

The crystal structures of schallerite and friedelite

by

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ABSTRACT

The crystal structures of schallerite and friedelite have been refined. (1) Schallerite. Space group: $P6_3$. $a = 13.420(4)$, $c = 14.320(5)$ Å. Structural formula: $Mn_{16}Si_{12}O_{30}(OH)_{17}(As_3O_6)$. $Z = 2$. Schallerite is a two-layered structure. The upper layer is formed by the symmetrical operation of 6_3 of the lower layer different from that of pyrosmalite layer. 'As molecules' of form of (As_3O_6) are present in the voids of twelve-membered rings. (2) Friedelite. Space group: $C2/m$. $a = 23.28(1)$, $b = 13.44(1)$, $c = 7.428(4)$ Å, $\beta = 104.98(1)^\circ$. Structural formula: $Mn_{16}Si_{12}O_{30}(OH, Cl)_{20}$. $Z = 2$. Arrangement of a tetrahedral sheet of friedelite is similar to that of pyrosmalite. However, the layer stacking is different.

Introduction

Pyrosmalite, schallerite and friedelite are a homologous series of layered manganese silicates. Once, it was considered that pyrosmalite was a one-layered trigonal, schallerite a two-layered hexagonal and friedelite a three-layered rhombohedral (Frondele and Bauer, 1953). The crystal structure of manganpyrosmalite has been determined by Takeuchi *et al.* (1969), partially refined by Kashaev (1969) using pyrosmalite, and more completely refined by Kato and Takeuchi (1983) with crystals of manganpyrosmalite and iron-rich manganpyrosmalite. Takeuchi *et al.* (1969) also discussed possible polytypic relations between manganpyrosmalite and schallerite-friedelite. Recently Dunn *et al.* (1981) compiled additional chemical data on schallerite and suggested that arsenic is present in stoichiometric quantities, indicating a unique crystallographic arsenic site. G. Donnay *et al.* (1980) proposed a new mineral, mcGillite, once, its cell dimensions were reported $a = 13.498$, $c = 85.657$ Å and space group $R\bar{3}m$ or $R3m$. Kato and Takeuchi (1980) found that the crystal structure of mcGillite could be definitely determined by the limitations imposed by layer stacking in this structure (Space group, $R3m$ was selected). However, Iijima (1982a, 1982b) showed that the structure of mcGillite is really monoclinic through his observation using HRTEM. Ozawa *et al.* (1983) have examined mcGillite and friedelite by X-ray and electron diffraction methods

and found both minerals have the same one layered monoclinic cell and proposed a structural model. Dunn and Peacor (1984) have proposed a new mineral, nelenite because they believe that the arsenic content is essential and non-variable though once this mineral was known as "ferroschallerite". Members of pyrosmalite family are listed in Table 1.

Table 1. Pyrosmalite family.

Name	Formula	Cell dimensions	Space group
Pyrosmalite	$(\text{Fe, Mn})_{16}\text{Si}_{12}\text{O}_{30}(\text{OH, Cl})_{20}$	$a = 13.36, c = 7.16\text{\AA}$	$P\bar{3}m1$
Manganpyrosmalite	$(\text{Mn, Fe})_{16}\text{Si}_{12}\text{O}_{30}(\text{OH, Cl})_{20}$	$a = 13.422, c = 7.165\text{\AA}$ (Kato and Takeuchi, 1983)	$P\bar{3}m1$
Schallerite	$\text{Mn}_{16}\text{Si}_{12}\text{O}_{30}(\text{OH})_{17}(\text{As}_3\text{O}_6)$	$a = 13.420, c = 14.320\text{\AA}$ (This study)	$P6_3$
Friedelite	$\text{Mn}_{16}\text{Si}_{12}\text{O}_{30}(\text{OH, Cl})_{20}$	$a = 23.28, b = 13.44,$ $c = 7.428\text{\AA}, \beta = 104.98^\circ$ (This study)	$C2/m$
McGillite	$\text{Mn}_{16}\text{Si}_{12}\text{O}_{30}(\text{OH})_{16}\text{Cl}_4$ (Donnay <i>et al.</i> , 1980)	$a = 23.312, b = 13.459,$ $c = 7.423\text{\AA}, \beta = 105.17$ (Ozawa <i>et al.</i> , 1983)	$C2/m$
Nelenite	$(\text{Mn, Fe})_{16}\text{Si}_{12}\text{O}_{30}(\text{OH})_{14}$ $[\text{As}^{3+}_3\text{O}_6(\text{OH})_3]^*$ (Dunn <i>et al.</i> , 1984)	$a = 23.240, b = 13.418,$ $c = 7.382\text{\AA}, \beta = 105.21^\circ$	$C2/m$

*We have some doubt about this structural formula.

We have had a chance to refine the structures of schallerite and friedelite. Detailed results will be given in this paper.

Experimental

The schallerite crystals were supplied by the courtesy of Dr. Pete J. Dunn, Smithsonian Institution. The crystals were from Franklin, New Jersey. The specimen number is NMNH #C2873. Its chemical composition analyzed by Dunn *et al.* is given in Table 2.

Table 2. Crystal data of schallerite.

Structural formula	$(\text{Mn}_{13.42}\text{Mg}_{1.62}\text{Fe}^{3+}_{0.50}\text{Zn}_{0.44})_{16}\text{Si}_{12}\text{O}_{30}(\text{OH})_{17}(\text{As}_3\text{O}_6)$
Cell dimensions	$a = 13.420(4)\text{\AA}$ $c = 14.320(5)$
Space group	$P6_3$
Z	2

Structural formula is based on data by Dunn *et al.* (1981).

The friedelite crystals from Aderville, France, were provided by Prof. C. Guillemin. The chemical composition of this material is given in the Handbuch der Mineralogie von Carl Hintze (1938) as shown in Table 3. In this book, the results of two chemical analyses were described. Presence of 3.40% Cl was confirmed in one analysis. However, the derived formula from these analyses was not so reliable, so an ideal formula was adopted in the refinement of the structure.

Table 3. Crystal data of friedelite.

Chemical Formula	(1) $(\text{Mn}_{14.72}\text{Mg}_{1.44})_{16.16}\text{Si}_{11.84}\text{O}_{30}(\text{OH})_{17.20}$
	(2) $(\text{Mn}_{15.22}\text{Mg}_{0.62}\text{Ca}_{0.14})_{16.02}\text{Si}_{12}\text{O}_{28}(\text{OH}_{22.32}\text{Cl}_{2.02})$
Ideal formula	$\text{Mn}_{16}\text{Si}_{12}\text{O}_{30}(\text{OH}, \text{Cl})_{20}$
Cell dimensions	$a = 23.28(1)\text{\AA}$ $b = 13.44(1)$ $c = 7.428(4)$ $\beta = 104.98(1)^\circ$
Space group	$C2/m$
Z	2

Two chemical analyses are given in Handbuch der Mineralogie von Carl Hintze (1938). (1) Analyzed by Bertrand (1876). (2) Analyzed by Gorgeu bei Bertrand.

Crystals of schallerite ($0.023 \times 0.014 \times 0.008\text{cm}$), and friedelite ($0.023 \times 0.014 \times 0.008\text{cm}$) were selected for this study. The cell dimensions of both crystals were determined using 25 reflections measured on a Philips PW-1100 single crystal diffractometer, respectively. The crystal data of schallerite and friedelite, are given in Tables 2 and 3, respectively. Intensity data were collected on the same computer-controlled diffractometer with graphite monochromated $\text{Mok}\alpha$ radiation ($\lambda = 0.71069\text{\AA}$). The $\theta - 2\theta$ scan mode was applied. The search range was $1^\circ < \theta < 30^\circ$. The reflections with $F > 3\delta$ (F) were considered to be significant. The numbers of observed reflections were 1481 for schallerite and 1371 for friedelite, respectively. The absorption correction was made using a program ACA-CA based on a procedure provided by Wuensch and Prewitt (1965).

In the refinement of the schallerite structure, 3 space groups, $P6_3$, $P6_3/m$, and $P6_322$ were selected because these space groups satisfy the extinction rule of $00l; l = 2n$. A model which satisfies the symmetrical condition of $P6_3$ was selected. The refinement was carried out using a full-matrix least-squares program, FLS-4, written by Sakurai *et al.* (1974). A difference Fourier map was made and the As atoms and extra oxygen atoms were located. In the course of the refinement, the values of isotropic temperature factors of many atoms became negative, so these were fixed at 0.30. The final R was 0.130. The final atomic para-

meters are given in Table 4. The selected bond distances are listed in Table 5.

Table 4. Atomic parameters of schallerite.

Atom	x	y	z	B(Å ²)
Mn(1)	.3333	.6667	.1039(37)	0.30*
Mn(2)	.0809(8)	-.0809(8)	.1130(37)	0.30*
Mn(3)	-.1756(8)	.1653(10)	.0999(38)	0.36
Mn(4)	-.4138(8)	.4169(8)	.0860(37)	0.30*
Mn(5)	.0907(7)	.4240(8)	.0972(38)	0.30*
Mn(6)	.3346(9)	.4133(8)	.0909(38)	0.55
Si(1)	.2418(13)	-.0044(14)	-.0988(39)	0.30*
Si(2)	.2349(11)	.2265(12)	-.0940(39)	0.30*
Si(3)	.4460(21)	.0974(19)	.2873(40)	2.04
Si(4)	.4250(12)	.3423(14)	.2839(39)	0.87
As(1)	.4993(17)	-.5166(17)	.4057(41)	1.86
As(2)	.2503(8)	-.2428(8)	.3966(37)	0.86
O(1)	.2511(31)	-.0060(33)	.0133(50)	0.30*
O(2)	.2520(30)	.2586(31)	.0181(45)	0.30*
O(3)	.4190(30)	.0826(31)	.1779(48)	0.30*
O(4)	.4178(30)	.3322(36)	.1705(46)	0.30*
O(5)	.3422(44)	-.0012(44)	-.1452(52)	3.01
O(6)	.3412(48)	.3450(45)	-.1427(51)	2.37
O(7)	-.1136(31)	.1129(32)	-.1392(43)	1.95
O(8)	.1222(46)	-.1254(46)	-.1244(49)	3.92
O(9)	-.2185(32)	.2146(31)	.3122(44)	1.01
O(10)	.5452(45)	-.5561(48)	.3387(50)	3.29
O(11)	.4993(54)	.5928(54)	.3437(58)	0.30*
O(12)	.3625(54)	.4556(59)	.3169(56)	0.30*
O(13)	.3333	.6667	.2792(52)	0.30*
OH(1)(1/3=O)	.5002(59)	-.5068(57)	.0202(54)	3.32
OH(2)(2/3=O)	-.0621(42)	.0583(41)	.1516(45)	1.84
OH(3)	-.2419(39)	.2555(37)	.0201(42)	0.30*
OH(4)	.1593(32)	-.1664(32)	.1725(41)	0.30*
OH(5)	.4257(33)	-.4175(35)	.1853(43)	0.55
OH(6)	.6667	.3333	.1643(58)	0.30*
OH(7)	.2553(32)	-.2521(35)	.0289(41)	0.30*
OH(8)	.0	.0	.0	0.30*

*Fixed.

Table 5. Selected bond lengths (Å) of schallerite.

Si(1) - O(1)* 1.61	Si(2) - O(2)* 1.65	Si(3) - O(3)* 1.60	Si(4) - O(4)* 1.63
- O(5) 1.48	- O(6) 1.67	- O(6) 1.65	- O(5) 1.49
- O(7) 1.79	- O(7) 1.60	- O(9) 1.75	- O(9) 1.77
- O(8) 1.66	- O(8) 1.69	- O(10) 1.63	- O(10) 1.70
Mean 1.64	Mean 1.65	Mean 1.66	Mean 1.65
Mn(1) - OH(5) 2.36		Mn(4) - O(3) 2.32	
- OH(5)' 2.36		- O(4) 2.30	
- OH(5)'' 2.36		- OH(1) 2.11	
- OH(7) 2.14		- OH(3) 2.07	
- OH(7)' 2.14		OH(3)' 2.24	
- O(13) 2.51		- OH(6) 2.21	
Mean 2.31		Mean 2.21	
Mn(2) - O(1) 2.44		Mn(5) - O(1) 2.28	
- O(2) 2.41		- O(3) 2.32	
- OH(2) 1.76		- OH(1) 2.30	
- OH(2)' 1.80		- OH(4) 2.30	
- OH(4) 2.09		- OH(5) 2.16	
- OH(8) 2.48		- OH(7) 2.12	
Mean 2.16		Mean 2.25	
Mn(3) - O(1) 2.45		Mn(6) - O(2) 2.08	
- O(2) 2.32		- O(4) 2.22	
- O(3) 2.28		- OH(1) 2.18	
- O(4) 2.08		- OH(4) 2.28	
- OH(2) 2.67		- OH(5) 2.39	
- OH(3) 2.15		- OH(7) 2.24	
Mean 2.33		Mean 2.23	
As(1) - O(10) 1.38		As(2) - OH(3) 1.77	
- OH(1) 1.67		- O(11) 2.19	
- O(11) 1.72		- O(12) 2.22	
- O(12) 2.11			
Mean 1.72		Mean 2.06	

* Apical. The hydroxyls bonded to arsenic are oxygens.

In the refinement of the friedelite structure several models which fit for the symmetrical condition of the space group $C2/m$ were devised and a model which gave the lowest R was selected for the correct model. The refinement was carried out using a block-diagonal least-squares program, BDLS-60 in the UNICS II system written by Sakurai *et al.* (1974). Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (Vol.4) (The same applied to schallerite). It was judged that the Cl atom concentrates in the OH(3) position. The final R was 0.203. The final atomic parameters are listed in Table 6 and the bond distances and angles are given in Table 7.

Table 6. Atomic parameters of friedelite.

Atom	x	y	z	B(Å ²)
Mn(1)	.0	.1236(9)	.0	0.47
Mn(2)	.0	.3711(10)	.0	1.06
Mn(3)	.1276(6)	.0	.0194(15)	0.70
Mn(4)	.1268(4)	.2486(6)	.0100(11)	0.77
Mn(5)	.1257(6)	.5	-.0132(16)	0.99
Mn(6)	.2521(4)	.1246(6)	.0181(10)	0.63
Si(1)	.2074(10)	.3866(16)	.3728(26)	2.14
Si(2)	.3217(10)	.2674(14)	.3769(25)	1.82
Si(3)	.4434(10)	.3825(16)	.3691(25)	2.12
O(1)	.0	.1657(114)	.5	8.04
O(2)	.0625(89)	.0	.5700(268)	17.14
O(3)	.1147(51)	.1647(91)	.5860(146)	12.37
O(4)	.1656(53)	.3287(93)	.4950(145)	10.31
O(5)	.2250(38)	.1670(70)	.5530(112)	7.26
O(6)	.2866(114)	.0	.5800(31)	21.10
O(7)	.1787(17)	.3731(26)	.1553(42)	0.24
O(8)	.3064(18)	.2504(32)	.1550(51)	0.89
O(9)	.4267(16)	.3783(26)	.1445(39)	0.11
OH(1)	.0570(28)	.0	.1757(74)	1.10
OH(2)	.0565(17)	.2477(28)	.1596(48)	0.59
OH(3)=Cl	.0603(18)	.5	.2207(47)	0.59
OH(4)	.1767(17)	.1260(28)	.1501(41)	0.21
OH(5)	.3036(27)	.0	.1580(71)	0.76
OH(6)	.3051(24)	.5	.1571(62)	0.37
OH(7)	.4272(17)	.1257(28)	.1446(39)	0.42

Table 7. Interatomic distances (Å) and angles (°) of friedelite.

				around Si
Si(1) - O(7)	1.59*	O(7) - O(4)	2.69	110.2
- O(4)	1.68	O(7) - O(5)	2.74	113.2
- O(5)	1.69	O(7) - O(6)	2.57	109.2
- O(6)	1.56	O(4) - O(5)	2.66	104.3
		O(4) - O(6)	2.68	111.1
Mean	1.63	O(5) - O(6)	2.64	108.7
		Mean	2.66	109.5
Si(2) - O(8)	1.61*	O(8) - O(3)	2.56	101.2
- O(3)	1.70	O(8) - O(4)	2.73	117.1
- O(4)	1.59	O(8) - O(5)	2.70	115.2
- O(5)	1.59	O(3) - O(4)	2.67	108.7
		O(3) - O(5)	2.64	106.9
Mean	1.62	O(4) - O(5)	2.55	107.0
		Mean	2.64	109.4
Si(3) - O(9)*	1.61	O(9) - O(1)	2.81	124.6
- O(1)	1.56	O(9) - O(2)	2.64	107.5
- O(2)	1.66	O(9) - O(3)	2.50	102.1
- O(3)	1.61	O(1) - O(2)	2.64	110.0
		O(1) - O(3)	2.58	109.1
Mean	1.61	O(2) - O(3)	2.51	100.7
		Mean	2.61	109.0
Mn(1) - O(9) (x2)	2.24	Mn(4) - O(7)	2.18	
- OH(1)(x2)	2.31	- O(8)	2.21	
- OH(2)(x2)	2.26	- O(9)	2.24	
		- OH(2)	2.20	
Mean	2.27	- OH(4)	2.13	
		- OH(7)	2.24	
		Mean	2.20	
Mn(2) - OH(7)(x2)	2.23	Mn(5) - O(7) (x2)	2.28	
- OH(2)(x2)	2.25	- OH(3)=Cl	2.59	
- OH(3)(x2)	2.54	- OH(5)	2.19	
= Cl		- OH(7)(x2)	2.17	
Mean	2.34	Mean	2.28	
Mn(3) - O(9) (x2)	2.23	Mn(6) - O(7)	2.31	
- OH(1)	2.24	- O(8)	2.20	
- OH(4)(x2)	2.13	- O(8)'	2.33	
- OH(8)	2.29	- OH(4)	2.22	
		- OH(5)	2.16	
Mean	2.21	- OH(6)	2.32	
		Mean	2.26	

* Apical

Discussion

The structure of schallerite is two-layered as predicted by Frondel and Bauer (1953). The relationship between the upper layer and the lower layer is illustrated in Fig. 1 (The upper layer is formed by the symmetrical operation of 6_3 of the lower layer).

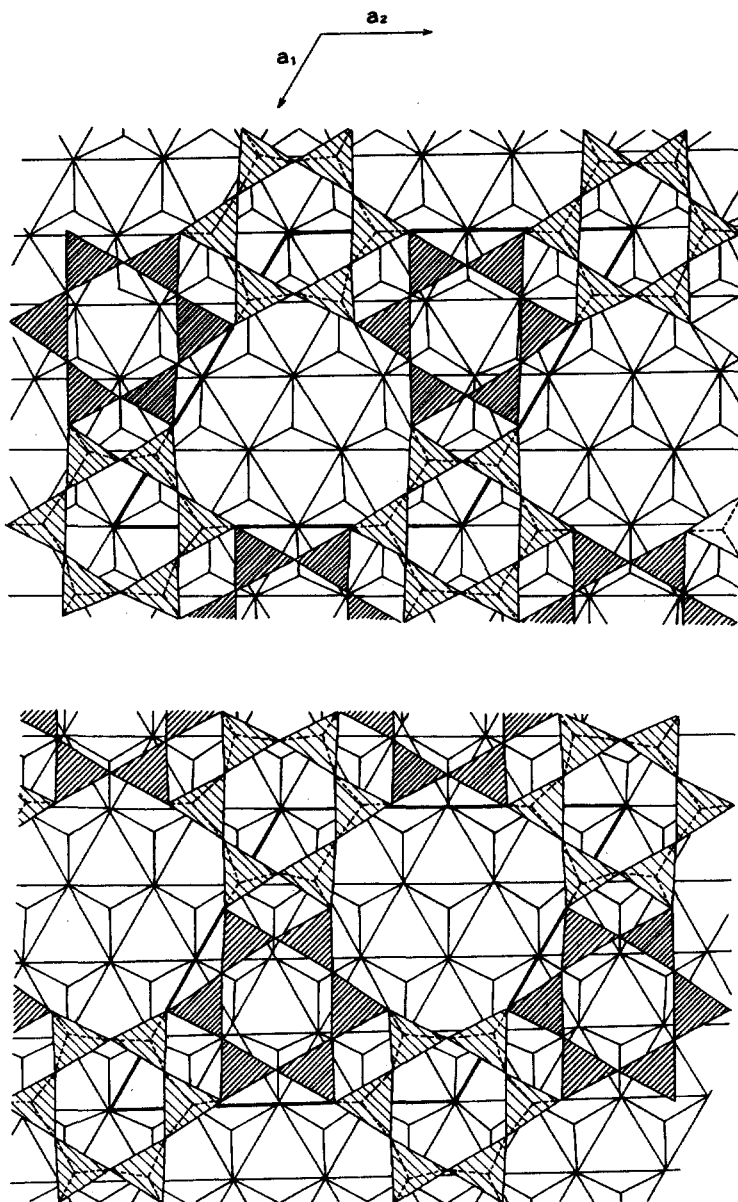


Fig. 1. The ideal structure of schallerite viewed down c . The above is the upper layer and the below is the lower layer. 'As molecules' are omitted.

Essentially, each layer is the same as that of the pyrosmalite or manganpyrosmalite layer. However, the origin of both structures is different. The six-membered rings are linked together to form twelve-membered rings and four-membered rings complete the continuity of the sheet. The question was how to find the As sites. Naturally, the As atoms were assumed to be present in voids of twelve-membered rings. We found two (or really three) peaks in a void using difference Fourier synthesis, and judged that these peaks were As sites. Also three additional peaks were found and these were judged to be the extra oxygens bonded only to arsenic atoms. As (1) has an occupancy of 2/6 and is four coordinated and bonded to OH(1) in an octahedral sheet, and two extra oxygens, O(11) and O(12), as well as O(10), a basal oxygen in a tetrahedral sheet. As(2) has an occupancy of 4/6 and is three coordinated and bonded to OH(3) in an octahedral sheet, and two extra oxygens, O(12) and O(13)(Fig. 2). It was judged that these hydroxyls bonded to As are replaced by

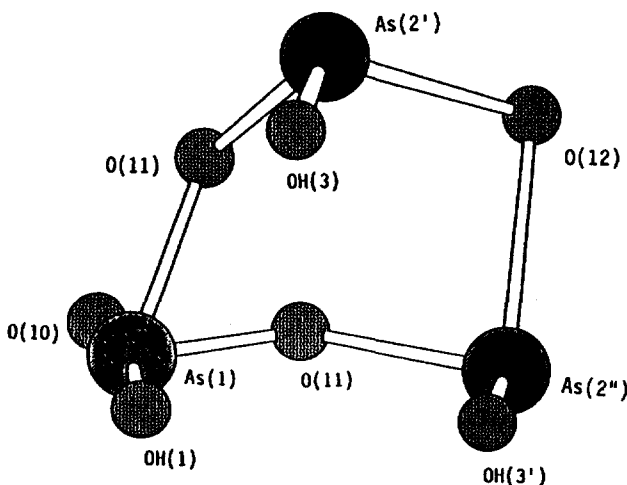
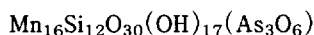


Fig. 2. A 'As molecule' in a void of the schallerite structure. Projected along the *c* axis. The hydroxyls bonded to arsenic are really oxygens.

oxygen atoms. Usually, trivalent As is three coordinated and bonded to three anions forming a trigonal pyramid with As as the principal vertex. It is possible to maintain a charge balance in this 'As molecule' if As (1) is not bonded to O(10), a basal oxygen in the tetrahedral sheet. However, the distance As(1) - O(10) is 1.38Å and the shortest among four bond lengths (Table 5), so As(1) was judged as four coordinated in spite of the fact that this As is trivalent. Thus, the 'As molecule' is expressed by the formula (As₃O₆). Note that a basal oxygen is also bonded to an As, As(1). Thus, the derived structural formula is:



and this formula agrees well with the *chemical* formula described by Dunn *et al.* (1981). The bond lengths listed in Table 5 are not so reliable because of low precision.

On the other hand, Takahata, Takeuchi and Ozawa (personal communication) concluded that schallerite was two-layer orthorhombic through studying it using HRTEM. At

the first stage of our X-ray study, we collected intensity data on schallerite adopting orthorhombic cell ($a = 22.50$, $b = 13.44$, and $c = 13.33\text{\AA}$, Space group, $Cmcm$ (This space group was different from that selected by Takahata *et al.*)). However, the best fit model was found to be hexagonal, so we recollected intensity data adopting a hexagonal cell. This contradiction remains to be solved.

Eleven years ago, Dunn wrote us that Peacor found that all of the schallerite that he studied showed diffuse superlattice reflections and thus were unsuitable for crystal structure work, although we could not confirm such results. Takahata *et al.* (private communication) described that the crystals of schallerite are markedly twinned, twin domains being up to only few hundreds Angstrom thick. If Peacor's results are correct, this might be a key to solving the contradiction described above. If this were true, our hexagonal cell must be a sub cell, and the statistical distribution of 'As molecules' must be partly responsible for the generation of superlattice reflections.

The structural model of friedelite obtained by our X-ray study coincides with the model proposed by Ozawa *et al.* (1983) (Figs. 3 and 4). The six-membered rings are linked together to form twelve-membered rings and four-membered rings to complete the continuity of the sheet. This is the same as that of pyrosmalite, however, pyrosmalite is trigonal while friedelite is monoclinic, and the detailed discussion of its layer stacking is given by Ozawa *et al.* (1983). It is possible to form 'As molecules' in the voids of twelve-membered rings in the nelenite structure, so we believe, though we could not obtain the correct cell and so could not collect intensity data on a four-circle using the sample supplied by Dunn. Low precision and the large values of isotropic temperature factors of the basal oxygens seems due to a considerable stacking disorder in the structure of friedelite. It seems that the octahedral sheets are very rigid. However, the tetrahedral sheets seems somewhat 'liquidified' by the stacking disorder. It was found that Cl atoms are concentrated in the position of OH(3). Also, the bond lengths and angles listed in Table 7 are not so reliable. Dunn *et al.* (1981) examined friedelite crystals and found that all crystals gave rise to superstructure diffractions indicative of a superstructure like that of mcGillite. Their results suggest the twinning in mcGillite described by Ozawa *et al.* (1983) is also common in friedelite. Ozawa *et al.* (1983) also examined friedelite from Harstig, Sweden using the precession method and found that the supercell reflections (those define a superstructure of pyrochroite by attaching sheet of silicon-oxygen tetrahedra) were completely streaked out along c^* and weaker than the sharp reflections of mcGillite.

Thus, the three structures of manganpyrosmalite, schallerite and friedelite in an interesting homologous series of the minerals of pyrosmalite group have been refined in our study although the quality of crystals of schallerite and friedelite is unsuitable for precise structure analysis by X-ray method.

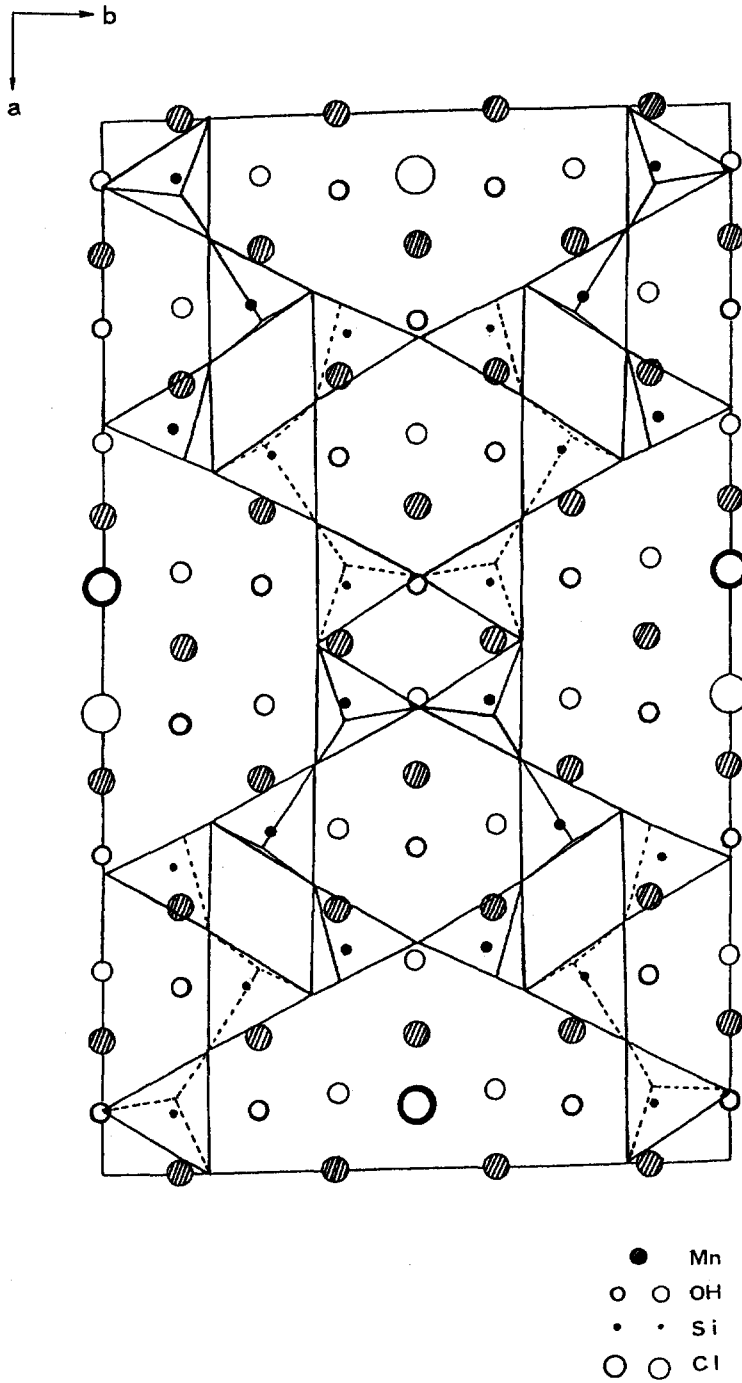


Fig. 3. The structure of friedelite viewed along the c^* axis.

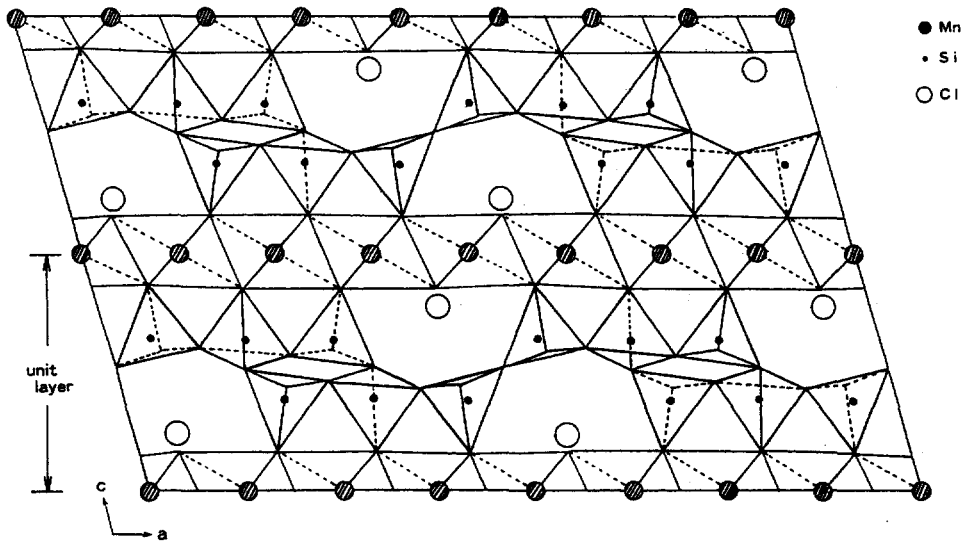


Fig. 4. The structure of friedelite viewed along the b axis.

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