

Composition Variation and Polymorphism of Tetrahedrite in the Cu-Sb-S System below 400°C

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Abstract

The phase relations of tetrahedrite have been studied in the Cu-Sb-S ternary system below 400°C. Tetrahedrite is stable in a wide solid solution range above 95°C with the composition of $\text{Cu}_{12+x}\text{Sb}_{4+y}\text{S}_{13}$ where $0.11 \leq X \leq 1.77$ and $0.03 \leq Y \leq 0.30$.

This tetrahedrite solid solution dissociates below 95°C into two immiscible phases with the same tetrahedrite structure. The dissociation is rapid and reversible. Cell dimensions and densities of the two phases indicate that they differ only in copper content. These copper-poor and copper-rich tetrahedrite phases change to each other by addition of copper or sulfur even at room temperature.

The homogeneous copper-poor and copper-rich tetrahedrite phases can exist at room temperatures only in a very narrow field with the end compositions near $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$, respectively. They are separated by a small field near Cu_3SbS_3 , where a superstructure appears with a cell edge two times larger than that of tetrahedrite ($a = 20.848 \pm 0.006$ Å for $\text{Cu}_3\text{Sb}_{0.99}\text{S}_3$). The superstructure phase, called pseudotetrahedrite, is stable up to 350°C, and transforms to the normal tetrahedrite phase, indicating its polymorphic relation with tetrahedrite. Because of the appearance of a high-temperature phase of Cu_3SbS_3 above 361°C, a part of the tetrahedrite solid solution dissociates into tetrahedrite and the Cu_3SbS_3 phase.

Introduction

Tetrahedrite is one of the widespread minerals commonly found in sulfide ore deposits in general. The mineral is cubic with space group $I\bar{4}3m$, and the structure was derived from the sphalerite structure (Pauling and Neuman, 1934; Wuensch, 1964). A chemical formula, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, has been widely accepted for tetrahedrite as an ideal formula based on its crystal structure. However, it contains many elements such as Fe, Zn, Ag, and Hg in solid solution in nature, and the majority of tetrahedrite from various localities has been considered to correspond to the general formula $(\text{Cu}, \text{Ag})_{10}(\text{Fe}, \text{Zn})_2(\text{As}, \text{Sb})_4\text{S}_{13}$ (Pauling and Neuman, 1934; Springer, 1969; Takéuchi, 1971).

Until recent studies of the phase relations in the Cu-As-S system by Maske and Skinner (1971) and in the Cu-Sb-S system by Skinner, Luce, and Makovicky (1972), only very few studies were reported on the phase relations of tetrahedrite. In order to provide a basic knowledge of the mineralogy and

crystal-chemistry of tetrahedrite, we initiated a study of the phase relations in the Cu-Sb-S system in 1969 and have mostly concentrated on elucidating the stable composition field of tetrahedrite in the system. In the course of this investigation, a detailed study on the Cu-As-S system (Maske and Skinner, 1971) was published. Upon inquiry, Professor Skinner kindly sent us the preprint of their excellent paper on the phase relations in the Cu-Sb-S system (Skinner, Luce, and Makovicky, 1972). In their investigation, they have established the general phase relations in the whole Cu-Sb-S system above 300°C. However, their description on the tetrahedrite solid solution is not yet complete below 400°C.

Our results on the phase relations in the Cu-Sb-S system confirm Skinner's results above 400°C (Tatsuka and Morimoto, 1972a and 1972b). However, we have studied the variation of the composition field of tetrahedrite below 400°C in some detail (Tatsuka and Morimoto, 1971) as will be described in this paper.

Because almost complete references to the earlier work on the Cu-Sb-S system have been given by Skinner, Luce, and Makovicky (1972), only addi-

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tional references necessary for describing our investigation are given here. The name abbreviations for the compounds in the Cu-Sb-S system used by Skinner, Luce, and Makovicky (1972) are mostly followed in this paper (Fig. 1).

Experimental Method

The crystals were synthesized dry from mixtures of sulfur, antimony, and copper. Copper and sulfur of 99.99 and 99.999 percent purity, respectively, were obtained as grains from the American Smelting Co. Antimony of 99.999 percent purity was purchased from Nakarai Chemical Ltd. The copper was reduced in hydrogen gas at 600°C.

The mixtures of the three elements in appropriate ratios were enclosed in evacuated silica tubes, and were kept for about 120 hours at 500° ± 3°C. They were slowly cooled to 300°C with the rate of 20°C/hour, kept at that temperature for more than 48 hours, and again slowly cooled to room temperature in about 10 hours. The products were ground under acetone, then dried and resealed in evacuated silica tubes. The procedures of heating, cooling, annealing, and grinding were repeated twice. Then the products were kept at 300° and 400° for appropriate periods from a week to a few months, and quenched into ice water or slowly cooled to room temperature. Grinding of the specimens was performed two or three times during the heating to accelerate reaction at 300°C and 400°C. Some crystals

were prepared by annealing after slow cooling to 300°C from the melt in evacuated silica tubes.

The reflection microscope and X-ray diffraction were employed to identify the phases in specimens of different compositions. The X-ray powder patterns were obtained by nickel-filtered CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The diffractometer was calibrated with respect to silicon of 99.999 percent purity, the cell edge of which was taken as 5.4306 Å at 20°C. The X-ray powder and single crystal methods were carried out at high temperatures for some specimens to confirm unquenchable phases.

The differential thermal analysis (DTA) was carried out for some specimens by sealing specimens in evacuated silica tubes. A differential scanning calorimeter (DSC) was also used to determine the reactions at low temperatures.

Tetrahedrite Solid Solution

In the study of the phase relations in the Cu-Sb-S system, Shima (1967 and 1968) and Sugaki and Shima (1969) found that the synthetic specimen with composition Cu₁₂Sb₄S₁₃ was not homogeneous, but always included a small amount of famatinite. They obtained an apparently homogeneous phase under the microscope only for the composition Cu₁₂Sb₄S_{12.7}. However, the X-ray powder patterns of this phase differed from those of natural tetrahedrite in that all the diffraction lines in the patterns had split into double peaks. No reason for this splitting was given by them.

In order to understand the reason for this line splitting, we synthesized tetrahedrite with widely different compositions around the composition of Cu₁₂Sb₄S_{12.7} at different temperatures and examined the products by the X-ray powder method and the reflection microscope. When rapidly cooled from 300°C, apparently homogeneous tetrahedrite has an extensive composition field in the Cu-Sb-S system, with or without splitting of the peaks in the powder patterns.

However, as described by Skinner, Luce, and Makovicky (1972), the field is always in an area more copper rich than Cu₁₂Sb₄S₁₃. The powder patterns of synthetic tetrahedrites (Fig. 2) illustrate that the splitting of peaks typical of Cu_{12.88}Sb_{4.09}S₁₃ results because Cu_{12.88}Sb_{4.09}S₁₃ consists of two different phases with the compositions of Cu_{12.11}Sb_{4.09}S₁₃ and Cu_{13.72}Sb_{4.09}S₁₃ (Tatsuka and Morimoto, 1971). The powder data of the two phases are listed in Tables 1 and 2. Skinner, Luce, and Makovicky (1972) independently describe the dissociation of tetrahedrite grown at elevated temperatures into two immiscible, but structurally similar, phases on

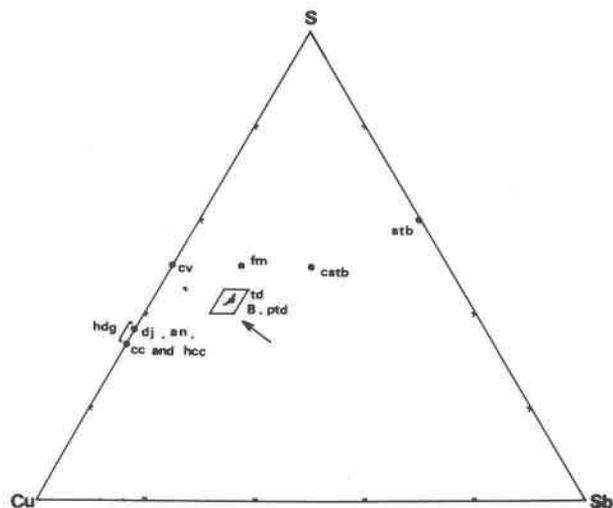


FIG. 1. Synthetic and natural phases in the Cu-Sb-S system. The area studied in the present study is indicated by the arrow. Abbreviations used in this figure are mostly after Skinner, Luce, and Makovicky (1972) and are used in subsequent figures and tables. They are as follows: cv, covellite (Cu₂S); cc, chalcocite (Cu₂S); hcc, high chalcocite (Cu₂S); dj, djurelite (Cu₁₁S); an, anilite (Cu₁₁S); hdg, high digenite; stb, stibnite (Sb₂S₃); fm, famatinite (Cu₂SbS₃); cstb, chalcostibite (CuSbS₂); td s.s., tetrahedrite solid solution; td two-phase, tetrahedrite two-phase region; B, Cu₁₂Sb₄S₁₃; ptd, pseudotetrahedrite (see text).

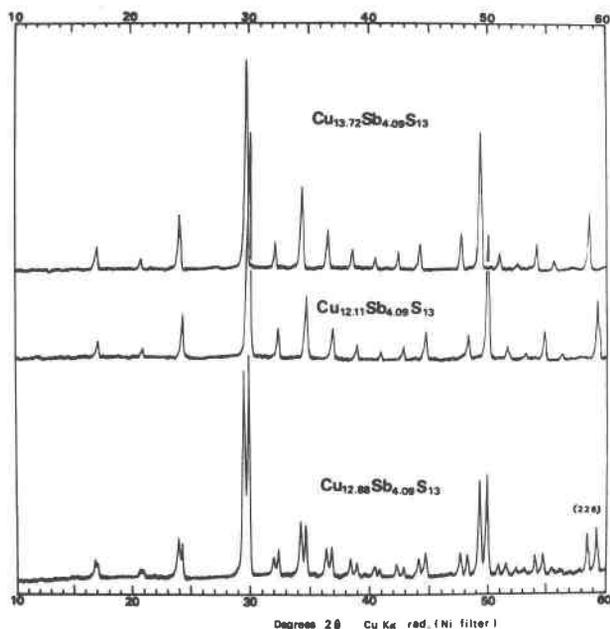


Fig. 2. X-ray powder patterns of synthetic tetrahedrite. The typical splitting of peaks is observed in the pattern of $\text{Cu}_{12.88}\text{Sb}_{4.09}\text{S}_{13}$, and indicates that this phase is really a mixture of two immiscible tetrahedrite phases, $\text{Cu}_{12.11}\text{Sb}_{4.09}\text{S}_{13}$ and $\text{Cu}_{13.72}\text{Sb}_{4.09}\text{S}_{13}$. The powder data of the two tetrahedrite phases are given in Tables 1 and 2.

quenching, without giving an exact relation between cell edge and composition.

Our efforts were concentrated on finding a possible composition field of tetrahedrite (tetrahedrite solid solution) in which only a single phase of tetrahedrite occurred for specimens rapidly cooled to room temperature from 300°C. Based on X-ray powder patterns and observations with the reflection microscope, the tetrahedrite solid solution field appeared to cover a curved strip, running, almost but not quite, from $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ to $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$ in composition (Fig. 3). The cell edges of tetrahedrite solid solutions increase with the copper content from 10.33 Å at the copper-poor end ($\text{Cu}_{12.11}\text{Sb}_{4.09}\text{S}_{13}$) to 10.45 Å at the copper-rich end ($\text{Cu}_{13.77}\text{Sb}_{4.09}\text{S}_{13}$) (Fig. 4 and Table 3). However, the shape of the solid solution field looks unusual and the phase determination (by the methods mentioned) was difficult for the specimens of the central part of the strip. Consequently, some single crystals with the compositions near the central part of the field were examined by X-ray single crystal method. A superstructure with a cell edge double that of tetrahedrite was confirmed in a small field near the composition Cu_3SbS_3 . This field separates the tetra-

TABLE 1. X-ray Powder Data for the Copper-Poor Tetrahedrite of $\text{Cu}_{12.11}\text{Sb}_{4.09}\text{S}_{13}$ *

d (Å)	I/I ₁	hkl	d (Å)	I/I ₁	hkl
5.16	8	002	1.594	2	145
4.22	4	112	1.557	25	226
3.65	16	022	1.523	4	136
2.981	100	222	1.491	2	444
2.760	12	123	1.460	4	017,055
2.582	25	004	1.405	2	127,255
2.434	14	033,114	1.380	2	246
2.309	6	024	1.312	4	237,156
2.202	4	233	1.291	4	008
2.108	6	224	1.271	4	118,147
2.205	12	015,134	1.234	4	356
1.885	8	125	1.200	6	057,138
1.826	40	044	1.185	6	266
1.771	6	035,334	1.114	4	129,167
1.721	2	006,244	1.089	4	039,158
1.675	10	116,235	1.065	4	239,367
1.633	4	026	1.054	6	448

* The intensity was estimated by the diffractometer and $I_1/I_{\text{corundum}}=2.75$. $\text{CuK}\alpha$ radiation was used. The cell edge (a) obtained from this data is 10.330 ± 0.003 Å.

hedrite solid solution field into two parts: one copper-rich, the other copper-poor. The superstructure phase here called pseudotetrahedrite is polymorphically related to the normal tetrahedrite solid solution as described below.

Tetrahedrite Two-Phase Field

Examination of specimens rapidly cooled to room temperature from 300°C revealed the copper-rich

TABLE 2. X-ray Powder Data for the Copper-Poor Tetrahedrite of $\text{Cu}_{13.72}\text{Sb}_{4.09}\text{S}_{13}$ *

d (Å)	I/I ₁	hkl	d (Å)	I/I ₁	hkl
5.22	8	002	1.612	2	145
4.27	4	112	1.575	20	226
3.69	20	022	1.540	4	136
3.016	100	222	1.508	4	444
2.792	10	123	1.478	4	017,055
2.612	25	004	1.422	2	127,255
2.463	14	033,114	1.396	2	246
2.336	8	024	1.327	4	237,156
2.228	4	233	1.306	4	008
2.133	8	224	1.286	4	118,147
2.049	10	015,134	1.249	4	356
1.908	12	125	1.215	4	057,138
1.847	45	044	1.198	4	266
1.792	6	035,334	1.127	4	129,167
1.741	2	006,244	1.101	4	039,158
1.695	10	116,235	1.078	4	239,367
1.652	4	026	1.066	4	448

* The intensity was estimated by the diffractometer and $I_1/I_{\text{corundum}}=2.68$. $\text{CuK}\alpha$ radiation was used. The cell edge (a) obtained from this data is 10.448 ± 0.003 Å.

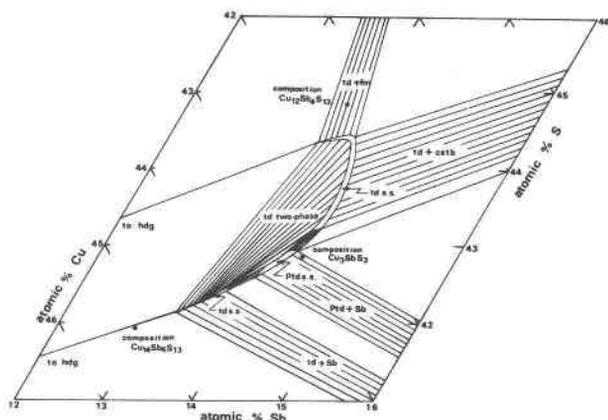


FIG. 3. The composition field of the tetrahedrite solid solution at room temperature in the Cu-Sb-S system. Compositions are in atom percent. The field is bounded by the three-phase and two phase assemblages indicated. The details of the phase relations in the central part of the field are explained in the text. The compositions $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, Cu_3SbS_3 and $\text{Cu}_{11}\text{Sb}_1\text{S}_{13}$ are represented as solid circles.

and copper-poor tetrahedrite phases to coexist over a wide composition field, here called the tetrahedrite two-phase field, in the antimony-poor region of the tetrahedrite solid solution strip mentioned above (Fig. 3). In one specimen the coexistence of the two phases was revealed not only by the splitting peaks in the X-ray powder patterns but also by observations with a reflection microscope after etching the specimen with a 20 percent KCN solution as described below. However, if the bulk composition of the specimen was close to that of the central

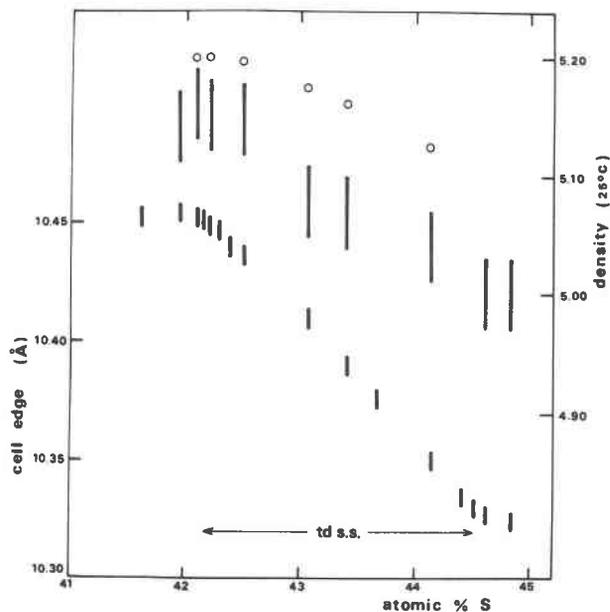


FIG. 4. Cell edges and density of the tetrahedrite solid solution plotted against atom percent of sulfur. Precise values for the cell edges and compositions are given in Table 3. The measurements were carried out at room temperature for the specimens rapidly cooled from 300°C. The cell edge for the specimen with 42.85 atom percent of sulphur represents that of the subcell of pseudotetrahedrite described later. The calculated values of density (open circles) were calculated by assuming 13 sulfur atoms in the unit cell.

part of the tetrahedrite solid solution, the two possible phases were very close to each other in composition, and X-ray single crystal methods were needed to distinguish them.

TABLE 3. Cell Edges and Composition of the Tetrahedrite Solid Solution*

Composition			Chemical formula (S=13)			Cell edge a_0 (Å)	density at 25°C ±0.03	Additional phases
Mole per cent		S	Cu	Sb	S			
Cu	Sb							
41.38	13.79	44.83				10.324	5.00	fm
41.46	13.94	44.60	12.08	4.06	13	10.327	5.00	fm
41.47	14.02	44.51	12.11	4.09	13	10.330		
41.50	14.10	44.40	12.15	4.13	13	10.335		
41.64	14.23	44.13	12.26	4.22	13	10.350	5.02	
41.90	14.44	43.66	12.48	4.30	13	10.376		
42.25	14.35	43.40	12.66	4.30	13	10.390	5.07	
42.71	14.23	43.06	12.89	4.30	13	10.411	5.08	
43.75	13.75	42.50	13.38	4.21	13	10.436	5.15	
44.07	13.56	42.37	13.52	4.16	13	10.441		
44.29	13.43	42.28	13.81	4.13	13	10.447		
44.53	13.28	42.19	13.72	4.09	13	10.448	5.15	
44.65	13.21	42.14	13.77	4.08	13	10.451		
44.78	13.13	42.09				10.452	5.16	hdg
45.16	12.90	41.94				10.453	5.13	hdg
45.90	12.50	41.60				10.452		hdg, Sb

* The cell edges were measured at room temperature for the compounds synthesized at 300°C.

To study the variation with temperature of the tetrahedrite two-phase field as well as its relationship with the tetrahedrite solid solution in the Cu-Sb-S system, X-ray powder studies were made at high temperatures with specimens consisting of two phases in evacuated silica capillaries. It was immediately found that the splitting of the peaks in the powder patterns took place by dissociation of homogeneous tetrahedrite at high temperatures into two immiscible phases on quenching. The dissociation is rapid and reversible.

As temperature increases, the two 226 peaks gradually approach and become single at 95°C for the specimen with bulk composition $\text{Cu}_{12.88}\text{Sb}_{4.09}\text{S}_{13}$ (Fig. 5). The gradual change in the d -values of 226 reflections for the two coexisting phases (Fig. 6) indicates that the two phases gradually change their compositions with temperature and finally become a single phase at 95°C. This temperature was confirmed by the differential scanning calorimeter (DSC) curve for the same specimen. According to Skinner (1972, private communication), however, the two coexisting phases for a crystal of composition $\text{Cu}_{12.59}\text{Sb}_{4.03}\text{S}_{13}$ homogenized at 125°C. This suggests that homogenization temperature is composition-dependent.

The degree of tetrahedrite solid solution has a tendency to become smaller with temperature increase above 300°C (Skinner, Luce, and Makovicky, 1972; Tatsuka and Morimoto, 1972a) and the dissociation of the tetrahedrite solid solution into two immiscible tetrahedrite phases is very rapid and reversible at about 100°C. Because the reactions of the tetrahedrite solid solution with other phases are not likely in the Cu-Sb-S system below 300°C, except for dissociation of the solid solution, the phase relations of the tetrahedrite solid solution obtained from the specimens rapidly or slowly cooled to room temperature from 300°C (Fig. 3) are considered to represent the phase relations at room temperature. On the other hand, the tetrahedrite solid solution at 300°C is obtained only by extending the tetrahedrite solid solution over the entire tetrahedrite two-phase field in Figure 3, except for the appearance of the pseudotetrahedrite solid solution described later.

Main experimental runs for the determination of the phase relations at 300°C and room temperature are presented in Tables 4 and 5. All the experimental data are available from the authors upon request.

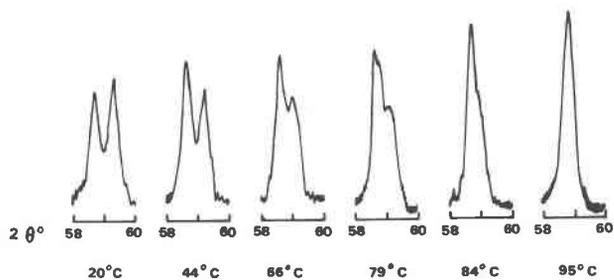


FIG. 5. Decrease in splitting of the 226 peaks for $\text{Cu}_{12.88}\text{Sb}_{4.09}\text{S}_{13}$ as temperature is increased from 20°C to 95°C.

Mobility of Copper Atoms in Tetrahedrite

Because the tie lines in the tetrahedrite two-phase field are approximately parallel to the join connecting $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$, the two coexisting phases differ mainly in copper content. In order to find the structural reason for the change in chemical composition along the strip of single-phase tetrahedrite solid solution at room temperature, the densities of the specimens of different compositions were measured by pycnometric method (Fig. 4). Because both cell edges and densities increase in the solid solution from the copper-poor phases to copper-rich phases, the composition change is attributed mainly to addition of copper atoms into interstices of the

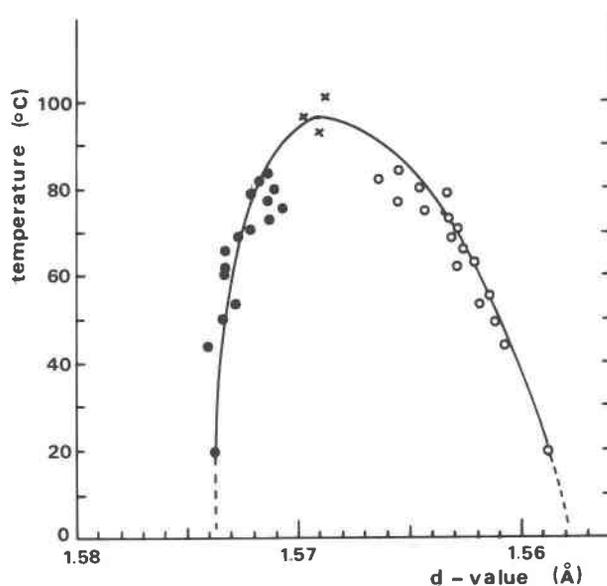


FIG. 6. Gradual change of the d -values for the 226 reflections of the two co-existing phases (solid and open circles) as temperatures for the specimen of $\text{Cu}_{12.88}\text{Sb}_{4.09}\text{S}_{13}$ are increased from 20° to 95°C.

normal tetrahedrite structure at compositions close to $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (Pauling and Neuman, 1934; Wuensch, 1964). The most copper-rich end member of the solid solution has about 3.32 more copper atoms in each unit cell in comparison with the most copper-poor end member.

Under the reflection microscope, it was difficult to distinguish the copper-poor tetrahedrite from the copper-rich tetrahedrite in air and in oil. However, after etching with KCN (20%) and KOH, cracks that were found to be the boundaries of the two phases were observed in the crystal grains under the micro-

TABLE 4. Significant Experimental Runs for the Phase Relations of the Tetrahedrite Solid Solution in the Cu-Sb-S System*

Composition, atomic %			Heating time, days	Products
Cu	Sb	S		
42.43	13.22	44.35	100	td+fm+hdg
48.75	8.75	42.50	37	td+fm+hdg
41.90	13.60	44.50	87	td+fm+hdg
41.58	13.75	44.67	29	td+fm
41.70	13.80	44.50	87	td+fm
41.57	13.91	44.52	49	td+fm
41.43	13.99	44.58	30	td+fm
41.38	13.79	44.83	100	td+fm
41.40	14.04	44.56	94	td+fm+cstb
41.20	14.04	44.76	30	td+fm+cstb
41.24	14.16	44.60	44	td+fm+cstb
41.34	14.13	44.53	43	td+cstb
41.50	14.20	44.30	94	td+cstb
41.90	14.44	43.66	42	td+cstb
42.13	14.47	43.40	21	td+cstb
41.59	13.95	44.46	30	td
41.74	13.91	44.35	45	td
41.47	14.02	44.51	44	td
41.55	14.08	44.37	49	td
41.59	14.16	44.25	44	td
41.64	14.23	44.13	30	td
41.74	14.21	44.05	44	td
42.04	14.30	43.66	42	td
41.97	14.37	43.66	42	td
42.25	14.26	43.49	21	td
42.25	14.35	43.40	42	td
42.55	14.19	43.26	79	td
42.71	14.23	43.06	36	td
43.75	13.75	42.50	79	td
44.25	13.25	42.50	44	td
42.40	13.80	43.80	44	td
42.00	13.70	44.30	103	td
42.40	13.60	44.00	103	td
43.00	13.50	43.50	87	td
43.40	13.30	43.20	87	td
43.21	13.93	42.86	79	td
44.07	13.56	42.37	55	td
44.53	13.28	42.19	98	td
44.65	13.21	42.14	98	td
43.75	13.40	42.85	44	td

TABLE 4, Continued

Composition, atomic %			Heating time, days	Products
Cu	Sb	S		
42.86	14.28	42.86	164	td+Sb
43.00	15.50	41.50	105	td+Sb
40.00	20.00	40.00	105	td+Sb
43.20	14.05	42.70	30	td+Sb
43.01	14.34	42.65	36	td+Sb
44.50	13.50	42.00	104	td+Sb
42.14	15.00	42.86	79	td+cstb+Sb
42.58	14.45	42.97	35	td+cstb+Sb
40.40	15.80	43.80	105	td+cstb+Sb
42.10	13.60	44.30	103	td+hdg
42.50	13.50	44.00	103	td+hdg
43.20	13.30	43.50	87	td+hdg
43.50	13.20	43.20	87	td+hdg
44.80	12.99	42.20	60	td+hdg
44.00	13.00	43.00	44	td+hdg
44.78	13.13	42.09	98	td+hdg
45.16	12.90	41.94	105	td+hdg
45.09	13.04	41.87	60	td+hdg+Sb
43.70	15.56	40.74	44	td+hdg+Sb

* The specimens were annealed at 300°C for times indicated. The identification of phases was mainly carried out a few months after rapid or slow cooling to room temperature. Phase abbreviations are given in Fig. 1.

scope. A photomicrograph (Fig. 7) for the specimen of $\text{Cu}_{12.88}\text{Sb}_{4.09}\text{S}_{13}$ etched with KCN (20%) for two seconds clearly indicates that each grain of $\text{Cu}_{12.88}\text{Sb}_{4.09}\text{S}_{13}$ dissociated to two immiscible copper-poor (white) and copper-rich (black) phases. Because such a dissociation below 100°C as found in the tetrahedrite solid solution is very rare in sulfides in general, the characteristics of the two immiscible phases of tetrahedrite were studied in more detail.

The diffusion of copper atoms in the tetrahedrite structure can take place not only in the heating experiments described above, but also in simple reactions at room temperature. Thus a mixture of copper and of copper-poor tetrahedrite powders in equal amounts was covered by platinum foil and pressed for 30 seconds under 5 ton/cm² pressure in 10⁻² Hg mm. In the pressed specimen, half of the copper-poor tetrahedrite changed to the copper-rich tetrahedrite in thirty minutes and this reaction proceeded to completion in a day. Similarly, copper-poor tetrahedrite was obtained by pressing a mixture of sulfur and of copper-rich tetrahedrite powders.

Copper-poor tetrahedrite was also obtained by immersing a copper-rich tetrahedrite in a carbon disulfide solution containing five percent sulfur for several hours. When the resulting copper-poor tetrahedrite was observed under the reflection microscope, a thin film of copper sulfide covered the

TABLE 5. Single Crystal Experiments for the Stable Field of Pseudotetrahedrite[#]

Composition, atomic %			Synthesis	Heating temperature and time		Cooling	Products
Cu	Sb	S	temperature °C	°C	days		
41.38	13.79	44.83	500	300	1	slow (one day)	td+fm
41.67	13.89	44.44	500	300	2	slow (one day)	td
41.74	13.91	44.35	500	300	2	slow (one day)	tó
41.81	13.94	44.25	500	200	2	rapid	}td
			500	300	2	slow (one day)	
42.55	14.19	43.26	705	—	—	slow (one day)	td
42.86	14.28	42.86	720	—	—	slow (one day)	ptd+Sb
			710	300	60	rapid	ptd+Sb
			710	360	1	rapid	td+Sb
42.71	14.23	43.06	710	300	1	rapid	ptd+cstb (trace)
43.25	14.05	42.70	710	300	1	slow (one day)	ptd+Sb
43.75	13.75	42.50	710	300	1	slow (one day)	ptd
45.16	12.90	41.94	710	300	60	rapid	td+Cu sulfides*
44.00	13.00	43.00	550	—	—	slow (20 days)	Copper-poor td+ Copper-rich td+dg
44.44	14.82	40.74	705	—	—	slow (one day)	td+Sb+Cu sulfides*

[#] The experiments were carried out at room temperature. The results are illustrated in Fig.10. The phase with * were not precisely determined because of complex relations of copper sulfides at low temperature.

crystal, indicating the outward diffusion of copper atoms from the copper-rich tetrahedrite to produce the copper-poor tetrahedrite. These outward diffusing copper atoms then reacted with the sulfur atoms in the solution.

Thus, Cu atoms are mobile even at room temperature. Although this mobility of Cu atoms is closely connected with the appearance of two different but similar tetrahedrite phases, the mechanism of the formation of the two phases remains unknown at this stage of the study.

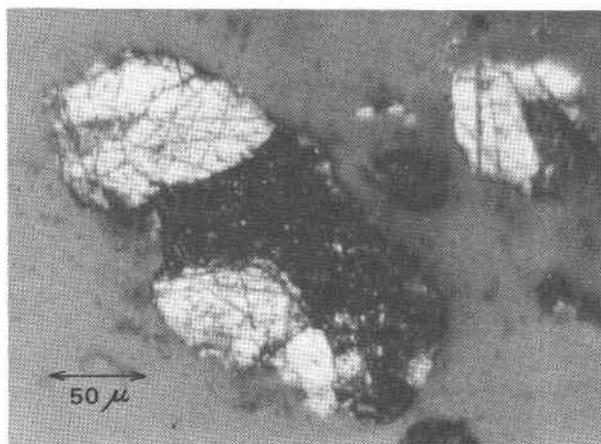


FIG. 7. Photomicrograph of synthetic $\text{Cu}_{12.88}\text{Sb}_{4.06}\text{S}_{13}$ in polished section etched two seconds with KCN (20%). The white (scratch) reveals copper-poor tetrahedrite, the black (deposit) represents copper-rich tetrahedrite, and the dark gray is cold-setting plastic.

Pseudotetrahedrite Solid Solution

A phase with the composition of Cu_3SbS_3 was first described by Cambi and Elli (1965) and later by Shima (1967 and 1968) and Godovikov *et al* (1971). Skinner, Luce, and Makovicky (1972) called it phase B or B'. They have found that (1) phase B is only stable above $359^\circ \pm 2^\circ\text{C}$; (2) below this temperature the compositional equivalent chalcostibite (CuSbS_2) + tetrahedrite + antimony becomes stable; but (3) phase B metastably persists below 359°C for a long time and transforms to phase B' at $122^\circ \pm 3^\circ\text{C}$. Though this transition temperature is in good agreement with ours, our results indicate that phase B decomposes below $361^\circ \pm 2^\circ\text{C}$ into tetrahedrite + antimony.

When a melt of composition Cu_3SbS_3 was cooled slowly to room temperature (or re-annealed at 300°C after rapid cooling to room temperature), phase B did not appear. The product was apparently a tetrahedrite phase and a very small amount of antimony representing the stable assemblage of composition Cu_3SbS_3 at room temperature (Fig. 3). Crystals obtained from the product were examined by the single crystal method. They were found to have a superstructure of tetrahedrite with the cell edge of $a = 2a' = 20.848 \pm 0.006 \text{ \AA}$, where a' is the cell edge of tetrahedrite. The crystals of this superstructure are cubic and are named pseudo-tetrahedrite in this paper as already mentioned. A precession photograph of pseudotetrahedrite is compared with that of tetrahedrite ($\text{Cu}_{12.24}\text{Sb}_{4.08}\text{S}_{13}$)

(Fig. 8). The composition of this pseudotetrahedrite is considered to be $\text{Cu}_3\text{Sb}_{0.99}\text{S}_3$, judging from the amount of antimony in the decomposition products of Cu_3SbS_3 .

In order to determine the temperature range where pseudotetrahedrite is stable, a high-temperature precession camera was used. The superstructure reflections of pseudotetrahedrite of composition $\text{Cu}_3\text{Sb}_{0.99}\text{S}_3$ disappear at $350^\circ \pm 5^\circ\text{C}$. When the crystal was rapidly cooled from that temperature, the normal tetrahedrite structure was preserved even at room temperature. However, annealing at 300°C again changed the crystal to pseudotetrahedrite. It is, therefore, evident that pseudotetrahedrite is polymorphically related to tetrahedrite. For the composition Cu_3SbS_3 , pseudotetrahedrite is stable together with a very small amount of antimony up to 350°C , where upon pseudotetrahedrite transforms to tetrahedrite. Above $361^\circ \pm 2^\circ\text{C}$, tetrahedrite and antimony change to phase B. When etched by KCN (20%), pseudotetrahedrite is dark brown rather

than black under the reflection microscope, and is closer in appearance to the copper-rich tetrahedrite.

To determine a possible composition field of pseudotetrahedrite at room temperature, the single crystal method was applied to several tetrahedrite-like crystals which were produced near and in the tetrahedrite solid solution area. The compositions of the crystals examined and the results are given in Table 5. The appearance of pseudotetrahedrite near the compositions Cu_3SbS_3 results in the separation of the tetrahedrite solid solution into copper-poor and copper-rich phases. At room temperature, the boundaries between pseudotetrahedrite and the copper-poor tetrahedrite and between pseudotetrahedrite and the copper-rich tetrahedrite are at about $\text{Cu}_{12.8}\text{Sb}_{4.3}\text{S}_{13}$ and $\text{Cu}_{13.5}\text{Sb}_{4.2}\text{S}_{13}$, respectively. However, the stable field of pseudotetrahedrite is considered to diminish to $\text{Cu}_3\text{Sb}_{0.99}\text{S}_3$ with temperature increase as illustrated in Figures 3 and 9a.

Because the intensities of the superstructure reflections are weak compared with those of the main reflections in pseudotetrahedrite, the difference in structure between pseudotetrahedrite and tetrahedrite is considered not great. The crystal structure of pseudotetrahedrite is now under investigation.

Variation of the Tetrahedrite Solid Solution

Based on the results obtained in this study, the change of the tetrahedrite solid solution and its relations to other phases are illustrated in the isothermal sections at various temperatures below 400°C (Figs. 3 and 9).

The nonstoichiometric composition of the tetrahedrite solid solution is evident at room temperature from the present study. However, the copper-poor and copper-rich fields in the tetrahedrite solid solution, separated by the pseudotetrahedrite solid solution, extend more toward the compositions of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$, respectively, with temperature decrease. Because most of the experimental data have been obtained from the synthetic specimens rapidly or slowly cooled from 300°C and the reaction rate is generally very slow below 300°C , it might be possible that these stoichiometric compositions are included within the tetrahedrite solid solution in the Cu-Sb-S system at room temperature. When partial substitutions of Cu by other ions such as Fe and Zn and of Sb by As take place in the tetrahedrite solid solution, only the copper-poor phase with a stoichiometric composition such as $(\text{Cu, Zn, Fe})_{12}(\text{Sb, As})_4\text{S}_{13}$ seems to remain stable

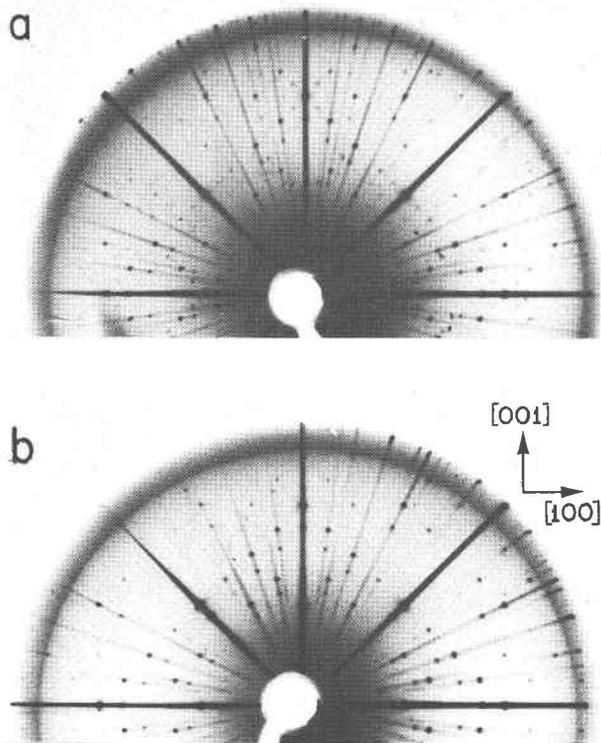


FIG. 8. Precession photographs perpendicular to the a -axis of (a) pseudotetrahedrite with a superstructure, and (b) tetrahedrite ($\text{Cu}_{12.21}\text{Sb}_{4.06}\text{S}_{13}$).

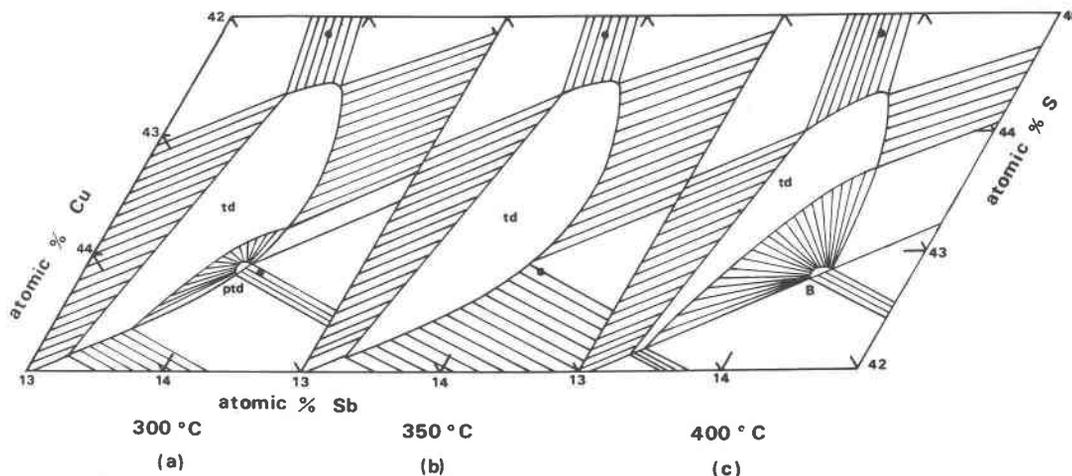


FIG. 9. Possible variation of the composition fields of tetrahedrite and pseudotetrahedrite with temperature. Compositions are in atom percent. The compositions $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and Cu_3SbS_3 are represented as solid circles.

according to the chemical composition of natural tetrahedrites (Springer, 1969; Takéuchi, 1971).

The existence of a three-phase field involving the copper-rich and copper-poor tetrahedrite phases plus pseudotetrahedrite is not clear in this investigation, but assumed in Figure 3. The two-phase field of tetrahedrite disappears and is included in the tetrahedrite solid solution above about 95°C, though pseudotetrahedrite remains stable in a very small field until 350°C. The two-phase field with tetrahedrite and pseudotetrahedrite is assumed in the isothermal section at 300°C (Fig. 9a).

When pseudotetrahedrite transforms to tetrahedrite, only tetrahedrite remains (Fig. 9b) as a stable ternary compound in the area given in Figure 9. Phase B of composition Cu_3SbS_3 appears at $361^\circ \pm 2^\circ$ and the two-phase field with phase B and tetrahedrite expands into the tetrahedrite solid solution field (Fig. 9c). These relations are also given by Skinner, Luce, and Makovicky (1972) with minor differences from ours. The tetrahedrite solid solution field becomes smaller with further increase of temperature and such solid solutions finally decompose to high digenite + famatinite + phase B at $543^\circ \pm 2^\circ$ as described by Skinner, Luce, and Makovicky (1972).

In nature, tetrahedrite is almost invariably a complex solid solution in which Sb and As show extensive mutual substitution and Fe, Zn, and Ag commonly substitute for Cu. To apply the phase relations to natural minerals, the study of more complex systems such as Cu-Fe-As-Sb-S is necessary. In order to examine the effect of other ions

to the phase relations in the Cu-Sb-S system, some experiments were carried out by adding several percent Fe or Zn instead of Cu in the Cu-Sb-S system. The change of the phase relations was remarkable. The tetrahedrite two-phase field disappeared and a single tetrahedrite solid solution remained stable even at room temperature. A similar effect by replacement of Sb by As was reported by Maske and Skinner (1971). The phase relations obtained in this investigation must, therefore, provide important basic knowledge for understanding the more complex systems.

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