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The crystal structure of spangolite, a complex copper sulfate sheet mineral

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Abstract

The crystal structure of spangolite, $Cu_6Al(SO_4)(OH)_{12}Cl\cdot 3H_2O$, trigonal, $a = 8.254(4)$ Å, $c = 14.354(8)$ Å, $V = 846.8(8)$ Å^3, space group = $P31c$, has been solved by direct methods and refined to an R index of 6.5% using Mo$K\alpha$ X-ray data. There are two distinct Cu positions, and each Cu^{2+} cation is coordinated by six anions in [4 + 2]-distorted octahedral arrangements typical of the Jahn-Teller-type distortion characteristic of divalent $^{[6]}$Cu. There is one distinct S position coordinated by a very regular tetrahedral arrangement of O anions, and one distinct Al position coordinated by a fairly regular octahedral arrangement of O anions. The Cl anion is only bonded to the Cu^{2+} cations.

The structure consists of an edge-sharing sheet of $Cu\phi_6$ and $Al\phi_6$ octahedra, decorated on one side by SO_4 tetrahedra. The $Cu\phi_6$ octahedra are associated together in edge-sharing trimers lying on threefold rotation axes; the sulfate tetrahedron links to the central anion on one side of this trimer. These clusters link outward by sharing edges with $Al\phi_6$ octahedra that lie on adjacent threefold axes, producing a continuous $M\phi_2$ sheet. These sheets then link along the **c**-axis by H-bonding between OH and H_2O anions of one sheet and sulfate O atoms of the adjacent sheet.

Introduction

Spangolite is a hydroxy-hydrated copper aluminum sulfate mineral. It is a widespread secondary mineral often associated with cuprite, tenorite, azurite, malachite, chrysocolla, and other less common copper oxysalts in secondary alteration zones around Cu deposits. Spangolite exhibits two distinct morphologies (Palache et al., 1951). It is commonly found as thin hexagonal plates or tablets with prominent {001} and minor {100} and {h01}. Less commonly, it is hemimorphic with well-developed (001) and {101} and minor or absent {100}. As part of a general study of copper oxysalt minerals, we have solved and refined the crystal structure of spangolite.

Experimental

The crystals used in this work are from Majuba Hill, Nevada. The material is very delicate. Spangolite has a perfect {001} cleavage and usually occurs as thin plates. X-ray diffraction patterns of such plates generally showed smeared reflections suggestive of displacement between subdomains in the crystal; such displacement may have been engendered by handling or by the stress caused by the drying of the glue that was used to attach the crystals to a glass fiber. We finally obtained some crystals that showed a hemimorphic habit with a small {100} prism and a well-developed {101} pyramid. Although these were also very delicate, we were able to obtain a crystal that had fairly sharp reflections.

This crystal was mounted on a Nicolet R3m automated four-circle diffractometer equipped with a Mo X-ray tube. Twenty-five reflections were measured on a random-orientation photograph and aligned automatically on the diffractometer. From the resulting setting angles, least-squares refinement gave the cell dimensions listed in Table 1, together with the orientation matrix. Intensity data were measured according to the procedure of Hawthorne and Groat (1985). A total of 5695 reflections was measured to a maximum 2θ angle of 60°. Ten strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector). These data were used to calculate an absorption correction, modeling the crystal as an ellipsoid and reducing the azimuthal R index from 6.5 to 3.7%; this correction was then used on the normal intensity data. Data were corrected for Lorentz and polarization effects, averaged, and reduced to structure factors; the R index for the averaging procedure was 4.4%. A reflection was considered as observed if its magnitude exceeded that

Table 1. Crystallographic data for spangolite

a (Å)	8.254(1)	Crystal size (mm)	0.24 × 0.26 × 0.30
c	14.354(3)	Radiation	Mo$K\alpha$
V (Å^3)	846.8(8)	Total $\|I\|$	5695
Space group	$P31c$	Unique $\|F_o\|$	1672
Final R (%)	6.5	No. of $\|F_o\| > 4\sigma$	1387

Unit-cell contents: $Cu_6Al(SO_4)(OH)_{12}Cl\cdot 3H_2O$

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Table 2. Atomic coordinates and displacement factors for spangolite

Atom	x	y	z	U_{eq}
Cu1	0.0915(2)	0.4649(3)	0	147(5)
Cu2	0.7979(2)	0.0405(2)	−0.0132(1)	137(4)
S	0	0	−0.2246(3)	283(12)
Cl	⅓	⅔	0.1495(4)	346(14)
Al	⅔	⅓	−0.0143(4)	122(10)
O1	0.1835(15)	0.0346(17)	−0.2593(7)	570(65)
O2	0	0	−0.1217(8)	212(30)
O3	0.8086(10)	0.2492(10)	−0.0830(5)	150(25)
O4	0.5283(11)	0.4121(10)	0.0584(5)	143(26)
O5	0.2962(10)	0.4517(10)	−0.0618(5)	158(29)
O6	0.0364(9)	0.2176(9)	0.0484(6)	140(27)
O7A	0.552(4)	0.0071(4)	0.255(1)	*471(38)
O7B	0.644(4)	0.097(3)	0.250(1)	*471(38)
H3**	0.81	0.25	0.85	120
H4**	0.53	0.41	0.13	120
H5**	0.30	0.45	0.87	120
H6**	0.04	0.22	0.12	120

* Constrained to be equal during refinement.
** Fixed during refinement.

Table 3. Selected interatomic distances (Å) and angles (°) in spangolite

Cu1-O4a	1.935(5)	Cu2-O3	1.957(9)
Cu1-O5	1.958(9)	Cu2-O5d	2.004(6)
Cu1-O5a	1.979(6)	Cu2-O6c	1.978(6)
Cu1-O6	1.979(8)	Cu2-O6d	1.977(8)
Cu1-O3b	2.425(7)	Cu2-O2c	2.424(7)
Cu1-Cl	2.835(4)	Cu2-O4d	2.352(9)
⟨Cu1-O⟩	2.185	⟨Cu2-O⟩	2.115
Cl-Cu1-O5	90.1(2)	O2c-Cu2-O3	93.5(3)
Cl-Cu1-O6	94.1(2)	O2c-Cu2-O5d	99.5(3)
Cl-Cu1-O4a	91.6(2)	O2c-Cu2-O6c	83.7(3)
Cl-Cu1-O5a	89.7(2)	O2c-Cu2-O6d	83.7(3)
O3b-Cu1-O5	106.2(3)	O3-Cu2-O4d	72.8(3)
O3b-Cu1-O6	77.0(3)	O3-Cu2-O5d	96.2(3)
O3b-Cu1-O4a	72.1(3)	O3-Cu2-O6c	89.3(3)
O3b-Cu1-O5a	101.0(3)	O4d-Cu2-O5d	76.7(3)
O5-Cu1-O6	82.1(3)	O4d-Cu2-O6c	101.7(3)
O5-Cu1-O5a	92.5(3)	O4d-Cu2-O6d	109.6(3)
O6-Cu1-O4a	97.4(3)	O5d-Cu2-O6d	81.0(3)
O4a-Cu1-O5a	87.9(3)	O6c-Cu2-O6d	93.7(4)
⟨O-Cu1-O⟩	90.1	⟨O-Cu2-O⟩	90.1
S-O1 × 3	1.480(12)	Al-O3 × 3	1.908(9)
S-O2	1.478(12)	Al-O4 × 3	1.886(9)
⟨S-O⟩	1.480	⟨Al-O⟩	1.897
O1-S-O1 × 3	109.3(4)	O3-Al-O3d × 3	95.7(3)
O1-S-O2 × 3	109.6(4)	O3-Al-O4d × 3	85.6(4)
⟨O-S-O⟩	109.5	O3-Al-O4e × 3	86.3(2)
		O4-Al-O4e × 3	92.4(2)
		⟨O-Al-O⟩	90.0
O3-H3f	0.97		
O4-H4	0.97	H4-O7Ae	1.88(2)
		H4-O7Be	1.87(2)
O4-H4-O7Ae	169(1)		
O4-H4-O7Be	162(1)		
O5-H5f	0.98	H5f-O7Ag	1.98(2)
		H5f-O7Bg	1.79(2)
O5-H5f-O7A	147(1)		
O5-H5f-O7B	165(1)		
O6-H6	0.98	H6-O1h	1.81(1)
O6-H6-O1h	171(1)		
Cl-O7Ae × 3	3.26(2)	Cl-O7Be × 3	3.51(2)
O1-O7Ai	3.01(4)	O1-O7Bj	2.93(3)
		O1-O7Bk	2.99(3)

Note: a: $y - x, 1 - x, z$; b: $x - 1, y, z$; c: $1 + x, y, z$; d: $1 - y, x - y, z$; e: $1 + y - x, 1 - x, z$; f: $x, y, z - 1$; g: $1 - x, 1 + y - x, -½ + z$; h: $y, x, ½ + z$; i: $y - x, -y, -½ + z$; j: $y, -x, -½ + z$; k: $-x, 1 - x + y, -½ + z$.

of 4 sd, based on counting statistics. Miscellaneous information pertaining to data measurement and structure refinement is given in Table 1.

Structure solution and refinement

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). R and R_w (statistical weights) indices are of the conventional form and are given as percentages.

The structure was solved by direct methods. The E statistics indicated that the structure was centrosymmetric, and initially we looked for a solution in space group $P\bar{3}1c$. However, we could only get a partial solution, and eventually we decided to go with the morphological indication that the structure lacks a center of symmetry. We obtained a solution in space group $P31c$, and this refined to an R index of ~7% for the observed reflections. At this stage, all displacement factors were anisotropic except that of O7, which was very large. When an anisotropic displacement factor was used for O7, the component in (001) became very large, suggesting positional disorder. Accordingly, the O7 atom was split into two half-atoms. Similarly, the component of displacement of the O1 atom in the (001) plane was also unusually large, but difference Fourier maps suggested a range of positions. Refinement was therefore continued with an anisotropic displacement factor for O1 rather than with a split atom model. The refinement of the structure converged to an R index of 6.7%. At this stage, difference Fourier maps indicated the positions of the H atoms bonded to the anions O3, O4, O5, and O6. These were inserted into the refinement but refined to anomalously short O-H distances, as is often the case for structure refinement of H positions with X-ray diffraction data. That made the interpretation of the H-bonding relationships confusing, and hence the H atoms were inserted into the refinement at fixed positions ~1.0 Å from the donor O atoms. The final R index was 6.7%. This is significantly higher than is usually obtained for well-ordered structures and may be the result of damage to the very delicate crystals during the experimental work.

Final atomic positions and isotropic displacement factors are given in Table 2; selected interatomic distances and angles are given in Table 3; observed and calculated structure factors together with the anisotropic displacement factors are listed in Table 4[1]; and empirical bond-valences are shown in Table 5.

[1] A copy of Table 4 may be ordered as Document AM-93-524 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 5. Empirical bond-valence table for spangolite

	Cu1	Cu2	Al	S	H3	H4	H5	H6	H7*₁	H7*₂	Sum
O1				1.481 ×3→				0.3		0.2	1.981
O2		0.127 ×3↓		1.490							1.871
O3	0.126	0.458	0.498 ×3→		1.0						2.082
O4	0.490	0.152	0.524 ×3→			0.8					1.966
O5	0.456 0.428	0.397					0.8				2.081
O6	0.248	0.429 0.431						0.7			1.988
O7						0.2	0.2		0.8	0.8	2.000
Cl	0.157 ×3↓								0.2 ×3↓		1.071
Sum	2.085	1.994	3.066	5.933	1.0	1.0	1.0	1.0	1.0	1.0	

* H atoms $H7_1$ and $H7_2$ are part of the H_2O group that occupies the O7 position. They were not located in the refinement procedure, but stereochemical considerations show that they must adopt the H-bond configurations shown here.

DISCUSSION

Local coordination

There are two unique Cu positions in the spangolite structure. Cu1 is coordinated by five O atoms and one Cl atom in a very distorted octahedral arrangement. Cu2 is coordinated by six O atoms in a distorted octahedral arrangement. Each $Cu\phi_6$ octahedron (ϕ = unspecified anion) has four short equatorial bonds (⟨1.963⟩ and ⟨1.979⟩ Å, respectively) and two long apical bonds (⟨2.360⟩ and ⟨2.388⟩ Å, respectively). This is the typical Jahn-Teller-type distortion found for $^{[6]}Cu^{2+}$: in a symmetric arrangement, there is an electronic degeneracy, and the local structure spontaneously distorts to relieve this degeneracy. The $Cu\phi_6$ polyhedra also show strong angular distortions (Table 3), the larger deviations from 90° tending to involve apical-equatorial bonds. However, when Cl is the apical ligand, the apical-equatorial bond angles are fairly close to their ideal values of 90°.

S is tetrahedrally coordinated with nearly ideal T_d symmetry, reflecting the unconstrained character of the interpolyhedral linkages involving the tetrahedron. Al is coordinated by six O atoms in an octahedral arrangement that is distorted from ideal O_h symmetry by contraction of edges shared with adjacent $Cu\phi_6$ octahedra. Cl is coordinated by three Cu1 cations, the $(ClCu_3)^{5-}$ groups forming a triangular pyramid.

Connectivity of the structural unit

Each Cu cation is in a general position and is coordinated to an anion on a threefold axis, and thus the rotation operations produce edge-sharing trimers of the form Cu_3O_{13} (Fig. 1). The $[Cu1_3(OH)_{12}Cl]^{7-}$ trimer lies on the threefold axis at ⅓ ⅔ z, and the $[Cu2_3(OH)_{12}O]^{8-}$ trimer lies on the threefold axis at 00z. These two distinct trimers knit together by sharing edges to produce an interrupted sheet of the form $[Cu_6(OH)_{12}OCl]^{3-}$, which contains octahedral interstices at ⅔ ⅓ z. These interstices are occupied by Al to produce a continuous edge-sharing sheet of octahedra with specific stoichiometry $[Cu_6Al(OH)_{12}OCl]^0$ and general stoichiometry $(M\phi_2)_7$. An SO_4 tetrahedron is attached to the single nonhydroxyl O atom of the $[Cu2_3(OH)_{12}O]^{8-}$ trimer to give the complete structural unit (Fig. 1), $Cu_6Al(SO_4)(OH)_{12}Cl$, an $M\phi_2$ sheet decorated on one side by TO_4 tetrahedra.

Bond-valence characteristics of the structural unit

The bond-valence table for spangolite, calculated with the values of Brown (1981), is shown in Table 5. It is fascinating how Nature manages to incorporate strong local Jahn-Teller distortions and a large anion such as Cl into the very simple stoichiometry of an $M\phi_2$ sheet and then link it to a very highly charged cation such as S^{6+}. In an $M\phi_2$ sheet, each anion is coordinated by three M cations. For simple divalent cations such as Mg in brucite, $Mg(OH)_2$, each cation contributes ~0.33 vu to each anion, and thus the local bond-valence requirements of the anions are satisfied by four bonds, 3 × 0.33 (Mg) + 1 × 1 (H) = 2 vu, with only very weak H bonding between the sheets. However, for a Jahn-Teller-type cation such as $^{[6]}Cu^{2+}$, the situation is very different. CuO_6 octahedra usually have four short equatorial bonds of ~1.97 Å and two long apical bonds of ~2.45 Å to O (longer to Cl, shorter to F), with bond valences of ~0.44 and ~0.13 vu, respectively. Thus there are four types of coordination possible for the anions of the sheet: (1) 0.13 × 3 = 0.39 vu; (2) 0.44 + 0.13 × 2 = 0.70 vu; (3) 0.44 × 2 + 0.13 = 1.01 vu; (4) 0.44 × 3 = 1.32 vu. If they are divalent, type 1 anions need an additional 1.61 vu and therefore must link to a $^{[4]}T^{6+}$ cation, the sulfate group in the case of spangolite. If they are monovalent (e.g., Cl^-), type 1 anions need an additional 0.61 vu. The only way in which this can be done is by H bonding. The usual strength of a H bond is ~0.20 vu (Brown, 1981; Hawthorne, 1992), and thus the monovalent type 1 anion needs three H bonds to satisfy its bond-valence requirements. Note that for both monovalent and divalent type 1 anions, the local bond-valence configurations and the local geometries both have trigonal symmetry. This corresponds to the O2 and Cl anions (Table 4) in spangolite. There are no type 2 anions in spangolite. Type 3 anions need an additional 0.99 vu to satisfy their bond-valence requirements. This is most easily done by bonding a H atom to the anion and having the H involved in only

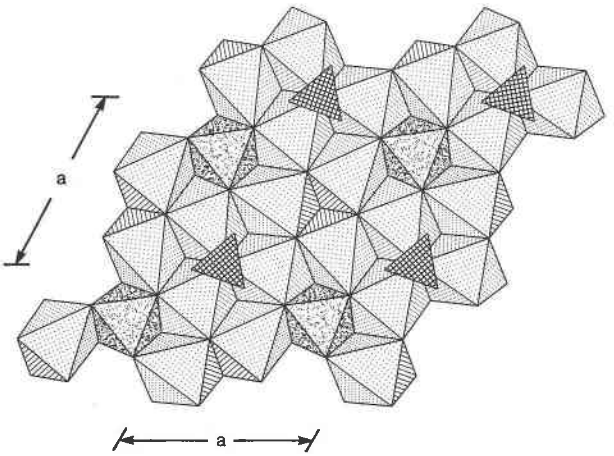

Fig. 1. The $Cu_6Al(SO_4)(OH)_{12}Cl$ sheet in spangolite viewed along [001]; $Cu\phi_6$ octahedra are shaded with dots in a regular pattern, $Al\phi_6$ octahedra are shaded in an irregular pattern, SO_4 tetrahedra are cross-hatched.

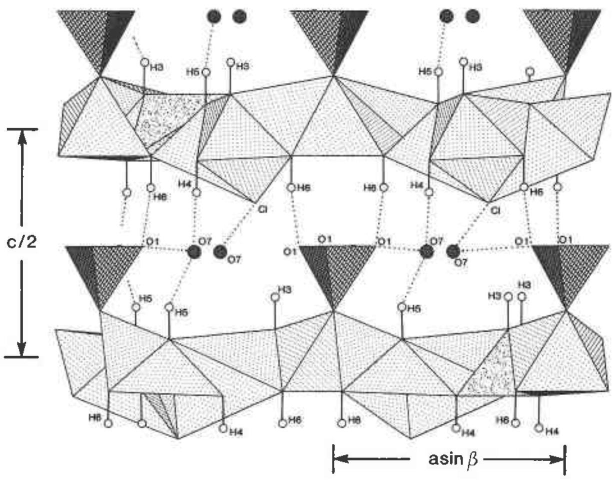

Fig. 2. The sheets in spangolite viewed down the **a** axis; shading as in Fig. 1, plus O7 (not split) atoms are shown as cross-hatched circles, H atoms are shown as small open circles, donor-H bonds as solid lines, and H-acceptor bonds as dotted lines.

weak H bonding. The O3 and O4 anions are of this type in spangolite. Type 4 anions need an additional 0.68 vu; this can be provided by bonding a H atom to the anion and having it involved in strong H bonding. The O5 and O6 anions (Table 4) are of this type.

It can be seen from this discussion that the cation occupancy pattern, anion type, and relative bond valences within the octahedral sheet in spangolite all fit together without obvious strain. Thus the incorporation of highly distorted $Cu^{2+}\phi_6$ octahedra into an $M\phi_2$ sheet is done without any obvious local strain or instability in the structure by a judicious combination of chemistry that complements the intrinsic bond-valence distribution in the distorted $Cu^{2+}\phi_6$ octahedra to produce satisfaction of all local bond-valence requirements throughout the sheet.

H bonding

The $Cu_6Al(SO_4)(OH)_{12}Cl$ sheets are linked solely by H bonds, accounting for the perfect {001} cleavage of spangolite. The H_2O group is not bonded directly to any cation (except H) but plays a crucial role in the H bonding between the sheets (Fig. 2). The O4 and O5 anions act as H-bond donors, with H4 and H5 bonding to the interstitial H_2O groups. One H atom of the H_2O group then forms an H bond across to a Cl atom in the adjacent sheet. The other H atom of the H_2O group forms an H bond to the O1 atom to the sulfate group (Fig. 2, Table 4). There is significant positional disorder associated with this H-bonding scheme, as both the H_2O and the sulfate groups show positional disorder. The origin of the positional disorder associated with the intersheet H bonding is not clear. This may be due to incomplete occupancy of the H_2O group, resulting in local rearrangements of the H-bonding scheme.

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