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CRYSTAL STRUCTURES AND MINERAL CHEMISTRY OF DOUBLE-SALT HYDRATES: I. DIRECT DETERMINATION OF THE CRYSTAL STRUCTURE OF TAMARUGITE

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Abstract

The structure of tamarugite, $NaAl(SO_4)_2 \cdot 6H_2O$, has been solved by reiterative application of Sayre's equation using three-dimensional photographic and counter data. The final R value is 7.3 percent (hydrogens included). The coordination polyhedra of sodium and sulphur are joined to form infinite chains parallel to c. The perfect (010) cleavage traverses only weak hydrogen bonds. The mean distances are: Na-O = 2.415 Å, Al-Ow = 1.883 Å, S-O = 1.488 Å, and Ow-O = 2.65 Å. The $Al(H_2O)_6$ octahedron and the two independent SO_4 tetrahedra are regular but the NaO_6 group deviates considerably from a regular octahedron.

Introduction

This study is the first of a series designed to elucidate the mineral structural chemistry of the double sulfate hydrates. Tamarugite was chosen because (1) optical and preliminary X-ray data have been reported by us (Robinson, Fang, and Bloss, 1967) and (2) tamarugite is a dehydration product of Na-alum whose dehydration mechanism we plan to investigate in our laboratory. Analysis by the direct method was desirable because the atoms are near enough in atomic numbers to make a Patterson approach difficult.

The crystals, from Alcaparrosa, Chile, were obtained from the U. S. National Museum, Smithsonian Cat. No. R 9117.

Crystal Data

$a = 7.353 \pm .002$ Å	Space group $P2_1/a$
$b = 25.225 \pm .005$ Å	$Z = 4$
$c = 6.097 \pm .002$ Å	D (calc) = 2.066 g/cm^3
$\beta = 95.2 \pm .1°$	D (meas) = 2.06 ± .01 g/cm^3

Intensity Measurements and Corrections

The crystal used in the analysis was a singly terminated prism, with dimensions 0.32×0.14×0.13 mm., mounted normal to its [001] elongation direction, the b axis coinciding with the axis of crystal rotation. Initially, intensities were collected by the standard multiple-film Weissenberg technique and were corrected for α_1–α_2 separation, Lorentz polarization and absorption.

At a later date, data collection was carried out using a 0.01 incrementing Buerger automated diffractometer and CuKα radiation. Crystal orientation and system stability was monitored by measurement of a standard reflection before and after each level. The reflections thus collected were then corrected for Lorentz polarization and absorption.

Any reflection which did not meet the condition $(C-\text{Bkgd}) \geq 3.0 * (C+\text{Bkgd})^{\frac{1}{2}}$ was rejected. During final refinement 3 sigma weighting was applied where

$$\sigma = F^2/2.0 * (C - \text{Bkgd}) * \sqrt{C + (t)(\text{Bkgd}) + (0.03[C + \text{Bkgd}])^2}$$

F^2 = Intensity corrected for Lorentz polarization and absorption

Bkgd = $(B_1 + B_2)^* t$

t = Scan time/2.0 * Bkgd time

C = Total integrated counts during scan

B_1, B_2 = background

DETERMINATION OF THE STRUCTURE

The structure was solved by reiterative application of Sayre's equation (Sayre, 1952). First, observed structure factors F_{h} are normalized to $E^2_{\text{h}}=1$, where

$$E^2_{\text{h}} = F^2_{\text{h}}/\epsilon \sum_{j=1}^{N} f^2_{j,\text{h}}$$

For the primitive monoclinic cell, $\epsilon=2$ for $0k0$ and $h0l$ reflections and $\epsilon=1$ for other reflections (Hauptman and Karle, 1959), and the sum of the squares of atomic scattering factors f_j extends over the N atoms of the unit cell. Second, the E_{h} are ordered in decreasing magnitude of

$$|E_{\text{h}}| \sum_{\text{h}'} |E_{\text{h}'}|\,|E_{\text{h}+\text{h}'}|,$$

and the three largest normalized structure factors which are linearly independent (Woolfson, 1961) are arbitrarily assigned a positive value in order to determine the origin. Third, the next n (n usually 4) strong reflections are given assumed signs. Fourth, the Sayre's equation is reiteratively applied to each of these starting sign sets, yielding 2^n solutions. The signs are calculated for reflections with $E \geq 1.5$ (in our case, the number of reflections with $E \geq 1.5$ is 161). The statistical averages for the normalized structure factors are listed in Table 1. Fifth, when each iterative process gives no more sign changes, then consistency index, C, defined as (Long, 1965).

$$C = \left\langle \left| E_h \sum_{h'} E_{h'} E_{h+h'} \right| \right\rangle \Big/ \left\langle \left| E_h \right| \sum_{h'} \left| E_{h'} \right| \left| E_{h+h'} \right| \right\rangle$$

where the sums are all pairs of h' and $h+h'$, and where $\langle\ \rangle$ means the average over all values of h'. The highest index usually indicates the true solution.

Using a starting set of seven signs (three origin-determining signs which are arbitrarily assigned as positive) and four other reflections, sixteen possible starting sets were considered so that each possible sign combination of the remaining four signs could be tried. The first seven reflections used were;

Table 1. Experimental and Theoretical Values of Normalized Structure Factors

	Experimental	Centrosymmetric	Non-Centrosymmetric
$\langle \lvert E \rvert \rangle$	0.809	0.798	0.886
$\langle \lvert E^2-1 \rvert \rangle$	0.894	0.968	0.736
$\lvert E \rvert \geq 3.0$	0.29%	0.3%	
$\lvert E \rvert \geq 2.0$	4.0%	5.0%	
$\lvert E \rvert \geq 1.0$	30.6%	32.0%	

h	k	l	E
1	3	−1	2.53
5	2	3	3.01
1	6	0	1.88
1	3	1	−2.64
1	1	5	−2.92
5	8	1	−3.11
4	7	−4	3.18

An E map (a three-dimensional Fourier map with E values rather than F values for the coefficients) was made using the 161 signed values of E from the set with the highest consistency index. The peaks which appeared in this map, however, were not at all meaningful. Although the true solution will usually be the most consistent one (*i. e.* it will have the highest consistency index) this is not always the case (Karle and Karle, 1964). Therefore, several more maps were calculated in the hope that the true solution would reveal itself. Our efforts proved fruitless.

We then recalled that our previous space group determination of $P2_1/m$ (Robinson, Fang, and Bloss, 1967) was based on several very faint reflections ($h0l$, $h \neq 2n$) which appeared only on the longest exposure films (96 hrs). Assuming those reflections to be the result of Renninger

TABLE 2. A COMPARISON OF THE SIXTEEN SOLUTIONS

Set No.	Signs of the First Seven	No. of Cycles	Consistency Index
1	+++++++	5	0.54606
2	+−+++−+	7	.58606
3	−+−++−+	7	.38555
4	−−−++−+	5	.49047
5	++++−−+	7	.40548
6	+−++−++	14	.57018
7	−+−+−−+	5	.44438
8	−−−+−++	12	.39839
9	++++++−	5	.56505
10	+−+++−−	4	.38448
11	−+−+++−	6	.52119
12	−−−++−−	7	.57154
13	++++−+−	5	.53848
14	+−++−+−	5	.66262
15	−+−+−−−	3	.85319
16	−−−+−+−	8	.63047

effect, the space group then became $P2_1/a$. This assumption was confirmed by the successful structure determination in $P2_1/a$ and by the fact that the occurrence of the spurious reflections was found to be dependent on the wavelength and techniques used in the taking of the photographs. Recalculation of the 16 possible solutions in $P2_1/a$ led to set No. 15 (Table 2) as the most likely choice. Subsequent E map calculation revealed seventeen peaks (there are 18 atoms, hydrogen atoms excluded, in the asymmetric cell). The 18th peak was later found to be very closely associated and almost masked by the highest peak.

Table 3 gives the coordinates and relative heights of the peaks and identifies the corresponding atoms. The R factor using all reflections with the coordinates given in Table 3 was 27 percent.

REFINEMENT OF THE STRUCTURE

The structure was then refined using the atomic coordinates obtained from the E map. The film data were initially used, and when the counter data became available, the refinement was carried out with this new set of data. The various stages in the refinement are tabulated below.

	Film Data	Counter Data
No. of reflections:	1179	744
Weighting scheme:	unit weight	Prewitt and Burnham (1966)
R factor, %:	27	8.9
	17.5	7.9
	16.0	7.3
	15.9	
	13.9	

TABLE 3. POSITIONAL PARAMETERS OBTAINED FROM THE E MAP

x	y	z	Peak height	Atom
0.640	0.184	0.210	269	S(1)
.710	.016	.755	251	S(2)
.135	.145	.680	231	Al
.620	.051	.190	144	Na
.385	.130	.640	122	Ow(3)
.820	.167	.140	117	O(2)
.730	.043	.560	117	O(6)
.910	.151	.735	107	Ow(4)
.150	.104	.925	101	Ow(6)
.530	.039	.800	99	O(7)
.680	.217	.430	96	O(4)
.840	.040	.910	95	O(8)
.070	.095	.510	93	Ow(2)
.515	.141	.230	92	O(3)
.220	.204	.840	91	Ow(5)
.570	.228	.065	84	O(1)
.120	.194	.425	82	Ow(1)
.290	.042	.245	(80)	O(5)

The scale factors and the positional parameters were varied in the first 3 cycles (film data). In the last cycle, (film data) the individual temperature factors were also varied. When the counter data were employed, the *R* factor was improved by nearly 5 percent. All parameters were varied in the two cycles using the counter data. No hydrogen contributions were included. At this stage Fourier and difference Fourier syntheses were calculated with the signs given in the last cycle (counter data). The electron density map showed clearly resolved non-hydrogen peaks with correct relative heights. However, the positions of the hydrogen atoms were not apparent in the difference electron density map. Therefore the expected hydrogen positions were calculated by placing the hydrogen atoms 0.97 Å away from Ow on the line Ow-O. Using the hydrogen positions thus obtained, another cycle of least-squares refinement was carried out in which all the positional parameters, including those of hydrogen, were varied. However, the shifts of some hydrogen atoms were so large as to give unreasonable Ow to H distances. At this stage, we returned to the Fourier method, and a difference map was recalculated using only those reflections with $\sin\theta/\lambda \leq 0.36$, as there is very little or no hydrogen contribution above this value. Again, the hydrogen positions could not be ascertained from the difference map. On the assumption that the difficulty in finding the hydrogen positions might be due to large anisotropic motions of heavier atoms, we then refined the structure anisotropically for one cycle. (The *R*-factor dropped by 1.6%; however, the β_{ij}'s of 3 oxygen atoms did not pass the positive-definitive test). A difference map was computed from this cycle, and the hydrogen positions were obtained. Another cycle of isotropic refinement was carried out, in which all positional parameters and nonhydrogen temperature factors were varied. The *R*-factor decreased from 8.7 to only 8.4 percent. Although it cannot be claimed that the H atoms were "found," a positive residual of electron density is present at each of the calculated hydrogen positions. It is not unusual or surprising to find a structure in which the determination of hydrogen positions is hampered by the presence of so many heavier atoms. In this case, of the 180 electrons present in the asymmetric unit of atoms, only 12 are involved in determining the hydrogens positions. (Since the average contribution of any atom to an intensity is proportional to the square of the scattering factor of that atom, one may also say that the contributions of the hydrogen atoms compared with the rest of the atoms for any one intensity is approximately one half of one percent for tamarugite). The observed and calculated structure factors are listed in Table 4 which has been deposited with The American Society for Information Science, The National Auxiliary Publications Service.[1]

RESULTS AND DISCUSSION

The final parameters (Table 5) are based on the refinement of 744 reflections, and yield the interatomic distances and bond angles shown in Table 6. The standard errors include the effects of correlations between parameters. The only high correlation coefficient above 0.500 is 0.526 between the scale factor and the temperature factor of S(2). The stereoscopic pair of the structure is shown in Figure 1.

The structure can be envisioned as consisting of four components: an Na polyhedron, an Al $(H_2O)_6$ octahedron, and two independent (SO_4) tetrahedra. The Na-O distances of the Na polyhedron (six fold) all lie between 2.26 Å and 2.51 Å, in close agreement with those given in the literature (International Tables, 1962). However, the O-O distances in this polyhedron show a considerable spread of 2.41 Å to 4.04 Å. The two short O-O distances are the edges which are shared with the S(2) tetrahedra. The water molecules about the Al atom form a slightly distorted octahedron (Table 6b). The average Al-Ow distance of 1.883 Å is identical (within standard deviation) with that of Na-alum (Cromer, Kay and Larsen, 1967). One could infer that in the course of dehydration of Na-alum, $NaAl(SO_4)_2 \cdot 12H_2O$, to form tamarugite, the $Al(H_2O)_6$ octahedron

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[1] For detailed paper, extended version, or supplementary material, order NAPS Document No. 00283 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc. 22 West 34th Street, New York, N.Y. 10001; remitting $1.00 for microfiche or $3.00 for photocopies.

TABLE 5. ATOMIC COORDINATES, TEMPERATURE FACTORS AND STANDARD ERRORS[a]

Atom	x	y	z	B
Na	0.6169(7)	0.0525(3)	0.1950(9)	1.8(1)
Al	.1424(5)	.1454(2)	.6785(6)	0.9(1)
S(1)	.6427(5)	.1830(2)	.2097(5)	1.2(1)
S(2)	.7076(5)	.0204(2)	.7515(6)	1.2(2)
O(1)	.5594(12)	.2214(5)	.0424(14)	1.9(2)
O(2)	.8171(12)	.1621(5)	.1392(15)	1.9(2)
O(3)	.5159(13)	.1391(5)	.2373(16)	2.3(2)
O(4)	.6811(12)	.2112(5)	.4229(14)	1.8(2)
O(5)	.2929(13)	.0400(6)	.2612(15)	2.0(2)
O(6)	.7571(13)	.0421(5)	.5380(16)	2.1(2)
O(7)	.5208(12)	.0381(4)	.7938(14)	1.5(2)
O(8)	.8391(12)	.0384(4)	.9326(14)	1.5(2)
Ow(1)	.1232(12)	.1870(5)	.4182(14)	1.5(2)
Ow(2)	.0611(12)	.0881(5)	.4987(15)	1.8(2)
Ow(3)	.3837(12)	.1260(4)	.6365(14)	1.5(2)
Ow(4)	.9020(12)	.1636(4)	.7299(15)	1.4(2)
Ow(5)	.2358(13)	.2020(5)	.8446(15)	1.9(2)
Ow(6)	.1389(13)	.1000(5)	.9307(16)	2.4(2)

[a] In parentheses.

is little disturbed, if any. The octahedron is linked to ten S tetrahedra through hydrogen bonds.

Each of the two crystallographically independent SO$_4$ tetrahedra is bonded to Al octahedra through hydrogens, and, in addition, the S(2) tetrahedron shares an edge with the Na polyhedron. It is evident from Table 6a that the results are in excellent agreement with that of Na alum and other sulphate hydrates (Baur, 1964), except for the S(2)-O(5) distance of 1.525 Å. This lengthening of the bond may have some possible significance, although a rather high standard deviation (of 0.025 Å) obscures any definite conclusion. Reported S-O distances seldom exceed 1.50 Å. However, Cruickshank (1964) has given a value of 1.51 Å in mercallite KHSO$_4$.

The coordination polyhedra of Na and S(2) are joined alternately to form an infinite, zig-zag chain along the *c*-axis. In this chain, O(6) serves as a bridge, and O(7) and O(8) form an edge shared by the two polyhedra. There is another chain parallel to the *c*-axis which consists of Al and S(1) polyhedra linked by hydrogen bonds. The bonding between the two chains is also of the hydrogen bond type. In contrast to this bonding scheme in the *a*-*c* plane, the bondings in the direction parallel to *b* are weak; the coordination polyhedra are solely linked by hydrogen bonds near $b=\frac{1}{4}$(Fig. 3). This arrangement accounts for the perfect, but not

TABLE 6. INTERATOMIC DISTANCES AND ANGLES

(a) Tetrahedral coordination around S

S(1) Tetrahedron		S(2) Tetrahedron	
S(1)-O(1)	1.498±.024 Å	S(2)-O(5)	1.525±.025 Å
S(1)-O(2)	1.485	S(2)-O(6)	1.488
S(1)-O(3)	1.467	S(2)-O(7)	1.489
S(1)-O(4)	1.487	S(2)-O(8)	1.472
Mean	1.484	Mean	1.493
O(1)-O(2)	2.44±.09 Å	O(5′)-O(6)	2.45±.09 Å
O(1)-O(3)	2.42	O(5′)-O(7)	2.44
O(1)-O(4)	2.42	O(5′)-O(8)	2.45
O(2)-O(3)	2.41	O(6)-O(7)	2.44
O(2)-O(4)	2.41	O(6)-O(8)	2.42
O(3)-O(4)	2.41	O(7)-O(8)	2.41
Mean	2.42	Mean	2.44
O(1)-S(1)-O(2)	110±2°	O(5′)-S(2)-O(6)	109±2°
O(1)-S(1)-O(3)	110	O(5′)-S(2)-O(7)	108
O(1)-S(1)-O(4)	109	O(5′)-S(2)-O(8)	110
O(2)-S(1)-O(3)	110	O(6)-S(2)-O(7)	110
O(2)-S(1)-O(4)	109	O(6)-S(2)-O(8)	110
O(3)-S(1)-O(4)	109	O(7)-S(2)-O(8)	109
Mean	109	Mean	109

(b) Octahedral coordination around Al

Al-Ow(1)	1.897±.024 Å	Ow(1)-Al-Ow(2)	87±2°
Al-Ow(2)	1.878	Ow(1)-Al-Ow(3)	92
Al-Ow(3)	1.880	Ow(1)-Al-Ow(4)	90
Al-Ow(4′)	1.880	Ow(1)-Al-Ow(5)	92
Al-Ow(5)	1.845	Ow(2)-Al-Ow(3)	89
Al-Ow(6)	1.920	Ow(2)-Al-Ow(4′)	92
Mean	1.883	Ow(2)-Al-Ow(6)	89
		Ow(3)-Al-Ow(5)	88
Ow(1)-Ow(2)	2.59±.10 Å	Ow(3)-Al-Ow(6)	92
Ow(1)-Ow(3)	2.71	Ow(4′)-Al-Ow(5)	92
Ow(1)-Ow(4′)	2.67	Ow(4′)-Al-Ow(6)	86
Ow(1)-Ow(5)	2.62	Ow(5)-Al-Ow(6)	93
Ow(2)-Ow(3)	2.62	Mean	90
Ow(2)-Ow(4′)	2.69		
Ow(2)-Ow(6)	2.66		
Ow(3)-Ow(5)	2.59		
Ow(3)-Ow(6)	2.73		
Ow(4′)-Ow(5)	2.67		
Ow(4′)-Ow(6)	2.59		
Ow(5)-Ow(6)	2.73		
Mean	2.73		

TABLE 6. (*Continued*)

(c) Coordination around Na

Na-O(3)	2.328±.026 Å	Na-O(7″)	2.504±.026 Å
Na-O(5)	2.472	Na-O(7′)	2.510
Na-O(6)	2.261	Na-O(8′)	2.415
		Mean	2.415
O(3)-O(5)	3.00±.09 Å	O(5)-O(7′)	3.43±.09 Å
O(3)-O(6)	3.45	O(6)-O(7″)	3.41
O(3)-O(7′)	3.72	O(6)-O(8)	3.79
O(3)-O(8)	4.04	O(7″)-O(7′)	3.20
O(5)-O(6)	3.67	O(7″)-O(8)	3.83
O(5)-O(7″)	2.44	O(7′)-O(8′)	2.41
		Mean	3.36
O(3)-Na-O(5)	77±2°	O(5)-Na-O(7′)	87±2°
O(3)-Na-O(6)	97	O(6)-Na-O(7)	91
O(3)-Na-O(7′)	100	O(6)-Na-O(8)	108
O(3)-Na-O(8′)	117	O(7″)-Na-O(7′)	79
O(5)-Na-O(6)	102	O(7″)-Na-O(8)	101
O(5)-Na-O(7″)	59	O(7′)-Na-O(8′)	59
		Mean	90

(d) Water molecules

Ow(1)-O(4′)	2.60±.10 Å	Ow(4)-O(2′)	2.63±.10 Å
Ow(1)-O(2′)	2.77	Ow(4)-O(4)	2.65
Ow(2)-O(6′)	2.55	Ow(5)-O(1′)	2.62
Ow(2)-O(5)	2.63	Ow(5)-O(1″)	2.68
Ow(3)-O(7)	2.58	Ow(6)-O(5′)	2.69
Ow(3)-O(3)	2.72	Ow(6)-O(8′)	2.70
		Mean	2.65

easy, (010) cleavage, as well as the often tabular habit {010} of tamarugite.

Although there is an uncertainty in regard to the hydrogen positions the hydrogen bonding scheme as illustrated (Fig. 2) should approximate the true picture. This is evidenced by Table 6d. The Ow-O distances range from 2.6 Å to 2.8 Å, and each Ow is bonded to two oxygens of the sulfate groups. There are two more oxygens at much larger distances, *viz.*, one at 3.2 Å and the other at 3.4 Å. These cannot reasonably be considered as hydrogen bonded. No bifurcated bond such as found in leonhardite, $MgSO_4 \cdot 4H_2O$, exists in tamarugite.

During the discussions of this work, there have been several instances in which the desirability of further investigation has been apparent. One of these would be a neutron diffraction study of tamarugite in locating

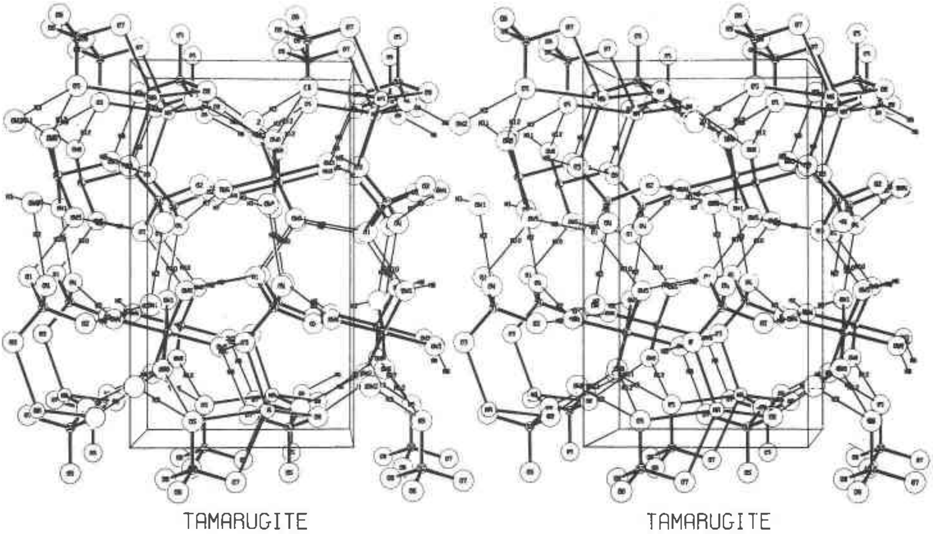

FIG. 1. Stereoscopic pair of the tamarugite structure (horizontal axis$=2a$; vertical axis $\approx b/2$; direction approximately normal to page$=c$; parallelpiped shown$=1a$, $\frac{1}{2}b$, $1c$.

hydrogen positions. Baur (1965) pointed out that the hydrogen positions can be calculated by considering only the electrostatic forces involved, and he has applied his MANIOC program to obtain the hydrogen positions in a number of single-sulphate hydrates. It would be of interest to extend his approach to double-salt hydrates. Aside from this, we plan to carry out dehydration studies of Na-alum to investigate the intermediate phase, mendozite, $NaAl(SO_4)_2 \cdot 11H_2O$ (?). It is of great interest to confirm or refute the existence of this species as well as to investigate the nature of the transformation mechanism. Also the crystal structure of the other end member, amarillite, $NaFe(SO_4)_2 \cdot 6H_2O$, might be determined. The mineral is reported in Dana's System of Mineralogy as having a different axial ratio from that of tamarugite. A complete structural analysis would yield important information in mineral chemistry regarding the differences in the electronic structures of Fe and Al.

COMPUTING METHODS

All computations were performed on an IBM 7040 at Southern Illinois University. The programs used were:

(1) α_1-α_2 intensity correction; CRAC by J. Cerven and P. Robinson, 1966.
(2) Diffractometer settings: TAPSET by D. Voet, 1966.
(3) Wilson plot and normalized structure factors; WILNORM by authors, 1967.
(4) Lorentz and polarization corrections: DSET4 by C. T. Prewitt, 1960.
(5) Absorption correction: GNABS by C. W. Burnham, 1966.

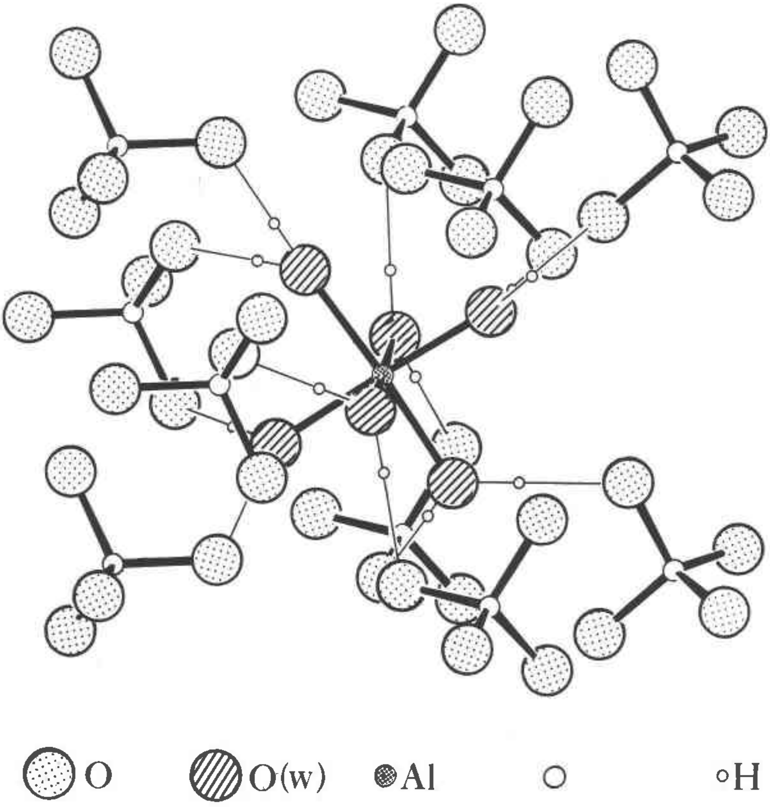

FIG. 2. Spatial arrangement of $Al(H_2O)_6$ octahedron and S tetrahedra.

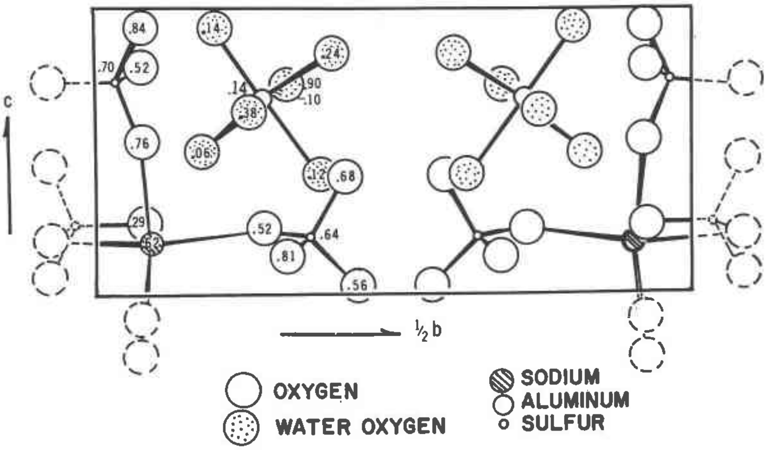

FIG. 3 Tamarugite structure projected on (100).

(6) Phase determination: by R. E. Long, 1965.
(7) Fourier summation: LOSA IV by Cromer, Larson and Roof, Los Alamos Scientific Laboratory, Los Alamos, N. M. 1965.
(8) Structure factors and least-squares: ORFLS by Busing, Martin, and Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1964.
(9) Structure factors and least-squares: BNLSI by W. C. Hamilton et al. Brookhaven National Laboratory, Upton, N. Y. 1965.
(10) Interatomic distances and angles; ORFFE by Busing, Martin, and Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1964.
(11) Stereo Plotting; ORTEP by Carrol K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1965.

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