THE AMERICAN MINERALOGIST, VOL. 52, JANUARY–FEBRUARY, 1967

THE Bi_2Te_3-Bi_2S_3 SYSTEM AND THE SYNTHESIS OF THE MINERAL TETRADYMITE

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ABSTRACT

A phase equilibria study of the Bi_2Te_3-Bi_2S_3 pseudobinary system has demonstrated that this system contains two compounds, a congruent melting γ-phase (called γ-tetradymite) and an incongruent β-phase (called β-tetradymite), as well as a region of solubility of Bi_2S_3 in Bi_2Te_3. The phase diagram is correlated with previous observations, including studies of the mineral "tetradymite." A mineral sample from Paonia, Colo. was identified as γ-tetradymite.

INTRODUCTION

The mineral tetradymite has the C33-type crystal structure and the space group symmetry $R\bar{3}m$, which is the same as the compounds Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3. The work of Harker (1934) on the structure and atomic positions of the atoms has shown that tetradymite (Bi_2Te_3S) consists of layers of atoms stacked in the following order along the c_H axis of the hexagonal lattice

-Te-Bi-S-Bi-Te-.

The synthesis of tetradymite as a single-phase composition has not been previously reported, and studies of the Bi_2Te_3-Bi_2S_3 phase system have not led to consistent results nor to a method for preparing tetradymite as a single phase.

Early work on this pseudobinary system is summarized by Mellor (1931). His phase diagram indicated that the only compound in this system was a congruent melting compound having the stoichiometry, $Bi_2Te_3 \cdot Bi_2S_3$. A more recent study of this system by Beglaryan and Abrikasov (1959) indicates that tetradymite is a congruent melting compound and is the only compound in this system, but a descrepancy appears in the composition scale for their diagram. It was reported by Soonpaa (1960, 1962) that reaction of the tetradymite composition above the liquidus produces Bi_2Te_3, tetradymite and a proposed phase $Bi_8Te_7S_5$. The simultaneous existence of these phases is evidence for possible incomplete reaction and may represent the difficulty in achieving equilibrium in this system.

For these reasons a detailed phase study of this pseudobinary system was undertaken to determine the true equilibrium phase diagram and to evaluate the conditions necessary for the synthesis of tetradymite. To

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achieve equilibrium, the samples used in this study were annealed at an elevated temperature in the subsolidus region for an extended period of time. The phase equilibria studies were performed by standard techniques employing X-ray diffraction, differential thermal analysis (DTA), and metallography.

EXPERIMENTAL PROCEDURES

Materials. Bismuth metal shot (99.999+%), elemental sulfur (99.999+%) and tellurium (99.999+%) were obtained from American Smelting and Refining Company and used in the preparation of the samples. A sample of the mineral tetradymite from Paonia, Colorado, was obtained from the U. S. National Museum (Catalog No. R-395).[1]

Sample preparation. For the phase equilibria studies of the Bi_2Te_3-Bi_2S_3 system, 37 three-gram samples covering the entire range of compositions were prepared. They were sealed in evacuated quartz ampoules and rotated in a 'Hevi-Duty' tube furnace; the temperature was raised above the liquidus for approximately 30 minutes and then cooled to room temperature. The samples were then placed in a high thermal capacity annealing furnace and initially annealed at 400°C for two weeks. After this initial annealing period, the alloys were removed from the ampoules, ground up with a vibrator and sieved to −50 mesh. They they were replaced in evacuated, sealed quartz ampoules and annealed at 400°C for approximately three more weeks. In addition, at periodic intervals during this three-week period the powdered samples were removed from the furnace and shaken with the vibrator to ensure homogenization of the composition. The samples were then cooled down to room temperature and used for the phase studies. This procedure was developed for synthesizing tetradymite in the subsolidus region by studying the effect of annealing time at 400°C on the resulting DTA thermograms and X-ray diffraction patterns, and was employed for preparing all compositions in this phase study.

Glatz (1965) has demonstrated that sample compositions in the bismuth-tellurium phase system prepared by this method do not deviate by more than 0.05 mole percent from the prepared composition.

Phase equilibria examination. The DTA thermograms were obtained by the conventional technique of plotting the difference in temperature between an aluminum oxide standard and the sample with a Honeywell X-Y recorder (Model 153X33). DTA samples were prepared by adding

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[1] This sample was identified as 'tetradymite' by Dr. E. N. Cameron of the University of Wisconsin.

750 mg of the alloy composition to 250 mg of α-Al_2O_3 (both sieved from -100 to $+200$ mesh). The alluminum oxide was added to the sample to minimize base-line drift. The standard and the sample were contained in sealed Vycor ampoules with concentric thermocouple wells and placed symmetrically in a high thermal capacity Kanthal furnace. The heating rate of the furnace was controlled at 5°C per minute with a cam-type program controller (Honeywell—Model 152). This DTA apparatus yields an accuracy of ±3°C for the reported transition temperatures.

The X-ray studies were performed at room temperature with a 14.3 cm Debye-Scherrer camera and nickel-filtered CuKα radiation, using the Straumanis method with the samples held in thin-walled silica tubes. The line positions were measured with a Norelco film reader accurate to 1/20 mm. Approximately 43 reflections were indexed for each composition on the basis of the hexagonal lattice. The lattice parameters were determined in extrapolation using Cohen's least-squares method with the function,

$$\tfrac{1}{2}\left[(\cos^2\theta/\sin^2\theta) + (\cos^2\theta/\theta)\right]$$

programmed in FORTRAN on a computer. For the calculation of the lattice parameters, 1.54051 Å and 1.54433 Å were assumed for the wavelengths of the Kα_1 and Kα_2 radiations, respectively, and 1.54178 Å was assumed for the wavelength of the unresolved doublet.

Some of the samples were examined by metallography at room temperature, using a Bausch and Lomb Research Metallograph. The powdered samples were mounted using a technique described by Skinner, and polished using a Fisher Vibramatic Polisher employing 0.05μ α-Al_2O_3 as a final abrasive.

EXPERIMENTAL RESULTS

Phase equilibria studies by DTA, X-ray diffraction, and metallography have established the phase diagram given in Figure 1 for the Bi_2Te_3-Bi_2S_3 system. This phase diagram shows the existence of two compounds: a congruent melting γ-phase (called γ-tetradymite) and an incongruent β-phase (called β-tetradymite). In addition, it also shows a limited solubility of Bi_2S_3 in Bi_2Te_3 (called the α-phase). The range of existence of these single-phase fields was established at room temperature by X-ray diffraction and the liquidus and solidus temperatures were determined by DTA studies.

Room temperature Debye-Scherrer X-ray diffraction patterns were obtained for various compositions from zero to 52 mole percent Bi_2S_3. The mineral sample of tetradymite from Paonia, Colo. was annealed at 400°C for one week to sharpen the diffraction lines in the back reflection region so that accurate values of the lattice parameters could be determined. A room temperature Debye-Scherrer X-ray diffraction pattern was obtained and was completely indexed. This pattern is similar to that published by Thompson (1949), Soonpaa (1960), and Peacock for tetradymite and is given in Table 1. All reflections obey the rhombohedral criteria, $-h+k+l=3\,n$, so that the true unit cell is rhombohedral. This indexed pattern was used to index the tetradymite patterns of the synthetic samples, and the hexagonal lattice parameters were determined

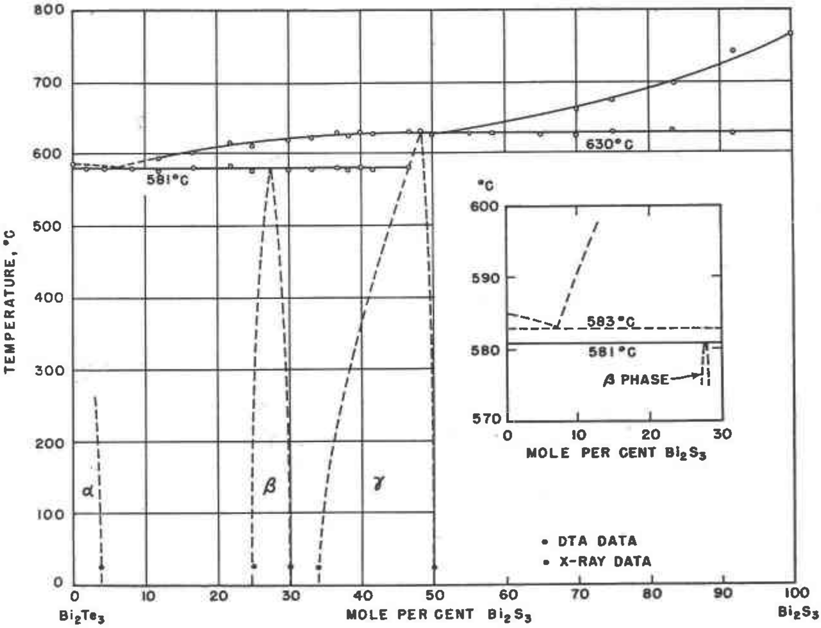

FIG. 1. Equilibrium phase diagram of the system Bi_2Te_3-Bi_2S_3.

by the procedure described above. The bismuth telluride patterns were indexed and the hexagonal lattice parameters determined by the method given by Glatz (1965). Measurement of the lattice parameters of these compositions were performed at room temperature and the results are given in Figure 2 along with the extent of the bismuth telluride and tetradymite patterns. The extent of the α-phase was determined from the compositional variation of the bismuth telluride lattice parameters and the bismuth telluride-rich boundary of β-tetradymite was determined by both the disappearance of the bismuth telluride pattern and the compositional variation of the tetradymite lattice parameters. The other phase boundary of β-tetradymite and the phase boundaries of γ-tetradymite

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR TETRADYMITE FROM PAONIA, COLO.

No.	*hkl*[1]	d (Å) obs.	d (Å) calc.	Int.
1	006	4.8634	4.9314	W
2	101	3.6114	3.6425	W
3	009 104	3.2595 —	3.2876 3.2878	W —
4	$\bar{1}05$	3.0967	3.1192	VS
5	107	2.7556	2.7714	W
6	108	2.5923	2.6052	W
7	00.12	2.4532	2.4658	W
8	10.10	2.2924	2.3036	VS
9	$\bar{1}0.11$	2.1594	2.1696	M
10	110	2.1108	2.1191	S
11	00.15	1.9652	1.9726	S
12	10.13	1.9293	1.9344	S
13	$\bar{1}0.14$ 021	1.8250 —	1.8316 1.8317	W —
14	119 024	1.7763 —	1.7812 1.7812	W —
15	205	1.7429	1.7528	M
16	027	1.6787	1.6834	VW
17	00.18 208	1.6382 —	1.6438 1.6440	S(bd) —
18	11.12	1.6030	1.6070	M
19	01.17	1.5690	1.5727	M
20	02.10	1.5556	1.5596	M
21	20.11	1.5126	1.5160	VW
22	11.15	1.4414	1.4439	M
23	02.13	1.4264	1.4286	W
24	00.21	1.4069	1.4090	VW
25	20.14 321	1.3826 —	1.3857 1.3857	VW —
26	01.20	1.4686	1.3722	W
27	125	1.3480	1.3506	S
28	11.18 128	1.2969 —	1.2989 1.2989	S —
29	21.10	1.2581	1.2561	M(bd)
30	00.24 12.11	1.2319 —	1.2329 1.2330	VW —
31	300	1.2223	1.2234	VW
32	01.23 303	1.2120 —	1.2141 1.2141	S —
33	21.13	1.1843	1.1846	W
34	11.21	1.1724	1.1733	VW
35	21.16	1.1083	1.1097	VW
36	00.27 30.12	1.0958 —	1.0959 1.0960	VW —
37	02.22 12.17	1.0851 —	1.0848 1.0848	W —
38	20.23 223	1.0526 —	1.0534 1.0535	M —
39	10.28	1.0145	1.0155	S
40	315	1.0027	1.0032	W
41	30.18 318	0.98605 —	0.98146 0.98148	W —
42	22.12 11.27	0.97276 —	0.97347 0.97343	VW —
43	$\bar{4}1.10$	0.96232	0.96260	W
44	12.23	0.94254	0.94330	M
45	02.28	0.91501	0.91578	M
46	045	0.90605	0.90675	VW
47	407 00.33 01.32	0.89598 — —	0.89670 0.89664 0.89664	M — —
48	22.18 $4\bar{4}8$	0.88994 —	0.89058 0.89059	M —
49	$\bar{5}22$ 21.28	0.84049 —	0.84068 0.84063	M —
50	327 20.32 11.33	0.82575 — —	0.82581 0.82576 0.82576	M — —

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[1] The *hkl* indices are referred to the hexagonal structure cell.

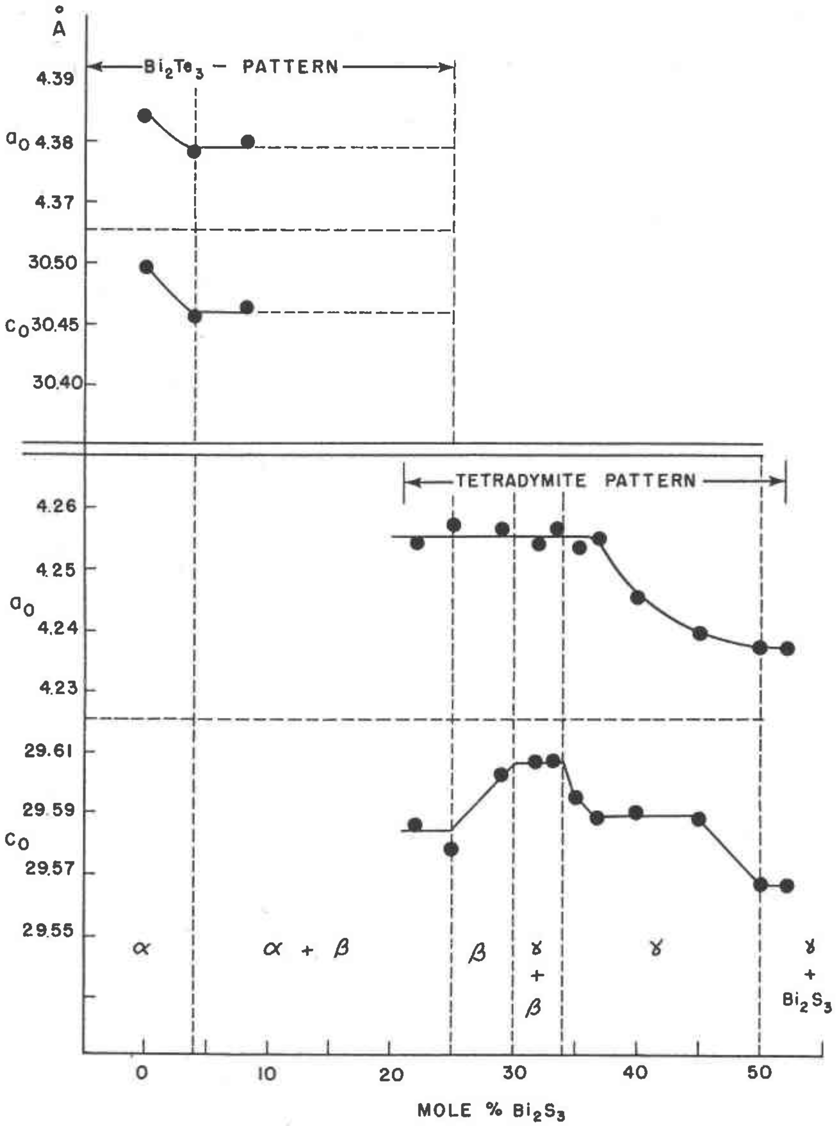

FIG. 2. Lattice parameters in the system Bi_2Te_3-Bi_2S_3 at room temperature.

were determined from the compositional variations of the tetradymite lattice parameters.

These results indicate that the extent of the α-phase at room temperature is not more than 4 mole percent Bi_2S_3. Recent X-ray studies by Gurieva, *et al* (1965) on cleavage faces of ingots grown by directional

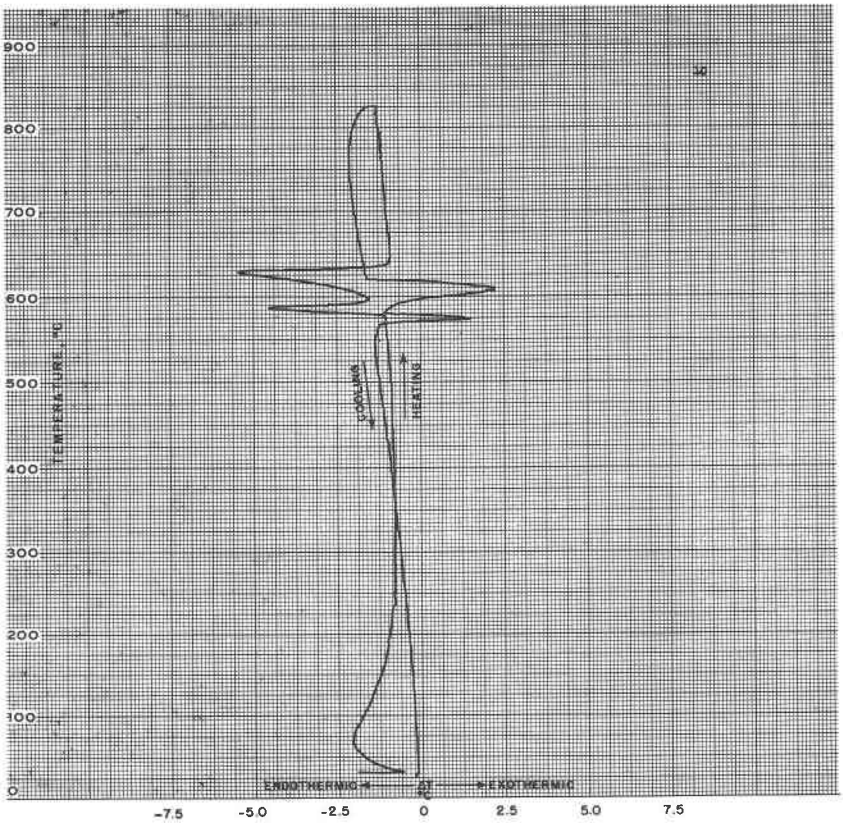

FIG. 3. DTA thermograms for $Bi_{40}Te_{42}S_{18}$.

crystallization from the melt indicated that the α-phase field extended up to 11 mole percent Bi_2S_3 at room temperature. These latter studies, however, have the disadvantage that the composition of the particular crystallite under investigation may deviate from the composition of the grown ingot and equilibrium may be difficult to achieve with such samples.

The existence of β-tetradymite as an incongruent compound was established by DTA studies. Shown in Figure 3 is a DTA thermogram for the composition $Bi_{40}Te_{42}S_{18}$ (30 mole percent Bi_2S_3). The heating curve of this thermogram shows the existence of a sharp enthalpic reaction followed by a liquid-solid enthalpic region to the liquidus temperature. DTA studies of all compositions in the region from 2 to $46\frac{2}{3}$ mole percent Bi_2S_3 show this sharp enthalpic effect for which the average temperature was established at 581°C, which is interpreted as being due to a peritectoid reaction of β-tetradymite.

The insert in Figure 1 for the region near Bi_2Te_3 and between 570 to 600°C has been inferred from DTA studies. The liquidus temperatures indicate the existence of a eutectic at approximately 8 mole percent Bi_2S_3, which is also shown on the previous phase diagrams for this system by Mellor (1931) and Beglaryan and Abrikasov (1959). This eutectic reaction temperature must be below the melting point of Bi_2Te_3, *i.e.* below 585°C, and equal to or greater than the reaction temperature of β-tetradymite at 581°C. Although this temperature interval is within the accuracy of the DTA apparatus, in all possible cases the enthalpic effects due to this reaction at 581°C were observed to be essentially completed before that of the liquid-solid region was initiated. An example of these enthalpic effects can be observed on Figure 3. Extrapolation of this latter enthalpic effect back to the baseline indicated an average temperature of approximately 583°C for the eutectic temperature. In addition, it is improbable that a eutectic and a peritectic would occur at the same temperature because this would be an invariant point. Therefore, the proposed phase diagram shown in the insert in Figure 1 indicates that β-tetradymite is a 'peritectoid' compound.

TABLE 2. REPORTED HEXAGONAL LATTICE PARAMETERS FOR TETRADYMITE AT ROOM TEMPERATURE

Investigator	*a* (Å)	*c* (Å)
Harker (1934)	4.316	30.009
Peacock	4.21	29.43
Soonpaa (1960)	4.24	29.56
Thompson (1949)	4.22	29.49
This work (USNM R-395)	4.2381	29.589

Shown in Table 2 are the hexagonal lattice parameters that have been previously reported for the mineral tetradymite as well as those obtained in this study. A chemical analysis of the mineral sample used in this study gave a composition that falls in the region now identified as γ-tetradymite. This result is verified by the fact that the lattice parameters given in Table 2 for this mineral are consistent with those given in Figure 2 for the synthetic sample of γ-tetradymite containing 45 mole percent Bi_2S_3. Table 2 also shows that some of the other reported lattice parameters for tetradymite deviate slightly from those obtained for the synthetic samples of β- and γ-tetradymite. This may be due to the fact that these mineral compositions did not lie exactly on the Bi_2Te_3-Bi_2S_3 tie line in the Bi-Te-S ternary system. Thompson (1949) reported that the chemical analysis of various tetradymite samples did not lie exactly on the Bi_2Te_3-Bi_2S_3 tie line and that some of the mineral samples contained appreciable amounts of other impurities. This deviation between the mineralogical and synthetic samples could also be due to the fact that the reported lattice parameters of the minerals were based upon too few diffraction lines, particularly in the back reflection region. From Table 2 observe that Harker's data (1934) is significantly different from the other data reported for this mineral. It is possible that the mineral sample used by Harker did not lie on the Bi_2Te_3-Bi_2S_3 tie line, and further work in the Bi-Te-S ternary system is required to resolve this point. Harker's work represents the only reported structural study of tetradymite and for this reason, it is unfortunate that Harker's x-ray data is significantly different from the other studies on tetradymite.

DISCUSSION

This phase equilibria study of the Bi_2Te_3-Bi_2S_3 system has demonstrated that this system contains two compounds and a region of solid-solubility of Bi_2S_3 in Bi_2Te_3. These compounds are: an incongruent β-phase (called β-tetradymite) which is probably a peritectoid phase and a congruent melting γ-phase (called γ-tetradymite). This study has demonstrated that at room temperature β- and γ-tetradymite exist as single phases from 25 to 30 and from 34 to 50 mole percent Bi_2S_3 respectively, and the γ-phase, which represents the solubility of Bi_2S_3 in Bi_2Te_3 exists as a single phase up to four mole percent Bi_2S_3. The incongruent reaction temperature of the β-phase is 581°C, and although the γ-phase is a congruent melting compound, it is a limiting case of peritectic compound with a peritectic reaction temperature and melting point of 630°C. In the region close to Bi_2Te_3 it is difficult to determine the exact form of the phase diagram because of the small temperature difference between the incongruent reaction of the β-phase and the liquidus temperatures. However, evidence is presented to show that it is probable that β-tetradymite is a peritectoid compound with a peritectoid reaction temperature of 581°C and there is a eutectic at 8 mole percent Bi_2S_3 with a eutectic temperature of 583°C.

The two compounds, β- and γ-tetradymite, are structurally very similar and correspond to mineral samples that have been identified as 'tetradymite.' The similarity of these two forms of tetradymite has apparently led to some confusion in the past. This phase study indicates that while γ-tetradymite can be prepared from the melt, it is difficult to synthesize β-tetradymite as a single phase by this method because of the difficulties in achieving equilibrium during a peritectoid reaction. However β-tetradymite can be synthesized as a single phase by solid-state reaction for an extended period of time below the peritectoid temperature of 581°C. The results are consistent with the observation by Soonpaa (1960, 1962) that reaction of the tetradymite composition produces bismuth telluride, tetradymite and a proposed phase $Bi_8Te_7S_5$. In addition, the proposed phase diagram given in Figure 1 is consistent with the composition $Bi_8Te_7S_5$ ($41\frac{2}{3}$ mole percent Bi_2S_3) as a single phase at room temperature.

This study of the Bi_2Te_3-Bi_2S_3 system has been performed on samples prepared in the subsolidus region in an attempt to achieve thermodynamic equilibrium employing conventional techniques of X-ray diffraction, DTA and metallography. The resulting phase diagram appears to correlate some of the previous observations and offer a reasonable explanation for some of the previous uncertainties for this system.

ACKNOWLEDGMENTS

I wish to acknowledge the assistance given by Dr. Brian Skinner of the U. S. Geological Survey for his many suggestions, and to Dr. Paul Desautels of the U. S. National Museum for providing the sample of tetradymite.

I also wish to thank Mr. Daniel Gaffaney, Mrs. Virginia Meikleham and Miss Karen Cordo for their assistance and helpful discussions, Mr. James Endress, Jr. for preparing the samples and performing the DTA measurements, and Dr. Robert Faxon of Syracuse University for taking the X-ray photographs.

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Manuscript received, April 18, 1966; accepted for publication, October 10, 1966.