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Disordered distribution of Cu in the crystal structure of leightonite, $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$

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ABSTRACT

The crystal structure of leightonite, $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$, *C*2/*c*, $a = 11.654(2)$, $b = 7.497(1)$, $c = 10.097(1)$ Å; $\beta = 125.21(1)°$, $V = 720.8(2)$ Å^3, $Z = 2$ has been solved by direct methods and refined to $R = 3.90\%$ for 1564 $F_o > 4\sigma(F_o)$, using Mo$K\alpha$ X-ray data from a crystal twinned on $\{20\bar{1}\}$. Structural sub-units $[Ca(SO_4)_2]^{2-}$ formed by one CaO_8 polyhedron and two opposite-sided SO_4 tetrahedra are linked by edge sharing. These sub-units are linked to each other by corner sharing to form a three-dimensional framework with channels, where the Cu atoms are located. The framework of CaO_8 polyhedra and SO_4 tetrahedra exhibits a perfect orthorhombic symmetry whereas the copper atoms located at the Cu1 and Cu2 sites are not equivalent because they have different partial occupancies (0.37 and 0.13, respectively). Both Cu1 and Cu2 are coordinated by O atoms to form two rhombically elongated octahedra (2 + 2 + 2 Jahn-Teller distortion). K and Ow are disordered on the same site. The crystal structure of leightonite closely resembles that of the triclinic polyhalite, $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$, with the main difference being the different distribution of Cu in leightonite with respect to Mg in polyhalite.

INTRODUCTION

Leightonite, from Chuquicamata, Chile, $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$, was first described by Palache (1938). A second occurrence from Tsumeb, Namibia, is reported by Keller (1977). The description given by Palache is also reported by Bandy (1938). Crystals of leightonite have the appearance of holohedral orthorhombic individuals. As inferred from the optical study by Palache (1938), this feature would result from microscopic, repeated lamellar twinning on (100) and (010) of a nearly rectangular triclinic lattice. On the basis of crystallographic and chemical similarities, Peacock (1938) stated that leightonite is the copper homologue of polyhalite, $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$. The crystal structure of polyhalite was solved by Schlatti et al. (1970) in space group $F\bar{1}$, thus supporting the hypothesis of Palache (1938) that leightonite is triclinic pseudo-orthorhombic.

The first X-ray diffraction study of leightonite was performed by Van Loan (1962) on a sample from Chuquicamata. On the basis of new goniometric measurements this author stated that the mineral is morphologically orthorhombic holohedral. Rotation and Weissenberg photographs yielded an orthorhombic unit-cell, with the calculated axial ratios close to those given by Palache (1938). According to Van Loan (1962), no evidence of twinning appeared on the films, and conditions for systematic absences were consistent with the *Fmmm* space group. Therefore he concluded that polyhalite differs from leightonite.

In the present paper we report the crystal structure of leightonite for a crystal from the type-locality.

SAMPLE CHARACTERIZATION

Crystals of leightonite from Chuquicamata, Chile (Royal Ontario Museum, no. 19490), are watery blue to greenish blue, transparent, and prismatic with {110} dominant. At Chuquicamata the mineral was found in the great open pit, confined to within 50 m of the original surface, and according to Palache (1938), formed under low acidity conditions. On the other hand, leightonite from Tsumeb was thought to form from acid solutions at fairly high temperature (Keller and Bartelke 1982).

A preliminary chemical analysis using EDS did not indicate elements ($Z > 9$) other than Cu, Ca, K, and S. The chemical composition was then determined from two polished crystals by means of a JEOL JXA 8600 electron microprobe operating at 8 kV and 20 nA with the beam defocused to 25 μm diameter. Results are given in Table 1. The WDS analyses were performed under unfavorable conditions because leightonite crystals decompose under the electron beam; however, the analyses substantially confirm the data obtained by Gonier, as reported by Palache (1938).

EXPERIMENTAL METHODS AND STRUCTURE SOLUTION

A preliminary X-ray investigation by means of Weissenberg photographs showed that the crystals exhibit overall diffraction symmetry *mmm*, with *hkl*, $h + k = 2n + 1$, $k + l = 2n + 1$, $h + l = 2n + 1$ reflections systematically absent. In addition, 0*kl*, *h*0*l*, and *hk*0 reflections appear to be present only when $k + l = 4n$, $h + l = 4n$, and $h + k = 4n$, respectively, thus suggesting the *Fddd* space group. More accurate measurements were performed with a Bruker *P*4 diffractometer. Values refined from 38 high-θ reflections gave the following parameters: $a = 11.654(2)$, $b = 16.499(1)$, $c = 7.497(1)$ Å; $\alpha = 90.00(1)$, $\beta = 90.00(1)$, $\gamma = 89.96(1)°$. Other crystals gave similar results. Taking into account the possibility that the real symmetry could

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TABLE 1. Chemical composition (wt%) for leightonite

	1	2	3
K_2O	14.68	13.93	14.82
Na_2O	–	0.56	–
CaO	17.45	18.41	21.09
CuO	12.39	11.97	10.36
SO_3	49.87	49.33	47.13
H_2O	5.61	5.71	n.d.
Total	100.00	99.91	93.40

Note: 1 = calculated for the ideal formula $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$; 2 = Palache (1938), analysis 3; 3 = this study.

be lower than orthorhombic, intensity data were obtained from the whole Ewald sphere ($2° < 2\theta_{Mo K\alpha} \leq 70°$). The intensities of 6366 reflections were measured and corrected for Lorentz-polarization and absorption following the semi-empirical method of North et al. (1968). Equivalent structure factors were merged according to *mmm* (R_{symm} = 3.67%), 2/*m* (R_{symm} = 3.32, 3.17, 2.95% assuming as monoclinic unique axis the **a**-, **b**-, and **c**-*orthorhombic* axes, respectively), and $\bar{1}$ symmetry (1.97%). A check of systematic absences, previously observed on the Weissenberg photographs, suggested space group *Fddd*. However, violations [$F_o/\sigma(F_o) > 5$] were found for 0*kl* (15) and *h*0*l* (13) reflections with $k + l$ and $h + l \neq 4n$, respectively. The first attempt to solve the structure by direct methods using SHELXS-97 (Sheldrick 1997) was performed in *Fddd*. The full-matrix least-squares program SHELXL-97 (Sheldrick 1997) was used to refine the structure. Isotropic full-matrix least-squares refinement led to R = 13.4% with unreliable atomic displacement parameters for the Cu and K atoms. The site occupancies were refined without any chemical constraint and indicated a disordered distribution of K and Ow atom (0.50 K + 0.50 O) on the same site and a partial occupancy for the Cu atoms (0.25Cu + 0.75□). Introduction of anisotropic atomic displacement parameters for all atoms led to an R index of 6.11% for 698 observed reflections [$F_o > 4\sigma(F_o)$] and R = 6.40% for all 804 independent reflections. At this stage a crystal which under the microscope appeared twinned was examined, and gave a similar final R value (5.80%). On the basis of this result as well as the above symmetry violations, it was hypothesized that the true symmetry was monoclinic with the apparent orthorhombic pseudosymmetry due to twinning. Among the three possible monoclinic subgroups of *Fddd* (i.e., *Fd*11, *F*1*d*1, *F*11*d*), the best internal consistency was found for *F*11*d* (*C*2/*c* as standard). The cell parameters were then transformed according to the matrix [1 0 0 / 0 0 $\bar{1}$ / –1/2 1/2 0] and the following values were obtained: a = 11.654(2), b = 7.497(1), c = 10.097(1) Å; α = 90.00(1), β = 125.21(1), γ = 90.00(1)°. The refinement in *C*2/*c* was performed following the method of Pratt et al. (1971) for twinned structures, assuming twinning on {20$\bar{1}$}. With monoclinic symmetry the Cu position splits into two non-equivalent positions with partial occupancies (0.37 and 0.13 for Cu1 and Cu2, respectively). The refined value of the fraction of the first twin component was 0.53, which accounts for the relatively low value (3.67%) of R_{symm} in the *mmm* Laue group. The final R index was 3.90% for 1564 observed reflections [$F_o > 4\sigma(F_o)$] and 4.15% for all 1596 independent reflections. Neutral scattering curves from the *International Tables for X-Ray Crystallography* (Ibers and Hamilton 1974) were used for O, S, K, Ca, and Cu. Details of data collection are given in Table 2; Table 3 reports fractional coordinates and anisotropic displacement parameters. A list of observed and calculated structure factors appears in Table 4[1].

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Selected bond distances and angles are given in Table 5. The Ca atom lies on a twofold axis (222 in *Fddd*) and links eight O atoms belonging to six different sulfate groups; in particular, the Ca polyhedron shares four vertices (O1 and O3, twice) and two edges (O2-O4) with the SO_4 tetrahedra. The Ca-O distances range from 2.382 to 2.599 Å with a mean value of 2.486 Å. However, because of the shared edge, distances are split into two separate sets of values: 2.385 Å (average value for Ca-O1 and Ca-O3) and 2.587 Å (for Ca-O2 and Ca-O4). The resulting coordination polyhedron resembles a distorted cube. The SO_4 tetrahedron deviates from ideality because of the edge sharing with the Ca polyhedron. The four S-O distances are split into two sets of values: 1.469 Å (average value for S-O1 and S-O3) and 1.482 Å (for S-O2 and S-O4). Likewise, the O-S-O angles form two groups: the O4-S-O2 angle is 105.7°, whereas all other values are in the range 109.6–110.9°. The shared edge O2-O4 (2.362 Å) is the shortest edge of the tetrahedron.

By considering one Ca polyhedron with two opposite-sided SO_4 tetrahedra linked by edge sharing, the $[Ca(SO_4)_2]^{2-}$ structural sub-unit results. These sub-units are linked together by corner sharing to form a three-dimensional framework with channels, parallel to the monoclinic **b** axis, in which Cu atoms are located (Fig. 1). The Cu atoms are disordered on two non-equivalent sites, Cu1 and Cu2, with partial occupancies of 0.37 and 0.13, respectively. Each Cu atom links four sulfate-oxygen atoms and two water molecules forming a distorted octahedron (Jahn-Teller effect). The Cu-polyhedra are connected to each other by corner-sharing (of water molecules) to form chains along [110] and [$\bar{1}$10] (Fig. 2).

The mean Cu-O distances are slightly different (2.116 and

[1]For a copy of Table 4, document item AM-02-007, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at http://www.minsocam.org.

TABLE 2. Crystal data and experimental details

Cell parameters	a = 11.654(2) (Å) b = 7.497(1) (Å) c = 10.097(1) (Å) β = 125.21 (1)° V = 720.8(2) (Å^3)
Space group	*C*2/*c*
Crystal size (μm)	80 × 90 × 120
Wavelength	Mo*K*α (30 mA × 50 kV)
Theta-range (°)	1–35
Scan mode	ω
Scan width (°)	2.50
Scan speed (°/min)	2.06
Independent refl.	1596
Refl. with $F_o > 4\sigma(F_o)$	1564
R_{merge} (%)	2.95
R_{obs} (%)	3.90
R_{all} (%)	4.15

Note: $R_{merge} = (\Sigma\{N\Sigma [w(\overline{F_O} - F_O)^2]\}/\Sigma[(N-1)\Sigma(wF_O^2)])^{1/2}$.
$R_{obs} = \Sigma(w^{1/2} |F_O - F_C|)/ \Sigma (w^{1/2} F_O)$.

TABLE 3. Fractional atomic coordinates and anisotropic displacement parameters U_{ij} (Å²) for leightonite

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
K/Ow	0.5889(2)	0.6223(2)	0.4264(1)	0.0186(8)	0.0155(3)	0.0210(3)	–0.0001(3)	0.0117(7)	–0.0027(4)	0.0182(2)
Ca	1/2	0.1261(1)	1/4	0.0101(7)	0.0094(2)	0.0133(2)	0	0.0062(6)	0	0.0112(1)
Cu1	1/4	3/4	0	0.0102(7)	0.0094(5)	0.0126(5)	–0.0036(5)	0.0054(6)	–0.0007(5)	0.0114(2)
Cu2	0	0	0	0.012 (2)	0.011 (1)	0.020 (2)	–0.003 (1)	0.010 (2)	0.011 (2)	0.0135(7)
S	0.6935(1)	0.1228(1)	0.6374(1)	0.0079(6)	0.0108(2)	0.0081(2)	–0.0017(2)	0.0035(5)	–0.0004(3)	0.0096(1)
O1	0.8544(3)	0.5914(4)	0.7579(4)	0.015(1)	0.022(1)	0.013(1)	0.004(1)	0.008(1)	–0.002(1)	0.0167(5)
O2	0.6599(3)	–0.0317(3)	0.5290(3)	0.018(1)	0.015(1)	0.016(1)	–0.003(1)	0.008(1)	–0.004(1)	0.0177(5)
O3	0.6546(3)	0.6558(4)	0.7624(4)	0.007(1)	0.022(1)	0.015(1)	0.004(1)	0.004(1)	0.001(1)	0.0161(5)
O4	0.6163(3)	0.2760(3)	0.5289(3)	0.019(1)	0.018(1)	0.018(1)	0.009(1)	0.010(1)	0.011(1)	0.0185(5)

TABLE 5. Selected interatomic distances (Å) and angles (°) for leightonite

K –	O1(*i*)	2.981(4)	Cu1–O1 (*ii,vi*)	2.454(3)
	O1(*ii*)	3.100(3)	O2 (*viii,ix*)	2.055(3)
	O1(*iii*)	3.150(3)	Ow(*ii,vi*)	1.840(2)
	O2(*x*)	2.738(3)	mean	2.116
	O2(*vii*)	2.777(3)		
	O3(*iv*)	3.023(3)		
	O3(*i*)	3.027(4)	Cu2–O3 (*viii,xi*)	2.475(3)
	O3(*v*)	3.130(3)	O4 (*viii,xi*)	2.070(2)
	O4(*i*)	2.745(3)	Ow(*viii,xi*)	1.831(2)
	O4(*v*)	2.784(4)	mean	2.125
	Ow(*vi*)	2.911(3)		
	mean	2.942		
Ca –	O1(*vii,viii*)	2.388(3)	S–O1(*xii*)	1.471(3)
	O2(*i,vi*)	2.599(3)	O2(*i*)	1.483(3)
	O3(*iv,v*)	2.382(3)	O3(*xii*)	1.467(3)
	O4(*i,vi*)	2.575(3)	O4(*i*)	1.481(3)
	mean	2.486	mean	1.476

O1(*vi*)–Cu1–O1(*ii*)	180.00	O3(*viii*)–Cu2–O3(*xi*)	180.00
O2(*ix,viii*)–Cu1–O1(*ii,vi*)	77.52(9)	O4(*viii,xi*)–Cu2–O3(*xi,viii*)	77.37(9)
O2(*ix,viii*)–Cu1–O1(*ii,vi*)	102.48(9)	O4(*viii,xi*)–Cu2–O3(*viii,xi*)	102.63(9)
O2(*ix*)–Cu1–O2(*viii*)	180.00	O4(*viii*) –Cu2–O4(*xi*)	180.00
Ow(*vi,ii*)–Cu1–O1(*vi,ii*)	86.71(8)	Ow(*viii,xi*)–Cu2–O3(*viii,xi*)	88.00(8)
Ow(*vi,ii*)–Cu1–O1(*ix,viii*)	93.29(8)	Ow(*viii,xi*)–Cu2–O3(*xi,viii*)	92.00(8)
Ow(*vi,ii*)–Cu1–O2(*viii,ix*)	89.18(9)	Ow(*viii,xi*)–Cu2–O4(*viii,xi*)	89.18(9)
Ow(*vi,ii*)–Cu1–O2(*ii,vi*)	90.82(9)	Ow(*viii,xi*)–Cu2–O4(*xi,viii*)	90.82(9)
Ow(*vi*)–Cu1–Ow(*ii*)	180.00	Ow(*viii*)–Cu2–Ow(*xi*)	180.00

O1(*xii*)–S–O2(*i*)	110.9(2)
O1(*xii*)–S–O4(*i*)	109.6(2)
O3(*xii*)–S–O1(*xii*)	109.8(1)
O3(*xii*)–S–O2(*i*)	109.9(2)
O3(*xii*)–S–O4(*i*)	110.9(2)
O4(*i*)–S–O2(*i*)	105.7(1)

Note: Symmetry codes are: (*i*): *x*, *y*, *z*, (*ii*): –1/2 + *x*, 3/2 – *y*, –1/2 + *z*, (*iii*): 3/2 – *x*, 3/2 – *y*, 1 – *z*, (*iv*): *x*, 1 – *y*, –1/2 + *z*, (*v*): 1 – *x*, 1 – *y*, 1 – *z*, (*vi*): 1 – *x*, *y*, 1/2 – *z*, (*vii*): 3/2 – *x*, 1/2 – *y*, 1 – *z*, (*viii*): –1/2 + *x*, 1/2 – *y*, –1/2 + *z*, (*ix*): 1 – *x*, 1 + *y*, 1/2 – *z*, (*x*): *x*, 1 + *y*, *z*; (*xi*): 1/2 – *x*, –1/2 + *y*, 1/2 – *z*; (*xii*): 3/2 – *x*, –1/2 + *y*, 3/2 – *z*.

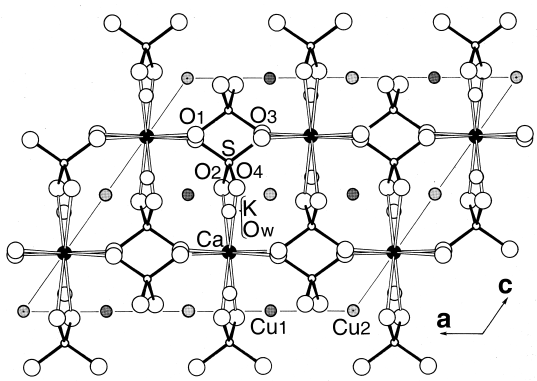

FIGURE 1. The crystal structure of leightonite projected along the **b** axis. The unit-cell is outlined.

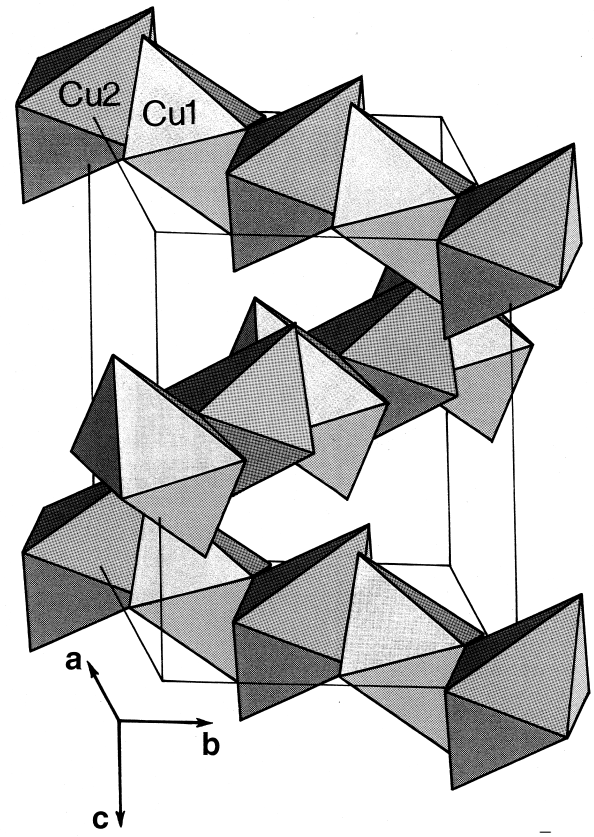

FIGURE 2. Cu-polyhedra chains running along [110] and [$\bar{1}$10].

2.125 Å for Cu1 and Cu2, respectively), in keeping with the two different site-occupancy values. On the other hand, both polyhedra exhibit a very similar kind of distortion; this can be evaluated from the similar values for quadratic elongation (λ = 1.0470 and 1.0489) and the variance of bond angles (σ^2 = 61.03 and 59.64). These values were computed according to the method of Robinson et al. (1971) where $\lambda = \Sigma_{i=1}^{6}(l_i / l_o)^2/6$ and $\sigma^2 = \Sigma_{i=1}^{12}(\theta_i - 90°)^2/11$. A further parameter ($\Delta = 1/6\ \Sigma[(l_i - l_o)/l_o]^2$) used to describe the polyhedral distortion for Cu^{2+} octahedra was introduced by Eby and Hawthorne (1993). Values of Δ calculated for Cu1 and Cu2, 0.014 and 0.016 respectively, fall within the range quoted by Eby and Hawthorne (1993) for a number of copper oxysalt minerals with octahedrally coordinated Cu^{2+} ions. However, an examination of the Cu-O distances reveals that in leightonite, Cu^{2+} octahedra are rhombically elongated with two short Cu-O distances (1.831 and 1.840 Å),

two long Cu-O distances (2.454 and 2.475 Å) and two intermediate Cu-O distances (2.055 and 2.070 Å). According to Burns and Hawthorne (1996), such a distortion is best referred to as a (2 + 2 + 2) distortion and can be considered a subclass of the (4 + 2) distorted octahedra, as the two intermediate Cu-O distances are closer to the shorter distances than to the long Cu-O distances. In leightonite the difference between the intermediate and the short Cu-O distances is 0.215 and 0.239 Å for Cu1 and Cu2, respectively. Burns and Hawthorne (1996) observed that in structures of Cu^{2+} oxysalt minerals with (2 + 2 + 2) distorted octahedra, this value is always greater than 0.10 Å. According to these authors, the degree of distortion for centrosymmetric (2 + 2 + 2) distorted Cu octahedra can be given by the parameter $\Delta_T = [(Cu\text{-}O_{short}) + (Cu\text{-}O_{inter.})]/[(Cu\text{-}O_{inter.}) + (Cu\text{-}O_{long})]$, which ranges from 0.857 (lubjibaite) to 0.923 (cyanochroite). A good correlation ($R = -0.84$) is observed when the Cu-O mean distance is plotted against Δ_T. Values calculated for leightonite (0.864 and 0.859 for Cu1 and Cu2, respectively) plot slightly off this trend (Fig. 3), since the mean distances (2.12–2.13 Å) appear to be shorter than expected (2.16 Å). This is likely due to the very short Cu-O distances (1.831–1.839 Å) which appear to be out of the expected range for equatorial distances (1.875–2.125 Å) given by Burns and Hawthorne (1996). On the other hand, it cannot be excluded that small amounts (lower than observable in the analyses) of smaller cations substituting for Cu^{2+} might lead to shorter cation-O atom distances.

The structure refinement indicated a disordered distribution of K (50%) and Ow (50%) at the same site. This implies short-range order; when H_2O enters the site, both Cu1 and Cu2 positions can be occupied by Cu atoms, whereas occupancy by K requires that both Cu1 and Cu2 positions be empty. When the site is occupied by K it forms bonds with ten sulfate-oxygen atoms and one Ow with a mean K-O distance of 2.942 Å.

The electrostatic valence balance, computed according to Breese and O'Keeffe (1991), is given in Table 6. The resulting empirical bond-valence sums for O1, O2, O3, and O4 are not far from 2.0 v.u., while Ow is strongly undersaturated, thus indicating that it belongs to a water molecule. However, the combined analysis of the ΔF-Fourier map and the interatomic O-O distances suitable for hydrogen bonds did not lead to reliable solution for the hydrogen bonding system.

On the whole the structure of leightonite closely resembles that of polyhalite which was described as triclinic by Schlatti et al. (1970). The framework of CaO_8 and SO_4 polyhedra, which in leightonite exhibits a perfect orthorhombic symmetry (Fig. 4), is topologically identical to that of polyhalite. However, in polyhalite K and Ow lie on two independent positions, which coalesce into the same position in the monoclinic structure of leightonite.

The main difference between the two minerals is the different distribution of the octahedral cations (i.e., Cu in leightonite and Mg in polyhalite). The Mg atom is located at the origin of the triclinic unit-cell of polyhalite, with 100% occupancy, and links four sulfate O atoms and two water molecules to form a fairly distorted octahedron ($\lambda = 1.0096$; $\sigma^2 = 28.67$). The Mg-O distances are 2.035 (× 2), 2.035 (× 2), and 2.155 (× 2) Å with a mean value of 2.075 Å. On the other hand, Cu in leightonite

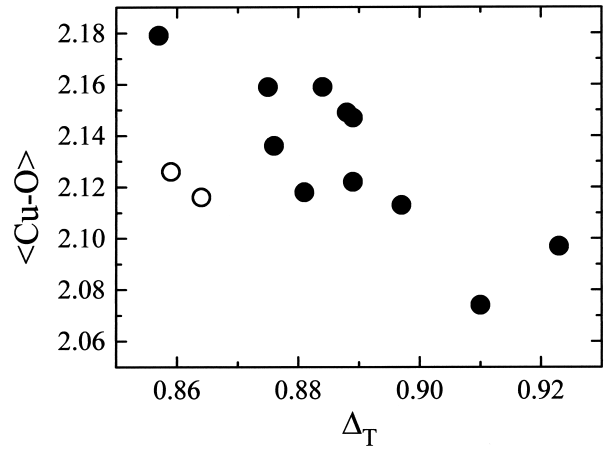

FIGURE 3. The <Cu-O> bond length vs. octahedral distortion Δ_T (see text). Solid circles = data reported by Burns and Hawthorne (1996), open circles = the present study.

TABLE 6. Empirical bond-valence values for leightonite

	O1	O2	O3	O4	Ow (50%)
Ca	0.32	0.18	0.33	0.19	
S	1.51	1.46	1.47	1.48	
Cu1 (37%)	0.05	0.13			0.24
Cu2 (13%)			0.02	0.05	0.09
K (50%)	0.12	0.18	0.12	0.18	0.06
Total	2.00	1.95	1.94	1.90	0.39

Note: The empirical parameters used in the calculations are those of Breese and O'Keeffe (1991).

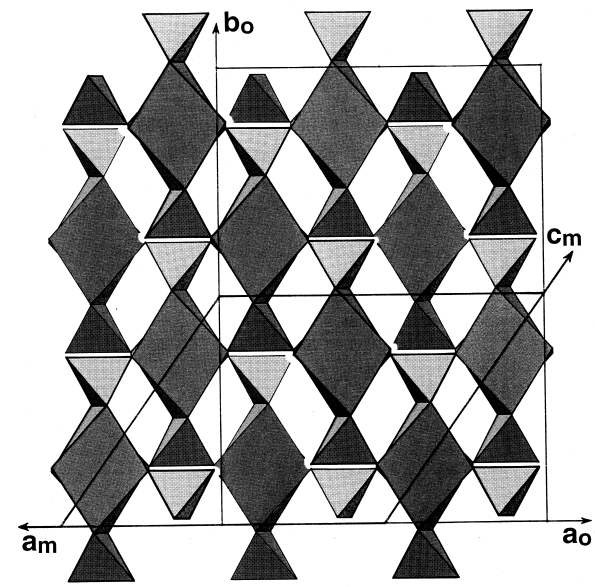

FIGURE 4. Polyhedral sketch of the CaO_8 and SO_4 framework. Both the monoclinic and orthorhombic unit-cells are outlined.

is disordered over two monoclinic sites (Cu1 and Cu2) with partial occupancies of 0.37 and 0.13, respectively. Because of the Jahn-Teller effect, the two independent Cu^{2+} polyhedra (mean Cu-anion distances of 2.116 and 2.125, respectively) exhibit more distortion ($\lambda = 1.0470, 1.0489$; $\sigma^2 = 61.03, 59.64$).

Moreover, there are Cu atoms (although with partial occupancy) in all the octahedral cavities within the $[Ca(SO_4)_2]^{2-}$ framework (see Fig. 1), whereas in polyhalite only one cavity out of four contains Mg atoms.

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