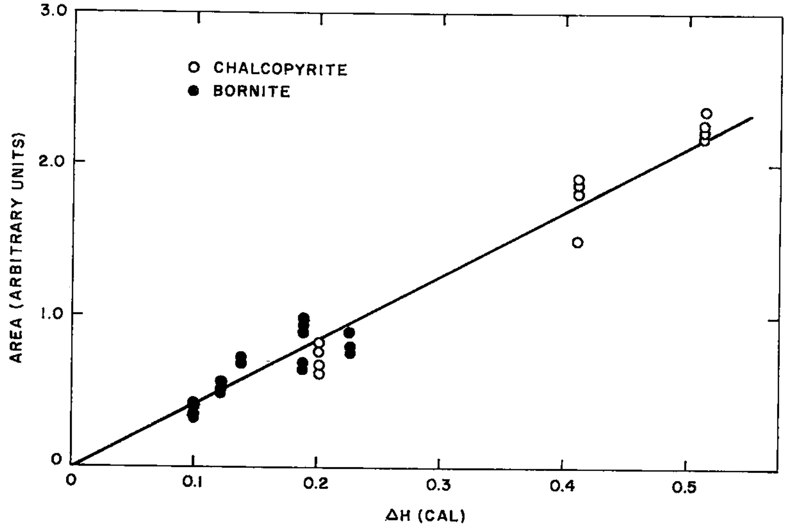

FIG. 4. — DTA calibration curve obtained for heating at 5°C/min with Inconel block.

fides. Considerable scatter exists and this is probably caused by the use of sealed glass tubes, the precise dimensions of which are somewhat variable. The peak areas depend on the heat flow to the couple, and differing thicknesses of glass in the thermowell or varying degrees of contact will affect the heat flow and hence the peak areas which were evaluated using the procedure of Ingraham & Marier (1965). The equation of the calibration curve was:

Area (arbitrary units) = $4.36\Delta H$ (cal) (1)

The error (98% confidence limits) associated with the curve was ±4% which is considered average for this type of DTA measurement.

The heats of transition in cubanite were computed by measuring the area produced by a given quantity of sulfide, by evaluating the associated heat effect, and finally by calculating the molar heat of transition taking into account the 92% purity of the cubanite concentrate used. This procedure was repeated using 20 different samples of cubanite, 10 from the concentrate provided by Dr. Cabri and 10 from the concentrate prepared in the present work. The heat of transition calculated for the former material was 5.26 kcal/mole with a maximum spread of ±1.10 kcal/mole; the corresponding value for the latter material was 5.88 kcal/mole with a maximum spread of ±1.44 kcal/mole. The average of the two values is about 5.6 kcal/mole.

Barton (1973) remarked that the heat effect of 2.4 kcal/mole reported for the chalcopyrite reaction at 557°C seemed large, but that it was consistent with his phase diagram. Although the molar heat effect for cubanite is twice that for chalcopyrite, the differences are less when the comparison is made on the basis of an equal number of atoms. Thus the heat effect for cubanite is 0.93 kcal/atom and for chalcopyrite it is 0.6 kcal/atom. Szymanski (1974), Cabri *et al.* (1973), and Fleet (1970) all concluded that the transition in cubanite is generally similar to the sphalerite-wurtzite transition in ZnS. The heat of the ZnS transition at 25°C is 3.2 kcal/mole (Barin & Knacke 1973); this heat is exchanged by the realignment of the *ABCABC* structure of the close-packed planes of sphalerite to the *ABAB* structure of the close-packed planes in wurtzite. The transition in cubanite requires, in addition to the transformation of the *ABAB* packing to the *ABCABC* packing, the movement of 1½ moles of the three moles of metal atoms across the sulfur planes and the subsequent randomization of these copper and iron atoms (Szymanski 1974). It is felt that substantial amounts of energy would be required to move the atoms across the sulfur plane but that relatively little energy would be required to effect the metal randomization. Thus, although the heat effect observed in cubanite is large, it appears generally consistent with the value expected for a sphalerite-wurtzite-type transition in this compound.

The heat of fusion of $CuFe_2S_3$ is unknown but this value can also be estimated from the area under the fusion peak. This procedure yielded a heat of fusion of 5 kcal/mole, a value which must be considered approximate since the heat of a fusion reaction is liberated in a different manner than that of a solid-solid transformation of the type used to calibrate the DTA. It is possible to improve the measured value to take into account the differences in calibrating temperatures and in methods of heat liberation by multiplying the measured value by the ratio of the calorimetric heat of fusion of $CuFeS_2$ (9.5 kcal/mole) to the DTA heat of fusion of $CuFeS_2$ (7.4 kcal/mole) measured in the present study and discussed later in this paper. When this is done, the heat of fusion of $CuFe_2S_3$ becomes 6.3 kcal/mole. Although this too must be considered an approximate value, it is probably fairly close to the true heat of fusion of $CuFe_2S_3$. The value is listed because no other appears to be available in the literature.

Figure 5 shows the type of DTA trace produced when chalcopyrite was heated at 5°C/min. in sealed silica tubes. The upper curve shows the entire DTA trace and the lower curve presents part of an actual trace obtained in the vicinity of the low-temperature peak. There are no transitions in chalcopyrite to 560 ± 10°C where the tetragonal form of $CuFeS_2$ reacts to cubic *iss* and pyrite (Barton 1973). The amount of pyrite formed seems to be small and the bulk of the heat effect is probably attributable to the tetragonal-cubic reaction in $CuFeS_2$. This reaction was sharp and the peak was symmetrical. The tetragonal-cubic reaction was reported to occur at 557°C by Pankratz & King (1970) and at 558°C by Conard *et al.* (1975); the value of 560°C found in the present study is in good agreement with these previous works.

The inset in Figure 5 reveals a broad endothermic peak at about 650°C; the great width of this peak relative to its height makes it difficult to give an accurate temperature for this transition. Pankratz & King (1970) reported this weak transition to occur at 657°C and attributed it to a second-order transformation in the cubic *iss* of composition $CuFeS_2$. Conard *et al.* (1974) also noted this transition to occur at 657°C, but they attributed it to the reaction:

$$iss + \text{pyrite} \longrightarrow iss + S_{(l)} \qquad (2)$$

Barton's (1973) phase diagram work indicated that reaction 2 does occur at approximately this temperature. The present author tends to support the Conard *et al.* (1974) interpretation of this reaction (except for the nature of the sulfur species) because of both the shape of the endothermic peak and the magnitude of the evolved heat. Both low-temperature reactions in chalcopyrite are reversible and both were apparent during cooling in the DTA apparatus.

The fusion of $CuFeS_2$ was observed to occur at 880 ± 10°C on either heating or cooling. The fusion peak is very broad and there is a strong suggestion of two closely superimposed peaks; that is, the melting may occur incongruently. Kullerud *et al.* (1965) reported that $CuFeS_2$ commenced melting at 865°C and was completely molten at 895°C; Conard *et al.*

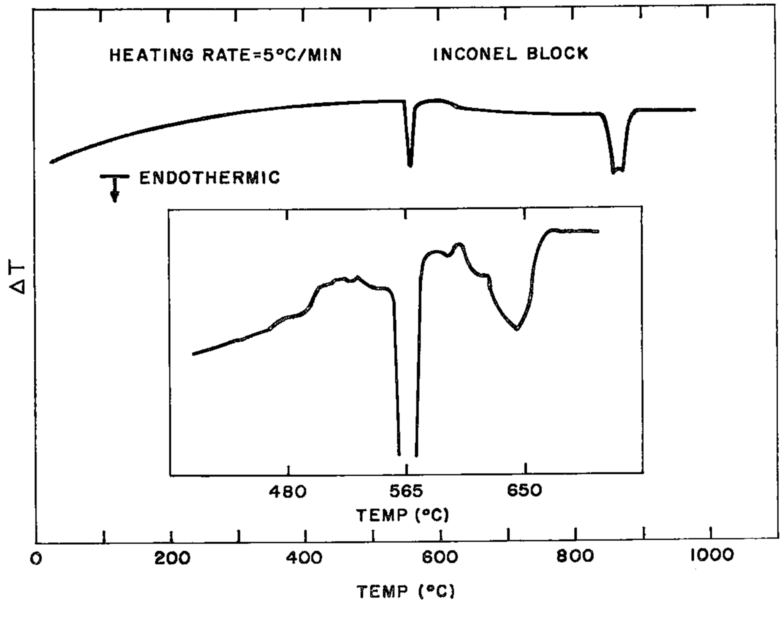

FIG. 5. — DTA curves for natural chalcopyrite.

(1975)* noted a fusion temperature of 882°C. Both studies indicated a range of fusion which suggests that chalcopyrite does not melt congruently but that the solidus and liquidus temperatures are close to each other. The present work agrees with these previous studies both in the "average" fusion temperature and in the fairly broad range of fusion. By contrast, Schlegel & Schuller (1952) reported that $CuFeS_2$ melted congruently at 950°C. The reason for this higher value is not known but recent works in this area all seem to favour a lower melting point for $CuFeS_2$.

It is possible to estimate the heat of fusion of chalcopyrite by measuring the area under the fusion peak and then using this area and Figure 3 to determine the total heat exchanged. This method is only approximate since the heat of a fusion process is liberated in a manner different than the heat of the solid-solid transformations which were used to calibrate the DTA apparatus. At the time of this work, there was no published value for the heat of fusion of $CuFeS_2$ and this approximate technique seemed justified to produce a needed value for this heat effect. Subsequently, Conard *et al.* (1975) determined a heat of fusion of chalcopyrite of 9.5 kcal/mole by calorimetric techniques. This value is to be preferred to the heat of fusion of 7.4 kcal/mole estimated by DTA methods in the present study.

Figure 6 shows the type of DTA trace obtained when mixtures of natural cubanite and natural chalcopyrite were heated at 5°C/min. As the concentration of cubanite is increased, the low-temperature transformation in cubanite becomes very clear and this is indicative of its large heat. By contrast, the solid-solid reaction in chalcopyrite becomes more feeble and appears to occur at lower temperatures with increasing concentrations of $CuFe_2S_3$. The observed peaks for the chalcopyrite reaction became significantly broader on the addition of $CuFe_2S_3$. For concentrations of $CuFe_2S_3$ much in excess of 50 wt. %, the chalcopyrite reaction was only faintly discernible against the background noise. Significantly, there is no exothermic peak for the reaction of $CuFeS_2$ and $CuFe_2S_3$ to form a single homogeneous solid solution during heating; such a heat effect might be expected to occur when these two materials react. When the mixtures were heated a second time, the cubanite peak vanished, but the chalcopyrite peaks were still readily discernible. The absence of a peak for the reaction of chalcopyrite and cubanite, together with the feeble chalcopyrite peak, may indicate that the reaction of the chalcopyrite to *iss* and pyrite and the reaction

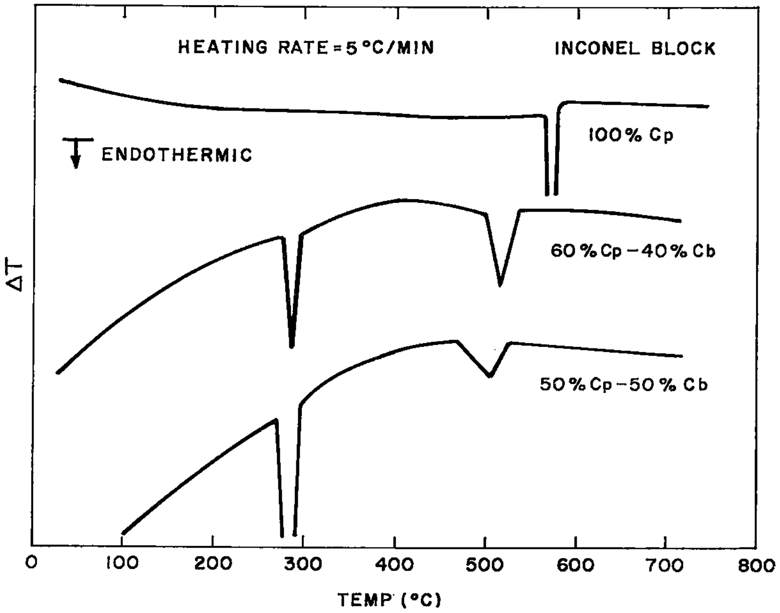

FIG. 6. — DTA curves for chalcopyrite-cubanite mixtures expressed in weight percentages.

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*Personal communication from B. R. Conard, R. Sridhar & J. S. Warner, International Nickel Company, J. Roy Gordon Research Laboratory.

of the $CuFeS_2$ and $CuFe_2S_3$ occur simultaneously with the two heat effects essentially annulling each other. This or some similar mechanism needs to be postulated to explain the absence of these heat effects, especially the chalcopyrite transition which should be discernible at very low chalcopyrite concentrations. The cubanite transition was detectable in mixtures containing only 5 wt. % cubanite.

Figure 7 presents some limited DTA data obtained for the pseudobinary $CuFeS_2$-FeS; this Figure summarizes the temperatures associated with the tetragonal-cubic reaction, the incongruent melting temperatures of $CuFeS_2$-$CuFe_2S_3$ mixtures as well as the liquidus values in the $CuFeS_2$-FeS system. Essentially identical values were obtained with $CuFeS_2$-$CuFe_2S_3$ mixtures as with $CuFeS_2$-FeS components. The incongruent melting temperature increased slightly as the bulk composition became richer in FeS. For compositions containing more than 50 mole % FeS, the peak for incongruent melting was split into two separate peaks whose separation increased as the composition became richer in FeS. The reason for this splitting was not determined. The liquidus temperatures dropped steadily from a value of 1170°C for a bulk composition of 100% FeS to 900°C at about 13 mole % FeS. The liquidus and solidus temperatures became indistinguishable for compositions containing less than 13 mole % FeS. Schlegel & Schuller (1952) investigated the phase system $CuFeS_2$-$FeS_{1.08}$ (4 experimental determinations) that should be quite similar to the system $CuFeS_2$-$FeS_{1.00}$. These workers reported a eutectic-type system in contrast to the generally peritectic-type diagram produced in the present study. In spite of this difference, however, there is a general agreement between the two studies for the FeS_x-rich portions if the different compositions of FeS_x are taken into account. Higher liquidus temperatures would be expected with $FeS_{1.08}$. The eutectic temperature of 896°C noted by Schlegel & Schuller is in good agreement with the incongruent melting temperature of about 900°C found in the present study. Schlegel & Schuller reported that $CuFeS_2$ melted congruently at 950°C and that it formed a eutectic with FeS_x. In these aspects the present study is not even in general agreement. A reaction in $CuFeS_2$ at about 950°C was looked for both on heating and cooling but none was detected. Conard *et al.* (1975) also looked for a reaction at this temperature and found none.

The addition of $CuFe_2S_3$ to $CuFeS_2$ seems to lower the tetragonal-cubic reaction in the latter compound as well as substantially diminishing the apparent size of the associated DTA peak. It is not known how closely these lower-temperature values approximate the true equilibrium temperature. No published data appear to exist for this reaction except for "pure" $CuFeS_2$, where the transformation is fairly well documented. It is not known what happens to this reaction at $CuFe_2S_3$ concentrations >50 wt. % (29 mole % FeS) because this peak becomes so feeble under these conditions it is difficult to distinguish against the background.

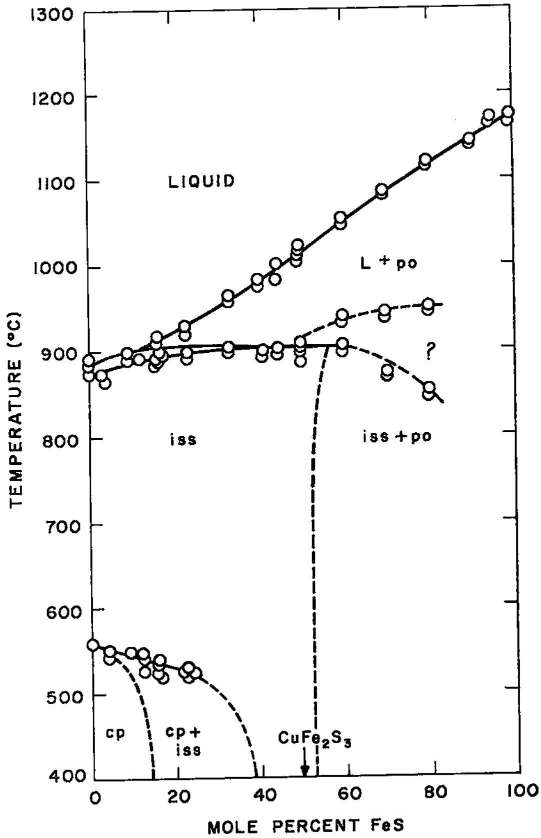

FIG. 7. — Partial phase diagram for the quasi-binary system $CuFeS_2$—FeS.

Microscopic examination of $CuFeS_2$-$CuFe_2S_3$ mixtures heated to 800°C and then slowly cooled revealed exsolution features similar to those noted by MacLean *et al.* (1972) and by Cabri (1973). Samples containing more than 50 wt. % $CuFe_2S_3$ (29 mole % FeS—71 mole % $CuFeS_2$) were characterized by "chalcopyrite" exsolved from the high-temperature cubic matrix as noted previously and shown in Figure 3. The mean size of the exsolution lamellae increased by at least 10 times on passing from

$CuFe_2S_3$ to 50 wt. % $CuFe_2S_3$–50 wt. % $CuFeS_2$. *X*-Ray diffraction analysis using a Guinier-de Wolff camera showed the above mixtures to consist of a chalcopyrite-like phase and cubic *iss*; the chalcopyrite-like phase was present in a slight excess at 50 wt. % $CuFe_2S_3$-50 wt. % $CuFeS_2$ and this could explain the weak DTA peak at this composition. Samples containing 25 wt. % $CuFe_2S_3$-75 wt. % $CuFeS_2$ (15.5 mole % FeS – 84.5 mole % $CuFeS_2$) consisted of a predominantly chalcopyrite matrix containing some grains which showed chalcopyrite exsolved from a cubic *iss* matrix. *X*-ray diffraction analysis confirmed the cubic phase to be present in only trace amounts at this composition. Mixtures containing less than 25 wt. % $CuFe_2S_3$ consisted only of chalcopyrite with no residual *iss* detectable. This was the basis for the construction of the chalcopyrite (cp) field in Figure 7.

Chalcopyrite-cubanite mixtures containing less than 25 wt. % $CuFe_2S_3$ (15.5 mole % FeS – 84.5 mole % $CuFeS_2$) behave essentially like chalcopyrite once they have been heated. An iron-rich tetragonal chalcopyrite predominates although some minor exsolution features are evident at 25 wt. % $CuFe_2S_3$; the most iron-rich chalcopyrite produced had the approximate formula $Cu_{0.92}Fe_{1.08}S_{2.00}$. Most of the grains appear to consist only of chalcopyrite with no evidence of retained *iss*. This iron-rich chalcopyrite undergoes the tetragonal-cubic reaction with the exchange of large amounts of heat. Karpenkov *et al.* (1974) reported a natural iron-rich chalcopyrite from the Noril'sk region, USSR; it had the formula $Cu_{0.90}Fe_{1.14}Ni_{0.01}S_{2.00}$ and produced a chalcopyrite *X*-ray pattern. This compound differs from other minerals reported in the central portion of the Cu-Fe-S system by having both a one-to-one metal to sulfur ratio as well as a substantial excess of iron over copper. The composition determined by Karpenkov *et al.* (1974) can be considered to consist of approximately 82 mole % $CuFeS_2$–18 mole % FeS and must be, according to the present study, near the iron-rich limit permitted for chalcopyrite. Presumably the addition of more iron would cause the compound to break down into iron-rich chalcopyrite and "cubanite". As the composition is increased beyond 25 wt. % $CuFe_2S_3$, the exsolution features predominate and the free grains of iron-rich chalcopyrite diminish in number. At 50 wt. % $CuFe_2S_3$ only small amounts of "free" chalcopyrite are present, and the DTA peak is correspondingly weak. The addition of still more $CuFe_2S_3$ results in a material consisting almost entirely of chalcopyrite-*iss* exsolved grains and the DTA detects only a minor heat effect.

CONCLUSIONS

The heat of the orthorhombic-cubic transformation in $CuFe_2S_3$ was found to be 5.6 kcal/mole at 260°C; the heat of fusion was estimated at 6 kcal/mole at the incongruent melting point of 902°C. The liquidus temperature for this composition was about 1015°C. Solid-solid reactions in $CuFeS_2$ were identified at 560°C and 650°C. This compound fused at 880°C and the fusion appeared to occur over a narrow temperature range. The addition of $CuFe_2S_3$ to $CuFeS_2$ elevates the incongruent melting temperature slightly and depresses the tetragonal-cubic transformation. The $CuFeS_2$-FeS pseudobinary system is generally of the peritectic type with an incongruent melting point of about 900°C.

ACKNOWLEDGEMENTS

The author would like to acknowledge the assistance of Dr. L. J. Cabri throughout this work. The X-ray diffraction analysis was done by S. Kaiman and the photographs were taken by P. Carrière. Some of the DTA experiments were done by C. Leblanc.

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Manuscript received May 1975, emended November 1975.