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Lyonsite, $Cu_3^{2+}Fe_4^{3+}(VO_4)_6^{3-}$, a new fumarolic sublimate from Izalco volcano, El Salvador: Descriptive mineralogy and crystal structure

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Abstract

Lyonsite, $Cu_3^{2+}Fe_4^{3+}(VO_4)_6^{3-}$, a new iron-copper vanadate mineral, has been discovered in the summit crater fumaroles of Izalco volcano, El Salvador. The mineral, which occurs with thenardite and a Na-Cu-Fe vanadate, formed as a sublimate product from the volcanic gases. Lyonsite occurs as euhedral, black lathlike crystals up to 230 μm in greatest dimension.

Lyonsite is orthorhombic, *Pmcn*, $a = 10.296(1)$, $b = 17.207(2)$, $c = 4.910(1)$Å. The atomic arrangement of the mineral has been determined and refined to $R = 0.028$, $R_w = 0.031$. The structure is based on a pseudohexagonal close-packed oxygen array. The fundamental building block consists of six isolated VO_4 tetrahedra that are linked, through corner sharing, to a central octahedron that is half-occupied by Cu^{2+} atoms. These "pinwheel" building blocks are connected on four sides by FeO_6 octahedra and on the remaining two sides by square-planar CuO_4 groups. The fundamental building block is isostructural with the silicate pinwheels in dumortierite.

Lyonsite is opaque and has a dark gray streak and metallic luster. $Z = 2$ and $D_{calc} = 4.215$ g/cm³. Lyonsite displays a good {001} cleavage. The mineral is creamy white in reflected light in air. Reflectance values measured on (010) are (λ, min., max.) 481 nm, 17.5, 23.1%; 547 nm, 16.6, 22.3%; 591 nm, 14.7, 20.7%; and 644 nm, 14.4, 18.8%.

The mineral is named after Dr. John B. Lyons of Dartmouth College. Milligram amounts of the phase exist and are on deposit at the NMNH, Smithsonian Institution.

Introduction

The fumaroles of Izalco volcano, El Salvador, were first investigated by R. E. Stoiber and colleagues from Dartmouth College. Early studies showed the presence of several high-temperature V minerals in the fumarole mineral suite (Stoiber and Duerr, 1963; Stoiber and Rose, 1974). Since that time, stoiberite ($Cu_5V_2O_{10}$), fingerite [$Cu_{11}O_2(VO_4)_6$], mcbirneyite [$Cu_3(VO_4)_2$], ziesite (β-$Cu_2V_2O_7$), blossite (α-$Cu_2V_2O_7$), bannermanite ($Na_xV_6O_{15}$), and scherbinaite (V_2O_5) have been described as minerals from the site. To these compounds is now added lyonsite, $Cu_3Fe_4(VO_4)_6$, the first iron-copper vanadate mineral known.

Lyonsite was collected from the "Y" fumarole of Izalco volcano and occurs with thenardite and a Na-Cu-Fe vanadate currently under study. The mineral is found as euhedral lathlike crystals up to 230 μm in greatest dimension. Specimens have been deposited at the NMNH, Smithsonian Institution. The authors are pleased to name the mineral lyonsite in honor of Dr. John B. Lyons, Frederick Hall Professor of Mineralogy at Dartmouth College. Dr. Lyons has had a long and distinguished career in the fields of igneous and metamorphic petrology, and it is fitting that he be so honored on the occasion of his retirement. The mineral and mineral name have been approved by the IMA.

Geologic setting

Izalco volcano is a basaltic composite cone that has been intermittently active since its birth in 1770. The volcano rises to an altitude of 1965 m, with 650-m relief, and has an approximate volume of 2 km³. The geology of the volcano is described by Meyer-Abich (1958), Rose and Stoiber (1969), and Stoiber et al. (1975).

Hughes and Stoiber (1985) described the conditions of mineral genesis in the fumaroles of Izalco volcano. They showed that the minerals formed as sublimates from a vanadium halogen or oxyhalogen gas that was exsolved from a basaltic magma when the magma was 550 m below the summit crater. As the gas rose to the fumaroles and mixed with the atmosphere, the oxygen fugacity rose from that of the magma to at least $10^{-3.5}$ bar. At the fumaroles, the vanadium compounds sublimated at temperatures up to ca. 800°C.

Chemistry

Single crystals of lyonsite were mounted and polished for electron-microprobe analysis. Qualitative energy-dis-

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TABLE 1. Chemical analyses of lyonsite

	Avg.*	Ideal $Cu_6Fe_8(VO_4)_{12}$
V_2O_5	47.74 (36)	49.44
Fe_2O_3	24.83 (12)	28.94
Mn_2O_3	3.41 (6)	—
TiO_2	2.27 (2)	—
CuO	21.99 (33)	21.62
Total	100.24	100.00

Formula (O = 48): $Cu_{6.09}(Fe^{3+}_{6.86}Ti^{4+}_{0.63}Mn^{3+}_{0.95})_{\Sigma = 8.44}V_{11.58}O_{48}$

* Analysis represents average of three analyses of type crystal. One standard deviation of least units given in parentheses.

TABLE 2. X-ray diffraction pattern and unit-cell parameters of lyonsite

d_{obs}*	d_{calc}**	I_{obs}	I_{calc}	*h*	*k*	*l*
8.79	8.835	20	<1.5	1	1	0
4.423	4.418	40	40.7	2	2	0
3.371	3.366	20	20.1	3	1	0
3.279 (b)	3.284	100	100.0	2	2	1
	3.264		35.2	1	5	0
	3.236		37.4	0	4	1
2.943	2.945	20	5.0	3	3	0
2.872	2.868	20	10.4	0	6	0
2.779	2.776	40	24.8	3	1	1
2.722	2.739	40	27.9	2	4	1
	2.718		17.2	1	5	1
2.526	2.526	60	56.7	3	3	1
2.477	2.476	10	17.5	0	6	1
2.259	2.260	10	8.9	4	1	1
2.215	2.216	10	2.0	2	0	2
	2.209		1.3	4	4	0
2.011	2.014	10	2.2	4	4	1
	2.008		3.8	3	6	1
1.887	1.886	10	15.8	3	3	2
1.805	1.803	10	3.7	5	3	1
1.718	1.716	20	7.9	6	0	0
1.671	1.670	20	11.9	3	9	0
1.591	1.592	40	10.7	6	2	1
1.550	1.549	40	11.1	2	10	1
+5 lines	<1.500 Å					

* 114.6-mm Gandolfi camera, in vacuo, Ni-filtered Cu radiation, visual intensity estimates; (b) = broad.

** Calculated from single-crystal diffractometer parameters: $a = 10.296(1)$, $b = 17.207(2)$, $c = 4.910(1)$ Å.

persive analyses demonstrated that Cu, Fe, and V were the major constituents, with minor Ti and Mn. Quantitative electron-microprobe analyses were performed on the Southern Illinois University Etec Autoscan microprobe with a Kevex 8000 energy-dispersive system using metal standards for Cu, Fe, V, Mn, and Ti. The results of these analyses are contained in Table 1. Based on knowledge of the conditions of mineral genesis and associated minerals, all elements were assumed to be fully oxidized. The subsequent crystal-structure determination confirmed the existence of Cu^{2+}, Fe^{3+}, and V^{5+}. The analyses demonstrate minor substitution of Mn^{3+} and Ti^{4+} for Fe^{3+}; however, in subsequent crystal-structure calculations, the Fe^{3+} octahedron was assumed to be occupied only by Fe^{3+}.

X-RAY CRYSTALLOGRAPHY

A diffraction pattern of lyonsite was obtained using a 114.6-mm Gandolfi camera and Ni-filtered Cu radiation, in vacuo. The indexed diffraction pattern is contained in Table 2.

A single-crystal precession study of lyonsite was undertaken using Zr-filtered Mo radiation. The euhedral form allowed rapid orientation of the crystals. Cone-axis and precession photographs were taken about all three principal axes. The photographs indicated Laue group *mmm*, and systematic extinctions $h + k \neq 2n$ for $hk0$ reflections and $l \neq 2n$ for $h0l$ reflections. The absences yield space group *Pmcn*, the *bca* setting of space group no. 62, *Pnma*. The unit-cell parameters of lyonsite were refined from 25 diffraction angles determined on a four-circle diffractometer and are given in Table 2.

CRYSTAL STRUCTURE

Experimental details

A euhedral single crystal measuring 0.23 × 0.06 × 0.025 mm was selected for the crystal-structure study. A complete suite of precession photographs showed no evidence of twinning or intergrown phases. The crystal was mounted on a CAD4 diffractometer utilizing graphite-monochromated Mo*Kα* radiation. Intensities were measured using a θ–2θ scan technique, with theta scan widths determined by the relationship $\theta = 0.60° + 0.34 (\tan \theta)$. A prescan of each peak during data collection determined counting time, with a maximum time of 4 min per reflection. One-third of the total counting time was spent determining background on both sides of the peak.

Three intensity standards were monitored every 4 h, and two orientation standards were monitored every 160 reflections. No significant deviation of intensity was noted during data collection (~3 d).

Intensity data were collected for the octant of reciprocal space compromising $+h$, $+k$ and $+l$, to 50° 2θ. The 946 resulting reflections were corrected for Lorentz and polarization effects, and absorption effects were corrected by an empirical technique employing intensity data obtained from 360° psi scans at 10° intervals for six reflections. Symmetry-extinct and "unobserved" data ($I < 4\sigma_I$) were removed from the structure-factor list. The final data set yielded 624 observed reflections. The zero-moment test yielded statistics not incompatible with the centrosymmetric space group; thus subsequent calculations were undertaken in space group no. 62, *Pmcn*.

All crystal-structure calculations were carried out using the Enraf-Nonius SDP-Plus programs. The phase problem was solved by direct methods as implemented in MULTAN and associated programs (Main et al., 1980). The phase set with the highest combined figure-of-merit ultimately revealed the positions of all atoms.

Final refinement was undertaken by refining positional parameters, scale factor, anisotropic temperature factors, an isotropic secondary extinction factor and the occupancy of the Cu(1) site, with a total of 96 parameters. The quantity $w(|F_o| - |F_c|)^2$ was minimized by full-matrix least-squares refinement, with $w = [\sigma_I^2 + (0.007F_o^2)^2]^{-1}$. Neutral-atom scattering factors, including terms for anomalous extinction, were taken from *Tables for X-ray Crystallography* (1974). Upon assigning the correct atomic positions, the structure routinely refined to $R = 0.028$, $R_w = 0.031$, with a goodness-of-fit of 2.1 for the 624 observed reflec-

TABLE 3. Atomic coordinates and equivalent isotropic *B* for lyonsite

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Cu(1)	¾	0.7497(2)	0.9080(6)	2.77(5)
Cu(2)	¼	0.82189(7)	0.2113(2)	1.33(2)
Fe	0.42409(8)	0.97289(4)	0.2476(2)	0.47(1)
V(1)	¼	1.05727(9)	−0.2293(3)	0.95(3)
V(2)	0.4716(1)	0.84431(5)	0.7208(2)	0.77(2)
O(1)	0.6129(4)	0.7959(2)	0.6585(9)	1.18(9)
O(2)	0.3859(4)	0.8739(3)	0.4245(9)	1.01(8)
O(3)	¼	0.9940(4)	0.053(1)	1.5(1)
O(4)	0.3849(4)	1.0358(3)	0.5747(9)	1.48(9)
O(5)	0.5054(4)	0.9272(2)	0.9130(9)	1.07(8)
O(6)	¾	0.6531(4)	0.656(1)	1.4(1)
O(7)	0.3766(4)	0.7917(3)	−0.0738(9)	1.27(9)

Note: Numbers in parentheses indicate one esd of least units given.

tions. The largest shift/error in the final cycle was <0.01. Refinement with all 741 nonabsent, $I > 0$ reflections yielded $R = 0.038$, $R_w = 0.034$. The highest negative peak in the final difference map is 1.02 e Å^{-3} [located midway between adjacent Cu(1) sites along *c*], and the largest positive peak is 0.86 e Å^{-3}, located 0.87 Å from Cu(2).

The atomic coordinates for lyonsite are listed in Table 3, and anisotropic thermal parameters are given in Table 4. Table 5 presents bond lengths and bond angles for all coordination polyhedra. Table 6 contains bond-valence sums for all atoms (Brown, 1981) and Table 7[1] contains a list of observed and calculated structure factors for the mineral.

Description of the structure

The small volume per oxygen atom in lyonsite (18.12 Å^3) suggested an atomic arrangement based on closest-packed oxygen atoms. The short *c* axis (4.910 Å) further suggested hexagonal closest packing with *c* corresponding to the hexad in the oxygen array. A plot of oxygen-atom positions projected on (001) revealed the hexagonal array (Fig. 1), in which the pseudo 6_3 axis coincides with the 2_1 axis parallel to *c*.

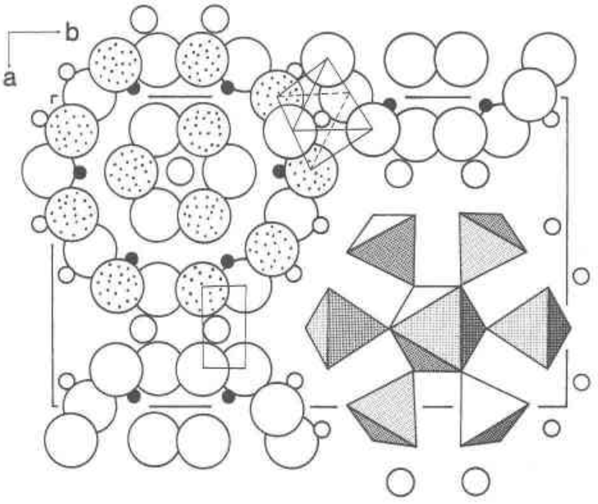

Fig. 1. Atomic arrangement of lyonsite projected on (001). Large circles are oxygen atoms, intermediate circles are Cu atoms, small open circles are Fe atoms, and small solid circles are V atoms. Upper left-hand portion of unit cell depicts inner and outer hexagonal rings of oxygen atoms. Stippled atoms in outer hexagonal ring are centered about plane at $z = 0.57$ (±0.02), and unstippled oxygen atoms in outer ring are centered at $z = 0.07$ (±0.02). For stippled oxygen atoms in inner ring, $z = 0.84$; unstippled oxygen atoms, $z = 0.34$. Lower right-hand portion of unit cell displays coordination polyhedra in fundamental building block. One Fe octahedron and one square-planar Cu(2) polyhedron that link fundamental building blocks are shown.

In lyonsite, all atoms are in the 8*d* general position or the 4*c* special positions [Cu(1), Cu(2), V(1), O(3), O(6)] that lie on the mirror planes at *x* = ¼, ¾. The atomic arrangement of lyonsite is defined by an hexagonal closest-packed (hcp) array of oxygen atoms. V atoms occupy tetrahedral interstices in the array, forming pseudohexagonal pinwheels of isolated VO_4 tetrahedra. The tetrahedra are tilted approximately 20° from those in an ideal hcp array, but tilted symmetrically outward from the pseudohexad. This tilting gives rise to two concentric hexagonal prisms of oxygen atoms; the basal oxygens in the tetrahedra form the outer hexagonal prism and the apical oxygen atoms of the six tetrahedra form the inner trigonal antiprism. The inner trigonal antiprism surrounds channels of face-sharing Cu(1)O_6 octahedra; these octahedra,

TABLE 4. Anisotropic thermal parameters for lyonsite

Atom	$\beta_{(1,1)}$	$\beta_{(2,2)}$	$\beta_{(3,3)}$	$\beta_{(1,2)}$	$\beta_{(1,3)}$	$\beta_{(2,3)}$
Cu(1)	0.0017(2)	0.00064(6)	0.071(2)	0	0	0.0026(6)
Cu(2)	0.00219(9)	0.00151(4)	0.0131(5)	0	0	−0.0039(2)
Fe	0.00136(6)	0.00034(2)	0.0044(3)	0.00007(7)	−0.0002(3)	−0.0002(2)
V(1)	0.0026(1)	0.00082(5)	0.0083(6)	0	0	0.0006(3)
V(2)	0.00191(8)	0.00067(3)	0.0073(4)	0.00039(9)	−0.0002(3)	−0.0001(3)
O(1)	0.0033(4)	0.0007(1)	0.013(2)	0.0003(4)	0.001(1)	0.0006(9)
O(2)	0.0026(4)	0.0009(1)	0.009(2)	−0.0005(4)	−0.002(1)	−0.0018(8)
O(3)	0.0044(7)	0.0013(2)	0.011(3)	0	0	−0.001(1)
O(4)	0.0051(5)	0.0010(1)	0.011(2)	−0.0009(5)	0.004(2)	−0.0017(9)
O(5)	0.0025(4)	0.0009(1)	0.011(2)	0.0003(5)	0.001(1)	0.0013(9)
O(6)	0.0033(6)	0.0015(2)	0.012(3)	0	0	0.001(1)
O(7)	0.0034(4)	0.0010(2)	0.012(2)	0.0011(5)	0.002(2)	−0.0010(9)

Note: Number in parentheses indicates one esd of least units given.

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[1] To obtain a copy of Table 7, order Document AM-87-356 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 5. Selected bond lengths (Å) and angles (°) in lyonsite

V(1)–O(3)	1.762(7)	O(3)–V(1)–O(4)a	107.8(2)	O(4)a–V(1)–O(4)b	106.8(2)
–O(4)a	1.730(5)	O(3)–V(1)–O(4)b	107.8(2)	O(4)a–V(1)–O(6)a	109.1(2)
–O(4)b	1.730(5)	O(3)–V(1)–O(6)a	115.9(3)	O(4)b–V(1)–O(6)a	109.1(2)
–O(6)a	1.687(7)				
Mean	1.727				
V(2)–O(1)	1.704(4)	O(1)–V(2)–O(2)	114.7(2)	O(2)–V(2)–O(5)	107.9(2)
–O(2)	1.776(4)	O(1)–V(2)–O(5)	109.1(2)	O(2)–V(2)–O(7)	111.0(2)
–O(5)	1.745(4)	O(1)–V(2)–O(7)	110.1(2)	O(5)–V(2)–O(7)	103.5(2)
–O(7)	1.672(4)				
Mean	1.724				
Cu(1)–O(1)	2.031(5)	O(1)–Cu(1)–O(1)a	88.1(2)	O(1)a–Cu(1)–O(6)c	92.2(2)
–O(1)a	2.031(5)	O(1)–Cu(1)–O(1)b	91.9(2)	O(1)b–Cu(1)–O(1)c	88.1(2)
–O(1)b	2.030(5)	O(1)–Cu(1)–O(1)c	179.7(2)	O(1)b–Cu(1)–O(6)	93.0(2)
–O(1)c	2.030(5)	O(1)–Cu(1)–O(6)	87.4(2)	O(1)b–Cu(1)–O(6)c	87.4(2)
–O(6)	2.072(7)	O(1)–Cu(1)–O(6)c	92.2(2)	O(1)c–Cu(1)–O(6)	93.0(2)
–O(6)c	2.070(7)	O(1)a–Cu(1)–O(1)b	179.7(2)	O(1)c–Cu(1)–O(6)c	87.4(2)
Mean	2.044	O(1)a–Cu(1)–O(1)c	91.9(2)	O(6)–Cu(1)–O(6)c	179.4(3)
		O(1)a–Cu(1)–O(6)	87.4(2)		
Cu(2)–O(2)	1.963(4)	O(2)–Cu(2)–O(2)c	90.9(2)	O(2)c–Cu(2)–O(7)b	91.6(2)
–O(2)c	1.963(4)	O(2)–Cu(2)–O(7)b	164.8(2)	O(2)c–Cu(2)–O(7)c	164.8(2)
–O(7)b	1.982(4)	O(2)–Cu(2)–O(7)c	91.6(2)	O(7)b–Cu(2)–O(7)c	82.2(2)
–O(7)c	1.982(4)				
Mean	1.973				
–O(7)a	2.576(4)				
–O(7)d	2.576(4)				
Fe–O(2)	1.953(4)	O(2)–Fe–O(3)	100.6(2)	O(3)–Fe–O(5)c	92.9(2)
–O(3)	2.064(3)	O(2)–Fe–O(4)	94.3(2)	O(4)–Fe–O(4)c	84.0(2)
–O(4)	1.978(5)	O(2)–Fe–O(4)c	86.8(2)	O(4)–Fe–O(5)a	85.7(2)
–O(4)c	2.157(5)	O(2)–Fe–O(5)a	170.4(2)	O(4)–Fe–O(5)c	164.8(2)
–O(5)a	2.026(4)	O(2)–Fe–O(5)c	96.1(2)	O(4)c–Fe–O(5)a	83.6(2)
–O(5)c	2.005(4)	O(3)–Fe–O(4)	95.9(2)	O(4)c–Fe–O(5)c	85.6(2)
Mean	2.031	O(3)–Fe–O(4)c	172.6(2)	O(5)a–Fe–O(5)c	82.2(2)
		O(3)–Fe–O(5)a	89.0(2)		

Note: Number in parentheses represents one standard deviation.

separated by only 2.455 Å, are half occupied. Adjacent hexagonal prism-pairs are linked by two edge-sharing FeO_6 octahedra on four sides and the square-planar Cu(2) atoms on the other two sides. It should be noted that the polyhedral arrangement of the fundamental building block of lyonsite was anticipated by Moore (1973) in his particularly prescient bracelet-and-pinwheel analysis of hcp arrays.

A comparison of the vanadate hexagonal prisms in lyonsite can be made to the silicate hexagonal prisms in dumortierite (Alexander et al., 1986; Moore and Araki, 1978). In dumortierite, isolated silicate tetrahedra form a pseudohexagonal array essentially identical to the array of vanadate tetrahedra in lyonsite. The inner channels in dumortierite, however, are occupied by $(Al,Fe)O_6$ octahedra that are approximately 80% occupied, in comparison to the half-occupied channel octahedra in lyonsite. Thus, in dumortierite, some face-sharing channel octahedral centers are separated by only 2.35 Å.

The Cu polyhedra in lyonsite deserve special mention. Cu(2), lying on the mirror planes at $x = 1/4$ and $3/4$, is coordinated to four oxygens in square-planar coordination typical for Cu^{2+}. In addition to these four oxygen atoms, Cu(2) is also weakly bonded to two more mirror-related oxygen atoms [O(7),O(7′)] at a much greater distance (2.576 Å). The two additional oxygen atoms do not complete a typical (4 + 2) polyhedron, as both additional oxygens are on the same side of the equatorial oxygen

TABLE 6. Bond-valence sums for atoms in lyonsite

	O(1)	O(2)	O(3)*	O(4)	O(5)	O(6)*	O(7)	Sum
V(1)*	—	—	1.09	1.19 (2×)	—	1.36	—	4.83
V(2)	1.29	1.04	—	—	1.14	—	1.42	4.89
Fe	—	0.59	0.43	0.33 0.55	0.51 0.48	—	—	2.89
Cu(1)*	0.37 (2×) 0.37 (2×)	—	—	—	—	0.33 0.32	—	2.13
Cu(2)*	—	0.45 (2×)	—	—	—	—	0.42 (2×) 0.09 (2×)	1.92
Sum	2.03	2.08	1.95	2.07	2.13	2.01	1.93	

* Denotes atom in 4*c* special position.

plane. If the two additional oxygen atoms are considered in the primary coordination polyhedron, it would be defined as a distorted trigonal prism, with Cu(2) lying on a prism face.

Cu(1) also lies on the mirror planes perpendicular to *a*. In addition, the Cu(1) atoms essentially lie on 2_1 screw axes ($y = \frac{1}{4}, \frac{3}{4}$) that are parallel to *c* and contained on the mirror planes, coincident with the 6_3 screw axis in the hexagonal close-packed array. This position yields symmetry-related $Cu(1)O_6$ octahedra that are separated by $c/2$ (2.455 Å) and share a common face. In addition, although the site symmetry does not preclude Jahn-Teller distortion, the octahedron is atypically regular for a CuO_6 octahedron, with bond lengths of 2.030 (2×) and 2.031 (2×) for the equatorial oxygens and 2.070 and 2.072 for the apical oxygens.

Initial least-squares refinement gave an unusually large isotropic thermal parameter ($B = 4.1$ Å^2) for Cu(1). This, coupled with the 2.455-Å separation of symmetry-equivalent Cu(1) sites and the stoichiometry of the compound, suggested half-occupancy of the Cu(1) site. Subsequent refinement of site occupancy yielded 2.36(1) Cu(1) atoms per unit cell (vs. 4.0 for the fully occupied special position), or 0.59 atoms in each Cu(1) channel octahedron. This value represents a small but significant deviation from half-occupancy and may indeed be real; when occupancy is fixed at 0.50 atoms per site, the temperature factor of Cu(1) becomes nonpositive definite. If the deviation from half-occupancy is real and not an artifact of the data, it is suggested that some Fe or Cu(2) sites may also be vacant.

The second peculiarity of the Cu(1) site involves its unusual regularity. Although Cu^{2+} atoms have been found to occupy more regular octahedral sites (Miller et al., 1973), Cu^{2+} typically shows a greater response to the Jahn-Teller effect than observed in lyonsite. However, two possibilities exist that may account for this apparent regularity. First, because of this unusual regularity of the Cu(1) octahedron, the Fe^{3+} octahedron affords a site with a similar mean bond length and a greater variation in bond length (1.953–2.157 Å) than the Cu(1) octahedron. It cannot be ruled out that there is disordering of Fe^{3+} and Cu(1) between the two octahedra, although the similarity of scattering factors between the two atoms mitigates against refinement of occupancy.

A second cause of the apparent Cu(1) octahedral regularity is indicated by the Cu(1) thermal parameters. The structure model places Cu(1), with fractional coordinates $x = \frac{3}{4}$, $y = 0.7497$, on a position that essentially lies on the 2_1 screw axis parallel to *c* ($x = \frac{3}{4}$, $y = \frac{3}{4}$) and on the mirror plane perpendicular to *a*. Displacement of Cu(1) along the 2_1 screw axis, however, would retain the special position symmetry. Thermal parameters of the Cu(1) atom display a marked anisotropy of electron density along the 2_1 axis, with $U_{(3,3)} = 0.086(2)$, $U_{(1,1)} = 0.0092(9)$, and $U_{(2,2)} = 0.0096(9)$ Å^2. The large rms displacement occurs along the 2_1 axis, through the octahedron face toward the adjacent unoccupied Cu(1) site [c.f. Al(1) in dumortierite of Moore and Araki (1978)]. The room-temperature structure may thus represent a space-average of disordered Cu(1) positions within the octahedron. Attempts to model the disordering were unsuccessful, however. It is felt that, because of the small crystal size and large aspect ratio of available crystals, the structure model for lyonsite is at the limits of its resolution.

PHYSICAL PROPERTIES

Lyonsite occurs as euhedral, lathlike crystals flattened on (010). The largest crystal isolated to date is 0.230 mm ([001]) × 0.060 mm ([100]) × 0.030 mm ([010]). The mineral is black with a metallic luster. The calculated density of lyonsite is 4.215 g/cm^3. Z = 2 for the formula $Cu_3Fe_4(VO_4)_6$.

Lyonsite displays a good {001} cleavage and a brittle fracture. The streak is dark gray.

The mineral is opaque. Lyonsite is creamy white in reflected light in air. Polished sections display a weak anisotropy in shades of gray with nicols 5–7° from crossed. Reflectivity for the mineral was measured in air on the polished (010) face, using a SiC standard. Average minimum and maximum reflectivity values for four wavelengths are 481 nm, 17.5, 23.1%; 547 nm, 16.6, 22.3%; 591 nm, 14.7, 20.7%; and 644 nm, 14.4, 18.8%.

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