MINERALOGICAL JOURNAL, VOL. 1, NO. 3, PP. 160-169, OCT., 1954

THE CRYSTAL STRUCTURE OF ORPIMENT (As_2S_3) REFINED

NOBUO MORIMOTO

Mineralogical Institute, University of Tokyo

ABSTRACT

The crystal structure of orpiment, As_2S_3, was refined by the Fourier synthesis. The unit cell has the dimensions, $a=11.46$ Å, $b=9.57$ Å, $c=4.22$ Å and $\beta=90.5°$, containing four As_2S_3. The space group is $C_{2h}^5-P2_1/n$. The structure is essentially the same as one described earlier.

Introduction

In the original analysis of orpiment, the usual trial-and-error method was used[7]. The crystal structure of realgar determined subsequently by the inequality relations and Fourier synthesis is considered much more precise. The relationship between these two related minerals has been discussed already[6].

The present study was undertaken in order to refine the atomic parameters of orpiment by means of the Fourier analysis, so that our discussion might be based on much more balanced data.

Experimental

Many experimental data were added to those used earlier. The specimens examined were the crystals from Saimoku, Japan[5]. The Weissenberg photographs were taken about the *a*, *b* and *c* axes by the multiple technique (Co $K\alpha$ radiation (1.79 Å)).

The relative intensities were estimated visually correcting for the Lorentz and polarization factors. No absorption correction was applied because of the difficulty due to the irregular shape of the

samples used. The effect of absorption, however, was reduced to minimum by comparing the relative intensity of a number of identical reflections from different samples.

The relative intensities were converted into the absolute ones by the method of Harker[4]. They were multiplied by a proportionality factor that minimized the sum of a certain number of the differences $||F_o|-|F_c||$.

The unit cell has the dimensions, $a=11.46\pm0.04$ Å, $b=9.57\pm0.02$ Å, $c=4.22\pm0.05$ Å and $\beta=90.5\pm0.5°$, containing four As_2S_3. The space group is $C_{2h}^5-P2_1/n$ with reflexions $h0l$ and $0k0$ absent respectively when $h+l$ and k are odd.[2]

Refinement by the Fourier synthesis

For summation the Beever-Lipson strips were used. The a and b axes were divided into 60 parts each with intervals of 0.19 and 0.16 Å, and the c axis into 30 parts with intervals of 0.14 Å.

The first summation of xy synthesis was carried out using 77 observed F_{hk0}'s whose signs were determined with certainity by the atomic parameters obtained in the previous study. The second summation was made with 91, and the third with 94 terms (all including zero terms), making successive adjustment of atomic positions. The xz synthesis was made in a similar way, the first one with 35, the second with 40, and the third with 41 terms (all including zero terms). In these syntheses, the effect of cutting off the higher-order Fourier terms was minimized by the method of Cochran.[3]

The final Fourier diagrams of electron density projected on (001) and (010) planes are given in Fig. 1. In these the maxima of contours of all the atoms in the cell are clearly resolved to read off immediately their parameters, excepting the z parameters of two of the sulfur atoms which overlap in the (010) projection. These were determined by a graphical method.[6]

The coordinates of atoms finally determined are given in Table 1,

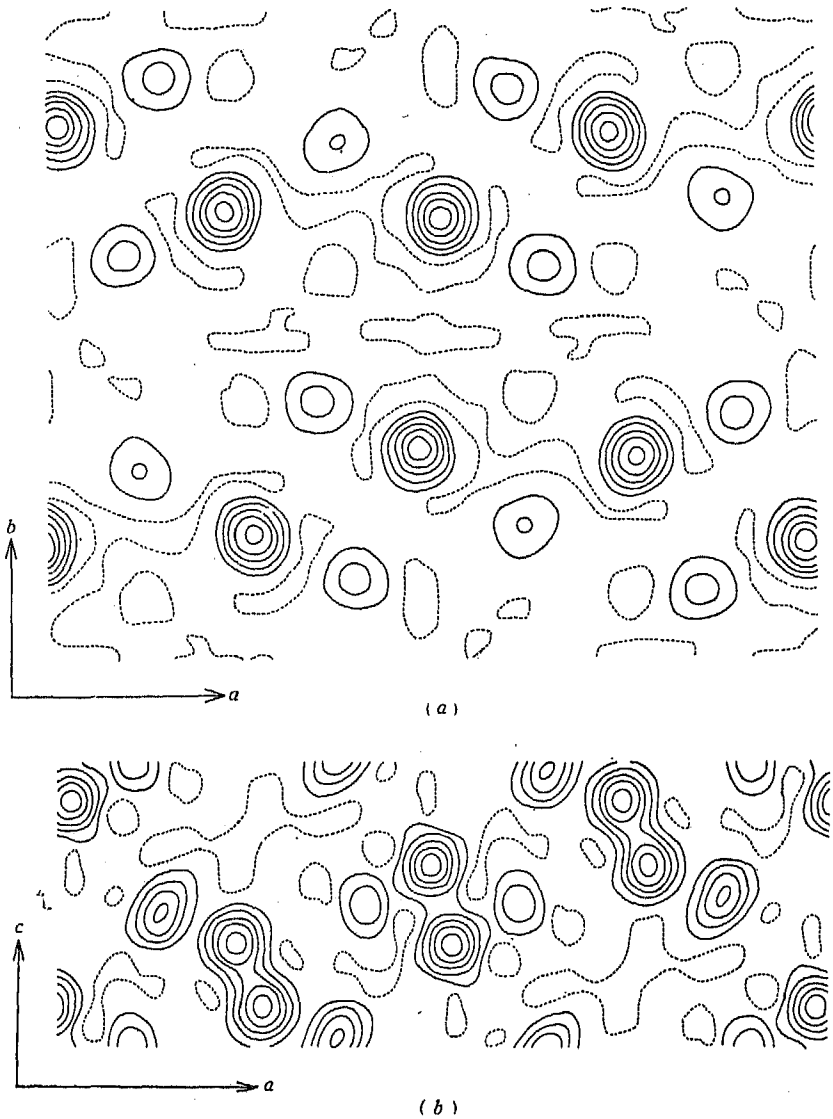

Fig. 1. Fourier projections of electron density on (a) (001) and (b) (010). Contours at intervals of 10 e. Å^{-2}, the zero-electron lines being broken.

Table 1. Coordinates of atoms

Atom	No. of atoms in the cell	*x/a*		*y/b*		*z/c*	
		(1)	(2)	(1)	(2)	(1)	(2)
As_1	4	.268	.267	.187	.190	.161	.143
As_2	4	.482	.484	.313	.323	.664	.643
S_1	4	.410	.395	.120	.120	.454	.500
S_2	4	.340	.355	.380	.397	−.046	.013
S_3	4	.125	.125	.305	.293	.455	.410

(1) Values by the previous study
(2) Final values by this study

compared with the original ones. Probable errors were estimated by the method of Booth[1] to be 0.04 Å for sulfur atoms and 0.02 Å for arsenic atoms. In Table 2, the structure factors calculated on the basis of the refined structure are given as also those experimentally determined. The reliability factor, $R=\Sigma||F_o|-|F_c||\div\Sigma|F_o|$, is 0.15 for *hk*0 reflexions, 0.21 for *h*0*l* reflexions, and 0.18 for *hkl* reflexions, all present and absent reflexions being counted.

The structure redescribed

The refined structure of orpiment as illustrated in Fig. 2, which like Fig. 1 is projected on (001) and (010) planes, is essentially the same as one originally described except for a few shifts in atomic positions which considerably improved the interatomic distances and the atomic bond angles.

The structure consists of As_2S_3 layers, in which spiral chains, AsS, running parallel to the *c* axis, can be seen (Fig. 3). The layers are parallel to (010) and held together by the van der Waals force.

In the structure, each arsenic atom is surrounded by three sulfur atoms and each sulfur atom is shared by two arsenic atoms. The covalent bond distances and the bond angles are given in Table 3. The mean value of the covalent bond distances between arsenic and

Table 2. Comparison of observed and calculated F-values

hkl	sin θ	F_{obs}	F_{calc}	*hkl*	sin θ	F_{obs}	F_{calc}	*hkl*	sin θ	F_{obs}	F_{calc}
200	.156	–	2.8	630	.546	91	90.8	560	.686	40	39.2
400	.312	63	67.8	730	.615	114	−103.2	660	.733	–	4.8
600	.468	–	− 0.8	830	.685	11	− 15.2	760	.786	–	0.8
800	.625	157	173.2	930	.756	42	48.4	860	.842	90	68.4
10.00	.781	–	7.2	10.30	.830	4	0.4	960	.903	22	18.0
				11.30	.906	65	− 72.4	10.60	.959	40	26.4
210	.182	72	− 62.4								
310	.252	38	49.2	040	.377	78	− 77.2	170	.664	–	13.6
410	.326	–	− 3.2	140	.384	74	− 75.6	270	.674	37	39.2
510	.411	56	49.2	240	.407	27	− 30.4	370	.696	10	− 14.4
610	.478	84	− 92.4	340	.443	135	133.4	470	.730	–	– 3.6
710	.564	72	71.2	440	.489	29	27.2				
810	.631	–	− 4.4	540	.543	45	− 35.6	080	.744	107	−102.8
910	.710	29	− 38.6	640	.601	17	− 18.4	180	.756	21	22.0
10.10	.786	74	− 88.8	740	.664	78	72.4	280	.768	–	11.6
11.10	.865	–	9.6	840	.729	10	26.0	380	.789	21	2.4
				940	.796	–	12.8	480	.815	152	−131.2
020	.188	203	−185.6	10.40	.865	40	− 13.3	580	.843	72	− 62.8
120	.204	29	42.4					680	.881	–	6.8
220	.244	–	9.2	150	.471	31	31.6				
320	.300	94	− 86.8	250	.497	52	49.2	190	.850	70	− 53.2
420	.364	106	− 96.8	350	.526	138	130.8	290	.860	–	– 2.4
520	.434	72	63.2	450	.564	14	22.4	390	.879	57	− 56.0
620	.505	14	14.4	550	.612	14	16.4	490	.901	40	− 33.2
720	.578	113	−104.8	650	.664	14	17.6				
820	.653	104	− 88.8	750	.722	47	34.2	101	.209	61	− 64.0
920	.728	51	− 65.2	850	.781	–	– 2.4	301	.314	202	217.6
10.20	.803	–	− 7.6	950	.841	10	− 10.8	501	.425	–	3.6
11.20	.879	40	− 34.0	10.50	.902	46	61.6	701	.587	108	113.6
								901	.726	26	9.2
130	.294	52	− 53.2	060	.564	102	96.4	11.01	.883	178	156.8
230	.322	87	− 90.8	160	.570	31	28.4				
330	.367	135	−137.2	260	.586	23	27.2	002	.425	67	54.0
430	.412	–	− 8.0	360	.612	117	116.2	202	.452	45	78.8
530	.481	100	− 77.6	460	.646	138	132.0	402	.527	132	−109.6

Table 2.—*Continued*

hkl	sin θ	F_{obs}	F_{calc}	*hkl*	sin θ	F_{obs}	F_{calc}	*hkl*	sin θ	F_{obs}	F_{calc}
602	.631	69	48.4	511	.455	38	30.0	241	.460	–	20.8
802	.757	22	22.8	611	.524	27	28.8	341	.492	16	− 23.6
10.02	.890	144	131.8	711	.595	84	76.0	441	.533	141	−142.4
				811	.666	14	6.0	541	.582	24	19.2
103	.640	107	−107.6	911	.740	–	2.0	641	.636	51	60.4
303	.680	41	− 59.2	10.11	.815	40	44.8	741	.696	16	14.0
503	.748	41	− 36.8	11.11	.890	34	− 33.2	841	.760	54	− 47.6
703	.840	89	50.0					941	.827	60	− 68.8
				021	.284	90	67.2	10.41	.894	44	51.6
004	.851	56	− 77.2	121	.293	46	53.6				
				221	.324	93	93.2	051	.516	160	186.4
$10\bar{1}$	.209	124	144.0	321	.368	111	−115.6	151	.523	40	− 31.6
$30\bar{1}$	.316	38	54.8	421	.422	114	112.8	251	.540	19	41.6
$50\bar{1}$	.425	29	23.2	521	.482	29	− 17.6	351	.569	–	− 11.6
$70\bar{1}$	.587	103	− 84.8	621	.547	94	−104.4	451	.604	–	− 12.8
$90\bar{1}$	.726	28	11.2	721	.615	118	-110.4	551	.650	19	− 20.8
$11.0\bar{1}$	.883	66	50.0	821	.685	45	41.6	651	.699	37	33.5
				921	.758	32	36.0	751	.752	27	− 21.6
$20\bar{2}$	.452	55	− 75.2	10.21	.830	27	− 16.0	851	.811	66	90.8
$40\bar{2}$	.527	95	−116.8	11.21	.907	56	− 70.4	951	.872	12	2.0
$60\bar{2}$	.631	79	− 55.2								
$80\bar{2}$	.757	39	25.6	031	.353	106	−102.0	061	.604	59	53.2
$10.0\bar{2}$	.890	156	−130.0	131	.362	12	− 0.8	161	.599	16	18.4
				231	.386	29	− 46.8	261	.624	51	− 60.4
$10\bar{3}$	.640	–	7.6	331	.424	–	24.4	361	.641	78	83.2
$30\bar{3}$	.680	64	− 83.2	431	.471	102	−107.6	461	.681	86	79.6
$50\bar{3}$	.748	40	− 66.4	531	.526	44	− 44.0	561	.720	26	17.6
$70\bar{3}$	.840	162	−165.6	631	.586	46	− 64.4	661	.766	43	− 32.0
				731	.652	11	8.4	761	.815	93	123.6
$20\bar{4}$	.864	–	− 19.2	831	.716	60	− 58.4	861	.870	52	41.2
$40\bar{4}$	.902	114	−126.2	931	.788	36	45.4				
				10.31	.859	59	− 89.6	071	.693	47	− 55.2
211	.280	23	23.2					171	.698	54	46.8
311	.330	38	− 38.0	041	.432	135	−125.2	271	.711	–	− 2.8
411	.389	55	93.6	141	.445	43	− 48.4	371	.731	24	18.0

Table 2.—*Continued*

hkl	sin θ	F_{obs}	F_{calc}	*khl*	sin θ	F_{obs}	F_{calc}	*khl*	sin θ	F_{obs}	F_{calc}
47$\bar{1}$	.759	17	27.6	52$\bar{1}$	.482	87	− 42.4	55$\bar{1}$	.650	43	34.4
57$\bar{1}$	.795	66	59.6	62$\bar{1}$	.547	126	−115.2	65$\bar{1}$	.699	57	− 42.0
67$\bar{1}$	.839	50	35.2	72$\bar{1}$	.615	25	28.2	75$\bar{1}$	.752	60	50.4
77$\bar{1}$	.882	12	1.6	82$\bar{1}$	.685	58	− 51.6	85$\bar{1}$	.811	111	108.0
				92$\bar{1}$	.758	28	26.4	95$\bar{1}$	.872	12	7.6
081	.782	32	35.6	10.2$\bar{1}$	.830	53	− 28.0				
181	.788	48	46.0					16$\bar{1}$	.599	78	82.0
281	.800	21	− 24.4	13$\bar{1}$	.362	30	28.0	26$\bar{1}$	.624	11	− 13.2
381	.819	93	−110.4	23$\bar{1}$	.386	39	42.0	36$\bar{1}$	.641	15	− 19.6
481	.846	−	0.8	33$\bar{1}$	.424	46	40.8	46$\bar{1}$	.681	63	− 71.2
581	.875	46	− 26.8	43$\bar{1}$	.471	100	−104.0	56$\bar{1}$	.720	31	31.6
681	.910	56	58.4	53$\bar{1}$	.526	74	− 71.2	66$\bar{1}$	.766	14	− 3.2
				63$\bar{1}$	.586	42	46.0	76$\bar{1}$	.815	16	12.4
091	.873	58	− 76.4	73$\bar{1}$	.652	60	69.3	86$\bar{1}$	.870	23	− 7.2
191	.889	60	− 41.6	83$\bar{1}$	.716	75	− 59.2				
291	.909	19	− 25.2	93$\bar{1}$	.788	47	36.8	17$\bar{1}$	.698	40	− 35.6
391	.929	24	4.0	10.3$\bar{1}$	.859	87	92.8	27$\bar{1}$	.711	34	38.6
								37$\bar{1}$	.731	99	−104.8
21$\bar{1}$	.280	14	− 12.0	14$\bar{1}$	.445	37	− 26.0	47$\bar{1}$	.759	−	6.4
31$\bar{1}$	.330	150	−196.0	24$\bar{1}$	.460	15	14.8	57$\bar{1}$	.795	34	22.8
41$\bar{1}$	.389	84	87.2	34$\bar{1}$	.490	12	− 9.6	67$\bar{1}$	.839	53	28.8
51$\bar{1}$	.455	−	14.8	44$\bar{1}$	.533	122	122.8	77$\bar{1}$	.882	138	−142.8
61$\bar{1}$	.524	25	− 18.0	54$\bar{1}$	.582	44	34.8				
71$\bar{1}$	.595	121	−105.2	64$\bar{1}$	.636	65	63.6	18$\bar{1}$	.788	62	− 55.6
81$\bar{1}$	.666	28	6.0	74$\bar{1}$	.696	31	15.2	28$\bar{1}$	.800	85	− 88.0
91$\bar{1}$	.740	−	0.4	84$\bar{1}$	.760	85	68.0	38$\bar{1}$	.819	−	0.4
10.1$\bar{1}$	.815	27	− 34.0	94$\bar{1}$	.827	54	− 38.0	48$\bar{1}$	.846	−	− 5.2
11.1$\bar{1}$	.890	170	−140.0	10.4$\bar{1}$	.894	51	50.0	58$\bar{1}$	.875	69	− 61.2
								68$\bar{1}$	.910	16	8.0
12$\bar{1}$	.293	61	− 86.8	15$\bar{1}$	.523	35	30.8				
22$\bar{1}$	.324	71	74.4	25$\bar{1}$	.540	61	− 55.2	19$\bar{1}$	.889	11	− 11.6
32$\bar{1}$	.368	−	− 7.6	35$\bar{1}$	.569	80	86.4	29$\bar{1}$	.909	19	− 18.8
42$\bar{1}$	.422	117	112.6	45$\bar{1}$	.604	14	0.8	39$\bar{1}$	.929	57	71.6

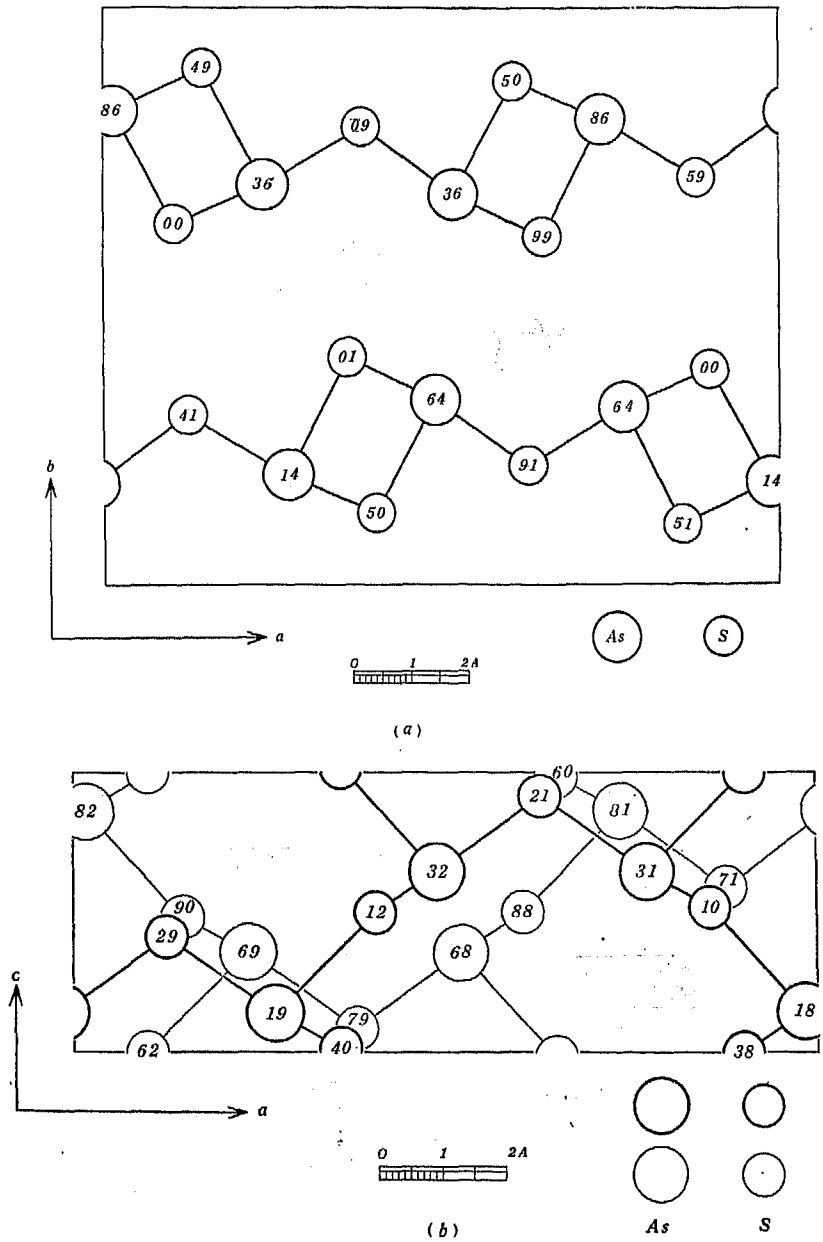

Fig. 2. The structure of orpiment, projected on (a) (001) and (b) (010). (The figure corresponds to Fig. 1). Numbers give the height of each atom in the cell expressed as a percentage of the c and b translation.

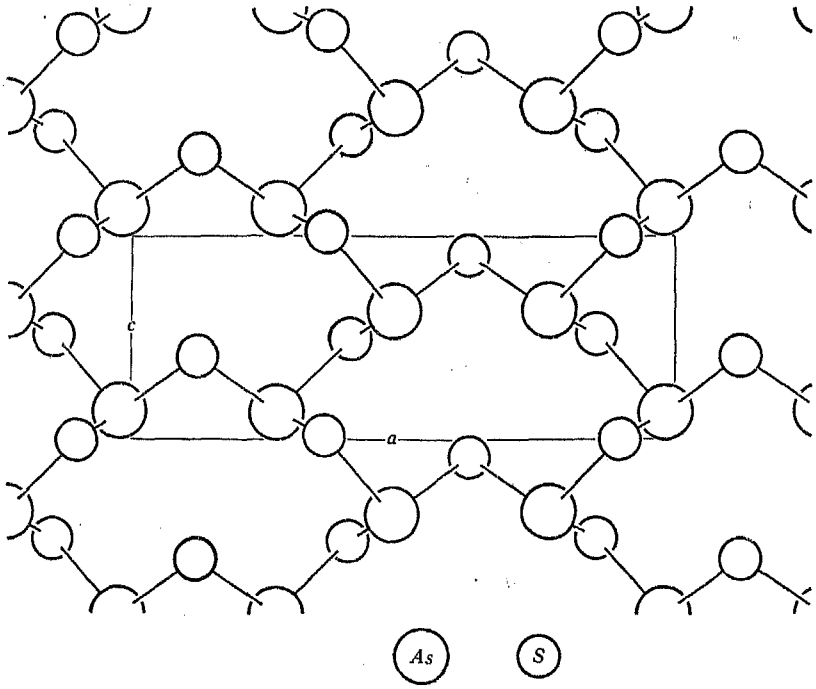

Fig. 3. The layer in the orpiment structure (projected on (010)). The spiral chains, AsS, composing the layer are to be seen.

Table 3. Interatomic distances and bond angles

1. Covalent bond distances (Å)

As_1-S_1	2.21	As_2-S_1	2.26
As_1-S_2	2.28	As_2-S_2	2.26
As_1-S_3	2.22	As_2-S_3	2.23

2. Bond angles (°)*

$\angle As_1-S_1-As_2$	102.8	$\angle S_1-As_1-S_2$	97.1
$\angle As_1-S_2-As_2$	100.6	$\angle S_2-As_1-S_3$	94.5
$\angle As_1-S_3-As_2$	94.4	$\angle S_3-As_1-S_1$	106.5
		$\angle S_1-As_2-S_2$	95.2
		$\angle S_2-As_2-S_3$	106.1
		$\angle S_3-As_2-S_1$	92.7

* Bond angles obtained by construction

3. Non-bonded distances (Å)

As_1-As_2	3.25	S_1-S_2	3.36
	3.49		3.36
	3.49	S_2-S_3	3.30
			3.58
		S_3-S_1	3.55
			3.24

sulfur atoms is 2.24 Å, and the mean values of the bond angles ∠As–S–As and of ∠S–As–S are respectively 99.3° and 98.7°.

The highly perfect cleavage of orpiment after (010) is parallel to the As_2S_3 layers.

It is interesting to note that the bond angles of the sulfur atoms added in between the spiral chains differ from those of the sulfur atoms in the chains. This would mean that the former sulfur atoms play a different role from the latter in the orpiment structure.

In conclusion the writer wishes to express his sincere thanks to Prof. Ito for suggestion and guidance throughout the work.

References

1) Booth, A. D.: Fourier Technique in Organic Structure Analysis. (Cambridge, University Press, 1948).
2) Buerger, M. J.: Amer. Miner., 27, 301 (1942).
3) Cochran, W.: Acta Cryst., 1, 138 (1948).
4) Harker, D.: Amer. Miner., 33, 764 (1948).
5) Ito, T. and K. Sakurai: Wada's Minerals of Japan, 3rd Ed., 26 (1947).
6) Ito, T., N. Morimoto and R. Sadanaga: Acta Cryst., 5, 775 (1952).
7) Morimoto, N.: X-rays, 5, 115 (1949).

Manuscript received August 19, 1954.