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# On the Chemical Formula of Chalcopyrite

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# On the Chemical Formula of Chalcopyrite

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*With 3 Text-figures*

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## Historical

The chemical formula of chalcopyrite was first given by R. PHILLIPS<sup>1)</sup> as  $\text{CuS} + \text{FeS}$ . Later, G. ROSE<sup>2)</sup> corrected it to  $\text{Cu}_2\text{S} + \text{Fe}_2\text{S}_3$ , arguing that mineral would be magnetic if its iron content were in the form of  $\text{FeS}$ . A. KNOP<sup>3)</sup> maintained the same opinion as PHILLIPS for his experiment of immersing the mineral in HCl for 8 weeks proved that all of the iron content was extracted as ferric salt, while little copper went into the solution. He concluded that iron atoms in chalcopyrite are trivalent and copper atoms are univalent though the mineral was finally covered by covellite.

C. F. RAMMERSBERG<sup>4)</sup> observed that one quarter of the total sulphur content was removed when the mineral was heated in a stream of hydrogen or on charcoal, the product being  $\text{Cu}_2\text{S} \cdot 2\text{FeS}$ . From this fact, he concluded that the real formula of chalcopyrite is  $\text{CuS} \cdot \text{FeS}$  and not  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ .

P. v. GROTH and K. MIELEITNER<sup>5)</sup> assume the existence of a hypothetical acid of the composition  $\text{Fe}(\text{SH})_3 - \text{H}_2\text{S} = \text{S} \cdot \text{Fe} \cdot \text{SH}$ , and chalcopyrite  $\text{S} = \text{Fe} \cdot \text{S} \cdot \text{Cu}$

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1) R. PHILLIPS, Ann. Phil. 3 (1882) 301. ref. C. DOELTER u. H. LEITMEIER, Handb. d. Mineralchem., Bd. 4, Erste Ht., 143.

2) G. ROSE, ref. op. cit.

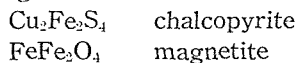
3) A. KNOP, Neues Jahrb. Min. etc. (1861) 562.

4) C. F. RAMMERSBERG, Mineralchem. (1875) 70; (1895) 32.

5) P. v. GROTH u. K. MIELEITNER, Mineralogische Tabellen, (1921) 22.

is a salt which is formed by replacing the hydrogen atom of the acid by univalent copper atom. Their opinion concerning the valency of Cu- and Fe-atoms is, therefore, the same as that of ROSE and KNOP.

F. RINNE<sup>1)</sup> noticed the similarity of Laue photograph of chalcopyrite to that of magnetite. He writes the formulae of the two minerals



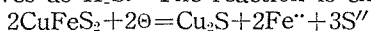
and explains that chalcopyrite is to be taken as a substitution product of magnetite in which the divalent iron atom of the latter is replaced by two univalent copper atoms and O<sub>4</sub> by S<sub>4</sub>, the degree of symmetry being lowered by the morphotropic effect of this replacement. In short, his opinion about the valency of metallic atoms in chalcopyrite is the same as that of ROSE, KNOP, GROTH and MIELEITNER. P. NIGGLI<sup>2)</sup> also writes the formula of chalcopyrite as  $[\text{Fe}_2\text{S}_4]\text{Cu}_2$  in his *Lehrbuch der Mineralogie*.

An experimental investigation of MORGAN and SMITH<sup>3)</sup> denies the assumption that iron atoms are trivalent. In the experiment of these authors, the mineral was decomposed by the action of dry hydrochloric acid under high temperatures, and ferrous iron of the product was determined by titration. This has proved that all the iron content of the mineral was in ferrous state.

In order to determine the formula of chalcopyrite, therefore, it is necessary to pay some further attention to the determination of the valency of metallic atoms and especially the molecular weight of the mineral. The results of the present investigation have proved that the correct formula is CuS·FeS as was given by RAMMERSBERG. In this paper, our experimental researches are reported, and a new way of representing the structural chemical formula is proposed.

### Valency of atoms in chalcopyrite

If a chalcopyrite electrode is polarised cathodically in not very dilute sulphuric acid in a closed vessel, iron goes into the solution as ferrous sulphate; copper remains on the electrode surface as Cu<sub>2</sub>S while sulphur dissolves as H<sub>2</sub>S. The reaction is expressed by the equation<sup>4)</sup>:



A question arises here which of the three kinds of atom in the mineral is reduced by the addition of electrons. To solve this question, the writer found it convenient to examine the time variation of the anode potential when the acidity of the solution is not very strong and current density is small. The experiment was carried out by employing a constantly rotating interruptor, the potential having been measured out, say, in every 10 seconds using a calomel electrode as the reference.

1) F. RINNE, *Neues Jahrb. Min. etc.*, (1916), Bd. 2, 103.

2) P. NIGGLI, *Lehrb. d. Min.*, (1920) 301.

3) L. P. MORGAN and E. F. SMITH, *Amer. Journ. Chem. Soc.*, vol. 23, (1901) 107.

4) A. MATSUBARA u. J. TAKUBO, Anniversary Volume dedicated to Prof. M. CHIKASHIGE by his Pupils in Celebration of his Sixtieth Birthday, Kyoto, (1930) 311.

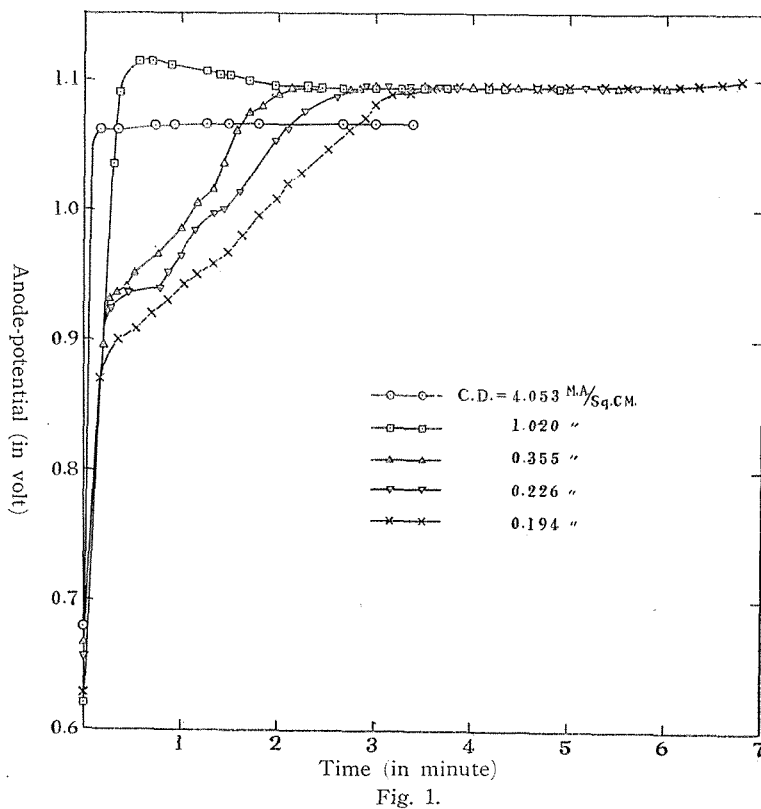


Fig. 1 shows some of the results when the mineral was anodically polarised in  $0.01\ n\ H_2SO_4$ . For purposes of comparison, some of the time-potential curves of pyrite-anode, which had previously been reported,<sup>1)</sup> are reproduced in Fig. 2.

As is seen in Fig. 1, chalcopyrite anode has a strong tendency to acquire passivity by anodic polarisation: its potential rises quickly until it reaches approximately to that of an oxygen electrode as soon as a current of sufficient strength passes. When the current density is less than ca. 0.4 milliamperere per sq. cm., a period of potential variation occurs during which the potential rises gradually until it settles at nearly the oxygen potential just as in Fig. 2. This period of gradual potential rise in pyrite electrode was already found to correspond with that of the oxidation of  $Fe^{II}$  to  $Fe^{III}$  of the electrode material, and it begins always at an anode potential of ca. 0.9 volt.<sup>2)</sup> So it is possible to conclude that the iron atoms in chalcopyrite electrode are also originally in ferrous state and become ferric only after the anodic oxidation.

1) A. MATSUBARA, Memoirs of the College of Science, Kyoto Imp. Univ., Ser. B, vol. 10 (1934), 73.

2) A. MATSUBARA, op. cit.

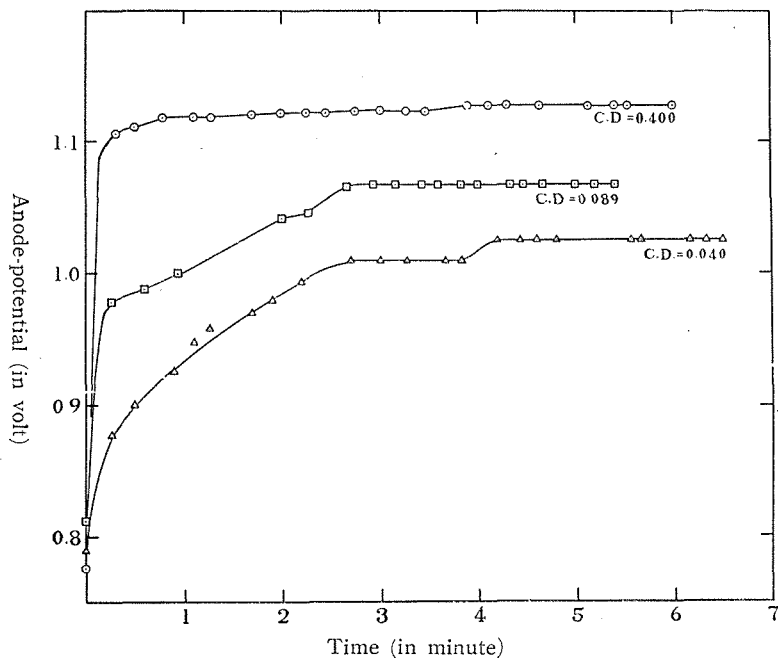


Fig. 2.

A question may arise here whether the gradually oxidized atoms may be copper- and not iron-atoms. To solve this question, a chalcosite( $\text{Cu}_2\text{S}$ )-electrode was anodically polarised under exactly the same conditions as above and the time-variation of the potential was observed. The results are represented in Fig. 3.

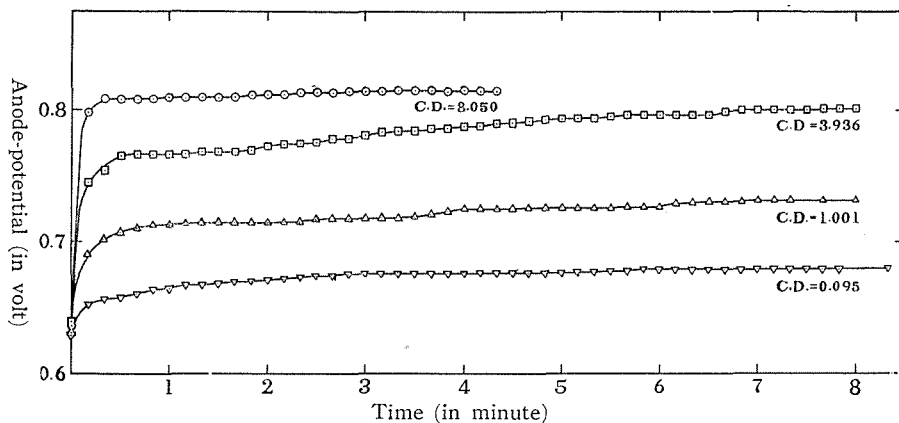


Fig. 3.

The curves in Fig. 3 have no oblique portion representing the gradual rise of potential, though the experiment was carried out in a wide range of current density. Moreover, the final settled potentials are markedly low:

even under a current density of 8 milliampere per sq. cm., the final potential is 0.81 volt. These facts suggest that the oblique portion of the curve in Fig. 1 does not correspond to the stage of  $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$

Finely pulverized chalcopyrite may be decomposed by hydrochloric acid and the iron content of the mineral can be extracted to a certain extent. To examine whether the extracted iron is ferrous or ferric, we have gone through the following experiment:

A current of  $\text{CO}_2$  was passed for a long time into the reaction vessel containing the pulverized mineral and into another vessel containing 6*n* HCl before they were mixed so as to remove any oxygen or dissolved chlorine. After mixing the reactants in the atmosphere of  $\text{CO}_2$ , the passing of the same gas into the mixture was continued for some time to remove any oxygen adhering to the mineral particles. Then the reaction vessel was left standing at the room temperature, shaking occasionally for two weeks after which the solution was analysed.

The resulting solution showed no trace of turbidity due to the formation of free sulphur and contained no trace of sulphuric acid and only a minute trace of ferric iron. The solution was essentially that of ferrous chloride. During the decomposition of the mineral, some amount of  $\text{H}_2\text{S}$  was produced and dissolved into the solution, but the absence of free sulphur proves that no reduction due to this gas has taken place.

In short, all the above experiments gave the same conclusion that iron atom in chalcopyrite is divalent as was ascertained by MORGAN and SMITH.

The final stage in the curves of Fig. 3 represents the oxidation potential of cuprous to cupric state under the prevailing conditions. Since any cupric atom formed by the electrolysis may directly go into the solution, the settled potential should undergo no change as long as all the electrode material is consumed. Should the copper atoms in chalcopyrite be univalent, we would obtain a similar halting point in the time-potential curves in Fig. 1. However, no trace of such halting points of low potential could be observed in repeated experiments. So it may be safe to conclude that the copper atoms are also originally divalent.

It follows, then, that it can be only copper atoms which are reduced by the cathodic polarisation, and the originally divalent iron atoms must go into the solution without suffering any reduction. Since two molecules of  $\text{CuFeS}_2$  take up no more than two electrons, sulphur atoms should also be originally divalent as they go into the solution in the form of  $\text{S}''$ .

#### Determination of molecular weight by means of cryoscopic method

Molecular weight of certain sulphide minerals can be determined by cryoscopic method employing  $\text{Sb}_2\text{S}_3$  in the melted state as the solvent. J. M. GUINCHANT and H. CHRETIEN<sup>1)</sup> have determined the constant of the mole-

1) J. M. GUINCHANT et H. CHRETIEN, *Compt. rend.* 138 (1904) 1269.

cular depression of  $\text{Sb}_2\text{S}_3$ , employing  $\text{Ag}_2\text{S}$  and  $\text{PbS}$ . They found it 793.6 in the case with  $\text{Ag}_2\text{S}$  and 788.7 with  $\text{PbS}$ . Since the two values do not differ more than 0.6 %, they concluded that the constant is to be taken as 790. A calculation of the heat of fusion from the above value gives 16.7 calori for 1 gr.  $\text{Sb}_2\text{S}_3$ , though the direct determination of the authors gave 17.5 calori.

H. PELABON<sup>1)</sup> has also determined the constant of the molecular depression of  $\text{Sb}_2\text{S}_3$ . He found it 797 when the solute was  $\text{Cu}_2\text{S}$ , and 788 when it was  $\text{HgS}$ . As he found the melting point of  $\text{Sb}_2\text{S}_3$  as 554° C., the heat of fusion calculated from VAN'T HOFF's equation becomes 17.1 calori in the case of  $\text{Cu}_2\text{S}$  while it assumes 17.3 calori in the experiment with  $\text{HgS}$ .

So far as the writers are aware, no experiment has hitherto been carried out with chalcopyrite as the solute. Nothing is known about the presence or absence of any property of this mineral to form solid solution or compound with  $\text{Sb}_2\text{S}_3$ . Our preliminary experiments showed, however, that the melting point of  $\text{Sb}_2\text{S}_3$  is regularly lowered by the addition of at least several percent of its weight of chalcopyrite and a distinct eutectic point appears in the cooling curve. The microscopic examination of the solidified mass also shows that the eutectic ground mass fills up the interstices of large stibnite crystals, and no other perceptible substance is present. The cryoscopic measurement in this system was, therefore, considered to be possible.

The results of measurement are summarized in the following table in which  $W$  represents the weight of chalcopyrite added to 100 gr. of stibnite,  $\Delta t$  is the depression of temperature of solidification in degrees centigrade, the solidification temperature of pure stibnite from Ichinokawa having been determined to be 550.3° C.

Exp. No.	1	2	3	4
$W$	2.00	3.31	4.60	5.73
$\Delta t$	8.6	14.4	20.4	26.3
$\Delta t/W$	4.30	4.35	4.43	4.58

From the graphical extrapolation,  $(\Delta t/W)_{W=0}$  was found to be 4.14. Taking the constant of molecular depression  $\Delta t_m$  to be roughly 790, we get 190 as the molecular weight of chalcopyrite. If 17.5 calori is taken as the correct figure of the melting heat of  $\text{Sb}_2\text{S}_3$ ,

$$\Delta t_m = \frac{0.0198 \times (550 + 273)^2}{17.5}.$$

This value of  $\Delta t_m$  gives 185 as the molecular weight of chalcopyrite while its true value is 183.53 if the molecular formula of the latter is  $\text{CuFeS}_2$ .

The above result indicates that the mineral is monomolecular and not  $\text{Cu}_2\text{Fe}_2\text{S}_4$ . The small deviation of the measured molecular weight from the theoretical value is to be attributed to the slight dissociation of the mineral in the mixed melt.

1) H. PELABON, Compt. rend. 140 (1905) 1389.

**Chemical behaviour of chalcopyrite in HCl-gas  
and in melted NaOH.**

The next problem to be solved is the type of compound to which the mineral belongs. That it is not a molecular compound is almost beyond dispute, for it does not decompose into CuS and FeS even at temperatures above 500° C. as we have seen already. The problem now remains to discover whether the mineral is a double salt or a complex compound.

The solution of this problem is never easy for we can not prepare the aqueous solution of the mineral in order to examine the ion reactions. In complex compounds, however, constituent atoms in the "outer sphere" are more loosely combined into the molecule than the atoms in the "inner sphere." And the authors who consider the mineral a complex compound assume without exception that copper atom is in the "outer sphere." If this assumption be true, it may be expected that copper atoms are more liable to be replaced or attacked by various chemical reagents.

By employing an aqueous solution of hydrochloric acid as the reagent, FeS-content only is extracted as we have seen before, but this phenomenon may be caused by the difference in solubility products. A more interesting reaction is that of dry HCl gas upon the mineral which was studied by MORGAN and SMITH.<sup>1)</sup> Unfortunately, however, these authors gave no information about the reaction of copper content in the mineral except that iron content was quantitatively changed into ferrous chloride.

To examine the reaction of copper content, the present authors repeated the experiment of MORGAN and SMITH. Finely pulverized chalcopyrite was exposed to the action of a stream of dry hydrochloric acid after completely expelling the air from the reaction vessel by passing nitrogen gas. The reaction vessel consisted of a quartz tube heated in an electric furnace.

To catch the reaction products of volatilizing nature, the exhaust gas was passed through a series of flasks containing normal solution of CuSO<sub>4</sub>. The temperature of the furnace was kept at 740° C. in the first experiment, and at 798° C. in the second. A visible deposition of free sulphur in the conducting tube began at the temperature of ca. 650°. At the higher temperatures, a copious accumulation of sulphur and cupric sulphide took place in the CuSO<sub>4</sub>-solution. This sulphur may possibly be carried out partly in the form of some chlorine compound. Ferrous chloride together with a very small amount of cupric chloride were also evolved, and condensed mainly on the cooler portion of the quartz tube, but an appreciable amount of ferrous chloride passed into the absorbing bottle.

The experimental results are summarized in the following table:

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1) L. P. MORGAN and E. F. SMITH, *op. cit.*



Experiment No.		1	2	
Temperature in °C.		740	740 798	
Duration of reaction in hour		1	1 2	
Original sample	Total weight in gr.		2.0307	1.9075
	Calculated weight of components in gr.	Cu	0.7035	0.6608
		Fe	0.6177	0.5804
		S	0.7095	0.6664
Insoluble residue in boat	Total weight in gr.		1.4311 (70.47%)	1.1748 (61.59%)
	Result of analysis (gr.)	Cu	0.7045 (49.23%)	0.6297 (53.59%)
		Fe	0.2937 (20.52%)	0.2075 (17.67%)
		S	0.4329 (30.25%)	0.3376 (28.74%)
	Calculation from analytical data	CuFeS <sub>2</sub> (undecomposed)	0.9651 (67.44%)	0.6824 (58.09%)
		Cu <sub>2</sub> S (formed)	0.4660	0.4924
Volatilized substances	Total weight in gr.		0.5996 (29.53%)	0.7327 (33.41%)
	Calculated from the analysis of residue	Cu	none	0.0311
		Fe	0.3240	0.3728
		S	0.2756	0.3288
	Caught by analysis	Cu	none	0.0223
		Fe	0.3227	0.3712
S		0.0891	0.1650	

In the first experiment, no copper chloride was produced; all the copper content of the mineral remained in the boat. The analytical result accurately shows that the decomposed portion of the mineral changed completely into Cu<sub>2</sub>S, so far as we assume that the undecomposed portion of the mineral remained as such in the boat and a ternary compound Cu<sub>3</sub>FeS<sub>3</sub> was not formed. A recent investigation of MERWIN and LOMBARD<sup>1)</sup> showed that there can exist 5 ternary compounds of Cu, Fe and S, but none of them coincides with a formula Cu<sub>3</sub>FeS<sub>3</sub>. Presumably the final residue in the boat was a mixture of CuFeS<sub>2</sub> and Cu<sub>2</sub>S.

Iron content in the decomposed portion of the mineral changed completely into FeCl<sub>2</sub> and vapourized as was already reported by the previous

1) H. E. MERWIN and R. H. LOMBARD, Econ. Geol. Supplement to Vol. 32 (1937) 203.

investigators, and the whole amount of vapourized iron was caught in the analysis as is seen in the above table. The vapourized sulphur, however, could not be completely caught by the analysis partly because it formed a hard incrustation on the wall of the quartz tube and no effort was made to take it out completely and partly because it may have escaped with the exhaust gas in some form of chlorine compound.

In the second experiment, a small amount of copper volatilized in the form of chloride as was actually recognized by the green colour of the incrustation. Otherwise the result was the same as in the first experiment.

From these results it is seen that, contrary to our expectations, the iron content of the mineral is far more easily attacked by hydrochloric acid than its copper content. If the mineral be a complex compound, such a formula as  $[\text{CuS}_2]\text{Fe}$  may be suspected to be the real one. However, it is more reasonable to consider that the mineral is decomposed first into  $\text{CuS}$  and  $\text{FeS}$ , and  $\text{FeS}$  thus produced reacts with  $\text{HCl}$ -gas while  $\text{CuS}$  dissociates into  $\text{Cu}_2\text{S}$  and  $\text{S}$ .

In the next experiment, the reaction between the mineral and  $\text{NaOH}$  was examined with the hope of getting any  $\text{Na}$ -salt of the complex anion in problem. Finely pulverized mineral was decomposed in a melt of  $\text{NaOH}$  at a temperature of ca.  $350^\circ\text{C}$ . for about 20 minutes, after which the melt was cooled very slowly.

The cooled cake contained a large amount of needle crystal of steel black colour, which was partly microscopical, and large, light yellowish crystals having perfect cleavage. The latter substance was found to be very unstable against water: it even decomposes in the air absorbing its moisture. To accomplish an optical examination of the crystals, a small fragment of the cake was crushed in a drop of soft Canada balsam on a slide glass and was examined under a polarisation microscope. The crystal flakes were more or less distinctly prismatic in form and were terminated by oblique faces somewhat like the cleavage flakes of gypsum. The angle between the trace of the oblique terminal face and that of the prism was about  $50^\circ$ , and the extinction angle referred to the trace of the prism was ca.  $35^\circ$ , the double refraction being very strong.

In water, the crystal decomposes rapidly giving  $\text{Fe}(\text{OH})_2$  and  $\text{NaHS}$ . So it is quite evident that the substance is some form of sodium sulphoferite.

Exactly the same substance can be prepared by fusing pyrrhotite with  $\text{NaOH}$ . Finely pulverized pyrrhotite is decomposed completely by melted  $\text{NaOH}$  also at a relatively low temperature giving light yellowish white cake. The latter is rapidly decomposed by water in the same manner as the above described substance. If the cake is examined under a microscope as above, the facial angle, extinction angle and strength of double refraction of the crystal coincide exactly with the above description. In this case, the composition of the crystal may presumably be  $\text{NaFeS}$  as the cake was uniform consisting wholly of the same crystal. It follows then that the similar crystals in the cake which was prepared with chalcopyrite, may also be  $\text{NaFeS}$ , although the exact analysis is lacking.

The black needle crystals may be separated from the fused mass by extracting the latter with formalin and subsequent decantation, any ferrous hydroxide in suspension being thus easily removed. After repeated washing of the residue with formalin in this manner, the fine needle crystals were collected in a filter and dried at 100° C. A quantitative analysis of the sample thus prepared gave the following result:

Sample taken:

	Weight %	Atomic ratio	Theoretical Wt. % in NaCuS
Cu	48.27	1.00	53.59
Fe	4.54	0.11	
Na	17.06*	0.98	19.39
S	28.56	1.18	27.02
Insol.	1.57		<hr/> 100.00

\*Calculated from the difference

The above result indicates that the needle crystal is essentially NaCuS or Na<sub>2</sub>S·Cu<sub>2</sub>S. Small amounts of iron and sulphur may be the contamination.

According to BODLÄNDER and IDASZEWSKI<sup>1)</sup> NaCuS can be prepared by fusion of an equivalent mixture of Na<sub>2</sub>S and Cu<sub>2</sub>S. Since the description of the crystal and the chemical composition given by these authors coincide with those of our crystals, they may both perhaps be the same substance, and a new method of preparation is thus found. The same compound may also be prepared by fusion of the mixture of CuS and NaOH and by subsequent slow cooling.

In this way, our effort to get any natrium salt of Fe<sub>2</sub>S<sub>4</sub>''-ion failed. By melting the mineral with NaOH, NaFeS and NaCuS were produced, showing that iron and copper atoms are equally liable to form similar complexes. Since these complexes may also be prepared by fusing FeS and CuS separately with NaOH, it seems reasonable to conclude that the mineral is decomposed first into FeS and CuS in the melt of NaOH and afterwards the natrium salts of the new complex anions are formed. The atomic arrangement in the crystal of chalcopyrite also affords no ground to conceive the presence either of Fe<sub>2</sub>S<sub>4</sub>''- or Cu<sub>2</sub>S<sub>4</sub>''-anion.

### Conclusion

The present researches have revealed that both copper and iron atoms in chalcopyrite are divalent, and that the compound is monomolecular and not Cu<sub>2</sub>Fe<sub>2</sub>S<sub>4</sub>. Though it does not decompose even at temperatures above 500° C., the FeS content is selectively attacked by the action of dry HCl gas under appropriate conditions. By fusion of the mineral with NaOH, NaFeS and NaCuS are formed and no Na-salt of Fe<sub>2</sub>S<sub>4</sub>'' anion is produced, showing that the mineral is first decomposed to CuS and FeS in the melt of NaOH.

1) G. BODLÄNDER u. K. S. IDASZEWSKI, Z. Elektrochemie, Bd. 11 (1905) 181.

From the above reasons, the present authors came to the conclusion that chalcopyrite is a double salt, and according to the usual expression of double salt, its formula is to be written as  $\text{CuS}\cdot\text{FeS}$  as was first given by RAMMERSBERG. Any other formulae such as  $\text{Cu}_2\text{Fe}_2\text{S}_4$ ,  $\text{CuFeS}_2$ ,  $\text{Cu}_2\text{S}\cdot\text{Fe}_2\text{S}_3$  etc. should be rejected.

It is a difficult matter to give a structural chemical formula for crystallized chalcopyrite as is the case with all crystallized substances, as the co-ordination number is, in general, independent of the number of valency bond. In a solution, for instance, in the melt of  $\text{Sb}_2\text{S}_3$ , the two molecules  $\text{CuS}$  and  $\text{FeS}$  may be combined by their "residual valencies" so that  $\text{CuS}\cdot\text{FeS}$  may be a quite correct structural formula. In such a free state of molecule,

even a formula  $\begin{array}{c} \text{S} \\ \diagdown \quad \diagup \\ \text{Cu} \quad \text{Fe} \\ \diagup \quad \diagdown \\ \text{S} \end{array}$  might be considered to represent the true structure

although this is quite erroneous in the case of a crystal.

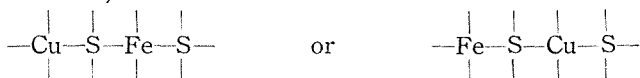
According to the latest investigation of S. Kôzu and his co-workers,<sup>1)</sup> chalcopyrite crystal belongs to the space group of  $V_d^2$ . It has three sets of four equivalent positions, one of which is

$$\frac{1}{4}, \frac{3}{4}, \bar{u}; \frac{1}{4}, \frac{3}{4}, u; \frac{3}{4}, \frac{1}{4}, u; \frac{3}{4}, \frac{1}{4}, \bar{u}.$$

This set of positions is considered to be occupied by sulphur atoms, and  $u$  was found to be ca. 0.25. A previous investigation made by R. GROSS and N. GROSS<sup>2)</sup> gave also the same result except that  $u=0.21$ .

Assuming that the above arrangement is correct, we have four sulphur atoms situated at the corners of a tetragonal sphenoid, which is very near to a tetrahedron, with an iron atom at its center. The relation is exactly (if  $u=0.25$ ) or nearly (if  $u=0.21$ ) the same with copper atom: the latter is also surrounded by four sulphur atoms arranged at the corners of a tetragonal sphenoid whose center is the position of copper atom.

In order to give a structural chemical formula coinciding with the above construction, we have to write either



but these formulae do not represent the valency relation at all, and before all, we have to write a number of free bonds which is not permissible in a chemical formula in the usual sense. Not to have the free bonds, an infinite number of molecules should be written and combined with each other. This may perhaps be the real feature of a crystal, as a crystal itself may be considered a large, polymerized molecule.

It will be convenient to express the structural formula in the above manner with the understanding that the formula can have any number of free bonds, and that each bond represents not one complete valency bond, but

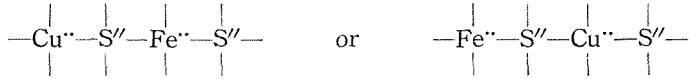
1) S. Kôzu, K. TAKANE and Y. KITAMI, Ganshiki-Kobutu-Kosyogaku, vol. 12, pp. 1-14.

2) R. GROSS u. N. GROSS, Neues Jahrb. Min. etc., Beil. Bd. 48 (1923), 113.

its fraction. The valency of each atom may be represented by the usual symbols attached to each of them. Thus in the case of sodium chloride and zinblende,



will represent their structural formulae respectively. In our case of chalcopyrite



are the required formulae, exactly coinciding with its crystalline construction.

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