

The crystal structure and bonding of lorandite, $\text{Tl}_2\text{As}_2\text{S}_4$ *[✓]

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Auszug

Die Kristallstruktur von Lorandit $\text{Tl}_2\text{As}_2\text{S}_4$, in der AsS_3 -Tetraeder zu spiralförmigen Ketten parallel [010] angeordnet und die Ketten durch Tl-Atome verbunden sind, wird bestätigt und bis zu $R = 0,09$ verfeinert. Die Gitterkonstanten sind $a = 12,28 \text{ \AA}$, $b = 11,30 \text{ \AA}$, $c = 6,10 \text{ \AA}$, $\beta = 104^\circ 5'$; $Z = 4$. Raumgruppe ist $P2_1/a$. Die S-Atome werden von den As- und Tl-Atomen in den Ecken schwach deformierter Tetraeder umgeben. S-Atome, die aufeinanderfolgende As-Atome in der Kette verbinden, haben außerdem noch zwei Tl-Atome zu Nachbarn. Jedes S-Atom, das nur an ein As-Atom gebunden ist, hat drei nächste Tl-Nachbarn; sein Abstand zum As-Atom ist auffallend klein (2,08 und 2,20 \AA entsprechend den zwei nicht-äquivalenten As-Atomen der Struktur).

Jedes Tl-Atom liegt einer der AsS_3 -Pyramidenketten näher als den übrigen; die S-Umgebung der Tl-Atome bildet deformierte tetragonale Pyramiden mit Tl in der Spitze.

Lage und Ausbildung der Spaltbarkeit hängt unmittelbar von Zahl und Typ der Bindungen zwischen den Ketten ab. Die kurzen (As–S)-Abstände weisen darauf hin, daß diese Bindungen bis zu einem gewissen Grad den Charakter von π -Bindungen haben. Die geringe Differenz der Elektronegativitäten von Tl und S, die scheinbare Wechselwirkung zwischen benachbarten Tl-Atomen und der Vergleich mit Tl-haltigen organischen Verbindungen legen die Annahme nahe, daß zwischen den Tl-Atomen und den AsS_3 -Ketten kovalente Kräfte bestehen.

Abstract

Lorandite ($\text{Tl}_2\text{As}_2\text{S}_4$) is monoclinic with $a = 12.28(1) \text{ \AA}$, $b = 11.30(1) \text{ \AA}$, $c = 6.101(6) \text{ \AA}$, $\beta = 104^\circ 5'(2')$, space group $P2_1/a$, $Z = 4$. The crystal structure, consisting of spiral chains of AsS_3 pyramids oriented parallel to [010] and connected by Tl atoms, has been confirmed and refined by full-matrix least-squares analysis of three-dimensional diffractometer data to give a value of the conventional residual index of 0.09. The positions of the S and As atoms are mark-

* Dedicated to Professor M. J. Buerger on the occasion of his 70th birthday.

edly different from those reported in the literature. The present study has shown that the bonds from the two non-equivalent As atoms to the non-bridge S are quite short (2.08 Å and 2.20 Å), that each S is tetrahedrally coordinated to As and Tl and that each Tl position is more closely related to one AsS₃ pyramid chain than to adjacent chains, the nearest-neighbor S environment of each being a distorted square-pyramidal configuration.

The development of cleavage in lorandite is directly related to the number and type of the interchain bonds. It is suggested that the short As non-bridge S distances in this mineral and in other sulfosalts indicate some degree of π -bonding character in these bonds. Finally, the small difference in the electronegativities of Tl and S, the apparent bonding interaction between adjacent Tl atoms and comparisons with Tl-bearing organic compounds suggest that Tl atoms are bound by covalent forces to the AsS₃-pyramid chains.

Introduction

The sulfosalt lorandite, Tl₂As₂S₄, is found in low-temperature mineral assemblages in association with orpiment, realgar, pyrite and certain other sulfide minerals; the most familiar locality being Allchar, Macedonia. It has monoclinic symmetry with $a = 12.27$ Å, $b = 11.34$ Å, $c = 6.11$ Å, $\beta = 104^\circ 12'$ (HOFMANN, 1933), space group $P2_1/a$, $Z = 4$. The mineral is deep red and, because of the prominent development of cleavage [(100) excellent, ($\bar{2}01$) very good, (001) good], it appears flexible in hand specimen, separating easily into cleavage lamellae and fibres (DANA'S *System of mineralogy*, 1946).

Table 1. Positional parameters of ZEMANN and ZEMANN

	x	y	z
Tl(1) in 4e	0.051	0.313	0.160
Tl(2) in 4e	0.101	0.056	0.732
As(1) in 4e	0.190	0.820	0.237
As(2) in 4e	0.151	0.585	0.554
S(1) in 4e	0.125	0.320	0.750
S(2) in 4e	0.150	0.580	0.200
S(3) in 4e	0.125	0.790	0.510
S(4) in 4e	0.200	0.030	0.200

The crystal structure of lorandite was determined from $h0l$ and $hk0$ reflections (ZEMANN and ZEMANN, 1959), giving the positional parameters in Table 1, and consists essentially of spiral chains of AsS₃ pyramids oriented parallel to [010] and linked together by irregularly coordinated Tl atoms. KNOWLES (1965) reported on a refinement of

the structure based on three-dimensional intensity data, suggesting that the S and As positions were poorly defined in the original study and that the Tl atoms appeared to be in twofold coordination with S.

Experimental

The present study was made on material from Allchar obtained through David New Minerals, Hamilton, Montana. Some difficulty was encountered in obtaining a single crystal from the hand specimen because the mineral deforms very readily when handled so that crystals reduced to a suitable size invariably have bent or twisted cleavage surfaces. The crystal selected was a tabular (010) cleavage fragment bounded by plane surfaces, 0.003 cm thick with a calculated volume of $0.11 \cdot 10^{-6} \text{ cm}^3$; it was mounted on the b axis to minimize possible errors in the absorption correction. Reflections recorded on precession camera films of the crystal did not show any evidence of deformation. The systematic absences on these films confirmed the accepted space group for lorandite, $P2_1/a$. The lattice parameters, obtained by least-squares refinement of twelve centred reflections of the crystal on a four-circle diffractometer, are $a = 12.276(12) \text{ \AA}$, $b = 11.299(2) \text{ \AA}$, $c = 6.101(6) \text{ \AA}$, $\beta = 104^\circ 5'(2')$ —the standard deviations are in parentheses—and compare quite favourably with published data.

The x-ray intensity data for the structure analysis were taken on a Picker facs 1 four-circle diffractometer system at the University of Western Ontario. All hkl and $hk\bar{l}$ reflections with $2\theta \geq 45^\circ$ were measured using a scintillation detector, Zr-filtered $\text{MoK}\alpha$ ($\lambda = 0.7107 \text{ \AA}$) radiation and the 2θ -scan technique: 40 second stationary background counts, peak-base widths of $2.0^\circ 2\theta$ (uncorrected for dispersion) and a scanning rate of 0.5° per minute. The resulting data were processed by a data-correction routine which corrected for background, Lorentz and polarization effects, and absorption, and assigned standard deviations (σ) to the corrected data based on the summed variances of the counting rates of the peaks and associated backgrounds. Transmission factors for the absorption correction were calculated by the analytical method of DE MEULENAER and TOMPA (1965) using a value for the linear absorption coefficient of 485.6 cm^{-1} . The calculated transmission factors varied from 0.10 for $31\bar{6}$ to 0.22 for $12\ 2\ 1$. Each reflection whose intensity was less than the associated background plus 3σ was given zero intensity. The final data list contained 1078 reflections of which 404 were "unobserved".

Crystal-structure investigation

At this stage in the investigation the author was unaware that the structure had been confirmed by KNOWLES (1965), and it was considered desirable to redetermine the structure independently of the earlier work.

The structure factors were converted to normalized structure factors, E , using program FAME (R. B. K. DEWAR, Illinois Institute of Technology, Chicago), and, since the structure must be centrosymmetric, the phases of those normalized structure factors with $E \geq 1.5$ were assigned by a reiterative application of SAYRE'S equation using program REL 1 (adapted from R. E. LONG, Ph. D. Thesis, University of California, Los Angeles, 1965). E maps, prepared from the solution with the largest consistency index (0.998), clearly indicated two Tl positions, two probable and one possible As positions and various possible S positions. A value of the conventional residual index, R , of 0.33 was obtained using a trial set from these positions. A F_o Fourier synthesis resolved all the positional ambiguities, giving a set of atomic positions which resulted in a lowering of the residual index to 0.23 and which proved to be equivalent to the accepted structure of lorandite; the As and S atoms being associated to form spiral chains of AsS_3 pyramids oriented parallel to [010] (Figs. 1a and 1b) with two nonequivalent Tl atoms seemingly irregularly coordinated between them.

The structure was refined further by full-matrix, least-squares refinement using program RFINE (L. FINGER, Geophysical Laboratory, Washington). RFINE minimizes the function $\sum w (|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$, F_o is the observed and F_c the calculated structure factor, and calculates a conventional residual index, $\sum ||F_o| - |F_c|| / \sum |F_o|$ and a weighted residual index, $[\sum w (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. The scattering curves for Tl and As were taken from CROMER and MANN (1968) and that for S^{2-} computed for a nine parameter fit from data in the *International tables for x-ray crystallography*, Vol. III; the anomalous dispersion coefficients of CROMER (1965) for Tl, As and S were included. Isotropic and anisotropic thermal parameters were added successively to the refinement. However, the values of the anisotropic thermal parameters for the S atoms were somewhat erratic and inconsistent, suggesting that they were reflecting limitations in the data set rather than true thermal motions of the atoms, and the refinement was limited to anisotropic thermal parameters for Tl and As atoms and isotropic thermal parameters for S atoms. The values of the conven-

tional and weighted residual indices obtained for the non-zero intensities used are all isotropic, 0.105 and 0.114, and anisotropic Tl and As and isotropic S, 0.094 and 0.098. According to the procedure for

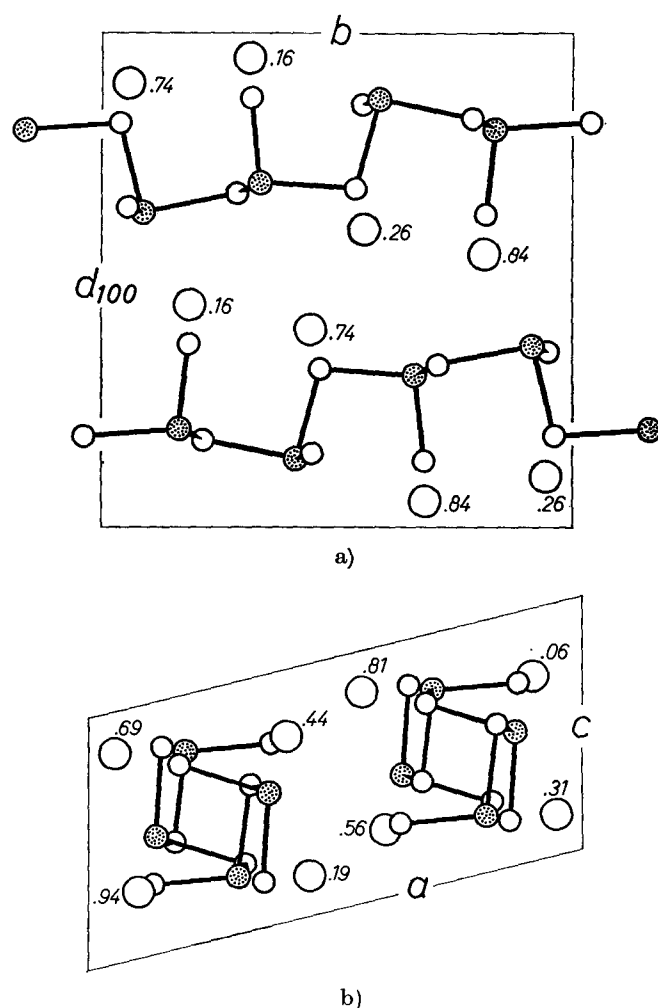


Fig. 1. The crystal structure of lorandite projected parallel to a) c axis, b) b axis; Tl: large open circles with the height in the projection indicated, As: small stippled circles, S: small open circles

testing weighted residuals (HAMILTON, 1965), the value of the residual index for the latter refinement is significant, compared to that using isotropic thermal parameters only, at the 0.005 level. The positional

Table 2. *Positional and thermal parameters* (standard deviations in parentheses)

Position	x	y	z	B_{11} (B)	B_{22}	B_{33}	B_{13}
Tl(1)	0.0519(3)	0.3121(4)	0.1619(6)	2.6(2)	2.1(2)	1.3(2)	3.4(6)
Tl(2)	0.1009(3)	0.0560(4)	0.7357(7)	3.0(2)	2.1(2)	1.3(2)	4.1(6)
As(1)	0.1960(8)	0.8353(9)	0.2266(15)	2.7(5)	1.5(5)	0.7(4)	1.8(1.5)
As(2)	0.1361(8)	0.5865(8)	0.5320(16)	3.3(5)	1.3(5)	1.3(5)	7.2(1.6)
S(1)	0.131(2)	0.316(3)	0.721(5)	3.3(6)			
S(2)	0.147(2)	0.553(2)	0.183(4)	1.6(4)			
S(3)	0.174(2)	0.786(2)	0.577(4)	2.2(5)			
S(4)	0.183(2)	0.038(2)	0.272(4)	1.7(5)			

and thermal parameters, and associated standard deviations for this refinement are given in Table 2.

The refinement was terminated when the changes to the positional and anisotropic thermal parameters were in the sixth places and the ratios of the changes in these parameters to the errors in the parameters were less than 0.005. The observed and calculated structure factors are given in Table 3. The refined structure was checked with F_o and $F_o - F_c$ Fourier maps; no significant residual peaks were detected.

Discussion of the structure

The positional parameters determined in the present study show marked discrepancies from those reported in the original work (ZEMANN and ZEMANN, 1959). As expected, the discrepancies are least for the heavy Tl atoms and greatest for the lighter S atoms. Thus, although the structure was outlined correctly, the bond distances and bond angles reported for the spiral chains of AsS_3 pyramids have little relation to the actual values. The ranges of the interatomic distances quoted by KNOWLES (1965) are similar to those of the present study, suggesting that the positional parameters of the two refinements would be quite comparable.

Some interatomic distances and bond angles of interest are given in Tables 4 and 5 respectively (the atom identification labels are consistent with the usage in Fig. 2; atoms marked by an asterisk are located in adjacent unit cells). The As—S bonds which form bridge bonds between the AsS_3 pyramids are similar in length (2.29 Å to 2.32 Å) to the average bridge bond (2.31 Å) obtained from a survey of well refined sulfosalt structures (TAKÉUCHI and SADANAGA, 1969). However, the non-bridge As—S bonds are somewhat shorter (2.08 Å

Table 3. Observed and calculated structure factors

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
0 0 2	523	473	1 6 -1	220	216	3 1 3	212	232	4 2 -4	68	49	5 6 -5	122	155	7 3 3	95	87
3	316	287	-4	81	80	4	59	26	-6	92	98	5 7 0	98	106	4	77	77
4	232	210	-5	73	54	-1	421	428	4 3 1	85	88	2	189	175	-1	140	121
0 1 2	174	149	1 7 1	120	128	-2	125	158	3	85	84	4	123	107	-2	74	82
3	278	243	2	57	51	-3	205	199	4	150	149	-1	61	65	-5	60	53
4	200	177	-1	180	181	-4	70	56	-1	190	191	-2	138	140	-6	140	176
5	201	188	-2	109	113	-5	68	83	-2	69	57	-4	76	70	7 4 3	148	142
0 2 1	130	125	-3	225	231	-6	93	98	-3	262	248	5 8 3	76	50	-1	204	189
2	82	72	-4	95	94	3 2 0	85	93	-4	65	49	5 9 0	56	67	-2	109	110
3	182	165	-5	77	74	1	126	136	-5	94	110	2	61	49	-3	143	127
4	226	219	1 8 3	95	106	2	136	143	5 10 0	94	102	-4	302	300	-4	302	300
5	120	129	1 9 0	60	70	4	166	189	4 4 2	51	57	-3	99	100	-5	111	101
6	119	127	2	70	78	5	66	76	5 11 0	99	93	5 11 0	99	93	7 5 0	151	123
0 3 1	291	309	4	146	142	-1	126	114	4 5 1	80	85	-1	115	120	1	81	95
2	105	97	-2	101	108	-3	166	150	3	62	54	6 0 0	80	82	2	89	83
3	193	178	-3	100	96	-4	220	213	4	62	64	1	364	435	3	90	77
4	24	25	-4	90	107	-5	209	221	-1	234	230	3	90	111	-1	126	116
0 4 1	32	47	1 10 1	151	185	-6	138	146	-3	278	260	4	62	62	-3	162	153
3	69	60	-2	140	130	3 3 0	133	156	-5	126	152	-1	270	336	-5	82	80
6	33	18	1 11 0	174	202	1	122	143	4 6 0	186	190	-2	222	285	7 6 0	171	174
0 5 1	175	181	2	108	114	3	224	227	1	120	124	-3	155	178	1	105	91
2	71	72	1 12 0	73	77	4	81	82	2	116	109	-4	143	168	2	138	133
3	114	110	2 0 0	88	111	5	211	223	3	80	81	-5	114	122	-1	143	135
0 6 1	169	176	1	144	190	-1	145	141	4	84	75	-6	118	85	-2	59	48
2	116	128	2	112	128	3	187	154	2	150	133	-3	184	191	3	166	78
3	99	93	3	179	186	-3	100	95	-3	80	87	2	50	45	7 7 3	62	63
4	108	106	5	234	221	-4	256	238	-5	118	128	3	122	132	-1	90	83
5	74	103	-1	49	87	-6	112	111	4 7 0	209	229	4	62	71	-2	79	73
0 7 1	31	57	-2	230	240	3 4 0	412	431	1	230	233	-1	87	96	-5	94	104
2	145	177	-4	288	256	1	122	143	2	150	133	-3	184	191	7 8 1	64	58
3	134	131	-5	323	293	2	107	103	3	199	176	-3	177	208	-1	85	87
4	31	62	-6	276	262	-1	70	71	-1	64	49	-4	189	209	-2	80	72
5	196	204	2 1 0	122	130	-2	260	240	-2	164	170	-5	67	77	7 9 1	124	106
0 8 0	386	442	1	311	338	-3	236	204	-3	92	94	-6	230	230	-1	126	119
1	30	52	4	168	157	-4	133	129	4 8 0	132	132	6 2 0	63	56	-3	134	130
2	258	254	5	133	122	-6	119	140	3	159	152	1	97	107	7 10 0	133	106
3	127	141	6	79	66	3 5 0	222	221	-2	227	218	2	193	201	-1	105	102
4	76	77	-1	70	62	1	124	130	-3	80	79	4	131	156	8 0 0	79	107
0 9 1	84	104	-2	475	426	2	121	121	-4	223	238	-2	101	97	1	270	285
2	91	99	-4	111	97	3	187	186	4 9 0	149	154	-3	119	133	3	189	191
3	40	71	-5	75	79	4	125	105	1	61	66	-5	171	206	-1	70	88
4	147	142	2 2 0	83	72	5	98	111	3	140	125	-6	86	64	-2	164	197
0 10 2	150	161	1	120	125	-1	98	93	-2	109	90	6 3 0	70	62	-4	128	144
3	98	107	2	78	71	-2	173	158	-3	86	70	2	124	122	-5	117	137
0 11 1	145	177	-1	335	323	-3	129	146	4 10 0	57	80	3	106	106	-6	108	120
1 1 0	53	48	-2	84	69	4	179	159	1	123	139	-1	266	257	8 1 2	79	93
1	70	69	-3	283	257	3 6 1	133	156	2	176	165	-2	190	192	3	71	70
2	164	158	-4	162	149	2	130	131	-1	233	241	-3	107	103	-1	198	198
3	110	99	2 3 0	51	47	3	80	78	-2	81	68	-5	96	115	-2	65	63
4	165	184	1	115	122	4	190	200	-3	78	61	-6	103	117	-3	61	58
6	152	157	2	247	258	-3	161	167	5 1 0	72	80	6 4 4	69	60	-4	94	127
-1	154	121	3	237	227	-5	92	116	1	56	66	6 5 0	54	40	8 2 0	187	180
-2	300	263	4	111	116	3 7 1	115	118	2	126	144	1	136	145	1	69	72
-3	288	265	-1	156	148	2	68	73	4	88	96	3	124	116	-1	146	131
-4	152	135	-2	202	182	3	139	121	-1	189	191	-1	245	228	-2	137	119
-5	77	39	-3	152	133	-1	179	183	-2	123	158	-2	90	93	-3	255	286
-6	174	158	-4	121	107	-3	85	71	-3	92	121	-3	123	121	-5	171	183
1 2 1	355	385	-6	199	209	3 8 1	65	70	-6	162	163	6 6 1	109	102	8 3 0	202	187
2	60	62	2 4 0	48	31	2	76	78	5 2 0	224	221	2	205	190	2	134	115
3	117	113	1	49	50	3	66	21	1	42	42	3	99	85	3	112	95
4	163	168	3	76	64	-2	120	118	3	120	135	4	115	121	-2	112	108
5	72	98	2 5 0	133	135	3 9 0	84	95	-1	123	120	-1	130	112	-3	61	63
-1	218	191	1	180	199	1	163	178	-2	65	69	-5	109	135	8 4 2	55	45
-2	199	175	2	272	263	2	114	109	-3	236	256	6 7 1	105	97	-1	90	90
-3	78	80	3	202	205	3	91	98	-5	96	92	2	67	55	-2	64	54
-4	102	80	4	202	207	-1	210	221	5 3 0	215	209	3	151	127	-3	54	25
1 3 0	320	330	5	77	95	-2	77	68	1	175	182	-1	99	97	8 5 0	211	203
1	208	214	-1	201	197	-3	132	151	-1	224	213	-2	75	74	1	59	70
2	208	200	-2	212	204	3 10 2	90	65	-2	394	366	-4	260	263	2	145	144
3	276	271	-4	152	152	-1	74	79	-4	262	260	6 8 0	97	96	3	119	101
4	53	6	2 6 1	153	165	3 11 1	102	103	-5	132	149	1	229	209	-1	93	79
5	74	89	-1	263	251	-1	75	72	-6	92	69	-1	205	186	-2	128	122
6	77	98	-2	76	85	-2	61	54	5 4 0	46	47	-2	182	178	-3	76	77
-2	189	163	-3	145	148	4 0 0	246	318	1	421	419	-3	90	77	-4	77	84
-3	54	29	-4	203	208	1	167	203	2	116	96	-4	103	102	-5	85	109
-5	132	131	-5	80	88	3	233	267	3	297	300	6 9 0	127	120	8 6 0	186	176
1 4 0	466	500	2 7 0	226	244	5	254	268	4	67	75	-2	93	60	3	58	21
5	219	235	1	75	91	-1	56	94	-1	120	113	-3	176	169	-2	88	85
-1	66	67	-1	144	139	-2	223	276	-3	162	139	6 10 -1	57	56	-3	239	247
-2	537	516	-2	245	233	-3	229	265	-4	224	208	-2	59	52	-4	93	102
-3	249	226	-4	194	186	-4	440	421	-5	135	139	7 1 0	123	124	8 7 1	94	89
-4	351	336	2 8 0	103	133	-5	165	149	-6	161	180	1	81	80	-1	157	135
-5	250	260	1	99	104	-6	94	68	5 5 0	88	88	2	71	84	-2	109	101
-6	121	125	2	214	205	4 1 0	388	405	1	146	161	3	145	162	-3	89	79
0 1 5	156	165	3	185	175	1	188	202	2	58	69	4	144	141	-4	103	117
1	161	174	4	66	63	2	102	105	-1	145	144	-3	179	197	-1	84	80
2	168	172	-2	98	76	3	240	268	-2	321	298	-5	172	211	8 9 -1	120	112
3	213	223	-4	160	163	-2	227	242	-3</								

Table 4. *Interatomic distances in lorandite*
(standard deviations in parentheses)

As(1)—S(1)	2.08(1) Å	Tl(1)—S(1)	3.31(3) Å	Tl(2)—S(1)	2.97(3) Å
As(1)—S(3)	2.29(3)	Tl(1)—S(1)*	3.07(3)	Tl(2)—S(2)	3.014(5)
As(1)—S(4')*	2.32(3)	Tl(1)—S(2')	2.96(2)	Tl(2)—S(3')	3.93(3)
As(2)—S(2)	2.20(2)	Tl(1)—S(2''')	3.19(2)	Tl(2)—S(4)	3.19(2)
As(2)—S(3)	2.30(3)	Tl(1)—S(3)	3.36(1)	Tl(2)—S(4)*	3.23(2)
As(2)—S(4)	2.32(1)	Tl(1)—S(3''')	3.69(2)	Tl(2)—S(3''')	3.89(1)
		Tl(1)—S(4)	3.48(2)	Tl(2)—S(4'')	3.63(1)
		Tl(1)—Tl(2)*	4.032(6)	Tl(2)—Tl(2'')	3.541(6)
S(1)—S(3)	3.35(2)				
S(1)—S(4')*	3.38(3)				
S(2)—S(3)	3.52(3)				
S(2)—S(4)	3.47(2)				
S(3)—S(4')*	3.42(3)				
S(3)—S(4)	3.31(3)				

Table 5. *Bond angles in lorandite*
(standard deviations in parentheses)

S(1)—As(1)—S(3')	100.2(1.1)°	As(1)—S(1)—Tl(1)	101.1(1.0)°
S(1)—As(1)—S(4')*	100.5(1.2)°	As(1)—S(1)—Tl(1)*	113.2(1.2)
S(3)—As(1)—S(4')*	95.9(1.0)	As(1)—S(1)—Tl(2)	103.2(1.2)
S(2)—As(2)—S(3)	102.9(1.1)	Tl(1)—S(1)—Tl(1)*	145.6(0.9)
S(2)—As(2)—S(4)	100.5(0.9)	Tl(1)—S(1)—Tl(2)	90.6(0.8)
S(3)—As(2)—S(4)	91.5(0.9)	Tl(1)*—S(1)—Tl(2)	83.7(0.8)
		As(2)—S(2)—Tl(1')	109.9(0.9)
S(1)—Tl(1)—S(1)*	145.6(0.9)	As(2)—S(2)—Tl(1''')*	94.7(0.9)
S(1)—Tl(1)—S(2')*	85.9(0.7)	As(2)—S(2)—Tl(2)	98.1(0.8)
S(1)—Tl(1)—S(2''')	131.1(0.7)	Tl(1')—S(2)—Tl(1''')*	100.4(0.6)
S(1)—Tl(1)—S(3)	60.3(0.6)	Tl(1')—S(2)—Tl(2)	133.9(0.8)
S(1)*—Tl(1)—S(2')*	79.6(0.8)	Tl(1''')*—S(2)—Tl(2)	113.2(0.8)
S(1)*—Tl(1)—S(2''')	76.7(0.7)	As(1)—S(3)—As(2)	101.1(1.1)
S(1)*—Tl(1)—S(3)	85.6(0.7)	As(1)—S(3)—Tl(1)	95.2(0.8)
S(2')*—Tl(1)—S(2''')	79.7(0.6)	As(1)—S(3)—Tl(2')*	98.4(0.8)
S(2')*—Tl(1)—S(3)	73.9(0.6)	As(2)—S(3)—Tl(1)	107.1(0.9)
S(2''')—Tl(1)—S(3)	150.4(0.6)	As(2)—S(3)—Tl(2')*	148.6(1.0)
S(1)—Tl(2)—S(2)	83.3(0.7)	Tl(1)—S(3)—Tl(2')*	95.2(0.6)
S(1)—Tl(2)—S(3')	147.1(0.7)	As(1')—S(4)—As(2)	102.1(1.0)
S(1)—Tl(2)—S(4)	88.2(0.7)	As(1')—S(4)—Tl(2)	87.3(0.8)
S(1)—Tl(2)—S(4)*	94.8(0.7)	As(1')—S(4)—Tl(2)*	102.3(0.9)
S(2)—Tl(2)—S(3')	72.8(0.6)	As(2)—S(4)—Tl(2)	122.5(0.9)
S(2)—Tl(2)—S(4)	67.5(0.6)	As(2)—S(4)—Tl(2)*	89.9(0.8)
S(2)—Tl(2)—S(4)*	77.0(0.6)	Tl(2)—S(4)—Tl(2)*	143.8(0.8)
S(3')—Tl(2)—S(4)	62.2(0.6)		
S(3')—Tl(2)—S(4)*	101.3(0.6)		
S(4)—Tl(2)—S(4)	143.8(0.8)		

and 2.20 Å) than the average for bonds of this type (2.26 Å) for other sulfosalts. The bond angles within the chains are within the ranges for bridged AsS_3 pyramids in sulfosalts, although the $\text{S}(3)\text{—As}(1)\text{—S}(4)$ and $\text{S}(3)\text{—As}(2)\text{—S}(4)$ bond angles are significantly smaller (95.9° and 91.5°) than the remainder, which fall in the range 100° to 103° .

In the present representation of the structure, each S atom is in tetrahedral coordination (Fig. 2); the bridge S atoms are coordinated to two As and two Tl whereas the non-bridge S atoms are coordinated

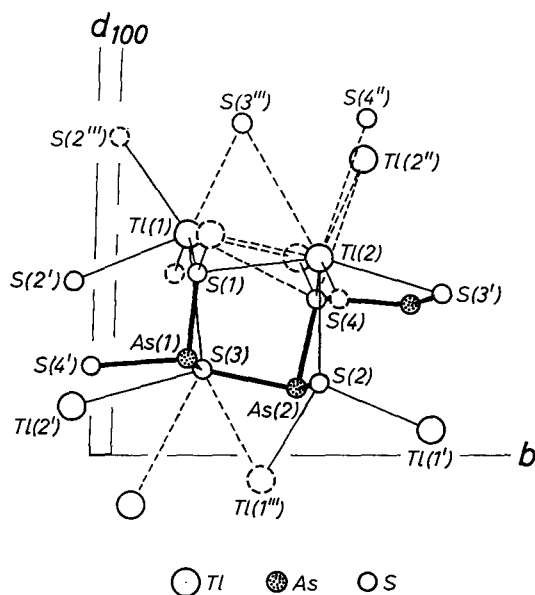


Fig. 2. Tl and S environments in lorandite; the structure is projected parallel to c axis and rotated 5° about $[100]$, dashed lines: interatomic distances greater than 3.40 Å, broken circles: atoms in unit cells above and below that represented

to one As and three Tl. Each tetrahedron is slightly distorted, but most of the bond angles do not depart too greatly from the ideal tetrahedral value.

Both Tl atoms are coordinated on the sides of the AsS_3 pyramid chains, adjacent to recesses formed in the chains. Each Tl position is more closely related to one chain than to neighboring chains. Although the S coordination polyhedra about the Tl atoms do appear irregular, closer inspection indicates many similarities in both positions. If an arbitrary limit of 3.40 Å is placed on the Tl—S distances,

each Tl atom is in fivefold coordination with S forming a flattened square pyramid. The bond distances and angles indicate considerable distortion from this ideal arrangement (Table 5). The Tl atoms are located beneath the base of each pyramid allowing for possible interactions with other Tl atoms and with more distant S and As atoms (Fig. 2). The closest Tl—S distances are, for both Tl(1) and Tl(2), to the non-bridge S atoms [S(1) and S(2)] and, these, presumably, correspond to the twofold coordination proposed by KNOWLES. However, although these bond distances may represent the strongest bonding interactions, the Tl—S bond distances do show a gradational increase between 2.96 Å and 3.89 Å making definition of the nearest-neighbor coordination polyhedra quite arbitrary.

The environments of the Tl atoms in lorandite are somewhat similar to the probable environment of Tl in the isomorphic sulfosalts, hatchite (MARUMO and NOWACKI, 1967) and wallisite (TAKÉUCHI and OHMASA, 1968), in which the Tl, Pb(2) positions are coordinated to two S (with interatomic distances of 2.99 Å and 3.14 Å) and more distant S and As. In hatchite the Tl, Pb(2) positions approach each other as close as 3.78 Å. Short Tl—Tl distances have been reported also from the sulfides of thallium. Tl₂S has a distorted Cd(OH)₂ (C6 type) structure, in which each Tl is coordinated to three S, with Tl—S distances ranging from 2.61 Å to 3.15 Å, and to twelve Tl with Tl—Tl distances from 3.50 Å to 4.63 Å (KETELAAR and GORTER, 1939). In TlS, Tl apparently exists in both the Tl⁺ and Tl³⁺ states (HAHN and KLINGLER, 1949). The Tl³⁺ is in tetrahedral coordination, with Tl—S distances of 2.60 Å, and the Tl⁺ is in eightfold coordination with Tl—S distances of 3.32 Å; Tl—Tl distances are 3.40 Å and 3.88 Å. In fact, in most of the investigated Tl-bearing sulfides and sulfosalts the Tl atoms have a tendency to interact with each other; in lorandite the closest Tl—Tl distances are 3.54 Å [Tl(2)—Tl(2)] and 4.03 Å [Tl(1)—Tl(2)].

The chains of AsS₃ pyramids are connected together in the lorandite structure by the Tl atoms. However the Tl atoms are associated more closely with one chain than with neighboring chains: of the ten Tl—S distances less than 3.40 Å in each formula unit, seven are within a single chain, only two connect directly chains lying within the same (100) plane and one connects chains lying within the same ($\bar{2}01$) plane: chains lying within the same (001) plane are connected directly by a strong Tl—Tl interaction. Clearly, the most cohesive bonding forces are within the chains (primarily As—S and Tl—S ones),

