The crystal chemistry of the hydrous copper silicates, shattuckite and planchéite

HOWARD T. EVANS, JR. AND MARY E. MROSE

U.S. Geological Survey, Reston, Virginia 22092

Abstract

The crystal structure of shattuckite, $Cu_5(SiO_3)_4(OH)_2$ has been refined in the orthorhombic space group $Pcab$ [$a = 9.885(1)$A, $b = 19.832(2)$A, $c = 5.3825(8)$A, $Z = 4$, $D(\text{X-ray}) = 4.128$ g/cm³] using 1980 reflections measured with $MoK\alpha$ radiation to $R = 0.056$. The structure consists of brucite-like $(CuO_2)_n$ layers with pyroxene-type $(SiO_3)_n$ chains joined to their surfaces. Adjacent complex sheets are linked by additional Cu atoms in square coordination, forming ladderlike ribbons along the chain axis $\parallel c$. The structure of planchéite, $Cu_8 (Si_4O_{11})_2(OH)_4 \cdot xH_2O$, has been solved in the orthorhombic space group $Pcnb$ [$a = 19.043(3)$A, $b = 20.129(5)$A, $c = 5.269(1)$A, $Z = 4$, $D(\text{calc}) = 3.815$ g/cm³] on the basis of 429 observed $hk0$, $hk1$, and $hk2$ reflections estimated from Weissenberg patterns, and the analogy of its structure to that of shattuckite. The structure is very similar to that of shattuckite, except that pyroxene-type chains are replaced by amphibole-type chains. There is evidence for the presence of free water in the structure, but $x < 0.43$ and is probably variable.

Introduction

The hydrated copper silicate shattuckite was first reported by Schaller (1915) and the closely related species planchéite by Lacroix (1908). Both minerals are fibrous in character, and are so similar in appearance that they have often been confused, and even said at times to be identical (Guillemin and Pierrot, 1961). Nevertheless, close attention to optical properties (Schaller, 1919), X-ray powder data (Newberg, 1964; Gastuche, 1967), and chemical analysis (Mrose and Vlisidis, 1966; Van Oosterwyck-Gastuche, 1968) has amply proven their validity as distinct species. In fact, the two species are usually distinguishable by their characteristic colors. With reference to the ISCC-NBS Color Name Charts (Kelly and Judd, 1955), the rosettes and prismatic crystals of shattuckite are deep blue (no. 179) to medium blue (no. 183), whereas the rosettes and feathery crystals of planchéite are light greenish blue (no. 172) to very light greenish blue (no. 171). Because of the close association of these minerals with each other as well as with chrysocolla, dioptase, *etc.*, and the difficulty of obtaining really pure bulk samples for analysis, the chemical constitutions of shattuckite and planchéite have remained uncertain until recently. The exact formula of each was finally established by crystal structure methods (Evans and Mrose, 1966; LeBihan,

1966, 1967). A comprehensive mineralogical, physical, and chemical study of shattuckite and planchéite, as well as of other copper silicate minerals, has been carried out by Van Oosterwyck-Gastuche (1974).

Our structure study has been based on crystals of shattuckite from Ajo, Arizona, and planchéite from Rioja, Argentina. Both structures were solved initially from Patterson syntheses of the *c*-axis projection using Weissenberg film data. Sufficient upper level data were measured to establish the three-dimensional structure for shattuckite for our first publication (Evans and Mrose, 1966). Subsequently, fine single crystals of shattuckite were found, which have given us the opportunity to make a full-scale structure analysis using counter data, providing bond-length information accurate to ± 0.005 A. Unfortunately, for planchéite the poor quality of the asbestos-like material has allowed only a semi-quantitative structure refinement, especially with respect to the *z* parameters. Our crystallographic and crystal structure studies are presented in full in this paper.

All except some earlier computations were carried out on an IBM 370/155 computer, using the program system XRAY72 written by J. R. Stewart and his colleagues at the University of Maryland.

Crystallography of shattuckite and planchéite

The orthorhombic unit cell of shattuckite was first established by Newberg (1964). Using the Buerger precession method we found an orthorhombic unit cell for planchéite that was very similar to that of shattuckite, but with the a axis doubled and a change in the space group. (The space groups of both crystals are uniquely determined by the observed extinction effects.) The significance of this close relationship subsequently became entirely clear from the determined crystal structures. Guinier-Hägg powder patterns of carefully purified samples of both, using $CrK\alpha_1$ radiation, yielded 49 lines for shattuckite and 53 lines for planchéite, from which refined unit-cell parameters have been obtained by least-squares analysis (Appleman and Evans, 1973). The unit-cell data are given in Table 1, and the powder data in Table 2.

Planchéite and shattuckite generally occur in silky, fibrous needles, but the shattuckite from Ajo sometimes has well-developed prismatic crystal forms. W. T. Schaller (unpublished data) measured several crystals and found the following forms (symbols assigned by us):

$b\{010\}$ ⎱
$a\{100\}$ ⎬ dominant
$m\{110\}$ ⎰

$w\{160\}$	$g\{210\}$	$q\{121\}$	$t\{161\}$
$u\{140\}$	$e\{201\}$	$r\{141\}$	$\phi\{321\}$
$n\{120\}$	$p\{111\}$	$s\{151\}$	

We measured the crystal that was finally used for counter measurements and found the dominant forms b, a, and ϕ, and the subordinate forms u, n, e, q, and t. The tips of the prismatic crystals are always pitted and irregular. A drawing illustrating the habit of our crystal, which may be considered as typical, is shown in Figure 1.

The optical properties, summarized in Table 1, serve readily to distinguish the two species. Agreement is general among the various reported refractive indices of shattuckite. Those given in Table 1 are taken from Larsen and Berman (1934). Wider variation in refractive indices has been reported for planchéite (Larsen and Berman, 1934; Van Oosterwyck-Gastuche, 1974), possibly because of variation in water content. The values given in Table 1 were determined by us on crystals from Rioja, Argentina. Contrary to many published observations, we find no appreciable pleochroism on clear single crystals of either shattuckite or planchéite. Many reported observations that were made on aggregates or very thin fibers or flakes may have led to misinterpreted results.

Structure analysis

Shattuckite

The structure of shattuckite was first solved from a set of intensities visually estimated from Weissenberg patterns made with MoKα radiation of the $hk0$ and $0kl$ nets. The structure was solved by interpretation of the $hk0$ Patterson map, using vector shift methods to locate the Cu atoms. When it was recognized that a very large interaction at $x, y = 0.25, 0.22$ represented two superposed Cu atoms, a feasible model was found to initiate a successful structure factor–electron density search for all the remaining non-hydrogen atoms. Least-squares analysis of 131 $hk0$ data on the basis of 22 x, y structure parameters and an overall temperature parameter converged to a structure for which the conventional reliability factor $R = 0.122$. The 11 z parameters and an overall thermal parameter were then refined, using 79 $0kl$ data, to $R = 0.093$. These results led to our earlier report (Evans and Mrose, 1966).

Subsequently, much better crystals were found and the automatic Picker single-crystal diffractometer became available to us. A new data set was measured using counter techniques, and the structure analysis was repeated. Within the limit of $2\theta = 75°$, MoKα radiation yielded 3218 independent reflections, of which 1980 had intensities larger than 3σ on the basis of counting statistics and were used for the structure refinement. The crystal was a prism of approximate

Table 1. Crystallographic data for shattuckite and planchéite

Property	Shattuckite	Plancheite
Composition	$Cu_5(SiO_3)_4(OH)_2$	$Cu_8(Si_4O_{11})_2(OH)_4 \cdot xH_2O$
Space group	Pcab (no. 61)	Pcnb (no. 60)
a, Å	9.885(1)	19.043(3)
b, Å	19.832(2)	20.129(5)
c, Å	5.3825(8)	5.269(1)
V, Å^3	1055.3(2)	2019.5(5)
Z	4	4
$a:b:c$	0.4984:1:0.2714	0.9460:1:0.2618
D(x-ray), g/cm^3	4.128	3.815 (x=0.4)
D(meas.), g/cm^3	4.11	3.65–3.80
n_α	1.753 ($\parallel$b)	1.697 ($\parallel$c)
n_β	1.782 ($\parallel$a)	1.718 ($\parallel$b)
n_γ	1.815 ($\parallel$c)	1.741 ($\parallel$a)
2V(character)	88° (pos.)	$88\frac{1}{2}°$ (pos.)
Color	intense blue	greenish blue
Absorption	variation slight	Z>X>Y

Table 2. X-ray powder data for shattuckite and planchéite

hkl	d(calc)	d(obs)	I	hkl	d(calc)	d(obs)	I	hkl	d(calc)	d(obs)	I
				A. Shattuckite (Ajo, Arizona)							
020	9.915	9.960	20	112	2.5122	2.5122	4	072	1.9512	1.9524	5
040	4.957	4.965	60	032	2.4928	2.4923	15	520	1.9389	1.9390	6
140	4.431	4.432	100	400	2.4715	2.4702	35	262	1.9226	1.9217	6
121	4.267	4.272	6	420	2.3981	2.3972	18	291	1.8850	1.8847	5
201	3.641	3.643	40	042	2.3654	2.3659	70	461	1.8577	1.8570	5
240	3.500	3.500	70	360	2.3335	2.3332	6	352	1.8452	1.8447	3
221	3.418	3.420	30	142	2.3005	2.3008	35	540	1.8365	1.8372	3
060	3.305	3.307	50	351	2.2931	2.2945	18	402	1.8204	1.8205	13
231	3.189	3.191	6	401	2.2461	2.2473	6	182	1.7931	1.7917	25
320	3.127	3.128	9	271	2.2358	2.2345	8	092	1.7049	1.7063	4
241	2.9345	2.9342	35	440	2.2118	2.2113	6	560	1.6967	1.6970	4
311	2.7827	2.7831	50	421	2.1906	2.1917	6	203	1.6867	1.6862	25
340	2.7443	2.7444	40	152	2.1726	2.1731	4	372	1.6790	1.6788	3
321	2.7040	2.7028	18	431	2.1266	2.1263	6	223	1.6628	1.6621	5
002	2.6915	2.6918	25	062	2.0870	2.0880	4	620	1.6254	1.6244	25
251	2.6820	2.6803	15	162	2.0420	2.0410	4				
331	2.5864	2.5861	35	371	1.9952	1.9950	9				
				B. Plancheite (Rioja, Argentina)							
020	10.064	10.105	100	360	2.9660	2.9672	30	042	2.3338	2.3335	13
200	9.552	9.557	40	521	2.9510	2.9500	18	142	2.3165	2.3170	25
120	8.898	8.931	15	441	2.8912	2.8910	20	731	2.2742	2.2722	8
220	6.917	6.936	70	531	2.8042	2.8048	7	821	2.1206	2.1197	10
320	5.369	5.383	5	261	2.7125	2.7135	3	062	2.0719 }	2.0704	10
101	5.078	5.087	10	611	2.6943	2.6963	30	920	2.0707 }		
140	4.865	4.869	50	451	2.6551	2.6539	2	262	2.0245	2.0256	5
400	4.761	4.766	4	541	2.6311	2.6337	6	622	1.9872	1.9883	5
420	4.304	4.304	3	720	2.6263 }	2.6242	25	362	1.9696	1.9686	4
221	4.191	4.196	5	621	2.6247 }			562	1.8200	1.8201	7
301	4.054	4.057	85	112	2.5878	2.5870	4	282	1.7872	1.7864	4
340	3.943	3.948	40	022	2.5484	2.5497	15	5.10.0	1.7796	1.7799	3
321	3.761	3.758	6	631	2.5197	2.5187	15	951	1.7648	1.7649	7
520	3.562	3.565	30	180	2.4944	2.4936	3	822	1.7396	1.7398	4
440	3.458	3.459	15	032	2.4521 }	2.4514	10	880	1.7292	1.7287	3
060	3.355	3.355	25	551	2.4495 }			11.2.0	1.7062	1.7055	18
160	3.304	3.306	40	280	2.4326	2.4322	13	881	1.6430 }	1.6426	2
600	3.174	3.174	15	701	2.4173	2.4168	18	413	1.6422 }		
501	3.087	3.088	10	740	2.3932	2.3935	3	10.5.1	1.6364	1.6357	3
540	3.037	3.038	30	800	2.3805	2.3802	13	971	1.6216	1.6217	5
620	3.027	3.029	2	720	2.3505	2.3492	13				

Guinier-Hägg method: CrKα₁ radiation, λ=2.28962 Å.
Internal standard: CaF₂, a=5.46375 Å.

dimensions 0.04 × 0.05 × 0.19 mm and had a calculated linear absorption coefficient of 101.8 cm⁻¹ (based on mass absorption coefficients of Cromer and Liberman, 1970). The absorption effect was calculated for all reflections using a Gaussian quadrature method of integration over 360 points in the crystal. The transmission factor was found to vary only between 0.57 and 0.63, a range comparable with the errors of measurement, and therefore was ignored. The usual Lorentz and polarization corrections and, in the last cycles, extinction and dispersion corrections (Cromer and Liberman, 1970) were applied. An extinction correction was included at the end according to the method of Larson (1967, eqn. 3), leading to a moderate value of the extinction parameter g on an arbitrary scale. The refinement [in which

the $|F(\text{obs})|$ values were weighted according to counting statistics] proceeded smoothly to $R = 0.056$ (weighted $R_w = 0.036$). This degree of refinement allows bond lengths to be determined to ± 0.005 Å.

In the hope that the single hydrogen atom in the asymmetric unit might be detectable, a ΔF Fourier synthesis was calculated using 245 data within the limit $(\sin\theta)/\lambda < 0.4$ ($R = 0.031$). The highest peak on this map occurred at $x, y, z = 0.71, 0.435, 0.63$, respectively, close to a line joining O(4) and O(7). This site lies 0.9 Å distant from O(7), and the O(4)–O(7) distance is 2.755(6) Å. Thus, the X-ray data appear to give direct confirmation of a hydrogen bond at this location. When the H atom was included in the low-angle structure factors, $R = 0.029$ was obtained for the low-angle data, but refinement of the
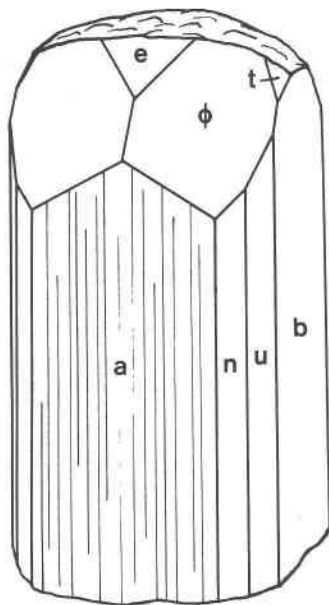
Fig. 1, Crystal habit of shattuckite. Forms shown are: $a\{100\}$, $b\{010\}$, $u\{140\}$, $n\{120\}$, $e\{201\}$, $t\{161\}$, $\phi\{321\}$.

H parameters was not attempted. The final structure and thermal parameters are set forth in Table 3, and the observed structure factors in Table 4.[1]

Planchéite

The poor quality of the available planchéite crystals has severely limited its structure refinement. A set of 168 $hk0$ data obtained by visual estimate from Weissenberg patterns made with a fair crystal was sufficient to obtain a solution of the structure. For this purpose, an interpretation of the $P_{,}(x,y)$ Patterson map, coupled with comparison with the shattuckite structure, led eventually to a clear electron density image of the planchéite structure that left no doubt about its constitution (Fig. 3). Holding thermal parameters fixed, the x and y parameters were first refined by full-matrix least-squares analysis, using the $hk0$ data. Unfortunately, the first crystal, which yielded this result, was lost, but an attempt was made to collect $hk1$ and $hk2$ data from another crystal of much poorer quality (the Weissenberg patterns consisted of spotty streaks spread over 10° to 15°

---

[1] Table 4 and Table 6 may be obtained by requesting document AM-77-042 from the Business Office, Mineralogical Society of America, Suite 1000, lower level, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

around the fiber axis). These 261 data were used to refine the 22 z parameters, whose approximate values had been obtained from careful model building based on the shattuckite structure. The 64 structure parameters were then refined using the full data set, still holding thermal parameters constant, leading to a conventional reliability factor $R = 0.146$. When 22 individual isotropic thermal parameters were allowed to vary, R was reduced to 0.129, an improvement that is significant at a confidence level better than 0.995 (Hamilton, 1965). Nevertheless, the U parameters for the oxygen atoms are very uncertain, and three of them, O(4), O(6), and O(14), became nonpositive definite, although by amounts less than 0.5 σ. In the last refinement stages, U for these atoms was held fixed at 0.015, 0.010, and 0.04 Å^2, respectively. The better quality of the $hk0$ data is revealed by the group R factors finally obtained separately, as follows:

Reflections		R
168	$hk0$	0.087
143	$hk1$	0.151
118	$hk2$	0.161
429	All	0.129

In all these refinements, convergence was slow and sometimes oscillatory, but cycling was continued until all shifts were less than 0.1 σ.

In the last stages, the population parameter of the water molecule O(14) was analyzed along with the U parameter, with which it has a correlation coefficient of 0.74. While the thermal parameter dropped to zero ($\pm$ 0.3 Å^2), the occupancy reached 0.37 $\pm$ 0.15. This result is consistent with the low electron density observed in the region of this atom in the Fourier synthesis. When structure factors are calculated with the water molecule entirely absent, a small increase in the R factor results, but according to the statistical test of Hamilton (1965), the change is significant at the 95-percent confidence level. When the U parameter was fixed at the more reasonable value of 0.04 Å^2, the occupancy was found to be 0.43, and this we regard as the best value.

The effect of the truncation of the data for planchéite at $l = 2$ is that the standard error in Å of the z parameters is about 3 times those of the x and y parameters. Thus, the oxygen positions are found to be uncertain by about $\pm$ 0.06 Å, but the actual expected error is probably at least twice this amount. The experimentally determined thermal parameters are less reliable still. The uncertainty is greatest for the water molecule, which probably has a greater thermal motion than any other atom in the unit cell.

Table 3. Structure and thermal parameters for shattuckite

A. Structure parameters

Atom	Equipt.	x	y	z
Cu(1)	4(a)	0.5	0.0	0.5
Cu(2)	8(c)	0.33090(8)	0.02547(4)	0.03970(16)
Cu(3)	8(c)	0.25205(10)	0.28125(3)	0.46765(16)
Si(1)	8(c)	0.54485(17)	0.13502(8)	0.2173(4)
Si(2)	8(c)	0.39742(17)	0.15706(8)	0.7265(4)
O(1)	8(c)	0.5054(4)	0.0554(2)	0.1996(9)
O(2)	8(c)	0.3426(4)	0.0805(2)	0.7439(9)
O(3)	8(c)	0.7076(4)	0.1512(2)	0.2203(9)
O(4)	8(c)	0.4913(5)	0.1735(2)	0.9708(9)
O(5)	8(c)	0.4907(5)	0.1670(2)	0.4777(9)
O(6)	8(c)	0.2836(4)	0.2163(2)	0.7193(9)
O(7)(OH)	8(c)	0.6779(4)	0.0243(2)	0.6426(8)
H	8(c)	0.71	0.435	0.63

B. Thermal parameters (U values in $\text{Å}^2 \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$\bar{u}$(rms, Å)
Cu(1)	88(5)	79(4)	93(6)	−32(5)	−30(5)	42(4)	0.093
Cu(2)	95(3)	80(3)	73(3)	−25(3)	−14(4)	20(3)	0.090
Cu(3)	108(3)	46(3)	66(3)	1(3)	−25(3)	−4(3)	0.085
Si(1)	62(7)	39(7)	52(7)	−4(6)	14(7)	6(7)	0.072
Si(2)	64(7)	34(6)	53(8)	1(6)	−2(7)	3(6)	0.072
O(1)	105(20)	51(18)	67(21)	−38(16)	−29(20)	31(16)	0.085
O(2)	157(22)	32(18)	119(23)	−29(16)	−22(22)	24(18)	0.100
O(3)	51(16)	57(17)	83(21)	−24(14)	5(18)	18(17)	0.080
O(4)	101(20)	73(18)	61(20)	−14(16)	−7(20)	−10(17)	0.089
O(5)	136(22)	71(21)	69(21)	7(17)	29(20)	−37(18)	0.096
O(6)	109(19)	51(16)	43(18)	32(15)	−23(18)	−23(18)	0.082
O(7)(OH)	91(18)	59(19)	69(19)	−21(17)	16(18)	−2(18)	0.085

Thus, while it is not reasonable to study the bond lengths in any detail in this structure, a good interpretation of its general configuration is possible.

The final structure and thermal parameters for planchéite are given in Table 5, and the observed structure factors are listed in Table 6.[2]

Comparison with published structures

To compare our structure for shattuckite with that proposed by LeBihan (1966, 1967), the corresponding parameters are set forth together in Table 7. The parameters of Table 3 (curtailed to 3 significant figures) are transformed by shifting our origin to (0, ½, 0) and then choosing another equipoint to make them equivalent to those of LeBihan.

Thus, we find fair agreement as far as the x and y coordinates are concerned, but the z parameters are grossly different. A calculation of interatomic distances in LeBihan's structure shows improbably close O–O approaches (as short as 2.2 A). Her structure analysis (LeBihan, 1966) was evidently based only on a set of $hk0$ data, and the three-dimensional structure in terms of the z parameters was evolved entirely

hypothetically from geometrical considerations. The geometrical analysis is incomplete, and as no experimental evidence is offered in support of the z parameters, LeBihan's structure must be incorrect.

The only suggestion about the structure of planchéite that has appeared was offered by Van Oosterwyck-Gastuche (1968), who evidently followed our allusion to "amphibole-like chains" (Evans and Mrose, 1966) and postulated a structure analogous to that of amphibole itself. In fact, there is no relationship between the two structures, except for the presence of the double silicate chain.

The crystal structures

Both shattuckite and planchéite are chain structures in terms of the silicate components. Shattuckite (Fig. 2) contains zigzag $(SiO_3)^{2-}$ chains that are quite similar to those found in the pyroxenes. Planchéite (Fig. 3) contains such chains joined in parallel pairs, forming double chains $(Si_4O_{11})^{6-}$ analogous to those found in the amphiboles. Thus, the c axis of all these minerals is about 5.3 A, representing the repeat unit of the silicate chains. Aside from these features, however, there is no analogy between the copper silicates and the pyroxene–amphibole group of structures.

In both shattuckite and planchéite, the apices of
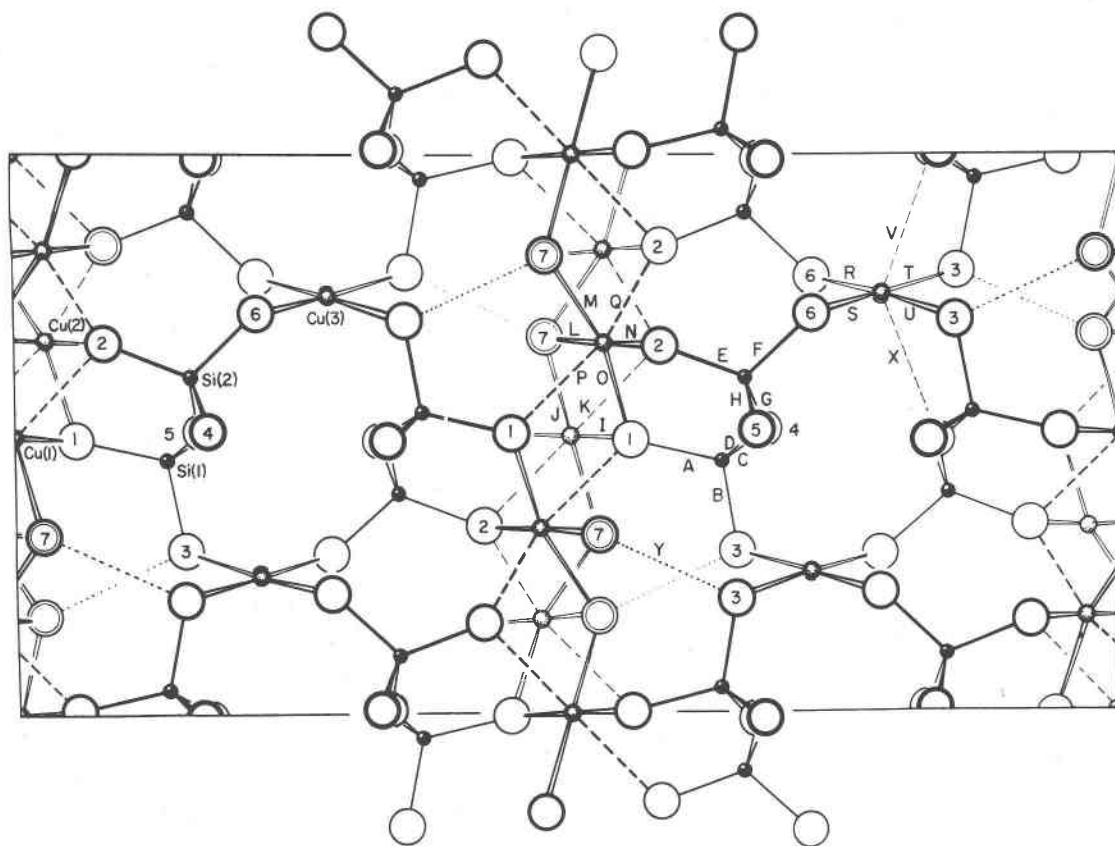
---

[2] See footnote, p. 494.

Fig. 2. Plan of the unit cell of the crystal structure of shattuckite, viewed along the c axis (b axis is horizontal). In the distorted octahedral Cu coordination, the longer apical bonds are dashed. Hydrogen bonds are dotted. Large, double circles represent OH groups. Numbers indicate atom numbers as listed in Table 3, and letters refer to bonds as listed in Table 8.

the silicate-chain tetrahedra are condensed on both sides of an extended copper–oxygen layer $(CuO_2)^{2-}$ that topologically is similar to that in brucite Mg-$(OH)_2$. The oxygen sites in the layer that are not supplied by the silicate tetrahedra are occupied by OH groups. The CuO_2 layer is strongly bent at the region of contact of adjacent silicate chains (the angle of bend is about 33°), giving the layers, which lie parallel to the a–c plane, a corrugated aspect. The structures may thus be considered as sheet structures in terms of the compact silicate–Cu–silicate triple layers referred to above.

The triple layers (two per unit cell) stack against each other along the b axis in both structures, with their corrugations nested, and the silicate chains in contact base-to-base. The triple layers are linked together by additional copper atoms having an unusual linkage. The copper atoms are bonded to the outer unshared oxygen atoms of the silicate chains from adjacent triple layers to form square-planar CuO_4

groups that are joined in ladder-like ribbons parallel to the c axis (Fig. 4). There are thus three levels of integrity in these structures. In terms of the overall bonding scheme, they are network structures; in terms of the compact triple layers, they are sheet structures; in terms of their strongest elements, the silicate chains, they are chain structures. The physical properties (optically positive, fibrous character) emphasize the last interpretation.

The thermal motions in shattuckite are quite small. They are defined by the U parameters shown in Table 3 and are illustrated as 75 percent probability ellipsoids in Figure 5. The ellipsoids are all oriented in a manner which would be expected from the restraints imposed by bonding to adjacent atoms. Thus, for example, all the copper atoms are vibrating with root-mean-square displacements $\bar{u}$ of ~0.07 A in the square plane and ~0.11 A normal to the plane, while the silicon atoms are vibrating nearly isotropically with $\bar{u} \sim 0.07$ A. Figure 5 may also be useful to gain

Table 5. Structure and thermal parameters for planchéite

Atom	Equipt.	x	y	z	$\bar{u}$, A
Cu(1)	8(d)	0.4592(5)	0.0100(5)	0.269(4)	0.14(1)
Cu(2)	8(d)	0.3746(5)	0.0329(4)	0.791(4)	0.14(1)
Cu(3)	8(d)	0.2925(5)	0.0563(4)	0.317(3)	0.14(1)
Cu(4)	8(d)	0.2518(7)	0.3085(4)	0.713(4)	0.19(1)
Si(1)	8(d)	0.6408(9)	0.1071(8)	0.941(8)	0.12(2)
Si(2)	8(d)	0.5635(9)	0.1239(8)	0.422(8)	0.12(2)
Si(3)	8(d)	0.4073(8)	0.1637(8)	0.505(8)	0.12(2)
Si(4)	8(d)	0.3323(9)	0.1873(8)	0.997(7)	0.12(2)
O(1)	8(d)	0.629(2)	0.028(2)	0.942(16)	0.14(4)
O(2)	8(d)	0.545(2)	0.047(2)	0.496(17)	0.11(6)
O(3)	8(d)	0.382(2)	0.087(2)	0.504(17)	0.13(4)
O(4)	8(d)	0.302(2)	0.112(2)	0.955(13)	0.12*
O(5)	8(d)	0.724(2)	0.126(2)	0.940(15)	0.17(4)
O(6)	8(d)	0.599(2)	0.144(2)	0.173(13)	0.10*
O(7)	8(d)	0.620(2)	0.140(2)	0.665(13)	0.08(7)
O(8)	8(d)	0.493(2)	0.165(2)	0.485(14)	0.10(5)
O(9)	8(d)	0.386(2)	0.195(2)	0.769(14)	0.08(7)
O(10)	8(d)	0.373(2)	0.204(2)	0.268(15)	0.14(5)
O(11)	8(d)	0.272(2)	0.246(2)	0.985(14)	0.11(5)
O(12)(OH)	8(d)	0.462(2)	0.062(2)	0.981(19)	0.15(4)
O(13)(OH)	8(d)	0.287(2)	0.005(2)	0.581(14)	0.16(4)
O(14)(H₂O)	4(c)	0.5	0.25	0.95(6)	0.20*

* Fixed value for least squares analysis.

additional appreciation of the various linkages in the structure.

The symmetry of the structures is determined first by the symmetry of the triple layers, and second by the way they are cross-linked by the CuO₄ squares. The symmetry of one triple layer in an orthorhombic unit cell with $b \sim 10A$ would be Pcaa for shattuckite and Pcna for planchéite; the shift in the b axis glide arises from the doubling of the silicate chains along the a axis and a change from an odd (3) to an even (6) number of copper atoms in the corrugated band. The joining of the triple layers by the CuO₄ square chains then leads to a doubled b axis and c axis glide in the b direction.

The complete structural integrity of these crystals makes it possible to write unambiguous chemical formulas for both of them, as shown in Table 1. Thus,

the Cu:Si ratio in shattuckite is 5:4, and in planchéite it is 1:1. The composition of shattuckite derived from the structure has been well confirmed by chemical analysis of carefully prepared samples by Vlisidis and Schaller (1967).

The only remaining question concerning composition is the amount of free water contained in planchéite. The structure analysis revealed a site between the hexagonal openings of opposite double-silicate chains in which a free water molecule could comfortably be placed. Electron density syntheses show a very weak density in this region, suggesting that the site is not fully occupied. The least-squares analysis of the structure factors indicates that, in the formula shown in Table 1, $x \sim 0.43$. The distances of this site on the 2-fold axis are 2.6 ± 0.1 A from O(9) and 3.0 A from O(8) and O(10), thus allowing reasonable space for the water molecule. Infrared spectra of planchéite and shattuckite prepared by I. A. Breger of the U.S. Geological Survey (Fig. 6) show absorptions at 3 μm for both crystals, corresponding to the OH groups in the structure, but at 6 μm only for planchéite, suggesting that this crystal also contains H₂O. It seems likely that planchéite does contain a small and probably variable amount of free water of crystallization.

The silicate chains

The detailed structure of the single silicate chain in shattuckite is entirely consistent with that found in pyroxenes. The Si–O bond lengths (see Table 8) for bridging oxygen atoms O(4) and O(5) have an average of 1.632 A, as compared with 1.647 A for eight well-refined pyroxene structures (Clark et al., 1969). For nonbridged oxygen atoms the average is 1.628 A, compared with 1.609 A for pyroxenes. Evidently this

Table 7. Comparison of present structure of shattuckite with that of LeBihan (1967)
Parameters of Table 3 (EM) transformed to setting of LeBihan (1967) (LB)

| Atom	No.		x		y		z	
	LB	EM	LB	EM	LB	EM	LB	EM
Cu	1	3	0.245	0.248	0.2805	0.2813	0.780	0.522
Cu	2	2	0.163	0.169	0.5209	0.5255	0.565	0.540
Cu	3	1	0.500	0.5	0.5000	0.5	0.500	0.5
Si	1	1	0.462	0.455	0.3685	0.3650	0.000	0.272
Si	2	2	0.585	0.603	0.3485	0.3429	0.500	0.726
O	1	3	0.302	0.292	0.3510	0.3488	0.00	0.780
O	2	1	0.473	0.495	0.4485	0.4446	0.05	0.801
O	3	4	0.502	0.509	0.330	0.3265	0.25	0.471
O	4	5	0.504	0.504	0.332	0.3330	0.75	0.977
O	5	6	0.698	0.717	0.2900	0.2837	0.50	0.281
O	6	2	0.645	0.658	0.4220	0.4195	0.53	0.257
O(OH)	7	7	0.684	0.678	0.548	0.5243	0.32	0.643
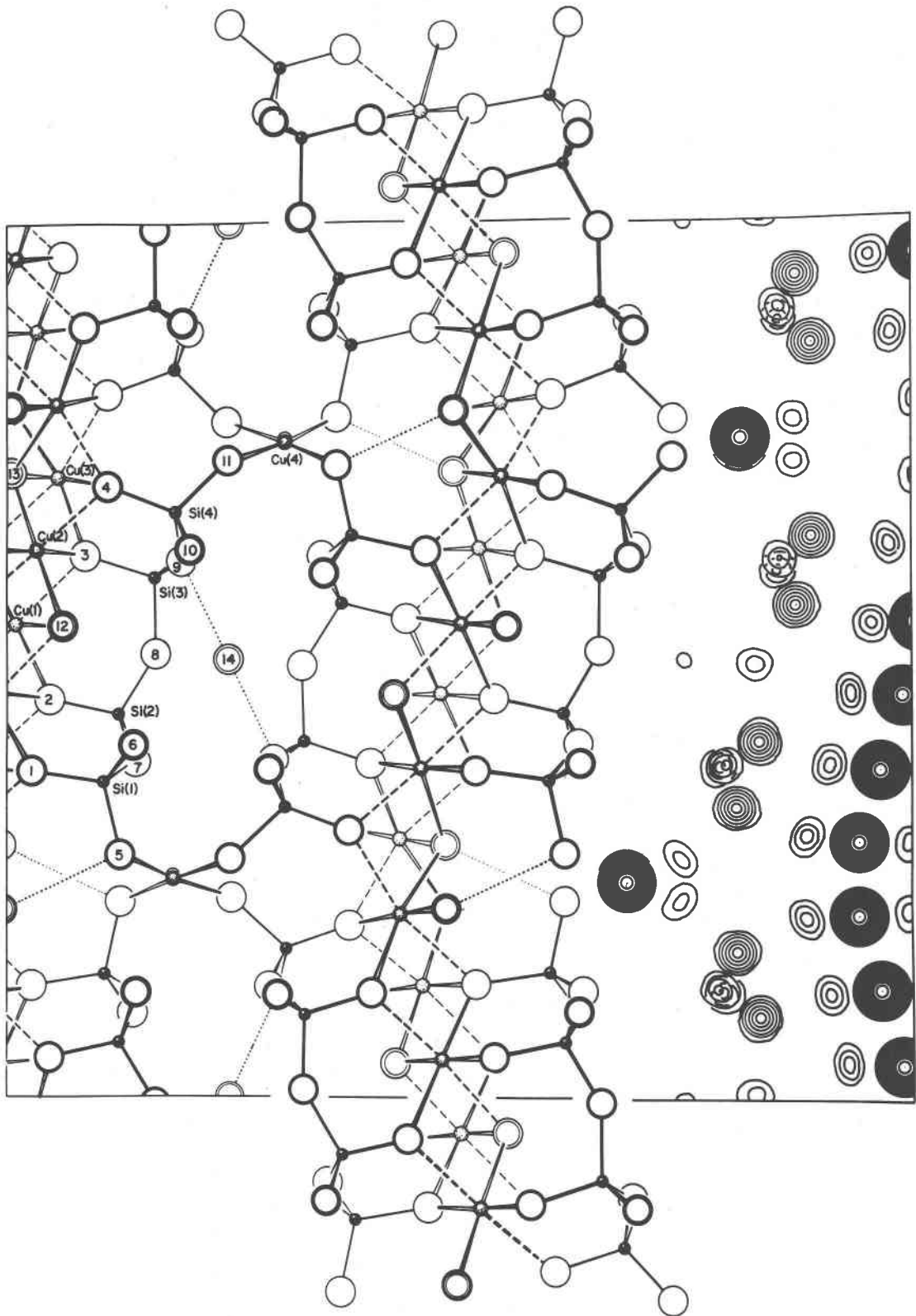
Fig. 3. Plan of the unit cell of the crystal structure of planchéite, viewed along the *c* axis (*b* axis is horizontal). Bonds are shown as in Fig. 2, and numbers indicate atom numbers as listed in Table 5. To the right, three-dimensional sections of the electron density synthesis are shown, with contours at 4, 6, 8, *etc.,* electrons/A³.
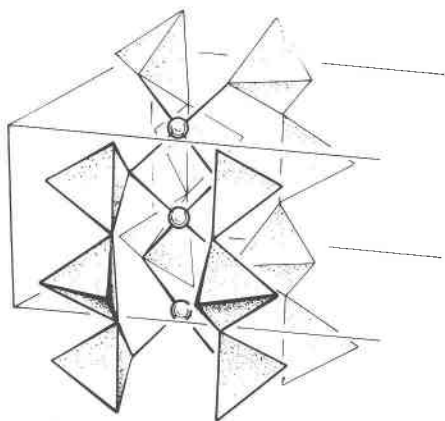
Fig. 4. View of a portion of the shattuckite (and planchéite) structure, showing the ladder-like manner in which square-planar coordinated Cu cross-links silicate chains from one triple layer to the next.
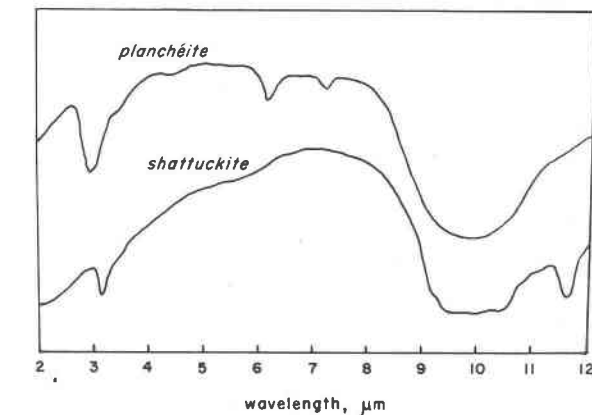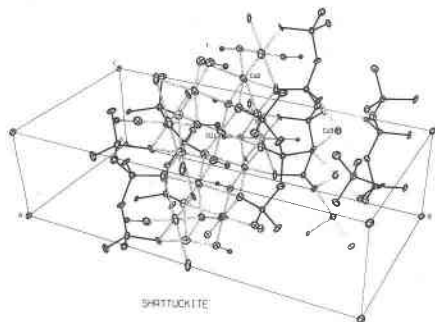

Fig. 6. Infrared transmission spectra of shattuckite and planchéite (prepared by I. A. Breger, U. S. Geological Survey). Transmission scale is relative, with the planchéite curve displaced upward for purposes of clarity.

distinction between two types of Si–O bonds is less distinct in shattuckite than in pyroxenes.

The linking angles Si–O–Si in shattuckite are 138.4(3)degrees at O(4) (vectors $C \wedge H$ in Fig. 2), and 147.7(3) at O (5) (vectors $D \wedge G$). The tetrahedron pair of the latter spans an elongated edge of the $Cu(2)O_6$ octahedron [O(1)–O(2) = 3.38 A], and hence the link angle is opened up more than in the former tetrahedron pair, which spans an equatorial edge of the octahedron [O(1)–O(2) = 2.98 A]. Typical pyroxene link angles range from 136 to 142 degrees (Clark *et al.*, 1969).

The bond lengths in planchéite are poorly determined ($\sigma > 0.1$ A) and are not amenable to detailed interpretation. An overall comparison of the configuration of the double chain shows a considerable departure from the near-mirror symmetry that prevails in the amphibole chains. Thus, the hexagonal rings are strongly skewed in a direction about 45° away from the chain axis (Fig. 7). This effect is clearly a

result of the Jahn-Teller distortion of the CuO_6 octahedra at the center of the triple layer.

The copper coordination

In shattuckite and planchéite, two distinct types of copper atoms are present. One type forms a con-

Table 8. Interatomic distances in shattuckite

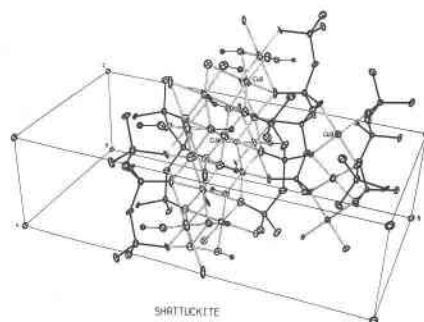| Atoms	Vector	Distance, Å	Atoms	Vector	Distance, Å
Si(1)–O(1)	A	1.630(5)	Cu(2)–O(7)	L	1.975(4)
–O(3)	B	1.641(4)	–O(7)'	M	2.054(4)
–O(4)	C	1.620(5)	–O(2)	N	1.934(5)
–O(5)	D	1.628(5)	–O(1)	O	2.017(4)
			–O(1)'	P	2.617(5)
Si(2)–O(2)	E	1.615(5)	–O(2)'	Q	2.310(5)
–O(6)	F	1.626(4)			
–O(4)	G	1.642(5)	Cu(3)–O(6)	R	1.896(4)
–O(5)	H	1.637(5)	–O(6)'	S	1.890(4)
			–O(3)	T	1.950(5)
Average Si–O		1.630	–O(3)'	U	1.939(5)
			–O(4)	V	2.692(5)
Cu(1)–O(1)	I(x2)	1.955(4)	–O(5)	X	2.781(5)
–O(7)	J(x2)	1.978(4)			
–O(2)	K(x2)	2.587(4)	O(3)–O(7)	Y	2.793(6)

Vectors are indicated in Fig. 2.

Fig. 5. Stereoscopic view of the crystal structure of shattuckite. All atoms (except H, shown as small spheres) are represented by 75-percent probability thermal ellipsoids. Si–O bonds are solid, Cu–O bonds are open.
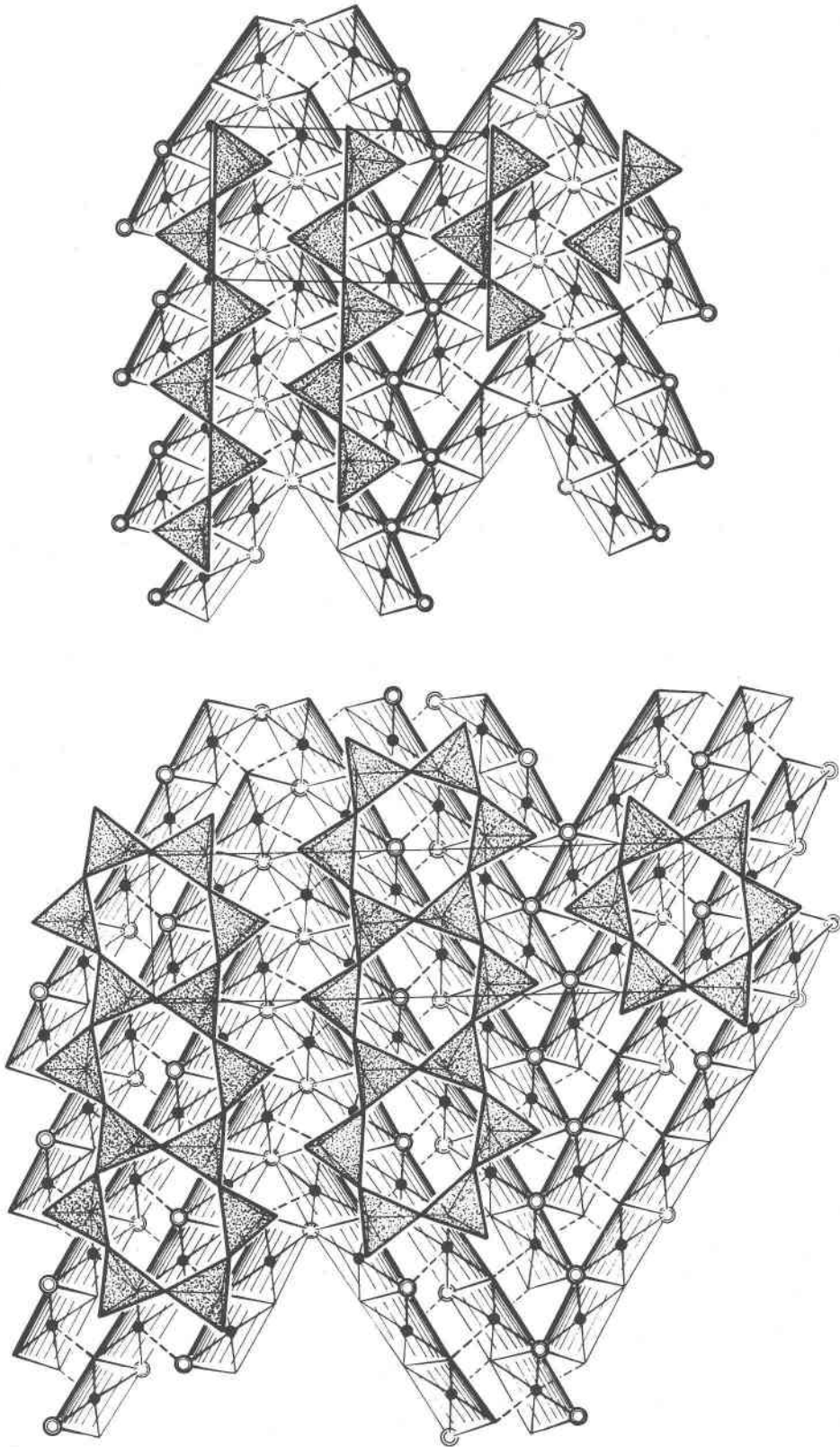
Fig. 7. Schematic views of the triple layers in shattuckite (top) and planchéite (bottom), viewed along the *b* axis (from the left in Fig. 2 and 3). The rows of planar CuO₄ groups are shown as crossed squares sharply tilted and arranged like Venetian blinds. The longer apical Cu–O bonds are dashed. The double circles represent OH groups.

densed octahedral brucite-like fabric at the center of the silicate–copper–silicate triple layer; the other type is in square coordination and ties the triple layers together with ladderlike CuO_2 ribbons. The shattuckite unit cell contains 6 atoms of the first type and 4 of the second; the planchéite cell contains 12 of the first and 4 of the second.

All of the CuO_6 octahedra in both shattuckite and planchéite have a strong tetragonal distortion in accord with the Jahn-Teller effect. In shattuckite, each copper atom has 4 oxygen atoms in a plane with Cu–O bond lengths in the range 1.89 to 2.05 A, (average 1.959 A) and two additional oxygen atoms completing the octahedron with lengths of 2.31 to 2.78 A (Table 8, Figure 2). The ranges are presumably the same in planchéite. A summary (Dubler et al., 1973) of 14 typical inorganic Cu(II) coordination groups recently determined shows that the average square plane distance is 1.961 A, while the apical oxygen atoms range from 2.3 to 2.9 A.

The ladderlike copper ribbons that join the triple layers together are unusual and apparently have no counterpart in any other known structure. Strictly square planar coordination is itself not common, as usually one or two additional ligands approach within 2.6 A along the normal to the square. One example is azurite, $Cu_3(OH)_2(CO_3)_2$ (Zigan and Shuster, 1972), in which one copper atom at a symmetry center has four ligands at 1.890(1) and 1.947(1) A in a square with an O–Cu–O angle of 88.2°. In another, the synthetic copper sodium silicate $Cu_3Na_2(Si_4O_{12})$ recently described by Kawamura and Kawahara (1976), two squares share one edge to form a nearly planar Cu_2O_6 group, with an average internal O–Cu–O angle of 78.1°, and average external angles of 93.9° (some of the angles given by the authors in their Table 5 are incorrect and have been recalculated). In shattuckite, the Cu(3) atom has four ligands at 1.896(4) and 1.890(4) A to O(6), 1.939(4) and 1.950(4) A to O(3) with an average O–Cu–O angle in the chain of 86.5° and an average lateral angle of 93.5°. The fact that the bonds to O(3) are longer may be related to the involvement of O(3) in a hydrogen bond with the hydroxyl group O(7). Two other oxygen atoms (links in the silicate chains) lie at distances of 2.69 and 2.78 A, in a very oblique direction to the square (~20° from the normal), and so must play a negligible bonding role. The string of squares along the chain are canted to each other at an angle of about 16°, with a distance of 2.692(1) A between Cu(3) atoms. The shared edge of the square is 2.630(5) A in length, and the lateral edges are 2.773(5) and 2.805(5) A.

The brucite-like arrangement of the CuO_2 layer at the center of the triple layer has apparently only been found in one other compound, $Cu(OH)_2$. According to Shishakov (1952), this form of the hydroxide (obtained by alkaline corrosion of Cu metal or brass) is hexagonal with $a = 3.30$ A and $c = 4.84$ A, and presumably has the brucite structure. The tetragonal elongations of the octahedra in the brucite-like layer are arranged in a particularly elegant way in the two present structures. In Figure 7, these octahedra are represented as crossed squares with two axes (dashed lines) normal to the squares, and from this representation we can see that the octahedra are arranged in rows in which the squares share opposite edges. In shattuckite, these rows are 3 squares in length, in planchéite 6; in both, the rows are condensed in imbricated manner with rows above and below, to generate one strip of the corrugated sheet. In the next strip, the rows, which are inclined to the c axis about 33°, are tilted in the opposite direction. Thus, the tetragonal distortion of the octahedra, the geometrical requirements of the coalesced silicate chains and the fit of adjacent chains at the corrugation folds, all combine in a beautiful way to build the complex but harmonious triple layer.

Note added in proof

A paper by A. Kawahara has appeared (*Mineral. J. (Japan)*, *8*, 193–199, 1976) in which a new structure determination of shattuckite is described. Weissenberg patterns made with $CuK\alpha$ radiation were used to estimate intensities of 251 *hkl* reflections, and the determined structure refined by least-squares analysis to $R = 0.128$. Kawahara's structure is the same as ours in all its structure parameters within 2σ (thus correcting LeBihan's structure), but his standard deviations are about 8 times ours.

References

Appleman, D. E. and H. T. Evans, Jr. (1973) Indexing and least-squares refinement of powder diffraction data. *U.S. Dept. Commerce, Natl. Tech. Serv. Publ. No. PB216188.*

Clark, J. R., D. E. Appleman and J. J. Papike (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineral. Soc. Am. Spec. Pap., 2*, 31–50.

Cromer, D. T. and D. Liberman (1970) Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys., 53*, 1891–1898.

Dubler, E., P. Korber and H. R. Oswald (1973) The crystal structures of barium hexahydroxocuprate(II) and strontium hexahydroxocuprate(II), $Ba_2[Cu(OH)_6]$ and $Sr_2[Cu(OH)_6]$. *Acta Crystallogr., B29*, 1929–1933.

Evans, H. T., Jr. and M. E. Mrose (1966) Shattuckite and planchéite: a crystal chemical study. *Science, 154*, 506–507.

Gastuche, M.-C. (1967) Sur l'existence de la planchéite et de la

shattuckite à Mindouli (Congo). *C. R. Acad. Sci., Ser. D, 264*, 1369–1371.

Guillemin, C. and R. Pierrot (1961) Nouvelles données sur la planchéite: identité de la planchéite et de la "shattuckite." *Bull. Soc. fr. Mineral. Cristallogr., 84*, 267–281.

Hamilton, W. C. (1965) Significance tests on the crystallographic *R* factor. *Acta Crystallogr., 18*, 502–510.

Kawamura, K. and A. Kawahara (1976) The crystal structure of synthetic copper sodium silicate $Cu_3Na_2(Si_4O_{12})$. *Acta Crystallogr., B32*, 2419–2422.

Kelly, K. L. and D. B. Judd (1955) *The ISCC-NBS Method of Designating Colors and a Dictionary of Color Names (with Supplement of Color Name Charts Illustrated with Centroid Colors)*. Natl. Bur. Stand. (U.S.), Circ. *553*, 158 p.

Lacroix, A. (1908) Sur une nouvelle espèce minérale, provenant du Congo français. *C. R. Acad. Sci., 146*, 722–725.

Larsen, E. S. and H. Berman (1934) The microscopic determination of the nonopaque minerals. *U.S. Geological Survey Bull. 848*

Larson, A. C. (1967) Inclusion of secondary extinction in least-squares calculations. *Acta. Crystallogr. 23*, 664–665.

LeBihan, M.-Th. (1966) Contribution à l'étude structurale des silicates de cuivre: structure atomique de la shattuckite. *C. R. Acad. Sci., Ser. D., 263*, 1801–1803.

—— (1967) Contribution à l'étude des silicates de cuivre. Diffé-renciation de la shattuckite et de la planchéite. Structure atomique de la shattuckite. *Bull. Soc. fr. Mineral. Cristallogr., 90*, 3–7.

Mrose, M. E. and A. C. Vlisidis (1966) Proof of the formula of shattuckite, $Cu_5(SiO_3)_4(OH)_2$ (abstr.). *Am. Mineral., 51*, 266–267.

Newberg, D. W. (1964) X-ray study of shattuckite. *Am. Mineral., 49*, 1234–1239.

Schaller, W. T. (1915) Four new minerals. *J. Wash. Acad. Sci., 5*, 7.

—— (1919) Planchéite and shattuckite, copper silicates, are not the same mineral. *J. Wash. Acad. Sci., 9*, 131–134.

Shishakov, N. A. (1952) Electronographic study of hydroxide films on metals (Mg, Al, Cu, Fe). *Zh. Fiz. Khim., 26*, 106–111.

Van Oosterwyck-Gastuche, [M.-C.] (1968) Les planchéites considérées comme une famille d'amphiboles cuivriques. *C. R. Acad. Sci., Ser. D, 266*, 1546–1548.

—— (1974) *Nomenclature et Structure des Silicates de Cuivre*. Thesis privately published (University of Liège).

Vlisidis, A. C. and W. T. Schaller (1967) The formula of shattuckite. *Am. Mineral., 52*, 782–786.

Zigan, F. and H. D. Shuster (1972) Verfeinerung der Struktur von Azurit, $Cu_3(OH)_2(CO_3)_2$, durch Neutronenbeugung. *Z. Kristallogr., 135*, 416–426.