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Abstract

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Crystallography

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The Crystal Structure of Liroconite

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Liroconite, $Cu_2Al[AsO_4][OH]_4 \cdot 4H_2O$, belongs to the crystal-chemical group of turquoise.

The determination of the structure of liroconite was carried out in order to provide additional information on the principle of construction of copper-arsenate (phosphate) structures.

The experimental material for the structural study consisted of rotation radiographs about the three axes of the monoclinic crystal $Cu_2Al[AsO_4][OH]_4 \cdot 4H_2O$ and goniometric developments of the zero and four higher layer lines of rotation about the b axis, as well as the zero, first, and second developments of rotation about c. In all cases MoK_α and CuK_α radiation was used. The intensities of the reflections were estimated by the method of blackening marks with a step of $\sqrt[4]{2}$.

Table 1

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cu	0.133	0.230	0.268	O_{III}	0.017	0.102	0.177
As	0.250	0.046	0	O_{IV}	0.039	0.272	0.425
Al	0	0	0	O_V	0.182	0.864	0.325
O_I	0.142	0.935	0	O_{VI}	0.107	0.473	0.120
O_{II}	0.247	0.149	0.125				

The Laue class $2/m$ and the cell parameters $a = 12.64$ Å, $b = 7.50$ Å, $c = 9.86$ Å, and $\beta = 91°18'$, as determined by us, agree well with earlier results ([1,2]). At a specific gravity of 2.88–2.98, the cell contains 4 formula units. The X-ray group $2/m1-/a$, following from the systematic extinctions, includes two space groups: $12/a$ and $1a$, which differ from one another by a center of symmetry. Intensity statistics made it possible to give preference to the group $12/a$ with 8-fold general and five 4-fold special positions; this at once restricted the possible positions of As and Al in the cell, reducing them to twofold axes and centers of symmetry.

From Patterson maps uvw and $uv0$, $uv\frac{1}{2}$, $uv\frac{1}{4}$, the coordinates of the As and Cu atoms were determined. This was sufficient to construct the projection of

Fig. 1. Projection of details of the structure of liroconite onto the plane $(01\bar{1})$

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Fig. 2. Projection of the structure of liroconite in polyhedra onto the xz plane

Figure 2: Fig. 2. Projection of the structure of liroconite in polyhedra onto the xz plane

the electron density onto the xz plane, on which, in addition to the Cu and As atoms that appeared in their assigned positions, peaks corresponding to the position of the Al atom and four independent oxygens were clearly distinguished. Application of the weighted-projection method made it possible to establish their vertical coordinates; to refine these and to reveal two further missing oxygen atoms, a three-dimensional Fourier synthesis was constructed.

Table 1 gives the coordinates of the basis atoms in liroconite; the discrepancy factors calculated from them for reflections of various types are less than 18%.

All cations of the structure proved to lie inside the polyhedra most characteristic of them. The interatomic distances in the Al octahedra do not exceed the known limits: Al—O = 1.85-1.93 Å and O—O = 2.66-2.67 Å.

In the As tetrahedra, two As—O distances are equal to 1.60 Å and the other two to 1.46 Å, with edge lengths O—O = 2.42-2.74 Å. The low value of two As—O bond lengths is probably connected with substitution of part of the As atoms by P atoms having a smaller ionic radius.

Each Cu has four nearest neighbors at distances
Cu—OII = 2.08; Cu—OII′ = 2.07; Cu—OIII = 1.98; Cu—OIV = 1.97 Å, forming a quadrilateral with sides OII—OII′ = 2.89; OII—OIII = = 2.96; OII′—OIV = 2.82 and OIII—OIV = 2.76 Å. Two more oxygens approach the Cu atom, completing this coordination to a strongly distorted octahedron, with distances Cu—OV = 2.87; Cu—OVI = 2.36 Å and angle OV—Cu—OVI 152.4°. The appreciable displacement of Cu from the plane of the above-mentioned quadrilateral in the direction of OVI indicates a tendency of copper toward fivefold coordination (with a coordination polyhedron in the form of a tetragonal pyramid). There are 8 Cu octahedra per cell, united pairwise by the common edge OII—OII′ into double groups analogous to those found in clinoclasite (3) $Cu_3AsO_4(OH)_3$ and cornétite (4) $Cu_3PO_4(OH)_3$.

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Al-octahedra and As-tetrahedra, linked by common oxygen vertices O_I, form chains extending along the a axis. The chains are connected to one another by groups of paired Cu-octahedra in such a way that the common vertices O_{II}, O'_{II} of two Cu-octahedra are simultaneously vertices of As-tetrahedra, while the oxygens O_{III}, O_{IV}, which enter into the coordination quadrilateral around Cu, also belong to two Al-octahedra. Figure 1 shows the connection of three chains $(x00; x\frac{1}{2}\frac{1}{2}; x11)$ by means of double Cu—Cu groups. In the same way, the chain $x\frac{1}{2}\frac{1}{2}$ is connected with $x10$ and $x01$. As a result, a three-dimensional framework is obtained. Figure 2 shows the view of the structure along the b axis.

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CITED LITERATURE

1. L. G. Berry, *Am. Mineral.*, **36**, 484 (1951).
2. V. I. Mikheev, *X-ray Determinative Tables for Minerals*, 1957.
3. S. Chose, M. Fenlmann, M. Sundaralingam, *Acta crystallogr.*, **18**, 777 (1965).
4. M. Fenlmann, S. Chose, J. S. Finney, *J. Chem. Phys.*, **41**, 7, 1910 (1963).

Note: Figure translations are in progress. See original paper for figures.