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Structure of Langite, $Cu_4[(OH)_6 | SO_4].2H_2O$

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Abstract. $M_r = 488{\cdot}29$, Pc, $a = 7{\cdot}137\,(3)$, $b = 6{\cdot}031\,(5)$, $c = 11{\cdot}217\,(1)$ Å, $\beta = 90{\cdot}00\,(1)°$, $V = 482{\cdot}8$ Å^3, $Z = 2$, $D_x = 3{\cdot}36$, $D_m = 3{\cdot}34$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 8{\cdot}78$ mm^{-1}, $F(000) = 476$, room temperature, 3093 unique reflections, $R = 0{\cdot}044$. The dominant structural feature is the arrangement of Cu—O polyhedra into dense sheets, parallel to (100). The sulphate groups are linked by a corner to one side of the sheets. Subsequent layers are connected to each other by hydrogen bonds. One water molecule is engaged in the Cu coordination, the other is attached between the sheets by hydrogen bonding.

Introduction. The crystal structure of langite was described by Wappler (1971) based on the chemical formula $Cu_4[(OH)_6 | SO_4].H_2O$. Wappler found double layers of close-packed OH^- ions with Cu^{2+} ions in octahedral interstices. Some of the anion sites are vacant causing two of the four Cu^{2+} ions to be really five-coordinated. Between the double layers there are SO_4 tetrahedra linked to one side of the layers by corner sharing. The tetrahedra are linked to one another by hydrogen bonds of water molecules and are also connected to the Cu–OH layers by hydrogen bonds.

Wappler used photographic data and two-dimensional Fourier syntheses for his investigation, so the accuracy of the structure determination is low ($R = 0{\cdot}14$) and there is some uncertainty as to the number and position of ligands.

Řidkošil & Povondra (1982) determined the chemical formula of natural langite from two localities in Czechoslovakia; they found it to be $Cu_4[(OH)_6 | SO_4].2H_2O$. The contents of two water molecules per formula unit had already been predicted by Dunn & Rouse (1975) and Mellini & Merlino (1979).

According to this information it seemed necessary to improve the structural description of langite.

Experimental. Natural crystal from Allihies Mine, County Cork, Ireland, 0·12 × 0·12 × 0·3 mm. D_m from Řidkošil & Povandra (1982). Syntex $P2_1$ diffractometer, Mo $K\bar{\alpha}$, graphite monochromator. Cell dimensions by least-squares refinement of 15 reflection angles. $\pm h, k, l$, $\sin\theta/\lambda \leq 0{\cdot}948$ Å^{-1}, ω–2θ scan. 3093 independent reflections, 2682 observed [$I > 1{\cdot}96\sigma(I)$]. Two standard reflections every 50 reflections, variation <2%. Absorption correction by the method of de Meulenaer & Tompa (1965). $w = 1/\sigma_F^2$. Scattering factors for Cu^{2+}, S, and O^- (*International Tables for X-ray Crystallography*, 1974). All calculations with the *XRAY* system (Stewart, 1976) on a Cyber 175 computer. For the solution of the structure the chemical composition $Cu_4[(OH)_6 | SO_4].H_2O$ (Pierrot & Sainfield, 1958; Wappler, 1971) was first assumed. Positions of Cu atoms by Patterson methods. Subsequent cycles of ΔF syntheses revealed the non-hydrogen atoms. At this stage of refinement (on F; $R = 0{\cdot}096$) one strong peak remained in the ΔF synthesis at $x, y, z = 0{\cdot}48, 0{\cdot}58, 0{\cdot}30$. Introduction of the O atom of a new interlayer molecule of H_2O as predicted by the chemical analysis reduced R to 0·082 and the peak disappeared. Anisotropic refinement of the temperature parameters and reflection weighting led to $R = 0{\cdot}047$ and $R_w = 0{\cdot}033$ (all reflections). Possible H positions were then calculated from shortest O—O distances. In final refinement cycle (isotropic temperature factor of H not refined) R dropped to 0·044, R_w to 0·031 (all reflections). Refinement of H-atom parameters results in too short O—H distances (down to 0·3 Å) owing to the mean positions of the electrons. Thus the bond lengths of hydrogen bonds were calculated using the unrefined H positions. Excursions on final $\Delta\rho$ map 0·26 to −0·39 e Å^{-3}. $(\Delta/\sigma)_{\max} = 0{\cdot}68$ for non-hydrogen atoms [x of O(7)], 2·17 for H atoms [z of H(5)]. Secondary-extinction coefficient $2{\cdot}64 \times 10^{-3}$, refined in *CRYLSQ*.

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Table 1. *Final atomic parameters (fractional* ×10⁴) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Cu(1)	0	−27 (1)	5000	0·8
Cu(2)	70 (1)	5081 (1)	4979 (1)	0·8
Cu(3)	−27 (1)	2448 (1)	2468 (1)	0·8
Cu(4)	−91 (1)	7456 (1)	2483 (1)	0·8
S	4226 (2)	1822 (2)	829 (2)	1·1
O(1)	4803 (6)	476 (7)	1861 (5)	2·1
O(2)	2173 (5)	2304 (5)	916 (4)	1·1
O(3)	5240 (5)	3938 (7)	792 (4)	2·0
O(4)	4598 (5)	9397 (7)	4720 (4)	2·2
O(5)	1391 (5)	7440 (6)	560 (4)	0·9
O(6)	8828 (6)	5100 (7)	6598 (5)	0·9
O(7)	8588 (5)	2463 (8)	9431 (4)	0·8
O(8)	1120 (6)	15 (6)	3398 (4)	0·9
O(9)	8754 (5)	60 (6)	6632 (4)	0·9
O(10)	1112 (6)	5040 (7)	8372 (4)	0·9
O(11)	7386 (5)	2620 (7)	4023 (5)	1·7
O(12)	4827 (7)	5795 (9)	3035 (5)	2·4

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu(1)–O(2)	2·332 (3)	Cu(2)–O(2)	2·418 (4)
Cu(1)–O(5)	1·942 (4)	Cu(2)–O(5)	1·920 (4)
Cu(1)–O(7)	1·918 (5)	Cu(2)–O(6)	2·020 (5)
Cu(1)–O(8)	1·966 (5)	Cu(2)–O(7)	1·921 (5)
Cu(1)–O(9)	2·035 (5)	Cu(2)–O(10)	1·951 (5)
Cu(1)–O(11)	2·670 (4)	Cu(2)–O(11)	2·650 (4)
Cu(3)–O(2)	2·346 (4)	Cu(4)–O(5)	2·363 (5)
Cu(3)–O(6)	1·952 (5)	Cu(4)–O(6)	1·989 (5)
Cu(3)–O(8)	1·978 (4)	Cu(4)–O(7)	2·380 (5)
Cu(3)–O(9)	1·981 (4)	Cu(4)–O(8)	2·046 (4)
Cu(3)–O(10)	1·996 (5)	Cu(4)–O(9)	1·958 (4)
Cu(3)–O(11)	2·542 (5)	Cu(4)–O(10)	2·000 (4)
S–O(1)	1·473 (5)	O(1)–S–O(2)	109·3 (3)
S–O(2)	1·496 (4)	O(1)–S–O(3)	111·3 (3)
S–O(3)	1·468 (4)	O(1)–S–O(4)	109·8 (3)
S–O(4)	1·469 (5)	O(2)–S–O(3)	108·4 (2)
		O(2)–S–O(4)	109·2 (2)
		O(3)–S–O(4)	108·8 (3)

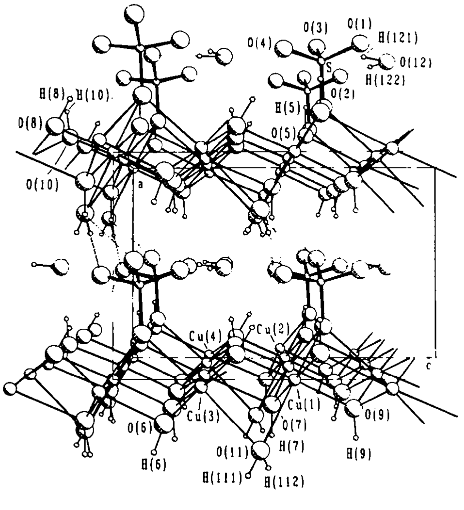

Fig. 1. Structure of langite as seen along **b**. Dashed lines are hydrogen bonds.

Discussion. Final atomic positional parameters and B_{eq} values for non-hydrogen atoms are listed in Table 1,* bond lengths and angles in Table 2.

The structure is made up of layers of six-coordinated Cu^{2+} ions parallel to (100) with anion sites occupied by OH^-, O^{2-}, and H_2O. The Cu^{2+} coordination is strongly distorted from an ideal octahedron owing to the Jahn–Teller effect. Sulphate tetrahedra are linked to one side of the pseudo-octahedral sheet by corner sharing. One of the two water molecules fills an anion site at the opposite side of the sheet; the other is attached between the sheets by hydrogen bonding. The connection between successive sheets is assured by hydrogen bonds.

Wappler assumed the cation O(11) to be a hydroxyl group instead of a water molecule, and he did not find the ligand at the O(5) position.

The crystal-chemical formula of the sheet is $^2_\infty[Cu_4(OH)_6|(H_2O)O]$ and is the same as determined for posnjakite (Mellini & Merlino, 1979). The difference between the two structures is the second molecule of water not linked to the sheets but involved in the hydrogen-bond system. This molecule induces a different connection between successive sheets and causes the monoclinic angle to change from 118° in posnjakite to 90° in langite.

Hydrogen-bond system and bond-valence balance. From all the distances between O atoms shorter than 3·2 Å and not belonging to the same polyhedron and on the basis of the balance of valences (details have been deposited) the hydrogen-bond network illustrated in Fig. 1 was derived. Acceptors in the hydrogen-bond system are the O atoms of the sulphate group not engaged in the Cu coordination [O(1), O(3), O(4)] and the O atom of the 'free' water molecule [O(12)]. One hydroxyl group [O(5)—H(5)] is not engaged in hydrogen bonding; one [O(7)—H(7)] forms a bifurcated hydrogen bond with O(3) and O(4).

The electrostatic valence was computed after Brown & Shannon (1973) with data from their Table 1 and the hydrogen-bond curve of Donnay & Donnay (1973).

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* Lists of anisotropic thermal parameters, H-atom parameters, remaining bond lengths and angles, structure factors, and a bond-valence summary have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39337 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dirhodium Triyttrium Disilicide, $Y_3Rh_2Si_2$

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Abstract. $M_r = 528{\cdot}7$, *Pbcm*, $a = 5{\cdot}5661\ (5)$, $b = 7{\cdot}7171\ (5)$, $c = 13{\cdot}043\ (1)$ Å, $V = 560{\cdot}26$ Å^3, $Z = 4$, $D_x = 6{\cdot}26$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 376{\cdot}1$ cm^{-1}, $F(000) = 940$, room temperature, final $R = 0{\cdot}045$ for 678 unique reflections. The structure is made of Y and Si trigonal prisms centred by Si and Rh atoms and can be derived from a hexagonal close-packed model using the concept of unit-cell twinning. The stacking of these units is the same as in binary alloys with Fe_3C- or Mn_5C_2-type structures.

Introduction. Structures of R_3M binary alloys of Fe_3C, Mn_5C_2 and CrB type have been studied (*e.g.* Moreau, Le Roy & Paccard, 1982). These structures can be derived from a hexagonal close-packed model through twinning of unit cells (Andersson & Hyde, 1974). Here, the study is extended to the three-component alloy $Rh_2Y_3Si_2$.

Experimental. Alloys made from commercially available elements of high purity (Y:99·9%, Rh:99·99%, Si:99·999%). Samples prepared by conventional arc-melting techniques. Small crystals of $Y_3Rh_2Si_2$ suitable for X-ray analysis isolated by mechanical fragmentation from crushed melt. Weissenberg photographs showed crystals to have space group *Pbcm* or $Pbc2_1$. Single crystal 40 × 60 × 80 μm, intensities measured with graphite-monochromated Mo $K\alpha$ radiation, CAD-4 Enraf–Nonius diffractometer, $\theta/2\theta$ scan mode; accurate cell dimensions by least-squares analysis of 25 θ values; three standard reflections monitored at intervals of 3600s, intensity variation during data collection <1%. Intensities of 1275 independent reflections, to limit of $\theta = 35°$, measured and corrected for background, Lorentz and polarization factors with *START* (Frenz, 1983). $0 \le h \le 8$, $0 \le k \le 12$, $0 \le l \le 20$. Structure solved by direct methods with *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Positions of Y, Rh and Si atoms revealed in corresponding *E* map for space group *Pbcm*. Full-matrix least-squares refinement of 36 positional and anisotropic thermal parameters converged after a few cycles using *F* values of 678 reflections* with $I > 3\sigma(I)$. $R = R_w = 0{\cdot}045$, Dunitz & Seiler (1973) weighting scheme where $w = \exp(36\sin\theta/\lambda)$ for each reflection. Zero Δ/σ in final least-squares cycle; peak height in final difference map $< |5{\cdot}0|$ e Å^{-3}. All calculations performed on PDP 11/23 computer using *SDP* (Frenz, 1983). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Atomic positions and equivalent isotropic temperature factors are listed in Table 1, interatomic distances are in Table 2.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39420 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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