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The crystal structure of chalcophyllite

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Abstract. Chalcophyllite, $Cu_9Al(AsO_4)_2(SO_4)_{1.5}(OH)_{12} \cdot 18\,H_2O$, crystallizes in space group $R\bar{3}$ with $a_{\mathrm{hex}} = 10.756$ and $c_{\mathrm{hex}} = 28.678$ Å. The structure was determined by Patterson and Fourier methods and refined by the least-squares technique to a final R index of 0.056. The dominant structural feature is the arrangement of Cu and Al polyhedra into complex sheets to which the As tetrahedra are attached by one face. The sheets are connected to each other by the hydrogen bonding system, where the sulphate groups are immersed. An interpretation of twinning with (100) as twin plane is given, and the partial occupancy of SO_4 tetrahedron is discussed.

Introduction

The present investigation on the crystal structure of chalcophyllite was undertaken as part of a program dealing with the crystal-chemical study of Cu/Al basic sulphate hydrated minerals.

Although this mineral was discovered nearly 140 years ago, its chemical composition and symmetry have been uncertain up to now. Berry and Steacy (1947) proposed the formula $Cu_{18}Al_2(AsO_4)_3(SO_4)_3(OH)_{27} \cdot 36\,H_2O$ with trigonal scalenohedral symmetry, space group $R\bar{3}m$, and with cell parameters $a_{\mathrm{hex}} = 10.77$ and $c_{\mathrm{hex}} = 57.51$ Å for the fully hydrated mineral. In this formula the SO_4 content appears overestimated in respect to several known analyses, in which the ratio of AsO_4 to SO_4 is in excess of 1 : 1 of the above composition. Moreover the specimen studied by Berry and Steacy (1947) was partially dehydrated and showed a well marked pseudo-cell with the c parameter halved in comparison with the fully hydrated material. Later Federico (1955), working on Laue and precession photographs obtained from a very thin cleavage lamina of a fully hydrated specimen, observed the presence of the threefold axis and the lack of symmetry planes. The author then stated the true symmetry class of chalcophyllite to be $\bar{3}$, the apparent symmetry $\bar{3}m$ being ascribed to a twinning of the laminae with $(10\bar{1}0)$ as twin plane.

The specimen studied in the present investigation appears to be a twinned and partially dehydrated chalcophyllite. The crystal structure determination leads to the chemical formula:

$Cu_9Al(AsO_4)_2(SO_4)_{1.5}(OH)_{12} \cdot 18\,H_2O$.

Experimental

A sample of chalcophyllite from Cornwall, England (No. 9772, Mineralogical Museum, Florence University), was used for the present work. The crystals are thin emerald-green plates, flattened parallel {0001}, with rhombohedral aspect. Attempts to find untwinned crystals were unsuccessful. The sample used for the unit cell determination and intensity data collection was an irregular platy fragment with a roughly triangular shape. The unit cell edges, determined from 25 high-angle reflections measured on a single-crystal diffractometer, are $a_{\text{hex}} = 10.756(2)$ and $c_{\text{hex}} = 28.678(4)$ Å. The true space group was determined by extracting from the composite pattern of the twinned crystal the set of reflections due to one individual. The only observed systematic extinctions are of the type $hkil$ with $-h + k + l \neq 3n$; this allows the space group to be $R\bar{3}$ or $R3$. The first one was chosen for structure determination and subsequently it was found to be correct.

Intensities of 2206 reflections from the whole twinned crystal were collected on a Philips 4-circle automatic diffractometer with graphite-monochromated Mo$K\alpha$ radiation, in the range $2° < \theta < 25°$, with ω-scan technique, scan range of 1.5°, and scan speed of $0.055\,s^{-1}$. Intensities were corrected for Lorentz and polarization effects. Because of the small size and of the complex shape of the crystal no absorption correction was applied; however, a partial compensation was achieved by averaging the intensities of equivalent reflections and of reflections belonging to both individuals of the twin.

As is illustrated in the following section, the 2206 starting 'twinned' reflections are considerably reduced after the handling and the averaging, obtaining an 'untwinned' set of data. Of the 1131 independent reflections 978 only were judged to be actually measured according to the criterion $I \geq 5\sigma\,(I)$.

Scattering factor curves for all atoms were taken from International Tables for X-ray Crystallography IV (1974). All computing was performed on the CII-10070 computer of Florence University.

The summarized crystal data are:

Formula: $Cu_9Al(AsO_4)_2(SO_4)_{1.5}(OH)_{12} \cdot 18\,H_2O$
$a_{\text{hex}} = 10.756(2)$; $c_{\text{hex}} = 28.678(4)$ Å; space group $R\bar{3}$.
$V = 2873.3$ Å^3; FW 1548.8; $Z = 3$.
$D_x = 2.684\,g\,cm^{-3}$; D_m (Federico, 1955) $= 2.69\,g\,cm^{-3}$.

Twinning

Figure 1 reports the reflection population due to the whole twinned crystal and relative to reciprocal lattice layers with $l = 3n + 1$ ($l = 1, 4, 7, \ldots$). Layers with $l = 3n + 2$ ($l = 2, 5, 8 \ldots$) can be represented by the same figure, with the only difference that solid circles substitute for open ones and *vice versa*. On the contrary the reciprocal lattice points of the layers with $l = 3n$ ($l = 0, 3, 6 \ldots$) are not superimposed to the points of the above layers, but they occupy the sites which are left free in the scheme of Fig. 1. The effect of the twinning is to superimpose exactly the reflections of the type $l = 3n$, all the remaining ones constituting two well-separated sets of data.

Taking into account only the geometry of reciprocal lattice, two twin laws are possible. The first, with a twofold axis as twin operator perpendicular to the layer lattice sketched in Fig. 1, makes hkl reflections of the A component related to $hk\bar{l}$ reflections of the B component. The other possibility, with the twin plane (100) as reported in Fig. 1, has hkl reflections of the A component corresponding to $\underline{k}\,\underline{h}\,\underline{l}$ reflections of the B component. Comparing the nonsuperimposed data no relationship between hkl and $hk\bar{l}$ was observed, whereas a nearly constant ratio between the intensities of hkl and khl reflections was found. This leads to the conclusion that the two individuals of the twin are related by the (100) mirror plane. Therefore the second of the

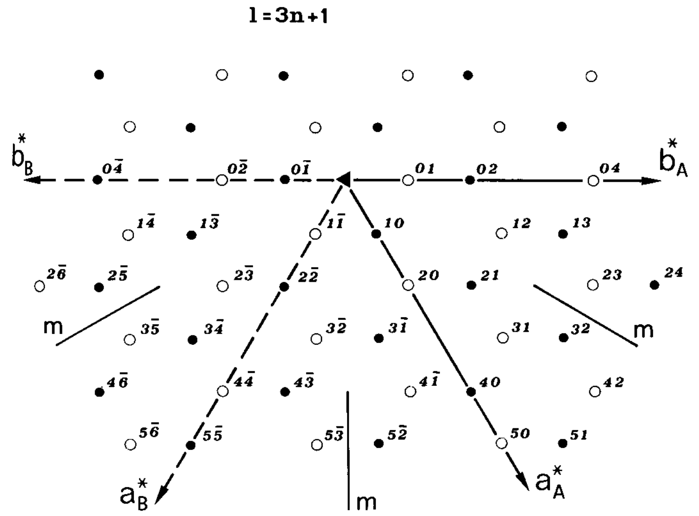


Fig. 1. A layer of the reciprocal lattice of the twinned crystal of chalcophyllite. The numbering refers to the h and k Miller indices of reflections, with $l = 3n + 1$. Solid circles represent the reflections with $-h + k + l = 3n$ belonging to the larger member of the twin (A individual); open circles those, with $h - k + l = 3n$, of the other member (B individual). The letter m denotes the mirror plane (100) which is the operator symmetry responsible for the twinning

above mentioned possibilities is true and Federico's statement was confirmed.

We have thus two different sets of data: reflections (with $l \neq 3n$) attributable separately to A and B individuals, and reflections (with $l = 3n$) overlapped by the twinning. From the intensities of 608 pairs of nonsuperimposed reflections of the first set, the relative volumes of the two individuals were easily computed. The knowledge of the volume ratio so determined ($A/B = 2.65$) allowed the composite intensities of the overlapped reflections to be subdivided into the intensities of A and B components, by solving the following expressions:

$$I_{hkl} = I^A_{hkl} + I^B_{khl}$$

$$I_{khl} = I^A_{khl} + I^B_{hkl}$$

where I is the observed intensity of the twinned crystal and I^A and I^B are the intensities of the two superimposed reflections. A program for the CII-10070 computer was written to solve the above equations and to correct and average the set of all experimental data, in such a way as to obtain a homogeneous set of reflections, as if the whole crystal were untwinned.

Structure determination and refinement

Assuming that, because of the micaceous aspect and the perfect {0001} cleavage of the crystals, dense sheets of Cu polyhedra are present in the structure of chalcophyllite and that the sheets are perpendicular to the c axis, a structural model with such copper-oxygen arrangement was chosen. This model, taken from the structure of serpierite $Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3\,H_2O$ (Sabelli and Zanazzi, 1968), was oriented in such a way as to fit the cell dimensions and the threefold symmetry of chalcophyllite. Owing to the threefold screw axis, three Cu – O sheets take place in the unit cell. They were located at $z = \frac{1}{6}, \frac{1}{2}$, and $\frac{5}{6}$.

The first remark was that a sheet with octahedral sites entirely occupied by copper requires the presence of 12 Cu atoms within the cell. This means that 36 atoms would take place in the whole unit cell, while 27 Cu atoms only are available on the basis of chemical analyses. This suggested that 9 out of the 12 possible octahedral sites were occupied by Cu atoms. The threefold axes were chosen to be free of Cu atoms, since such atoms as As, S, and Al are forced to take place on 3 and $\bar{3}$ point symmetry because of their low number of positions.

The Cu and O atoms of the sheet contribute to the structure factor calculation only for reflections with $h = k = 2n$ and $h - k = 6n$, showing the presence of a well-marked subcell. On the other hand these reflections are the strongest ones and it was considered helpful to leave out their contribution from the computation of a Patterson function. The highest peaks recognized

Table 1. Positional and thermal parameters ($\times 10^5$). The anisotropic temperature factor is: $\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$

Atom	x/a	y/b	z/c	B eq. (Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.89	41(13)	7(13)	73(2)	− 11(10)	14(3)	2(3)
Cu(2)	0.33719(7)	0.17841(8)	0.50598(3)	0.79	36(10)	4(9)	68(1)	7(7)	18(2)	0(2)
As	$\frac{2}{3}$	$\frac{1}{3}$	0.46011(5)	1.49	228(10)	228	87(2)	114	–	–
S	$\frac{1}{3}$	$\frac{2}{3}$	0.3257(2)	1.90	498(41)	498	68(7)	249	–	–
Al	0	0	$\frac{1}{2}$	0.62	2(29)	2	57(6)	1	–	–
OH(1)	0.3246(4)	0.3481(4)	0.5278(2)	0.73	147(47)	149(46)	36(6)	77(39)	− 16(12)	− 2(12)
O(2)	0.5218(4)	0.3333(4)	0.4822(2)	1.42	127(47)	30(47)	106(8)	− 11(39)	15(15)	− 1(14)
$H_2O(3)$	0.3467(5)	0.4588(5)	0.4334(2)	2.33	626(65)	538(62)	87(8)	278(55)	− 9(18)	18(18)
OH(4)	0.1296(4)	0.1620(4)	0.4639(2)	0.87	100(47)	119(47)	57(6)	57(38)	14(13)	− 1(13)
O(5)	$\frac{2}{3}$	$\frac{1}{3}$	0.4037(3)	2.33	541(71)	541	98(14)	270	–	–
O(6)	$\frac{1}{3}$	$\frac{2}{3}$	0.3763(6)	4.17	1104(164)	1104	148(29)	552	–	–
O(7)	0.2253(9)	0.5253(9)	0.3081(3)	4.65	945(129)	1081(140)	171(17)	225(102)	− 71(35)	−152(37)
$H_2O(8)$	0.3324(9)	0.3563(9)	0.2876(3)	5.94	2606(183)	1953(150)	98(13)	1400(132)	− 79(30)	− 40(29)
$H_2O(9)$	0.4137(8)	0.3088(9)	0.3727(3)	5.01	1486(122)	1823(130)	156(12)	1172(105)	−188(30)	−129(30)
H(1)	0.330	0.352	0.558							
H(2)	0.123	0.151	0.432							
H(3)	0.343	0.528	0.415							
H(4)	0.365	0.415	0.405							
H(5)	0.303	0.413	0.289							
H(6)	0.420	0.398	0.306							
H(7)	0.312	0.252	0.368							
H(8)	0.506	0.317	0.378							

on this synthesis were assigned to As – As, As – S, and As – O vectors. The coordinates of As and S, together with five oxygens and the two asymmetric Cu atoms, were used as a starting point for structure factor calculation. The Al atom and the remaining four oxygen atoms were located from Fourier syntheses, and the initial R index of 0.33 lowered to 0.18.

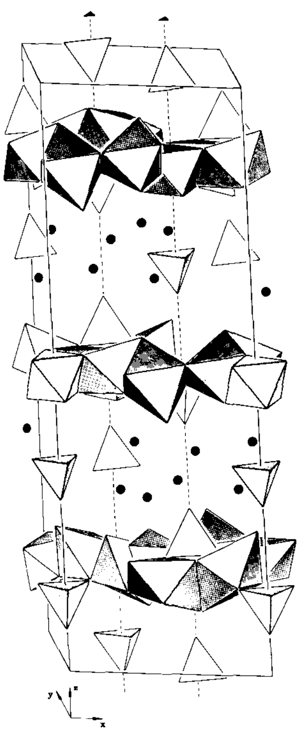
During three full-matrix isotropic ($R = 0.13$) and one anisotropic ($R = 0.08$) cycles of refinement the temperature factor for S atom and for the oxygen atoms of the tetrahedron, namely O(6) on the three fold axis and O(7) triplicated by the same axis, was observed to increase steadily to values too high for such atoms. This increase led to an attempt to refine the site occupancy of atoms of the SO_4 group. The S site occupancy lowered to values close to 0.75 while only a little decrease for O(6) and O(7) occurred. The R index dropped to 0.068. At this stage a final electron density difference map gave useful indication for positioning five out of the eight hydrogen atoms in the structure. The remaining three H atoms, all falling in positive but too wide areas, were placed in calculated positions at about 1 Å from the donor atom and approximately along the donor-acceptor line. Because of inconsistencies in their shifts, the H atom positions could not be refined and their temperature factors were fixed at 4 $Å^2$. The last cycle of refinement resulted in a final R index of 0.056 for the 978 'observed' reflections ($R = 0.068$ for all data).

Positional and thermal anisotropic parameters along with their standard deviations are given in Table 1. Observed and calculated structure factors were deposited at Akademische Verlagsgesellschaft, Wiesbaden.

Description and discussion of the structure

As already mentioned, the Cu atoms form edge-sharing polyhedra arranged in sheets parallel to (001), at $z = \frac{1}{6}, \frac{1}{2}$, and $\frac{5}{6}$ (Fig. 2). The two independent Cu polyhedra exhibit the well known tetragonal distortion due to the Jahn-Teller effect, with bond lengths (Table 2) in good agreement with other structure determinations. The equatorial atoms of Cu(1) polyhedron, on an inversion center, are two oxygens and two hydroxyl oxygens (mean distance of 1.966 Å) while the ones of Cu(2), in a general position, are one oxygen and three hydroxyls (mean distance of 1.969 Å). The axial bonds, which involve two water oxygens for Cu(1) and a hydroxyl and a water oxygen in the Cu(2) polyhedron, range from 2.416 to 2.486 Å. A considerable angular distortion can be observed mostly for the Cu(2) polyhedron, as evidenced by the O_{eq} – Cu – O_{axial} angles scattered in the range from 71.5 to 112.7°. This distortion is to be ascribed to the geometrical requirements of Al octahedra inserted within the sheets and of As tetrahedra stuck above and below them (Figs. 2 and 3).

As illustrated in Fig. 4 the Cu – O sheet in chalcophyllite has 3 unoccupied octahedral sites out of 12 available positions per unit cell. These holes house



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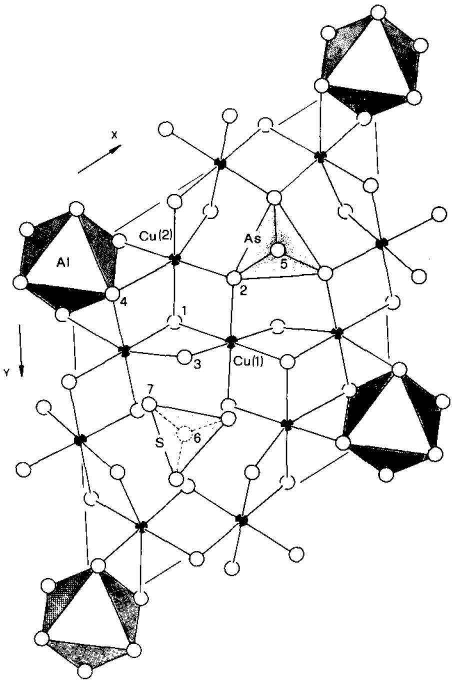

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Fig. 2. A view of the layer structure of chalcophyllite. On the edges of the unit cell two Al octahedra among the Cu polyhedra of the intermediate sheet are represented. The As tetrahedra are attached above and below the sheets while the S tetrahedra and water molecules (solid circles) are located in between. Dashed lines indicate the threefold axes inside the unit cell.

Fig. 3. Atomic connection viewed along the *c* axis. Free water oxygens and hydrogen atoms are missing. The atom numbering is that of Table 1

the threefold axes of the structure. The Al atom lies on the $\bar{3}$ point symmetry and so it binds six hydroxyl groups OH(4) to form a nearly regular octahedron participating in the sheet. The As atom is situated on the 3 point symmetry, just a little off the sheet, and binds three O(2) oxygens, bonded also by Cu(1) and Cu(2), and the O(5) oxygen outside the sheet. The As tetrahedra so formed are alternatively disposed above and below the sheet. The Cu–Cu approaches between neighboring ions are 3.001 and 3.184 Å for two different Cu(1)–Cu(2) distances and 3.161 Å for one Cu(2)–Cu(2) distance; the Cu(2)–Al distance is 3.147 Å.

Sheets of edge-sharing Cu coordination polyhedra are present in other basic copper minerals, but the sheet-type found in chalcophyllite shows a greater complexity and it is quite new. The Cu–O sheets in serpierite

Table 2. Distances (Å) and angles (°) in the coordination polyhedra

Cu(1) polyhedron	
Cu(1)−OH(1)	1.945(4) × 2
Cu(1)−O(2)	1.987(5) × 2
Cu(1)−H_2O(3)	2.416(6) × 2
OH(1)−Cu(1)−O(2)	81.4(2)
OH(1)−Cu(1)−H_2O(3)	83.3(2)
OH(1)−Cu(1)−O(2,1)	98.6(2)
OH(1)−Cu(1)−H_2O(3,1)	96.7(2)
O(2)−Cu(1)−H_2O(3)	90.5(2)
O(2)−Cu(1)−H_2O(3,1)	89.5(2)

Cu(2) polyhedron	
Cu(2)−OH(4,6)	1.951(3)
Cu(2)−O(2)	1.968(4)
Cu(2)−OH(1,6)	1.980(3)
Cu(2)−OH(1)	1.997(5)
Cu(2)−OH(4)	2.466(5)
Cu(2)−H_2O(3,6)	2.486(6)
OH(1)−Cu(2)−O(2)	80.5(2)
OH(1)−Cu(2)−OH(4)	73.3(2)
OH(1)−Cu(2)−OH(1,6)	169.0(2)
OH(1)−Cu(2)−H_2O(3,6)	109.2(2)
OH(1)−Cu(2)−OH(4,6)	96.8(1)
O(2)−Cu(2)−OH(4)	112.7(2)
O(2)−Cu(2)−OH(1,6)	94.8(2)
O(2)−Cu(2)−H_2O(3,6)	91.9(2)
O(2)−Cu(2)−OH(4,6)	174.0(2)
OH(4)−Cu(2)−OH(1,6)	97.6(2)
OH(4)−Cu(2)−H_2O(3,6)	155.5(1)
OH(4)−Cu(2)−OH(4,6)	71.5(2)
OH(1,6)−Cu(2)−H_2O(3,6)	80.8(2)
OH(1,6)−Cu(2)−OH(4,6)	88.9(1)
H_2O(3,6)−Cu(2)−OH(4,6)	83.9(2)

Al octahedron	
Al−OH(4)	1.903(4) × 6
OH(4)−OH(4,5)	2.765(5)
OH(4)−OH(4,6)	2.615(6)
OH(4)−OH(4,8)	2.766(6)
OH(4)−Al−OH(4,5)	93.2(2)
OH(4)−Al−OH(4,6)	86.8(2)

As tetrahedron	
As−O(2)	1.682(5) × 3
As−O(5)	1.617(9)
O(2)−O(5)	2.737(9)
O(2)−O(2,4)	2.699(7)
O(2)−As−O(5)	112.1(2)
O(2)−As−O(2,4)	106.7(2)

S tetrahedron	
S−O(7)	1.467(8) × 3
S−O(6)	1.450(16)
O(6)−O(7)	2.391(8)
O(7)−O(7,3)	2.384(7)
O(6)−S−O(7)	110.2(4)
O(7)−S−O(7,3)	108.8(5)

Symmetry code			
none	x	y	z
1	$1-x$	$1-y$	$1-z$
2	$\frac{1}{3}-x$	$\frac{2}{3}-y$	z
3	$1-y$	$1+x-y$	z
4	$1-y$	$x-y$	z
5	$-y$	$x-y$	z
6	y	$-x+y$	$1-z$
7	$\frac{1}{3}+y$	$\frac{2}{3}-x+y$	$\frac{2}{3}-z$
8	$-x+y$	$-x$	z

The second numbers in atom specifications refer to symmetry operations

$Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$ (Sabelli and Zanazzi, 1968) and devillite $CaCu_4(OH)_6(SO_4)_2 \cdot 3H_2O$ (Sabelli and Zanazzi, 1972) have the Cu sites completely occupied, with repetition unit ${}^2_\infty[Cu_2(OH)_3O]^-$. The same crystal-chemical formula characterizes the sheets found in ktenasite $Zn_2(Cu,Zn)_8(SO_4)_4(OH)_{12} \cdot 12H_2O$ (Mellini and Merlino, 1978), while the sheets of posnjakite $Cu_4(SO_4)(OH)_6 \cdot H_2O$ (Mellini and Merlino, 1979) have repeat unit ${}^2_\infty[Cu_4(OH)_6(H_2O)O]$. Except for a partial substitution of Cu for Zn in serpierite and ktenasite and of O for H_2O in posnjakite, the crystal-chemical formulae of these continuous sheets are the same. In chalcophyllite, on the contrary, one quarter of the sheet sites is free of Cu allowing Al to take

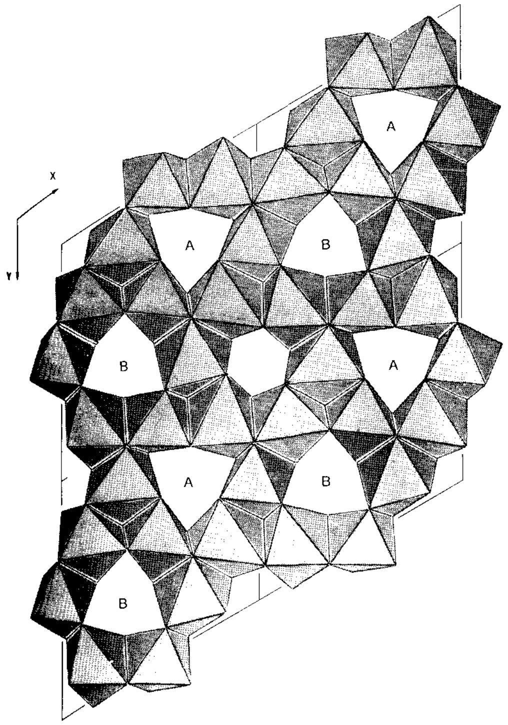

Fig. 4. The sheet of Cu polyhedra at $z = \frac{1}{2}$ through 4 unit cells. Only 9 out of 12 possible octahedral sites in each unit cell are occupied by Cu atoms. The Al octahedra are located within the sheet, on the threefold axes at the origin of the unit cells (in the holes with an hexagonal outline). The As tetrahedra, on the threefold axes at $x = \frac{2}{3}$ and $y = \frac{1}{3}$, are attached by three vertices above the sheet (*A* positions) and at $x = \frac{1}{3}$ and $y = \frac{2}{3}$ below the sheet (*B* positions)

place inside the sheet; As clings to the same sheet by one face of its tetrahedron. While Al atoms are therefore to be considered to participate strictly in the sheet, it is questionable if As tetrahedra too form a part of the sheet or if they are to be regarded as appendices. Not considering As atoms as belonging to the sheet, the crystal-chemical formula can be written ${}^{2}_{\infty}[Cu_9Al(OH)_{12}(H_2O)_6O_6]^{-3}$.

With regard to SO_4 tetrahedron, the mean S – O bond length of 1.463 Å is quite similar to 1.473 Å, the average S – O distance of well-refined structures of hydrated sulphates (Baur, 1964). The SO_4 groups are inserted (Figs. 2 and 5) between the Cu – Al sheets, together with the two free water molecules of the structure. A third water molecule, $H_2O(3)$, belongs to the sheet and its oxygen is the farthest atom coordinated both by Cu(1) and Cu(2). As can be seen in Fig. 5 the H-bonding system is of particular relevance for the cohesion of the structure. On the whole there are two free water molecules, one ligand water and two hydroxyls which supply the nine H-bonds of the asymmetric

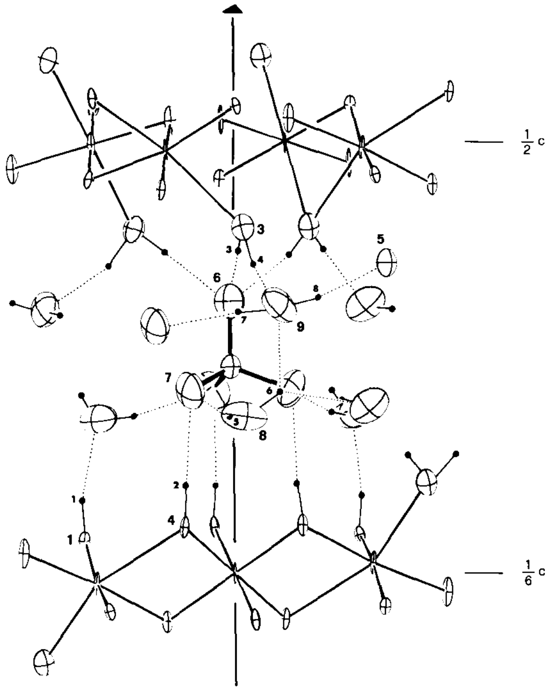

Fig. 5. Surroundings of a SO_4 group, placed between two adjacent Cu – Al sheets on a threefold axis. Dots represent the H atoms and dotted lines indicate the H bonds. Thermal ellipsoids for all atoms represent the 50% probability surfaces

unit (Table 3). There is an H-bond exceeding the eight independent hydrogens because the bond provided by H(6), belonging to $H_2O(8)$, was found to be most likely bifurcated on the basis of two possible donor(D)-acceptor(A) distances. Even the two related $A-D-A$ angles are close to the water angle. The overall $D-A$ average distance is 2.80 Å, the individual values ranging from 2.66 to 3.03 Å. Only four of these distances are to be considered strong bonds after Brown's (1976) criterion, which fixes 2.73 Å as the threshold between strong and weak H-bond.

Beside the greater complexity of chalcophyllite sheets in respect to the ones found in related basic copper sulphates, another important difference is provided by the position of SO_4. In other minerals the SO_4 groups are always linked to the sheet by corner sharing: on one side in langite $Cu_4(OH)_6SO_4 \cdot H_2O$ (Wappler, 1971) and in posnjakite and on both sides in serpierite, devillite, and ktenasite, while in chalcophyllite they are isolated groups. This particular feature of the sulphate group, isolated and 'trapped' in a close net of H-bonds, is similar to the one observed in the structures of alunogen, the most hydrated aluminum sulphate (Menchetti and Sabelli, 1974), of apjohnite $MnAl_2(SO_4)_4 \cdot 22H_2O$, a member of the halotrichite

Table 3. Hydrogen bonds in chalcophyllite

Donor atom (D)	Hydrogen atom	Acceptor atom (A)	Distance (Å)			Angle (°)		
			D...A	D–H	H...A	D–H...A	A...D...A	H–D–H
OH(1,1)	H(1)	$H_2O(8,7)$	2.70(1)	0.87	1.85	165	–	–
OH(4)	H(2)	O(7,2)	3.03(1)	0.92	2.11	175	–	–
$H_2O(3)$	H(3)	O(6)	2.83(1)	0.93	1.90	179		
$H_2O(3)$	H(4)	$H_2O(9)$	2.70(1)	1.01	1.74	158	103.5(4)	91
$H_2O(8)$	H(5)	O(7)	2.66(2)	0.82	1.86	165		
$H_2O(8)$	H(6)	O(9)	2.73(1)	0.97	2.12	118	102.7(4)	106
		O(9,7)	2.94(1)		2.17	135	100.8(3)	
$H_2O(9)$	H(7)	O(7,4)	2.88(1)	0.96	1.92	179		
$H_2O(9)$	H(8)	O(5)	2.75(1)	0.96	1.80	165	150.6(4)	151

series (Menchetti and Sabelli, 1976), and of aluminite $Al_2(OH)_4(SO_4) \cdot 7\,H_2O$ (Sabelli and Trosti Ferroni, 1978).

As can be seen in Fig. 5 there is a strong difference in the thermal behaviour of the SO_4 tetrahedron and free water oxygens in respect to the atoms of Al and Cu polyhedra. The noticeable thermal motion affecting the atoms of the 'soft' part of the structure in comparison with the layer atoms, constituting the 'rigid' part, accounts for a clear weakness of the inter-sheet portion of the structure.

Furthermore, as observed during the last stage of the refinement, the site of the S atom is 75 % statistically occupied, while the O(6) and O(7) oxygens of the tetrahedron vary in their occupancies from 0.75 to 1.0. As the S site, even the O(6) and O(7) sites are most likely occupied at 75 %, meaning 1.5 instead 2 SO_4 groups in the formula units as the charge equilibrium needs. The relatively greater O(6) and O(7) site occupancies found in the refinement can be explained as a probable partial substitution of tetrahedral oxygens for additional water molecules. On the basis of the observed electron density residual areas on the ΔF maps, it is possible also for this replacement to take place in positions slightly shifted with respect to the ones found for O(6) and O(7).

As concerns the change of the atomic arrangement responsible of the twinning, it appears clearly that the (100) twin plane pre-exists as a 'pseudo' symmetry operator in the Cu – Al sheets, owing to the particular coordinates of atoms involved, so that the sheets of an individual of the twin are practically interchangeable with those of its mate. The real change of the structure takes place in the 'soft' part of the structure, starting from the As tetrahedra forced by the twin operator to cling to the same side of the sheet; therefore at the twin boundary this portion of the structure becomes mirrored instead of being inverted as the true symmetry of chalcophyllite requires.

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