Synthetic Sulfide Minerals (I)

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1. Introduction

Sulfide minerals play most important rôle in metallic ore and occur persistently from ore deposits of various types. Therefore, studies on them are regarded to be important from the scientific and economic points of view. When the genesis of the ore-forming minerals in the ore deposits is discussed, it is necessary to ascertain the phase relations on equilibrium between sulfide minerals. The phase relations also play an important rôle to interpret behavior of the sulfide minerals in the smelting furnace. In the experimental works to determine the phase relatons between sufide minerals, artificially prepared sulfide minerals are used, owing to the difficulty of obtaing the necessary amounts of natural sulfide minerals of sufficient purity. Accordingly, the synthesis of sulfide minerals is the first step in the studiet on the phase diagram. In this paper, methods and results of sythetic experiments on simple sulfides, such as Cu_2S, CuS, $Fe_{1-x}S$, MnS, Bi_2S_3 and Sb_2S_3, and their identification will be described.

2. Apparatus of Experiments

The synthesis of simple sulfides was mostly done by dry method in evacuated rigid glass tube. Copper, iron, manganese, bismuth, antimony, and sulfur used as the starting materials, were accurately weighed by a chemical balance in appropriate proportion of the simple sulfides and then sealed in silica or hard glass tubes evacuated in 10^{-3} mm Hg by a rotary vacuum pump. The silica glass tube used is transparent and 7 mm in inside diameter with about 1 mm in wall thickness. As hard glass tube, Hario glass tube, 8 mm in inside diameter, made by Shibata Chemical Apparatus Co. was mainly used. Its quality is about the same as that of Corning's Pyrex glass. Sealing of evacuated silica or Hario glass tubes was practiced by using acetylene-oxygen or city gas-oxygen flames respectively. In order to prevent heating of the materials by flames, wet cloth was rolled on the tubes in which the materials were kept.

The sealed tube was heated in the electric furnace at desired temperature until metal and sulfur perfectly reacted to produce their sulfide compounds. After heating, it was quenched in air or sometimes in water. In the case of antimony sulfide, however, it had to be slowly cooled down in the furnace for long time to dissociate its vapor at temperatures higher than 600°C. The products formed by heating were taken out from the tube and ground in an agate motor with acetone to mix them completely. Then, they were usually sealed again in an evacuated rigid glass tube and heated in the furnace. By this reheating, the products became usually a homogeneous phase when observed under the microscope with a vertical illuminator. In this case, if they were heterogeneous or starting materials still remained, the procedure mentioned above should be repeated until homogeneous sulfide is formed.

A part of experiments on synthesis of monoclinic pyrrhotite and alabandite was carried out by wet method. Namely, monoclinic pyrrhotite was produced by reaction between aqueous

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solution of sodium sulfide and synthetic troilite in sealed glass tube at temperatures below 200°C. On the other hand, alabandite was also synthesized by heating in evacuated tube precipitate formed by reaction between aqueous solution of manganese chloride and gas of hydrogen sulfide.

The electric furnace used is cylindrical vertical type, 60 mm in inside diameter and 500 mm in length, wound by Kanthal wire, 1.8 mm in diameter. Temperature of the furnace was exactly measured by a potentiometer with a chromel-alumel thermocouple and automatically recorded continuously. An auto-regulator by potentiometric system was also employed to keep desired temperature for long time in the furnace within a range of ±2°C.

3. Identification of Synthetic Products

Microscopic study. A small quantity of synthesized product, generally in granule or powder, was mounted on polyester resin Rigorac, and then polished smoothly. The polished section was observed under reflecting microscope with illuminator about its homogenity, reflecting colour, anisotropism and etching reactions etc.

X-ray study. X-ray studies for synthetic minerals were examined by powder method employing X-ray diffractometer, Geigerflex. Manganese filtered FeK_α ($\lambda = 1.9373\text{Å}$) radiation or nickel filtered CuK_α ($\lambda = 1.5418\text{A}$) radiation were used for $Fe_{1-x}S$ and MnS or for Cu_2S, CuS, Bi_2S_3 and Sb_2S_3 respectively. The experimental conditions of X-ray powder diffraction were as follows:

Voltage; 30 KV, current; 10 mA (Fe) or 13 mA (Cu), scale factor; 16, time constant; 2 seconds, multiplire; 1, divergence slit; 1°, scattering slit; 1°, receiving slit; 0.2 mm, scanning speed; 1°/min., chart speed; 1 cm/min.

To measure exactly a spacing of index and a length of unit cell edges, 0.25°/min. in scanning speed was usually adopted. In this case, the diffraction angle 2θ was calibrated by using metallic silicon, 99.9999% in purity as standard.

Thermal study. The differential thermal analysis (D.T.A.) was performed on all synthetic minerals to detect their thermal behavior, such as phase transformation. It was carried out by method analizing in nitrogen atmosphere as described by one of the present writers in the previous paper1), or by method using sealed vacuum silica tube as sample holder. In the case using nitrogen gas, a small amount of the oxygen mixture in it was taken off by copper net heated at 550°C and also, moisture in it was absorbed by phosphoric oxide and calcium chloride. The thermal analysis was made in the purified gas under an atmospheric pressure led into the horizontal furnace employing. The analysis was also made, using evacuated sealed silica tube as sample holder in vertical furnace of removing type. The aparatus will be described in detail else where. Calcined aluminum oxide was used as inert material, which was placed in a porcelain box or evacuated sealed silica tube adjacent to it packed with the samples. The rate of increase of temperature was regularly 5°C/min. during the analysis with aid of an automatic program controller. Temperature was read by a millivoltmeter with chromel-alumel thermocouple.

4. Cu_2S (Chalcocite)

As the starting materials for synthesis2) of chalcocite Cu_2S, electrolytic copper of which purity is 99.99% in a chip-shaped form about 5 mm in size and sulfur crystal refined to 99.9 % by Kanto Chemical Co. as guaranteed reagent were utilized. When the metal was covered

Table 1. The data of X-ray powder diffraction for synthetic Cu_2S (low form)

1		2		
d (Å)	I	d (Å)	I	hkl
4.25	5	4.25	w	222
		3.86	w	251
3.83 B	6	3.83	vw	133
		3.79	w	062
3.74	30	3.73	m	242
3.60	20	3.60	m	162
3.51	4	3.482	vw	053
—	—	3.415	vw	080
—	—	3.333	w	233,153
3.32	25	3.317	m	322
3.28	30	3.271	m	024
3.19	35	3.182	m	262
3.16	35			
—	—	3.139	vw	351
3.06	20	3.058	m	342
2.96	35	2.957	w	280,400
		2.951	m	182
2.94	15	2.921	m	204,144
2.89	9	2.885	m	411
2.871	10	2.861	w	173,224
2.832	7	2.817	w	333
2.799	4			
2.768	10	2.773	m	431
2.732	45	2.731	m	362
		2.721	m	440
—	—	2.690	w	244
2.669	20	2.671	m	422
2.648	6	2.652	w	291,164
2.621	15	2.623	m	115,353
2.568	8	2.567	w	451
2.533	35	2.541	m	0.10.2
		2.532	m	442,135
2.477	40	2.481	m	1.10.2
		2.464	m	413,193
2.452	5	2.440	w	215
2.403	75	2.409	st	344
		2.401	st	084
—	—	2.393	w	433
—	—	2.370	w	373,235,153
2.333	35	2.333	m	2.10.2,471
2.243	20	2.244	m	480,502,255
—	—	2.231	vw	404
—	—	2.218	vw	315,075,026
2.213	40	2.208	m	522,106
2.172	15	2.180	w	126
—	—	2.137	vw	1.11.3,046
2.099	7	2.117	w	444
2.051	6	2.049	vw	533
2.027	7	2.028	w	2.12.2
2.010	15	2.012	w	562,246
2.001	10	2.002	w	464
—	—	1.992	vw	415
—	—	1.987	vw	195,166
1.983	45	1.982	m	600
1.977	80	1.973	st	3.12.0
—	—	1.958	vw	553
1.956	20	1.953	m	580,435,306
—	—	1.917	vw	631,493
1.911	15	1.908	w	266
1.897	7	1.895	w	3.12.2,117
1.881	100	1.882	st	346,086

1 : Synthetic Cu_2S 2 : Data for Cu_2S III by Djurle

by thin film of its oxides, it was reduced by hydrogen gas at temperatures from 600°C to 800°C for 2 hours before weighing. They were exactly weighed in proportion to two copper and one sulfur in molecular ratio and were sealed in Hario glass tube under vacuum in 10^{-3} mm Hg. The tube was put into a vertical electric furnace and was kept at 500°C for 24 hours after heating from room temperature up to 500°C during 6 hours. By this heating, copper and sulfur easily reacted each other to form a copper sulfide. Then the polished product was observed under microscope. If copper remained or the product was heterogeneous, the product was ground in an agate motor to get homogeneous mixture with acetone to prevent oxidation. Then, it was again sealed in the glass tube under vacuum and was reheated in the furnace usually at 500°C for 48 hours. By this reheating, homogeneous chalcocite was formed. Rarely, very fine hairs of metallic copper grew on the surface of the block of cuprous sulfide synthesized.

Chalcocite thus produced is aggregate of fine grains showing steel gray colour with metallic luster. Under the microscope, it is grayish white in reflecting light and shows anisotropism changing from grayish blue to grayish brown under the crossed nicols.

When etched with HNO_3 (1 : 1), it changes the colour into blue with strong effervescence. By KCN (20%), it immediately changes its colour from dark brown into black. By $FeCl_3$ (20%) and $HgCl_2$ (20%), it is stained with bluish gray and dark gray in colour respectively. However, it is negative to HCl (1 : 1) and KOH (sat.). These optical properties and etching reactions are in good accordance with those of natural chalcocite described by Farnham3), Short4), Uytenbogaardt5) and Ramdohr6).

The data of X-ray powder diffraction for synthetic chalcocite are given in Table 1 as compared with that of chalcocite formed by Djurle. The specimens synthesized were cooled in the air after keeping at 500°C for 48 hours. Therefore, it is regarded as a low temperature type of orthorhombic form. In fact, the result of X-ray diffraction indicates that they belong to chalcocite of low temperature form described by Buerger7), 8) and Djurle9).

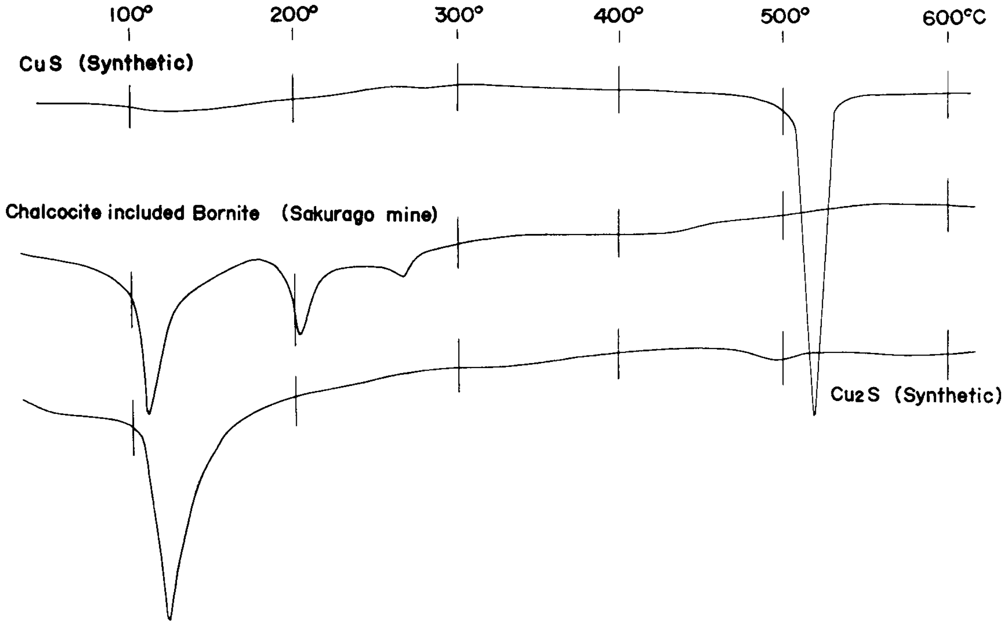

Fig. 1. Differential thermal curves for synthetic CuS and Cu_2S in comparison with the curve for chalcocite from the Sakurago mine, Yamaguchi Prefecture.

The D.T.A. curves of synthetic and natural chalcocite below 600°C are shown in Fig. 1. The curves have distinct endothermic peaks at 105°C which represent a latent heat of inversion from the orthorhombic form into the hexagonal form. While the inversion from hexagonal (intermediate) form into cubic (high temperature) form at 470°C found by Ueda[10], Hirahara[11] and Djurle[9] represents only as a very weak endothermic curve and sometimes, it is not observed by D.T.A. owing to its too small latent heat. The endothermic peaks of two steps at temperatures from 200°C to 270°C in the curve of natural chalcocite from the Sakurago mine may represent high-low inversion of bornite impurity intimate associated with chalcocite, as described by Frueh[13] and Morimoto and Kullerud[14].

5. CuS (Covellite)

Synthesis[2] of covellite was also carried out by reaction between electrolytic copper and crystal sulfur which were sealed in evacuated Hario glass tube after accurately weighing one copper and one sulfur in molecular ratio. They were treated at 300°C or 400°C for 48 hours after slow heating from room temperature up to 300°C during 6 hours. If the reaction between them was imperfect and yellow sulfur remained in the upper part of tube, the tube was maintained upside down in the furnace for long time so as to expend sulfur. If the product was found heterogeneous under the ore microscope, it was again sealed in evacuated glass tube after grinding and then reheated in the furnace at 400°C for 48 hours. After reheating, it was cooled in air. By this reheating, a homogeneous phase was usually obtained.

Covellite synthesized is in granular aggregate, indigo-blue in colour, with submetallic lustre megascopically. Under the microscope, it has distinct pleochroism changing from blue to purplish gray, and also shows very strong anisotropic property changing its interference colour from deep reddish brown to purple under the crossed nicols. Its hardness is low. When etched

Table 2. The data of X-ray powder diffraction for synthetic CuS

1		2		3		
d (Å)	I	d (Å)	I	d (Å)	I	hkl
3.29	7	3.28	4	3.285	14	100
3.22	20	3.22	2	3.220	28	101
3.05	50	3.04	28	3.048	67	102
2.818	80	2.806	51	2.813	100	103
2.727	100	2.723	100	2.724	56	006
2.321	7	2.315	5	2.317	10	105
2.101	5	2.409	2	2.097	6	106
2.044	10	2.044	14	2.043	7	008
1.897	55	1.899	30	1.902 1.896	25 75	107 110
1.736	35	1.738	29	1.735	34	108
1.633	2	—		1.634	3	201
1.610	5	—		1.609	8	202
1.573	10	1.573	6	1.572	15	203
1.557	30	1.558	14	1.556	37	116
		1.463	2			
		1.356	6			

1 : Synthetic CuS 2 : Covellite (Hanaoka mine) 3 : Data from A.S.T.M.

by HNO_3 (1 : 1), it is tarnished by fume and stains purple or reddish brown in colour. By HCl (1 : 1), KOH (sat.) and $FeCl_3$ (20%), it is slowly affected to change its colour from purple to reddish brown. KCN (20%) violently acts with it and rapidly changes its colour into reddish brown or black, while it is negative to $HgCl_2$ (20%).

The data of X-ray powder diffraction of synthetic covellite are given in Table 2 as compared with that of natural covellite.

The results of D.T.A. on synthetic covellite are shown in Fig. 1. The analysis is carried out by both methods of sealed vacuum tube and nitrogen atmosphere. These results were about the same. The curve represents a strong endothermic reaction beginning at 503°C which seems to indicate formation of digenite by dissociation of covellite[15]. The curve is nearly similar to that obtained by Hiller and Probsthain[16]. The optical properties, X-ray diffraction data and thermal analysis agree with those of natural covellite described by the authors.[3~6), 16~18]

6. $Fe_{1-x}S$ (Troilite and Pyrrhotite)

Stoichiometric and iron-deficient ferrous sulfides were synthesized by reaction between electrolytic iron powder under 100 mesh in size, and crystal sulfur, several millimeter in size, in evacuated silica tube. They were exactly weighed in proportion to compositions of $Fe_{1-x}S$ and then sealed in the silica glass tube under vacuum in 10^{-3} mm Hg. Then, the tube was kept in the furnace at 750°C for 48 hours after heating from 400°C up to 750°C for 2 hours, and the starting materials were completely reacted to produce iron sulfide. However, in many cases, the products were heterogeneous, and it was necessary to reheat them after thoroughly grinding under acetone and sealing in evacuated silica tube. The reheating at 750°C for 48 hours was generally enough to produce a homogeneous ferrous sulfide.

The iron sulfide thus formed is aggregates of fine granules of bronze yellow in colour with metallic luster. Under the microscope with vertical illuminator, it has pleochroism changing

Table 3. The data of X-ray powder diffraction for synthetic $Fe_{1-x}S$

1		2		3		4		5	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
						3.045	5	3.045	6
2.986	55	2.986	45	2.979	100	2.990	40	2.990	40
2.877	9	—	—	—	—	2.870	10	2.881	5
2.652	70	2.649	70	2.640	55	2.652	60	2.652	57
—	—	—	—	—	—	—	—	2.299	4
—	—	—	—	—	—	—	—	2.248	4
—	—	—	—	—	—	2.178	5	—	—
—	—	—	—	—	—	2.161	5	—	—
2.073	100	2.067	100	2.055	55	2.070	100	2.074	100
1.724	35	1.722	30	1.720	50	1.724	40	1.724	40
1.614	9	1.608	10	—	—	—	—	1.613	10
1.462	7	—	—	—	—				
1.439	10	1.433	8	1.424	20				
1.325	13	1.325	15	—	—				

1 : Synthetic $Fe_{0.917}S$ 2 : Synthetic $Fe_{0.893}S$ 3 : Synthetic $Fe_{0.862}S$ 4 : Pyrrhotite (Hitachi mine) 5 : Pyrrhotite (Kawayama mine)

Table 4. The data of X-ray powder diffraction for synthetic FeS

1		2	
d (Å)	I	d (Å)	I
2.986	60	2.98	4
2.661	60	2.66	6
2.528	7	2.52	1
2.141	4	2.14	1
2.094	100	2.09	10
1.955	4	—	—
1.927	10	1.923	3
1.749	7	1.748	1
1.723	30	1.719	5
1.637	6	1.634	3
—	—	1.595	1/2
—	—	1.501	1/2
1.467	5	1.469	3
1.447	8	1.445	2
—	—	1.422	1/2
1.329	12	1.331	4

1 : Synthetic FeS 2 : Data for troilite by Berry & Thompson

Table 5. Data of spacing d_{102} for synthetic pyrrhotites

x		Fe (mol%)	d_{102} (Å)
($Fe_{1-x}S$)	(FeS_{1+x})		
1.000	1.00	50.00	2.0928
0.980	1.02	49.50	2.0888
0.962	1.04	49.02	2.0848
0.943	1.06	48.54	2.0779
0.926	1.08	48.08	2.0738
0.917	1.09	47.85	2.0723
0.909	1.10	47.62	2.0695
0.893	1.12	47.17	2.0637
0.885	1.13	46.95	2.0624
0.877	1.14	46.73	2.0576
0.870	1.15	46.51	2.0568
0.862	1.16	46.30	2.0535
0.855	1.17	46.08	2.0523

from pale brown to yellowish cream. Under the crossed nicols, it shows strong anisotropism changing its interference colour from bluish gray to reddish brown. Its hardness is medium. When etched by HNO_3 (1 : 1), it changes its colour into brown with strong effervescence. By KOH (sat.) and $HgCl_2$ (20%), it is also stained into brown in colour. These optical properties and etching reactions are in good agreement with those of natural pyrrhotite by the authors.[3)~6)]

The X-ray powder data of synthetic pyrrhotite are given in Table 3 as compared with those of natural pyrrhotite, and the powder data of artificial and natural troilites are shown in Table 4. The value of spacing d_{102} in the diffraction pattern changes regularly in proportion to amounts of iron deficience as given in Table 5. The relation between the value of d_{102} and iron contents in molecular percentage is also shown in Fig. 2 as compared with data obtained by Arnold$^{19)}$. Both are in good agreement. The value of d_{102} was exactly measured at scanning speed of 0.25°/min. Therefore, composition of pyrrhotite can be obtained from X-ray powder data, especially by d_{102}.$^{20), 21)}$ Though pyrrhotite synthesized shows the diffraction of single peak for 102, corresponding with the value at 2θ from 55° to 57° by manganese filtered iron radiation, it of some natural pyrrhotites represents as two spliced diffraction. Such pyrrhotites may be thought to belong a monoclinic phase as mentioned by Grϕnvold and Haraldsen$^{22)}$, while pyrrhotites synthesized by present experiments are believed to be hexagonal pyrrhotite. The monoclinic pyrrhotite can be formed by annealing hexagonal pyrrhotite richer in sulfur than $Fe_{0.885}S$ at temperature below 325°C, high (hexagonal)-low (monoclinic) inversion point, for from 48 hours to 96 hours. For example when synthetic pyrrhotite $Fe_{0.862}S$ was kept at 300°C for 48 hours, it changed into monoclinic form representing two splitted peaks at 55.95° and 56.12° in 2θ (FeK_{α}). Also, monoclinic pyrrhotite can be produced reaction between 40% aqueous solution of sodium sulfide and synthetic iron sulfide FeS in sealed glass tube at 200°C for 168 hours. Recently, G. Moh described that monoclinic pyrrhotite was formed by treatment of stoichiometric FeS with ammonium disulfide at 130°C for 4 days. This experiment has been continuously made at present, and more detailed data on the synthesis of monoclinic pyrrhotite are expected in near future.

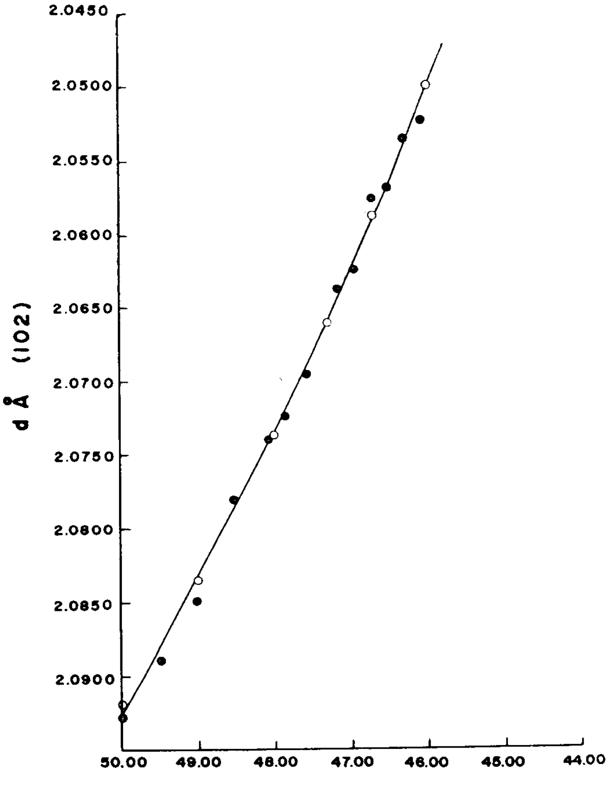

Fig. 2. Composition versus d_{102} relationship for synthetic pyrrhotites.
Black circle: Present writer's data
White circle: Data calculated by Arnold's equation.

The D.T.A. of synthetic iron sulfides was carried out in nitrogen atmosphere under an atmospheric pressure, with the results shown in Figs. 3, 4 and 5. In Fig. 3, the curves from $Fe_{1.000}S$ to $Fe_{0.943}S$ have an endothermic peak at temperatures from 100°C to 155°C. It seems to represent a latent heat of α-transformation from ordered superlattice to disordered hexagonal form. The peak removes to lower temperature side and becomes smaller with decreasing thermal contents of its latent heat in proportion to increase of amounts of sulfur. However, the peak is not found in D.T.A. curves of iron sulfides with more sulfur than $Fe_{0.926}S$. In the curves of synthetic pyrrhotites from $Fe_{0.926}S$ to $Fe_{0.893}S$, an endothermic peak is observed at temperatures from 190°C to 300°C. It is considered to show a magnetic γ-transition point at which their susceptibility increases rapidly. The endothermic peak at temperatures from 320°C to 345°C is found in all curves as shown in Figs. 3, 4 and 5. It is regarded to represent β-transformation corresponding to Neel point, above which arrangement of magnetic spins in sub-lattice becomes disordered. The transformation of $Fe_{0.870}S$, $Fe_{0.862}S$ and $Fe_{0.855}S$ is represented by a sharp peak divided into two steps as shown in Fig. 5. The D.T.A. curves of

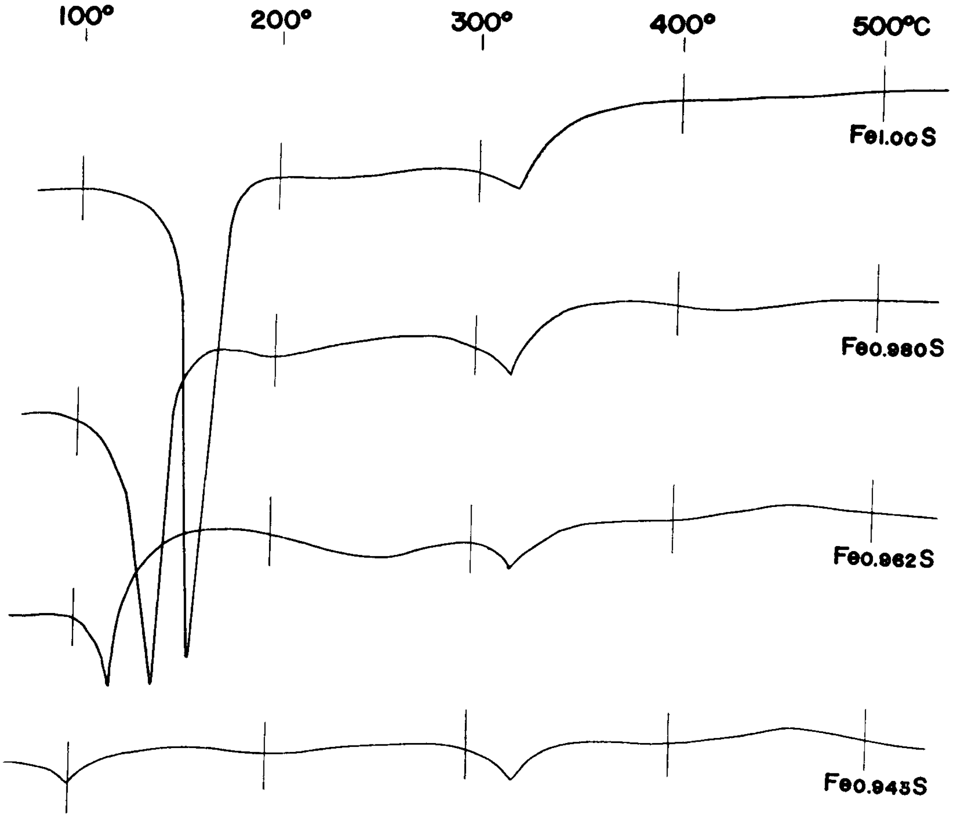

Fig. 3. Differential thermal curves for synthetic $Fe_{1.00}S$, $Fe_{0.980}S$, $Fe_{0.962}S$ and $Fe_{0.943}S$.

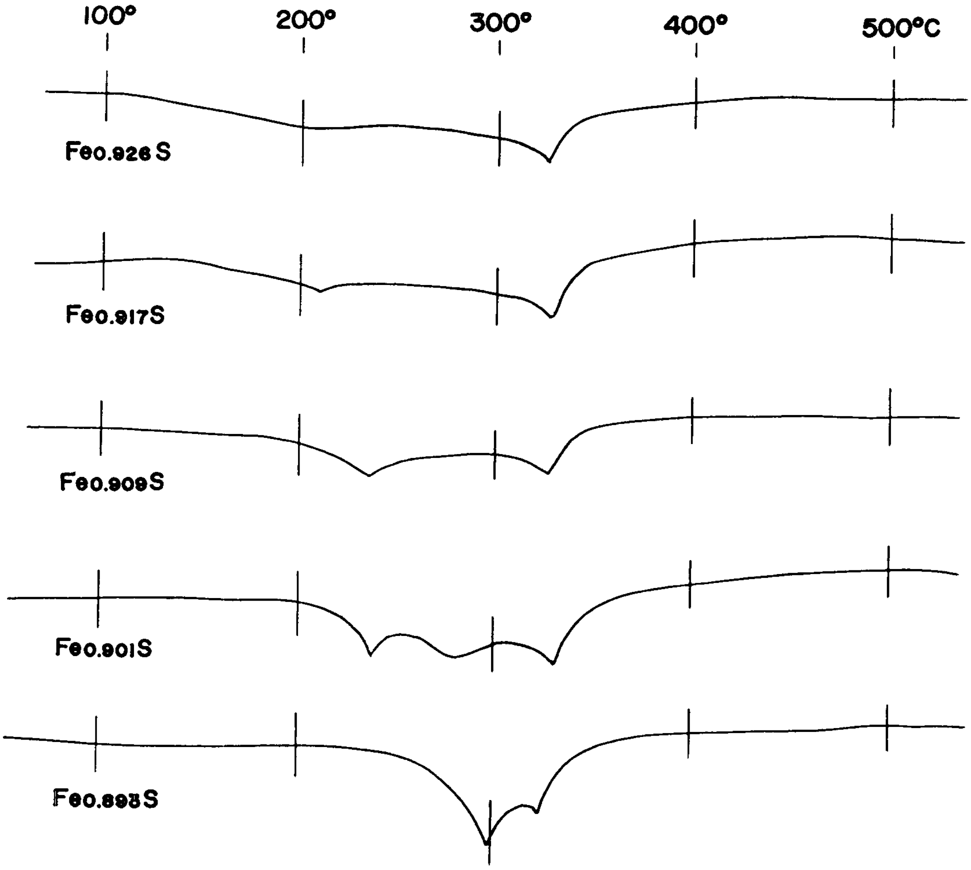

Fig. 4. Differential thermal curves for synthetic pyrrhotites, $Fe_{0.926}S$, $Fe_{0.917}S$, $Fe_{0.909}S$, $Fe_{0.901}S$ and $Fe_{0.893}S$.

natural pyrrhotites are given in Fig. 6 for comparison with the synthetic pyrrhotites. They show usually two endothermic peaks at temperatures about 240°C and 320°C which seem to indicate γ- and β-transformation respectively. However, α-transition observed at temperatures between 100°C and 165°C in synthetic ferrous sulfide is not found in natural pyrrhotites examined.

7. MnS (Alabandite)

As starting materials, powder of electrolytic manganese and crystal granule of sulfur, both 99.9% in purity, were used. After accurately weighing, they were sealed in evacuated silica glass tube. The tube was heated in electric furnace under program as follows: at 500°C for 72 hours after heating from room temperature up to 500°C for 8 hours; from 500°C up to

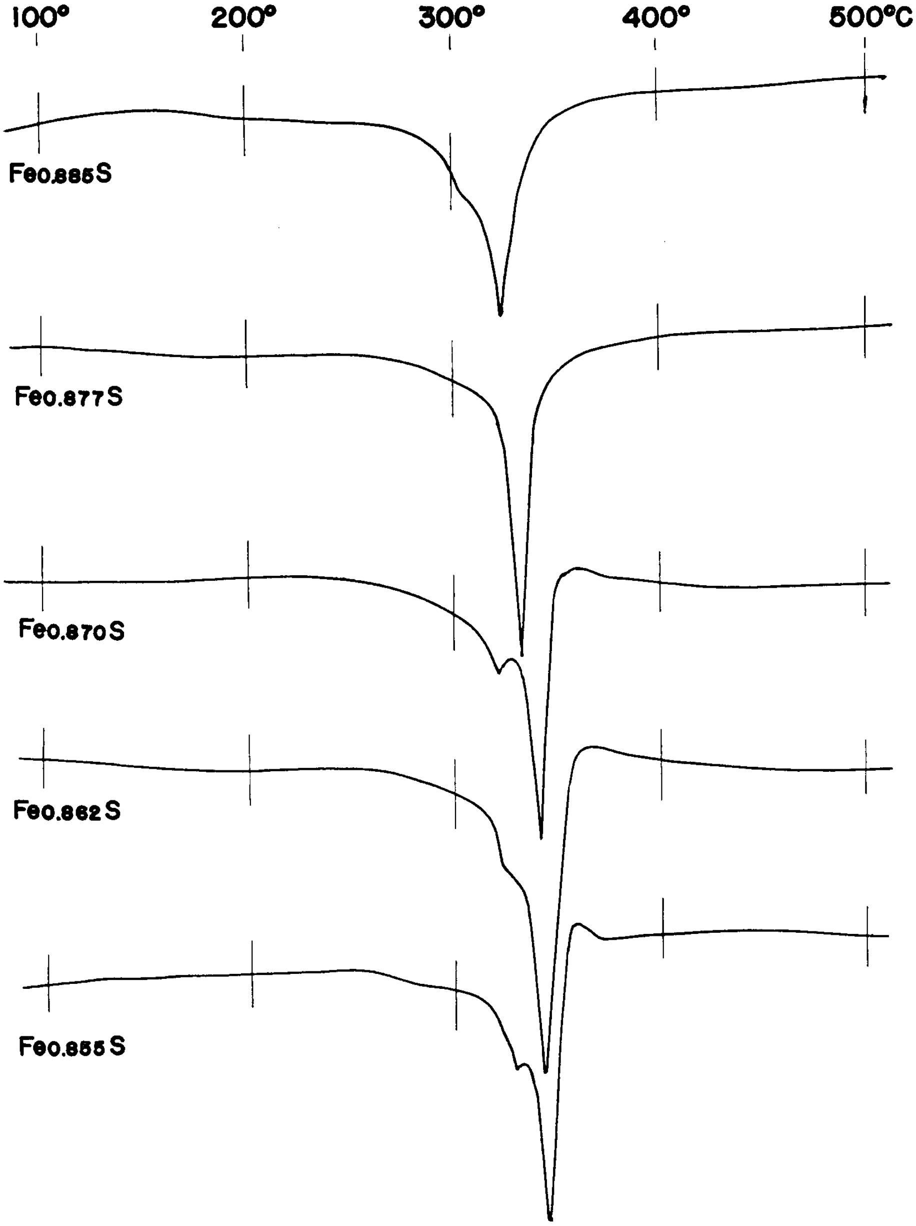

Fig. 5. Differential thermal curves for synthetic pyrrhotites, $Fe_{0.885}S$, $Fe_{0.877}S$, $Fe_{0.870}S$, $Fe_{0.862}S$ and $Fe_{0.855}S$.

800°C for 24 hours; at 800°C for 24 hours; at 850°C for 24 hours; at 900°C for 24 hours; at 990°C for 144 hours; slow cooling from 990°C down to room temperature in the furnace by cutting off electric current. The velocity of the reaction between manganese and sulfur was very slow. Accordingly, it was necessary to keep them at 990°C for 6 days or more to have all manganese and sulfur reacted to form alabandite. Alabandite produced, sometimes, reacted with silica glass of the sealed tube, and consequently the wall of the tube became very thin in thickness. The tube was often broken by difference of contraction between silica glass and manganese sulfide during cooling. In such case, the product was oxidized by air. Therefore, it should be cooled down very slowly in the furnace after heating.

The synthetic experiment of alabandite was also practiced by wet method. In this case, a solution was used, in which 27 g of manganese chloride, $MnCl_2 \cdot 4H_2O$, is dissolved in 75 cc of distilled water, and 50 cc of $3N\text{-}NH_4Cl$ was added always into the solution to prevent precipitation of manganese hydroxide. Also, pH of the solution was kept constant at 8.8 by addition of 15 cc to 20 cc of $3N\text{-}NH_4OH$. The manganese sulfide was precipitated by reaction between the solution and hydrogen sulfide. Its precipitate was amorphous paste-like form, pinkish rose in colour. It was quickly filtrated by means of a suction and then immediately removed into a porcelain boat. The boat was heated at 950°C for 6 hours in the horizontal furnace evacuated by rotary vacuum pump.

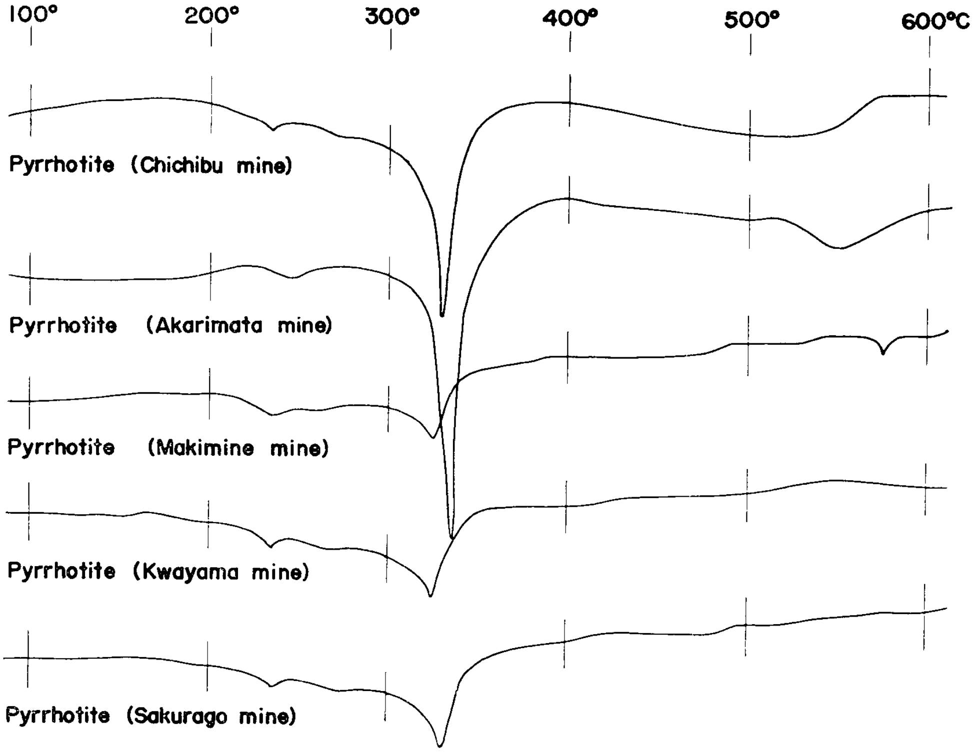

Fig. 6. Differential thermal curves for natural pyrrhotites.

The manganese sulfides synthesized by dry and wet methods are massive granular aggregates iron black in colour with submetallic lustre. Its powder and streak show green colour. Under the microscope with vertical illuminator, it is whitish gray in reflecting colour with internal reflection showing greenish iridescence. It is perfectly isotropic under the crossed nicols. When etched by HNO_3 (1 : 1), it instantly shows violent effervescence by liberation of hydrogen sulfide and is tarnished dark brown or black. By HCl (1 : 1), it also effervesces instantly and liberates gas of hydrogen sulfide. However, it is negative to KOH (sat.), KCN (20%), $FeCl_3$ (20%) and $HgCl_2$ (20%). These optical properties and etching reactions of synthetic alabandite as mentioned above agree with those of natural alabandite described by the authors.$^{3\sim6)}$

Table 6. X-ray powder diffraction data for synthetic MnS

1		2		3		
d	I	d	I	d	I	hkl
3.018	4	3.018	4	3.015	13	111
2.615	100	2.613	100	2.612	100	200
1.848	30	1.847	45	1.847	48	220
				1.575	6	311
1.509	8	1.508	11	1.509	19	222
1.306	6			1.306	8	400
1.168	10			1.168	19	420

1 : MnS synthesized by dry method 2 : MnS synthesized by wet method 3 : Data from A.S.T.M.

In Table 6, the X-ray powder data of alabandite synthesized by both methods of dry and wet are given for comparison with those of alabandite from A.S.T.M. It shows to be halite structure of face centered cubic form.

8. Bi_2S_3 (Bismuthinite)

Bismuth sulfide Bi_2S_3 was formed by dry method in evacuated Hario glass tube. As starting materials, granule of metallic bismuth and crystal fragment of sulfur, both 99.9% in purity, was used. They were exactly weighed at the rate of two bismuth and three sulfur in molecular ratio and then sealed in Hario glass tube under vacuum in 10^{-3}mm Hg. The tube was put into furnace and heated at 500°C for 48 hours after keeping at 300°C for 8 hours to 12 hours. By heating, the starting materials were entirely consumed and changed into bismuth sulfide. After heating, the product was taken out from the tube and ground into powder under acetone. Then, it was again sealed in evacuated glass tube and kept in the furnace maintained at 500°C for 48 hours. The product obtained by reheating was a homogeneous phase which was identified with bismuthinite.

The synthetic bismuth sulfide is massive, and lead-gray in colour. Under the ore microscope, it is aggregates of granular and blade-like crystals. It shows distinct pleochroism changing from creamy white to purplish gray, and has also strong anisotropism changing from pale brownish gray to dark violet in interference colour, with inclined extinction under the crossed nicols. When etched by HNO_3 (1 : 1), it is slowly stained brown with effervescence. By $HgCl_2$ (20 %), it changes its colour into brown. But, it is negative to HCl (1 : 1), KOH (sat.), KCN (20 %) and $FeCl_3$ (20%).

The powder data of X-ray diffraction by nickel filtered copper radiation for synthetic bismuth sulfide are given in Table 7. They are in good agreement with those of natural and synthetic bismuthinites described by Berry and Thompson$^{18)}$, and A.S.T.M.

The D.T.A. curve obtained by using evacuated sealed tube is shown in Fig. 7. A very

Table 7. The data of X-ray powder diffraction for synthetic Bi_2S_3

1		2		3		
d (Å)	I	d (Å)	I	d (Å)	I	hkl
5.68	55	5.68	2	5.65	20	020
5.06	18	5.10	2	5.04	19	120
3.98	22	4.00	3	3.97	38	220
3.76	3	3.77	1/2	3.75	20	101
3.58	100	3.58	10	3.56	94	130
3.54	20	—	—	3.53	60	310
3.26	4	3.25	1/2	3.256	18	021
3.12	20	3.14	5	3.118	100	230, 211
2.818	12	2.82	2	2.811	63	221
2.723	5	2.73	1	2.716	34	301
2.645	4	2.66	1/2	2.641	24	311
2.525	25	2.51	1/2	2.520	35	240
2.504	3	—	—	2.499	13	420
2.459	2	2.46	1/2	2.456	15	231
2.306	8	2.32	1	2.304	24	041
2.256	10	2.26	3	2.256	36	141
2.132	2	2.13	1/2	2.129	9	241
2.120	3	—	—	2.118	15	421
2.099	6	2.09	1	2.096	11	250
2.076	2	—	—	2.074	10	520
1.991	4	1.989	1	1.990	33	002
1.954	8	1.953	2	1.954	55	431
1.937	8	1.933	2	1.935	20	151
1.922	5	—	—	1.919	20	530
1.885	30	1.892	1	1.884	14	060
1.858	5	1.866	1/2	1.854	17	251
1.835	1	1.834	1/2	1.834	7	610
1.782	2	—	—	1.779	13	222
1.753	2	—	—	1.765	5	620
1.739	5	1.743	2	1.737	7	351
—	—	—	—	1.734	35	312
1.704	5	1.710	1/2	1.703	10	061
1.683	3	1.687	1/2	1.682	7	161
—	—	—	—	1.679	8	360
—	—	—	—	1.665	2	611
—	—	—	—	1.604	4	412
1.562	3	1.561	1	1.562	15	242
1.552	2	—	—	1.552	11	640
1.535	1	1.537	1	1.533	8	720
1.483	7	1.486	2	1.490	6	342

1 : Synthetic Sb_2S_3 2 : Data for bismuthinite by Berry & Thompson 3 : Data from A.S.T.M.

distinct endothermic peak is only found at 780°C in this curve. This represents a latent heat of melting of bismuthinite. From this fact, bismuthinite is regarded to be melt congruently.

These properties of optics, X-ray diffraction and thermal analysis of synthetic bismuth sulfide

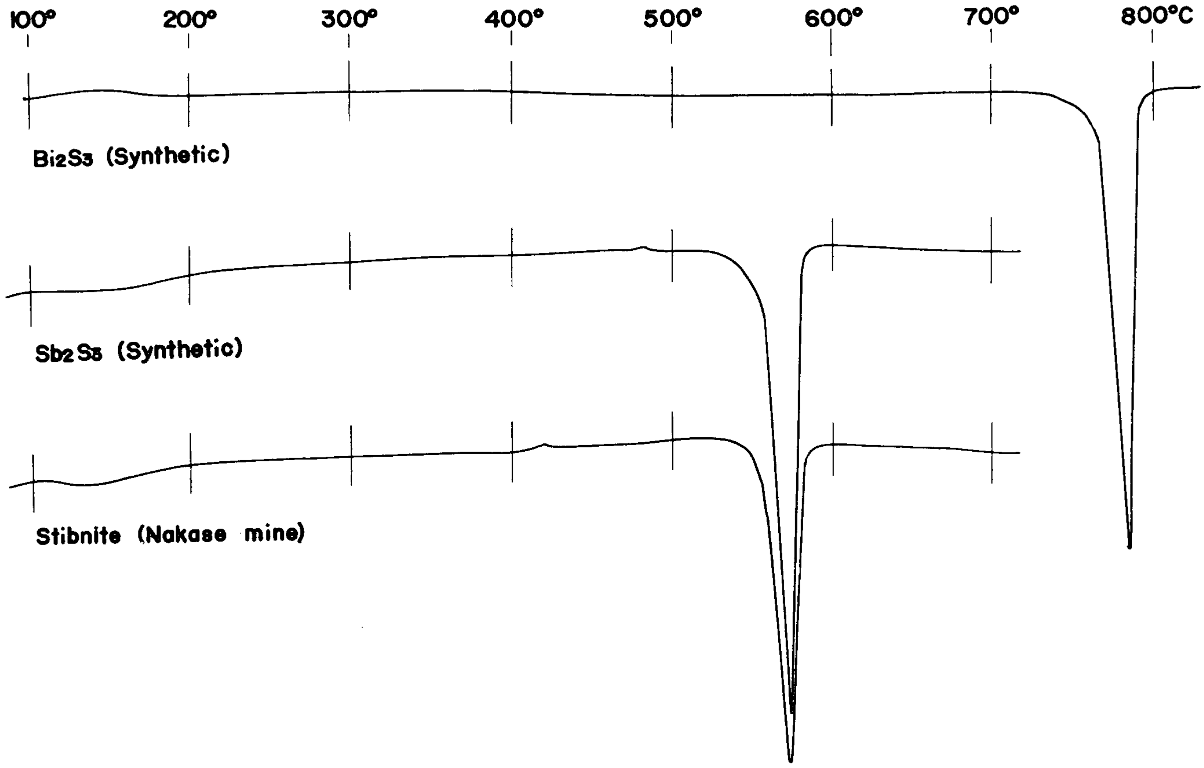

Fig. 7. Differential thermal curves for synthetic Bi_2S_3 and Sb_2S_3 as compared with the curve for stibnite from the Nakase mine, Hyogo Prefecture.

agree with those of bismuthinite occurred in nature.

9. Sb_2S_3 (Stibnite)

As starting materials of synthesis for stibnite, granular metallic antimony, from 0.5 mm to 2.0 mm in size and 99.9 % in purity, and crystal sulfur were employed. The synthesis was practiced by dry method in evacuated rigid glass tube. Namely, after antimony and sulfur were accurately weighed by chemical balance in proportion to two to three in molecular ratio, they were sealed in evacuated silica glass tube. Then, they were treated in the electric furnace under program of heating and cooling as follows: at 400°C for 24 hours after heating from room temperature up to 400°C for 2 hours; at 550°C for 36 hours; at 600°C for 36 hours; at 700°C for 24 hours; at 600°C for 24 hours and then cooling from 600°C down to room temperature for 30 hours. Though antimony sulfide was produced by the experiments mentioned above, the reaction between them was very slow at temperatures below 500°C. Consequently, the reaction was carried on in liquid state at about 700°C, at which temperature starting materials and product were entirely melted. Under such a condition, considerable amounts of the vapor were liberated from the product in the sealed tube. Accordingly, it was necessary to cool very slowly in order that the vapor was again absorbed in the solid product during cooling.

The product is radially fibrous aggregates, silver white in colour. Under the reflecting microscope, it is aggregates of long prismatic and needle-like crystals, and shows distinct pleochroism from grayish white to grayish brown. Under the crossed nicols, it has strong anisotropism changing its interference colour from dark brown to bluish gray and shows twinning.

Table 8. The data of X-ray powder diffraction for synthetic Sb_2S_3

1		2		3		4		
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	hkl
5.70	85	5.68	100	5.64	3	5.654	36	020
5.08	70	5.06	80	5.07	4	5.052	57	120
4.00	25	3.99	30	4.00	2	3.987	28	220
3.64	6	3.63	25	—	—	3.632	29	101
3.59	100	3.58	100	3.58	10	3.573	67	130
—	—	—	—	—	—	3.556	72	310
3.47	8	3.46	15	—	—	3.458	25	110
3.19	?	—	—	—	—	3.178	18	021
3.14	35	3.14	40	3.14	2	3.128	37	230
3.06	30	3.06	35	3.06	2	3.053	95	211
2.772	30	2.766	35	2.76	3	2.764	100	221
2.690	15	2.682	30	2.67	1	2.680	52	301
2.614	8	2.611	15	2.61	1/2	2.609	25	311
2.541	50	2.528	45	2.52	4	2.525	46	240
2.436	8	—	—	2.43	1	2.426	22	231
2.281	10	2.277	15	2.26	1	2.277	24	041
2.259	8	—	—	—	—	2.252	14	430
2.237	10	2.22	20	2.22	2	2.233	25	141
2.006	?	—	—	—	—	2.202	7	510
2.187	?	—	—	—	—	2.186	6	331
2.104	25	2.101	30	2.10	3	2.101	21	421
—	—	—	—	—	—	2.008	12	520
1.997	7	—	—	1.994	1/2	1.992	10	440
1.945	20	1.940	30	1.933	5	1.940	46	431
1.922	10	1.920	15			1.920	36	002, 151
1.890	15	1.886	7	1.881	1/2	1.885	9	060
1.870	?	—	—	—	—	1.871	9	600
1.863	5	1.862	7	1.852	1/2	1.858	5	160
1.848	?	—	—	—	—	1.846	9	610
1.762	3	—	—	1.781	1/2	—	—	—
1.731	10	1.728	7	1.728	3	1.729	19	351
—	—	—	—	—	—	1.725	20	531
1.692	15	1.691	30	1.692	4	1.691	34	132
1.640	?	—	—	1.639	1/2	1.636	8	232, 322
1.603	2	—	—	1.605	1/2	—	—	—
1.547	5	1.544	3	1.549	1	1.543	10	720
1.530	4	1.528	3	1.528	1	1.528	16	242
1.486	6	—	—	1.484	2	1.484	5	370
—	—	—	—	—	—	1.462	5	432, 342
1.444	5	—	—	1.445	2	1.444	7	271

1 : Synthetic Sb_2S_3 2 : Stibnite (Nakase mine) 3 : Data for stibnite by Berry & Thompson
4 : Data from A.S.T.M.

When etched by HNO_3 (1 : 1), it is sometimes tarnished darker in colour. By KCN (20%), it is affected to bleach its surface. By KOH (sat.), it stains reddish brown or orange in colour, and many fine pits appear on its polished surface by reaction. However, it is negative to HCl (1 : 1), $FeCl_3$ (20%) and $HgCl_2$ (20%).

The data of X-ray powder diffraction for synthetic antimony sulfide are given in Table 8 as comparison with those of natural stibnite.

As shown in Fig. 7, The curves of D.T.A. of natural and synthetic stibnites are quite similar and have only a distinct endothermic peak at 570°C which represents the latent heat of its congruent melting.

10. Conclusion

As mentioned above, the simple sulfides of copper, iron, manganese, bismuth and antimony could be synthesized by reaction between metals and sulfur in evacuated glass tube. Their optical properties, thermal behavior and X-ray diffraction data are good agreement with those of natural minerals.

Synthesis of such simple sulfides is important in order that they are often used as starting materials for synthesis of sulphosalt minerals. The present authors have synthesized many sulphosalt minerals, such as chalcopyrite $CuFeS_2$, bornite Cu_5FeS_4, wittichenite Cu_3BiS_3, enargite Cu_3AsS_4, famatinite Cu_3SbS_4 and tennantite $(CuFe)_{12}$ As_4 S_{13}, by using synthetic chalcocite, covellite, troilite, pyrrhotite, bismuthinite, stibnite and realger. These experimental data will be described in the next paper of this memoire.

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