

DETERMINATION OF THE CRYSTAL STRUCTURE OF LIROCONITE $\text{Cu}_2\text{Al}[\text{AsO}_4](\text{OH})_4 \cdot 4\text{H}_2\text{O}$

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Projections and sections of the Patterson function are used to determine the positions of the heavy atoms. The coordinates of the light atoms are derived from the three-dimensional electron-density distribution. The structure may be represented as a chain of Al octahedra linked by vertices to As tetrahedra, which are joined via paired Cu bipyramids.

This greenish-blue mineral belongs to the torquoise group. Our specimens (from Cornwall, Britain) were crystalline fragments of size 0.2 to 0.8 mm. Rotation and layer-line patterns (Weissenberg goniometer, Mo $K\alpha$ and Cu $K\alpha$) gave the cell parameters as $a = 12.64$, $b = 7.50$, $c = 9.86 \text{ \AA}$, $\beta = 91^\circ 18'$, which agree well with the values of [1, 2]. The unit cell contains four $\text{Cu}_2\text{Al}[\text{AsO}_4](\text{OH})_4 \cdot 4\text{H}_2\text{O}$ formula units. The absences indicate the x-ray group as $2/mI-a$, which includes space groups $I2/a$ and Ia . The statistics of the reflections of general type indicated the presence of a center of symmetry, which led us to choose group $I2/a$.

The As and Cu atoms led to hope that the Patterson function would solve the structure. The four As atoms can have only special positions in group $I2/a$, the most likely ones being on twofold axes. The $p(uv)$ Patterson projection (Fig. 1) showed that Cu lies in a general eightfold position with $x_{\text{Cu}} = 0.129$, $z_{\text{Cu}} = 0.261$.

The y coordinates of Cu and As were derived approximately from $p(uv)$. The strong peaks on the lines $u = 0$, $u = 0.121$, and $u = 0.242$ confirmed the x coordinates of the heavy atoms, but the y coordinates were found only roughly, because the two Cu-As peaks on the $u = 0.121$ line are replaced by one very strong one, from overlap of the two; this had $v \approx 0.208$, which gives $y_{\text{Cu}} \approx 0.250$ and $y_{\text{As}} \approx 0.042$. This explained why the lines $u = 0$ and $u = 0.242$ did not have two Cu-Cu' peaks, which both have $v = \frac{1}{2} - 2y_{\text{Cu}}$ but which differ by a factor two in weight: one of them coincides with the peak at the origin, and the other with the parameterless

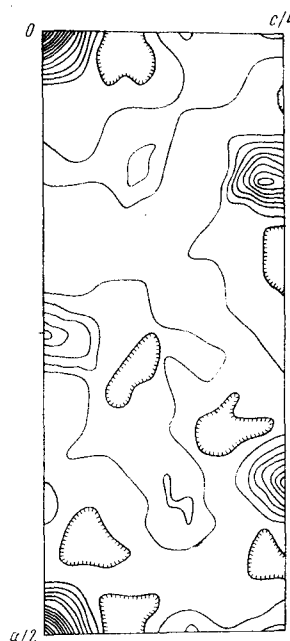


Fig. 1. The $p(uv)$ Patterson projection for liroconite.

(for this x_{Cu}) Cu-Cu' peak at $u = 0.242$, $v = 0$ (Fig. 2, a and b). The As-As' peak on $u = 0$ is represented by a peak of suitable height at $v = 0.402$, which gives $y_{\text{As}} = 0.049$. Further information was obtained from sections $P(\frac{1}{2}v, 0)$ and $P(0, 121v, 0.250)$ of the three-dimensional Patterson function. The y coordinates given by these were 0.048 (As) and 0.219 (Cu). Ordinary $\sigma(xz)$, $\sigma(xy)$ and weighted $\sigma_K(xz)$ ($K = 1, 2, 3, 4$) projections of the electron

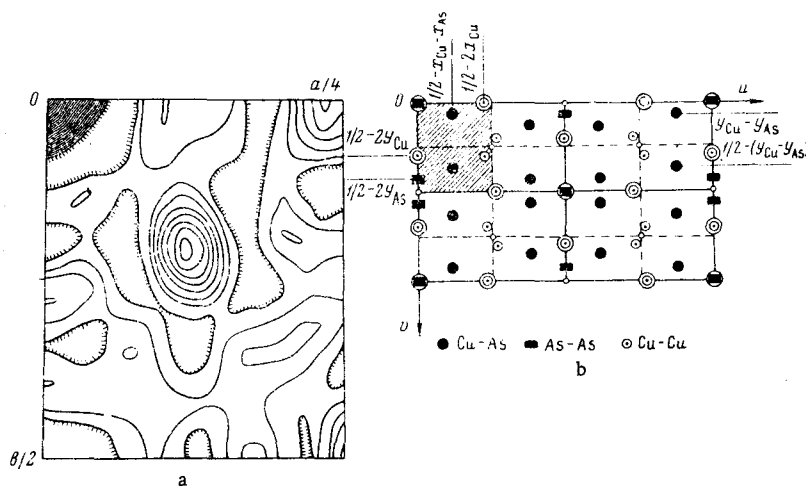


Fig. 2. a) $p(uv)$ Patterson projection for liroconite, b) symmetry of the projection and disposition of the peaks.

density allowed us to locate the Al and four of the six independent O atoms, leaving the positions of two O still uncertain. Weighted projections were used [3] to construct the three-dimensional electron density, which gave the coordinates of these last two atoms and also refined values for the others. At this stage $R_{hkl} = 0.16$. Least-squares refinement reduced this to $R_{hkl} = 0.11$. The discrepancies $\Delta = [(|F_o| - |F_c|) / |F_o|] \cdot 100\%$ were distributed as follows: $0 \leq \Delta \leq 10$ for 56.5% of the total non-zero reflections, $10 < \Delta \leq 20$, 24.4%, $20 < \Delta \leq 30$, 10.2%, $30 < \Delta \leq 40$, 4.9%, $40 < \Delta \leq 50$, 1.8%, and $\Delta > 50$, 2.2%. That is, discrepancies exceeding 20% occur for 97 reflections out of 508, and for these 97, 44 had intensities estimated as less than 10 (the weakest density was 3, the strongest 400), 18 had 10 to 15, nine had 15 to 20, seven 20 to 25, and four over 160. Thus, 82 of the 97 reflections with discrepancies over 20% were very weak, while four were very strong which naturally increased the error of measurement for these. The remaining 15 had intensities as follows: seven between 25 and 30, and the other eight between 30 and 110, of which

only two gave discrepancies greater than 31%: for 400, $\Delta = 56\%$; for 2.0.12, $\Delta = 33\%$.

Table 1 gives the numbers of finite reflections for various layer lines, and also R_1 (reliability factor taking account only of As and Cu), R_2 (from coordinates of all atoms from the three-dimensional electron-density synthesis), and R_3 (after least-squares refinement). The table also gives the corresponding isotropic temperature factors B_1 and $\max(\sin \theta/\lambda)$. Table 2 gives the final values for the coordinates of the basic atoms.

The Al atoms lie at inversion centers; as in many other structures, the nearest neighbors are six O atoms (Fig. 3a), which form an octahedron. The cation-anion distances are: $\text{Al}-\text{O}_1(\text{O}'_1) = 1.89$; $\text{Al}-\text{O}_3(\text{O}'_3) = 1.95$; $\text{Al}-\text{O}'_4(\text{O}_4) = 1.80 \text{ \AA}$; the first four agree well with known values, e.g., for epidote [4], where the Al-O bond lengths are 1.85-1.95 \AA , corundum [5], where three Al-O distances are 2.0 \AA and the other three 1.9 \AA , etc. The other two are somewhat shorter. The O-O here and subsequently are shown in the figures. The bond angles are: $\text{O}_1-\text{Al}-\text{O}'_4 = 85^\circ 57'$, $\text{O}_3-\text{Al}-\text{O}'_4 = 87^\circ 57'$, $\text{O}_1-\text{O}_3-\text{O}'_1 = 88^\circ 24'$.

TABLE 1. Reliability Factors for Layer Lines

Refl.	No. of $ F_o \neq 0$	R_1	B_1	R_2	B_2	R_3	B_3	$\max \sin \theta/\lambda$
$h0l$	128	0.37	0	0.18	0.4	0.11	0.57	1.146
$h1l$	112	0.36	0	0.11	1.4	0.08	1.4	0.636
$h2l$	106	0.37	0	0.18	0.6	0.11	0.4	0.774
$h3l$	96	0.37	0	0.17	0.4	0.11	0.4	0.713
$h4l$	63	0.32	0	0.18	1.6	0.12	1.11	0.554
$hk0$	49	0.29	0	0.16	1.0	0.13	0.75	0.711

TABLE 2. Coordinates of the Basic Atoms in Liroconite

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
As	0.250	0.047	0	O ₃	0.022	0.104	0.179
Cu	0.132	0.222	0.271	O ₄	0.040	0.290	0.429
Al	0	0	0	O ₅	0.187	0.879	0.340
O ₁	0.145	0.939	-0.005	O ₆	0.110	0.487	0.113
O ₂	0.243	0.165	0.134				

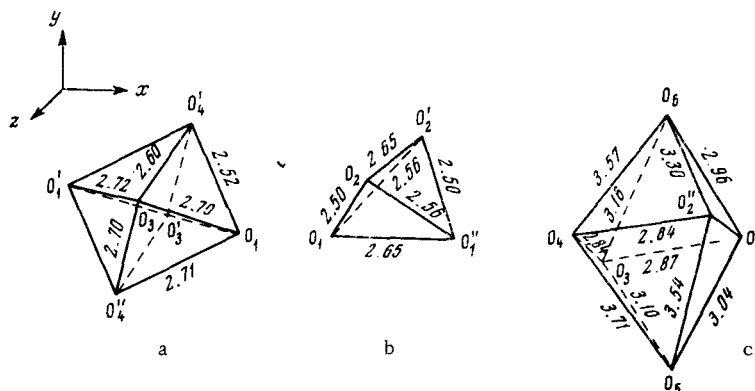


Fig. 3. Coordination polyhedra in liroconite. Primes denote atoms related to the basis ones by symmetry operations.

The As atoms lie on twofold axes, each having an oxygen tetrahedron (Fig. 3b) with $\text{As}-\text{O}_1(\text{O}_1'') = 1.56$; $\text{As}-\text{O}_2(\text{O}_2') = 1.59$ Å. The As-O bond lengths are appreciably less than those in clinoclase, where two As-O distances have an average of 1.73 Å and the other two have 1.68 Å [6], but they are only slightly less than for the corresponding in sim-ple-site $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, where $\text{As}-\text{O}_1 = 1.60$; $\text{As}-\text{O}_2 = 1.63$, and $\text{As}-\text{O}_3(\text{O}_3') = 1.69$ Å [7]. It may be that this is due to replacement of part of As in liroconite by P, which has a smaller ionic radius. A chemical analysis was not possible, as only a little material was available. The bond angles fall into two groups: $\text{O}_1-\text{As}-\text{O}_2'(\text{O}_1'-\text{As}-\text{O}_2) = 108^\circ 32'$; $\text{O}_1-\text{As}-\text{O}_2(\text{O}_1'-\text{As}-\text{O}_2')$ = $105^\circ 51'$ for the first and $\text{O}_1-\text{As}-\text{O}_1' = 135^\circ 24'$; $\text{O}_2-\text{As}-\text{O}_2' = 127^\circ 36'$ for the second.

The four oxygen atoms ($\text{O}_2, \text{O}_3, \text{O}_4, \text{O}_2''$) nearest the Cu (Fig. 3c) lie at 2.00, 1.87, 2.02, 2.01 Å, respectively; they lie roughly in a plane and form a quadrilateral, or rather two triangles $\text{O}_3\text{O}_2\text{O}_2''$ and $\text{O}_3\text{O}_4\text{O}_2''$ with $\text{O}_3\text{O}_2''$ as common side, the planes of the two lying at $179^\circ 30'$. The angles are: $\text{O}_4-\text{O}_3-\text{O}_2 = 89^\circ 17'$, $\text{O}_3-\text{O}_2-\text{O}_2'' = 89^\circ 57'$, $\text{O}_2-\text{O}_2''-\text{O}_4' = 94^\circ 24'$, and $\text{O}_2''-\text{O}_4-\text{O}_3 = 86^\circ 24'$. The Cu atom lies above this

plane by 0.045 Å. The coordination number is brought up to that most favorable as regards energy and most commonly found with divalent copper [8] by O_5 and O_6 , which lie at 2.75 and 2.55 Å, respectively, from the copper. The bond angles are: $\text{O}_2-\text{Cu}-\text{O}_6 = 80^\circ 02'$, $\text{O}_2-\text{Cu}-\text{O}_5 = 77^\circ 49'$, $\text{O}_3-\text{Cu}-\text{O}_6 = 89^\circ 57'$, $\text{O}_3-\text{Cu}-\text{O}_5 = 82^\circ 04'$, $\text{O}_4-\text{Cu}-\text{O}_6 = 102^\circ 25'$, $\text{O}_4-\text{Cu}-\text{O}_5 = 101^\circ 05'$, $\text{O}_2''-\text{Cu}-\text{O}_6 = 91.58^\circ$, $\text{O}_2''-\text{Cu}-\text{O}_5 = 94^\circ 51'$. The displacement of the plane of the quadrilateral towards O_6 shortens that bond relative to $\text{Cu}-\text{O}_5$, which indicates a tendency to fivefold coordination (tetragonal pyramid). The unit cell has eight Cu polyhedra linked via common $\text{O}_2-\text{O}_2''$ edges into four pairs via centers of symmetry, as in clinoclase and cornetite [9]. This $\text{O}_2-\text{O}_2''$ edge is much shorter than the other sides of the quadrilateral. The Cu-Cu distance in a pair is 3.03 Å, while the angle between the planes of the two quadrilaterals is about 180° .

Figures 4-6 show projections on the three coordinate planes, while Fig. 7 shows an axonometric projection. The Al octahedra and As tetrahedra are linked via common O_1 vertices and form chains along the a axis. Three such chains ($x00; x\frac{1}{2}\frac{1}{2}; x11$) are linked by two groups of paired Cu

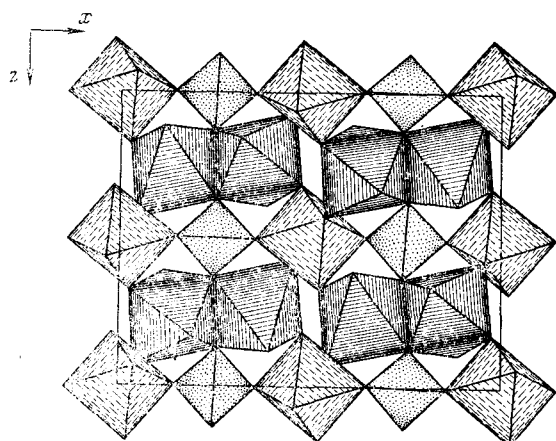


Fig. 4. Projection of the structure of liroconite on the xz plane.

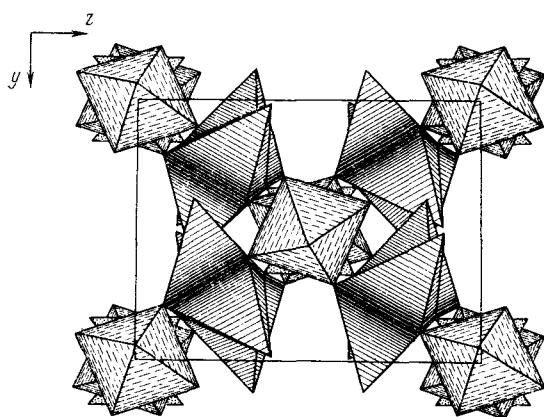


Fig. 5. Projection of the structure of liroconite on the yz plane.

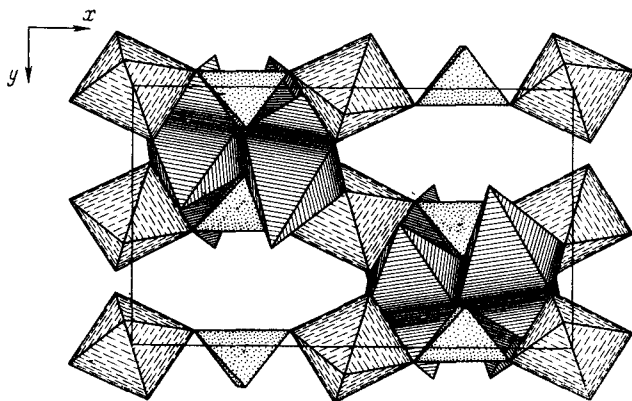


Fig. 6. Projection of the structure of liroconite on the xy plane.

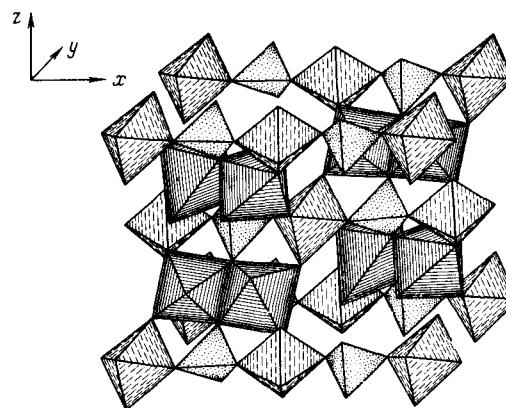


Fig. 7. Axonometric projection of the structure of liroconite.

polyhedra so that the common vertices O_2 and O_2'' of two Cu polyhedra are simultaneously vertices of two As tetrahedra, while O_3 and O_4 in the quadrilateral around Cu also belong to two Al octahedra. The other two groups of paired Cu polyhedra similarly link $x\frac{1}{2}y\frac{1}{2}$, $x10$, and $x01$ chains.

The protons were distributed between the oxygen atoms to form OH groups and H_2O molecules from the valency balance derived from Pauling's second rule. The sum of the bond strengths at O_1 is 1.75, while that at O_2 is 1.91; those at O_3 and O_4 are 0.83, and those at O_5 and O_6 are 0.33. Hence O_3 and O_4 are identified as OH groups, while O_5 and O_6 are H_2O molecules. The bonds are obviously longer for the last two, which confirms this conclusion, since H_2O lies before OH in the series of increasing addend field strength [8]. Figures 5 and 6 show that the water molecules lie in channels parallel to the a and c axes, the minimum distance between water molecules being 2.80 Å.

The structure explains the imperfect cleavage [1] or $(1\bar{1}0)$ and (011) . The packing coefficient is 0.56, so the bonds have a considerable proportion of homopolarity. Representation of the atoms as spheres in this case is purely formal, but if we do this and calculate the packing coefficients for major planes (Table 3), we get maximal values for $(1\bar{1}0)$ and (011) , the values being much higher than for the

TABLE 3. Packing Coefficients for Major Planes in Liroconite

Plane	(100)	(001)	(010)	(011)	(1 $\bar{1}0$)	(110)	(101)	(111)
k	0.60	0.55	0.45	0.73	0.57	0.42	0.50	0.41

other planes (the bar is connected with the choice of coordinate origin). Figures 5 and 6 illustrate this.

The grouping of many atoms close to these planes leads to stronger bonds in directions parallel to the planes and weaker ones perpendicular to them. The cleavage is imperfect because the centers do not lie exactly in these planes, and also because between the planes lie some of the atoms, which are linked to atoms in the planes.

The commonest $\{110\}$ and $\{011\}$ forms [1] are formed by the most densely populated planes.

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