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Cornetite: Modulated Densely-Packed Cu^{2+} Oxysalt

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With 5 Figures

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Summary

The crystal structure of cornetite, $Cu_3(PO_4)(OH)_3$, orthorhombic, a = 10.854(1), b = 14.053(3), c = 7.086(2) Å, V = 1080.8(3) $Å^3$, Z = 8, space group Pbca, has been refined to an R-index of 3.9% for 1231 observed reflections ($I > 3\sigma I$), measured with MoKα X-radiation on an automated four-circle diffractometer. The structure consists of edge-sharing zig-zag chains of distorted octahedra, cross-linked by edge-sharing octahedral dimers into complex octahedral layers. Adjacent layers are corner-linked together by neighbouring octahedra and PO_4 tetrahedra into a densely-packed heteropolyhedral framework, in which the phosphate tetrahedra share edges with the octahedral dimers. The polyhedral layers exhibit a commensurate modulation that results from the interaction between local relaxation of Jahn-Teller distorted octahedra and the long-range requirements of translational periodicity.

Zusammenfassung

Cornetit: Ein moduliertes, dicht gepacktes Oxosalz des zweiwertigen Kupfers

Die Kristallstruktur des Cornetits, $Cu_3(PO_4)(OH)_3$, orthorhombisch, a = 10,854(1), b = 14,053(3), c = 7,086(2) Å, V = 1080,8(3) $Å^3$, Z = 8, Raumgruppe Pbca, wurde mit 1231 beobachteten Röntgenreflexen ($I > 3\sigma I$), die mit MoKα-Strahlung auf einem automatischen Vierkreis-Diffraktometer gesammelt worden waren, auf einen R-Wert von 3,9% verfeinert. Die Struktur besteht aus kantenverknüpften Zickzack-Ketten verzerrter Oktaeder, die über kantenverknüpfte Oktaeder-Dimere zu komplizierten Oktaederschichten verbunden sind. Benachbarte Schichten sind über Ecken durch benachbarte Oktaeder und PO_4-Tetraeder zu einem dichtgepackten, heteropolyedrischen Gerüst verknüpft, in welchem die Phosphattetraeder mit den Oktaeder-Dimeren Kanten gemeinsam haben. Die Polyederschichten zeigen eine kommensurable Modulierung, die aus der Wechselwirkung zwischen der lokalen Relaxation von Jahn-Teller-verzerrten Oktaedern und den Forderungen der translatorischen Periodizität über größere Entfernungen resultiert.

Introduction

Cornetite, $Cu_3(PO_4)(OH)_3$, is a copper hydroxy-phosphate mineral first described by *Cesaro* (1912) from the L'Etoile du Congo mine, Katanga, Belgian Congo (now Zaire). The mineral was named by *Buttgenbach* (1916) and the correct formula was established by *Hutchinson* and *Macgregor* (1913). The morphology and derivation of the unit cell was given by *Berry* (1951), and the structure was solved by *Fehlmann* et al. (1964); it is the chemical analogue of clinoclase, $Cu_3(AsO_4)(OH)_3$, but the two minerals are not isostructural. Cornetite is a secondary mineral, and often occurs as crusts associated with other secondary copper oxysalts such as brochantite, libethenite, atacamite, malachite and pseudomalachite.

The coordination of Cu^{2+} in oxysalt minerals is strongly influenced by the Jahn-Teller effect. There has been a tendency to underestimate the coordination of Cu^{2+} in the past, and this has greatly retarded our understanding of Cu^{2+} oxysalts. Description of structures with [6]-coordination of Cu^{2+} (wherever possible) greatly simplifies the graphical (often called bond-topological) aspects, and makes apparent the structural relationships with other Cu^{2+} and non-Cu^{2+} oxysalts. The current work is part of an on-going study of copper oxysalt minerals (*Hawthorne*, 1985a, b, 1986; *Hawthorne* and *Groat*, 1985, 1986; *Groat* and *Hawthorne*, 1987; *Hawthorne* and *Eby*, 1985) that is examining the graphical consequences of incorporating Jahn-Teller distortions into networks with translational symmetry.

Experimental Methods

The crystals used in this work are from the Mine de L'Etoile, Katanga, and are subhedral prisms, sky blue and 0.30–1.0 mm in size. A crystal fragment was shaped into an ellipsoid and mounted on a Nicolet R3M automated four-circle diffractometer. The cell dimensions were refined from the setting angles of 25 intense reflections selected from a rotation photograph and aligned automatically; the resulting values are listed in Table 1, together with other information pertinent to data collection and refinement. Intensity data were collected according to the experimental procedures of *Hawthorne* (1985a). A total of 1882 reflections were measured out to a maximum two-theta value of 60°. An empirical absorption correction (psi-scan method) was applied to the data, reducing R(symmetric) for the azimuthal data to 1.4%. Lorentz, polarization and background corrections were applied, and the data were reduced to structure factors, resulting in 1231 unique observed reflections.

Refinement

Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from *Cromer* and *Mann* (1968) and *Cromer* and *Libermann* (1970). R-indices are of the form given in Table 1, and are expressed as percentages.

Systematic absences are compatible with the space group Pbca. The coordinates were taken from *Fehlmann* et al. (1964), and full-matrix least-squares refinement for an isotropic thermal model converged to an R-index of 5.6%. Conversion to anisotropic temperature factors and refinement of all variables resulted in convergence at an R-index of 3.9%; hydrogen atoms could not be located on the final

Table 1. *Pertinent data for cornetite*

Unit Cell: a = 10.854(1)Å
b = 14.053(3)
c = 7.086(2)
V = 1080.8(3)$Å^3$

Space group : Pbca

Portion of sphere collected : 1 octant

dens.(calc) = $4.14 g/cm^3$
dens.(meas) = $4.10 g/cm^3$

Number of reflections used in cell determination : 25
No. Reflections Collected : 1882

Total Observed $|F_o|$ I>3.0 : 1572
Total Unique $|F_o|$: 1231
No. of ψ-scan reflections : 10
No. of ψ-scan measurements : 360
Absorption corr. R-merge : 1.43%
min-max : 0.058 - 0.097
Cell contents : $8[Cu_3(PO_4)(OH)_3]$

R(obs) = 3.93% ; Rw(obs) = 2.97%

$R(obs) = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$Rw(obs) = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, w=1

Table 2. *Atomic parameters for cornetite*

	x	y	z	U(equiv)
Cu(1)	0.01900(6)	0.12739(5)	0.1876(1)	0.0127(2)
Cu(2)	0.19409(6)	0.24645(6)	0.40293(9)	0.0128(2)
Cu(3)	0.10041(6)	0.45217(5)	0.1092(1)	0.0121(2)
P	0.3800(1)	0.3864(1)	0.2070(2)	0.0114(4)
O(1)	0.2690(3)	0.4101(3)	0.0857(6)	0.016(1)
O(2)	0.9211(4)	0.4726(3)	0.1754(6)	0.013(1)
O(3)	0.4896(4)	0.3596(3)	0.0812(5)	0.016(1)
O(4)	0.3499(4)	0.3034(3)	0.3415(6)	0.015(1)
OH(1)	0.0564(4)	0.3390(3)	0.9551(5)	0.011(1)
OH(2)	0.1822(4)	0.1876(3)	0.1470(5)	0.013(1)
OH(3)	0.1343(4)	0.5679(3)	0.2450(6)	0.013(1)

Table 3. *Anisotropic temperature factors for cornetite*

	*U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Cu(1)	102(3)	166(4)	112(3)	10(3)	-7(3)	-29(2)
Cu(2)	115(3)	158(3)	110(3)	-8(4)	14(3)	-38(3)
Cu(3)	95(3)	128(3)	140(3)	-22(3)	0	8(3)
P	95(7)	149(7)	98(7)	-9(6)	6(5)	-8(6)
O(1)	79(17)	243(22)	165(20)	-11(19)	-10(16)	17(17)
O(2)	121(18)	127(19)	152(19)	33(17)	-6(17)	8(15)
O(3)	103(18)	249(22)	131(19)	13(18)	27(16)	19(17)
O(4)	157(19)	173(20)	115(20)	13(17)	-5(17)	-52(17)
OH(1)	110(18)	110(18)	100(20)	-22(15)	4(15)	17(16)
OH(2)	139(18)	145(19)	95(19)	5(16)	-23(16)	-21(16)
OH(3)	118(18)	131(19)	148(19)	-35(18)	10(16)	20(16)

*U(ij) = U(ij) x 10^4

difference-Fourier map. Final positional and thermal parameters are given in Tables 2 and 3, selected interatomic distances and angles are listed in Table 4; structure factor tables can be obtained from the authors.

Description of the Structure

This work confirms the validity of the original structure model of *Fehlmann* et al. (1964). There is one unique phosphorous position surrounded by four oxygen atoms in a tetrahedral arrangement; there is little distortion from the mean bond length of 1.532 Å, which falls within the range of commonly observed $\langle P\text{-}O \rangle$ distances (*Baur*, 1974). There are three unique divalent copper positions, designated Cu(1), Cu(2) and Cu(3). Each Cu^{2+} is surrounded by six oxygen and hydroxyl anions in an octahedral arrangement, and all the coordination polyhedra show typical Jahn-Teller distortion with four short Cu-φ bonds (φ = unspecified ligand) and two long Cu-φ bonds in a *trans* arrangement. Again we stress that it is these long Cu^{2+}-φ bonds that allow a better interpretation of the graphical aspects of these type of structures.

A bond-valence analysis for cornetite is given in Table 5; the longer Cu-φ bonds have very low calculated bond-valences, and we make no argument to justify

Table 4. *Selected interatomic distances (Å) and angles (°) in cornetite*

P-O(1)	1.518(4)	O(1)-P-O(2)a	111.4(2)	O(1)-O(2)a	2.522(6)
P-O(2)a	1.536(4)	O(1)-P-O(3)	109.9(2)	O(1)-O(3)	2.497(5)
P-O(3)	1.532(4)	O(1)-P-O(4)	110.3(2)	O(1)-O(4)	2.510(6)
P-O(4)	1.541(4)	O(2)a-P-O(3)	106.6(2)	O(2)a-O(3)	2.460(5)
<P-O>	1.532	O(2)a-P-O(4)	108.8(2)	O(2)a-O(4)	2.503(6)
		O(3)a-P-O(4)	109.8(2)	O(3)a-O(4)	2.514(6)
		<O-P-O>	109.5	<O-O>P	2.501
Cu(1)-O(2)b	2.470(4)	O(2)b-Cu(1)-O(3)c	120.8(2)	O(2)b-O(3)c	3.843(6)
Cu(1)-O(3)c	1.940(4)	O(2)b-Cu(1)-OH(1)d	77.4(2)	O(2)b-OH(1)d	2.815(5)
Cu(1)-O(4)a	3.087(4)	O(2)b-Cu(1)-OH(2)	101.4(2)	O(2)b-OH(2)	3.460(6)
Cu(1)-OH(1)d	1.996(4)	O(2)b-Cu(1)-OH(3)e	75.4(2)	O(2)b-OH(3)e	2.719(5)
Cu(1)-OH(2)	1.984(4)	O(3)c-Cu(1)-O(4)a	76.2(2)	O(3)c-O(4)a	3.229(6)
Cu(1)-OH(3)e	1.923(4)	O(3)c-Cu(1)-OH(2)	88.0(2)	O(3)c-OH(2)	2.726(5)
		O(3)c-Cu(1)-OH(3)e	98.2(2)	O(3)c-OH(3)e	2.919(6)
<Cu(1(-O>[4]	1.961	O(4)a-Cu(1)-OH(1)d	89.7(2)	O(4)a-OH(1)d	3.667(6)
		O(4)a-Cu(1)-OH(2)	100.3(2)	O(4)a-OH(2)	3.960(6)
<Cu(1)-O>[6]	2.233	O(4)a-Cu(1)-OH(3)e	81.4(2)	O(4)a-OH(3)e	3.384(6)
		OH(1)d-Cu(1)-OH(2)	81.7(2)	OH(1)d-OH(2)	2.602(5)
		OH(1)d-Cu(1)-OH(3)e	92.5(2)	OH(1)d-OH(3)e	2.830(5)
		<O-Cu(1)-O>	90.2	<O-O>Cu(1)	3.180
Cu(2)-O(1)f	2.679(4)	O(1)f-Cu(2)-O(4)	100.7(1)	O(1)f-O(4)	3.573(6)
Cu(2)-O(3)a	2.734(4)	O(1)f-Cu(2)-OH(1)d	68.6(1)	O(1)f-OH(1)d	2.679(5)
Cu(2)-O(4)	1.921(4)	O(1)f-Cu(2)-OH(2)	96.8(2)	O(1)f-OH(2)	3.527(6)
Cu(2)-OH(1)d	1.952(4)	O(1)f-Cu(2)-OH(2)f	88.9(1)	O(1)f-OH(2)f	3.293(5)
Cu(2)-OH(2)	1.998(4)	O(3)a-Cu(2)-O(4)	118.8(2)	O(3)a-O(4)	4.028(6)
Cu(2)-OH(2)f	1.966(4)	O(3)a-Cu(2)-OH(1)d	74.2(1)	O(3)a-OH(1)d	2.895(5)
		O(3)a-Cu(2)-OH(2)	103.0(1)	O(3)a-OH(2)	3.732(6)
<Cu(2)-O>	1.959	O(3)a-Cu(2)-OH(2)f	68.7(1)	O(3)a-OH(2)f	2.726(5)
		O(4)-Cu(2)-OH(2)	91.3(2)	O(4)-OH(2)	2.803(6)
<Cu(2)-O>	2.208	O(4)-Cu(2)-OH(2)f	93.5(2)	O(4)-OH(2)f	2.831(6)
		OH(1)d-Cu(2)-OH(2)	82.4(2)	OH(1)d-OH(2)	2.602(5)
		OH(1)d-Cu(2)-OH(2)f	94.2(2)	OH(1)d-OH(2)f	2.870(5)
		<O-Cu(2)-O>	90.1	<O-O>Cu(2)	3.130
Cu(3)-O(1)	1.930(4)	O(1)-Cu(3)-O(2)h	99.3(2)	O(1)-O(2)h	3.224(6)
Cu(3)-O(2)g	2.023(4)	O(1)-Cu(3)-O(3)i	109.3(2)	O(1)-O(3)i	3.909(6)
Cu(3)-O(2)h	2.280(4)	O(1)-Cu(3)-OH(1)j	86.3(2)	O(1)-OH(1)j	2.680(5)
Cu(3)-O(3)i	2.821(4)	O(1)-Cu(3)-OH(3)	96.9(5)	O(1)-OH(3)	2.885(5)
Cu(3)-OH(1)j	1.988(4)	O(2)g-Cu(3)-O(2)h	92.3(1)	O(2)g-O(2)h	3.115(6)
Cu(3)-OH(3)	1.925(4)	O(2)g-Cu(3)-O(3)i	58.3(1)	O(2)g-O(3)i	2.460(5)
		O(2)g-Cu(3)-OH(1)j	90.5(2)	O(2)g-OH(1)j	2.849(5)
<Cu(3)-O>[4]	1.967	O(2)g-Cu(3)-OH(3)	87.1(2)	O(2)g-OH(3)	2.721(5)
		O(2)h-Cu(3)-OH(1)j	82.0(1)	O(2)h-OH(1)j	2.815(5)
<Cu(3)-P>[6]	2.161	O(2)h-Cu(3)-OH(3)	94.0(2)	O(2)h-OH(3)	3.092(6)
		O(3)i-Cu(3)-OH(1)j	87.5(1)	O(3)i-OH(1)j	3.379(6)
		O(3)i-Cu(3)-OH(3)	94.7(1)	O(3)i-OH(3)	3.543(6)
		<O-Cu(3)-O>	89.9	<O-O>Cu(3)	3.056

Hydrogen bond donor...acceptor contacts:	OH(1)-O(4)k	2.712(5)
	OH(2)-OH(3)l	2.697(5)
	OH(3)-O(1)m	2.651(5)

Shared edges:	O(2)a-O(3)	2.459(5)	As and Cu(3)
	O(3)c-OH(2)	2.726(5)	Cu(2) and Cu(3)
	OH(1)d-OH(2)	2.602(5)	Cu(2) and Cu(3)
	O(2)g-O(2)h	3.115(6)	Cu(3) and Cu(3)

equivalent positions: a -1/2+x, y, 1/2-x; b 1-x, -1/2+y, 1/2-z; c -1/2+x, 1/2-y, -z; d x, 1/2-y, -1/2+z; e -x, -1/2+y, 1/2-z; f x, 1/2-y, 1/2+z; g -1+x, y, z; h 1-x, 1/2-y, -z; i -x, 1-y, 1-z; j x, y, z-1; k -1/2+x, y, 3/2-z; l 1/2-x, -1/2+y, z; m 1/2-x, 1-y, 1/2+z.

including these as bonds on this basis. Discounting hydrogen bonds, anion coordination numbers vary between [2] and [4], and the relative variation in bond lengths (and bond-valences) can be rationalized as resulting from local bond-valence requirements. The bond-valence sums around the (OH) anions are approximately equal to unity, confirming that these are hydroxyl anions. The anions O(1), O(4) and OH(3) have bond-valence sums less than 1.8 v.u., suggesting that they should be hydrogen-bond acceptors. The anions also have suitable donor-acceptor distances (Table 4), and a sensible hydrogen-bond scheme can be assigned; in Table 5, the H-O bond-valencies have been assigned on the basis of the curve of *Brown* and *Altermatt* (1985), giving reasonable bond-valence sums. The resulting hydrogen-bond scheme is illustrated in Fig. 1.

Table 5. *Bond-valence table for cornetite*

	Cu(1)	Cu(2)	Cu(3)	P	H(1)	H(2)	H(3)	
O(1)		0.070	0.498	1.328			0.22	2.116
O(2)	0.113		0.179 0.375	1.263				1.930
O(3)	0.482	0.062	0.051	1.277				1.872
O(4)	0.030	0.512		1.249	0.20			1.991
OH(1)	0.407	0.465	0.417		0.80			2.089
OH(2)	0.422	0.404 0.445				0.80		2.071
OH(3)	0.508		0.505			0.20	0.78	1.993
SUM	1.962	1.958	2.025	5.117	1.00	1.00	1.00	

*Bond-valence curves from Brown(1981).

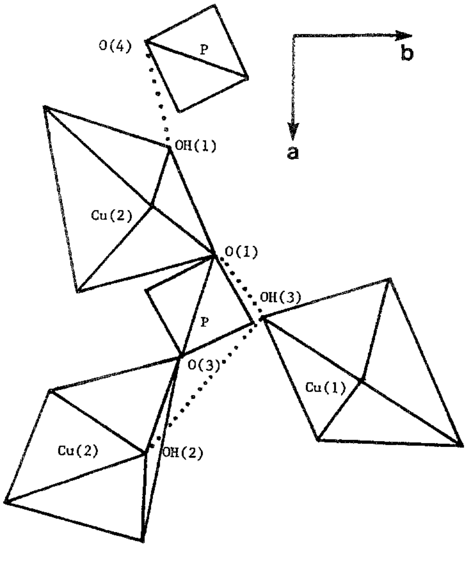

Fig. 1. The hydrogen-bonding arrangement in cornetite; this small fragment of the structure shows the OH...O donor...acceptor separations

The Cu(1) and Cu(2) octahedra share edges to form staggered chains extending along [001] (see Fig. 2). Cu(3) octahedra share edges to form dimers which share an edge with a (PO_4) group to form the second type of tightly-bonded unit. The chains are then linked into a complex sheet by edge-sharing with the $Cu(3)_2\varnothing_6(PO_4)$ clusters along [010], as shown in Fig. 3. This complex sheet then links to the next sheet by sharing octahedral corners along [100] (visible in Figs. 2 and 4) to form the densely-packed heteropolyhedral framework shown in Fig. 4. In this figure, alternate sheets are shaded and unshaded, and very apparent is the commensurate modulation of the sheet along [010]. In the structural schemes developed by *Hawthorne* (1983, 1985c, 1986b), cornetite is a heteropolyhedral framework structure.

The modulation of the structure shown in Fig. 4 arises from the polymerization of distorted octahedra across periodically repeated point symmetry elements, as indicated in Fig. 5. Two (symmetrically equivalent) distorted octahedra share an edge across a mirror plane (Fig. 5a); coupling and repetition of this situation by translationally symmetric mirror planes lead to a commensurate modulation of the resulting edge-sharing chains. Note how this type of effect results in octahedra that have two elongated axial bonds and four concommitantly shortened equatorial bonds, corresponding to the usual geometrical situation in Jahn-Teller distorted $(Cu^{2+}\varphi_6)$ octahedra. This commensurate modulation can thus be seen as the method whereby the local (electronic) relaxation around the Cu^{2+} is incorporated into a structure with translational periodicity. It has been noted previously in the structures of lammerite (*Hawthorne*, 1986a) and lindgrenite (*Hawthorne* and *Eby*, 1985), and is one of the more important mechanisms whereby Cu^{2+} oxysalts satisfy the requirements of both local (Jahn-Teller) distortion and translational periodicity.

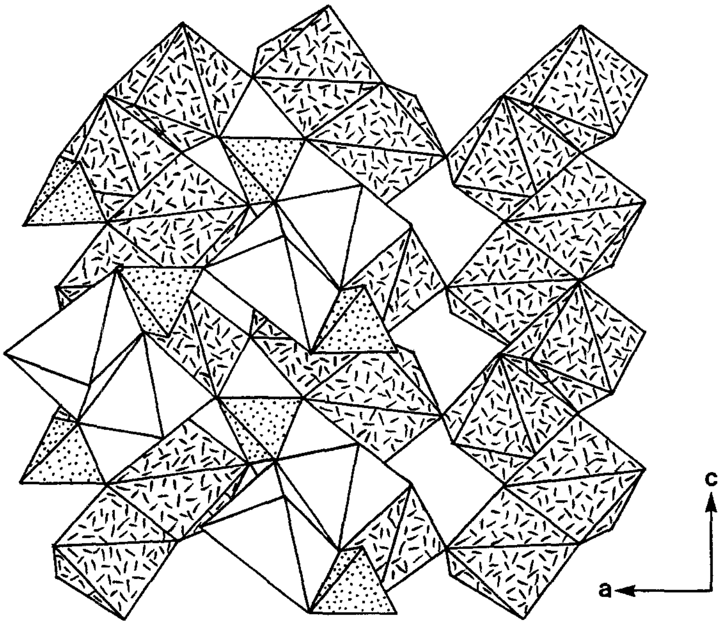

Fig. 2. The structure of cornetite, projected down [010]. Chains of Cu(1) and Cu(2) octahedra (dashes) are cross-linked by Cu(3) octahedral dimers (unshaded) and PO_4 tetrahedra (dotted); note the edge-sharing between PO_4 tetrahedra and Cu(3) octahedra

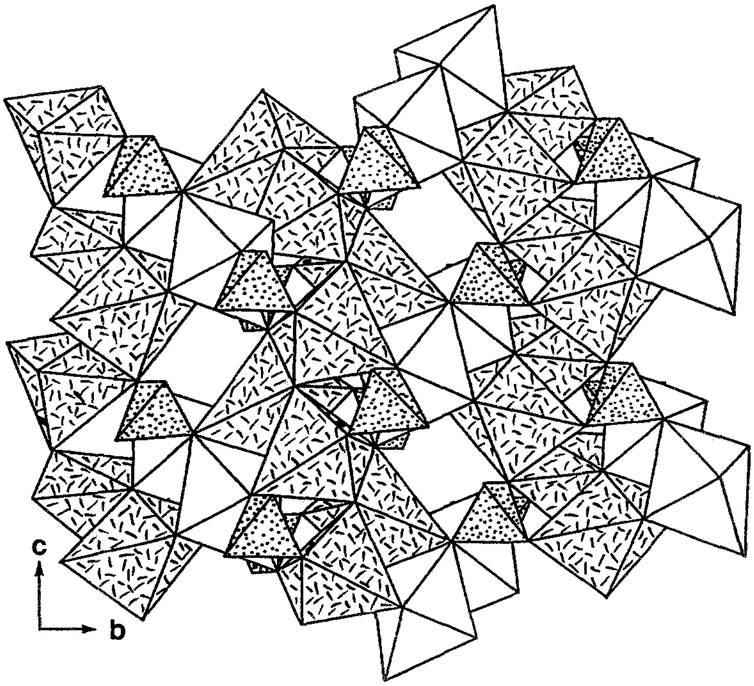

Fig. 3. The structure of cornetite projected down [100]. Note the edge-sharing of the dimers and chains along [010] to form layers parallel to (100)

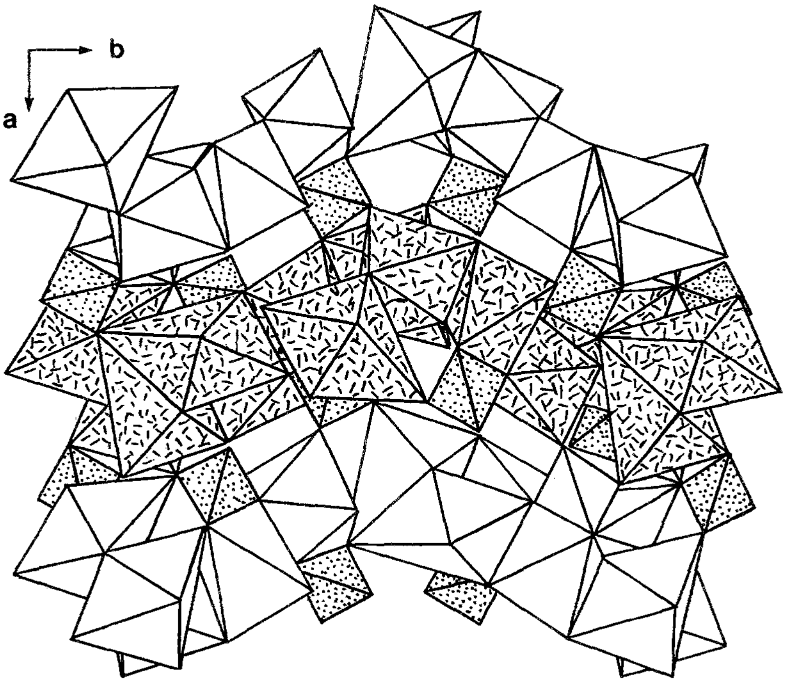

Fig. 4. The structure of cornetite projected down [001]. Note the densely-packed and modulated heteropolyhedral layers; the modulation is commensurate with the translational periodicity along [010]

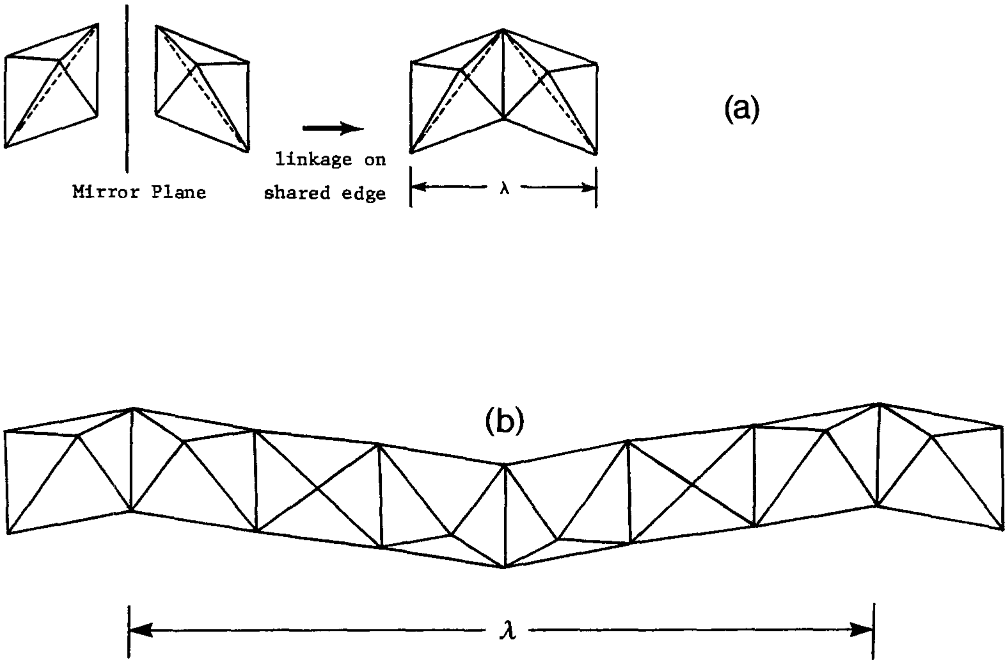

Fig. 5. (a) Distortion-coupling by edge-sharing of Jahn-Teller distorted octahedra across a mirror plane; (b) polymerization causing a waveform commensurate with structural periodicity

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References

Baur WH (1974) The geometry of polyhedral distortions. Predictive relationships for the phosphate group. Acta Cryst B30: 1195–1215

Berry LG (1950) On pseudomalachite and cornetite. Amer Mineral 35: 365–400

Brown ID (1981) The bond-valence method: an empirical approach to chemical structure and bonding. In: O'Keeffe M, Navrotsky A (eds) Structure and bonding in crystals, II. Academic Press, New York

Buttgenbach H (1916) Les Mineraux et les Roches. Liege

Cesaro, G (1912) Sur un nouveau mineral du Katanga. Ann Soc Geol Belgique 39: B241–B242

Cromer DT, Libermann D (1970) Relativistic calculation of anomalous scattering factors for X-rays. J Chem Phys 53: 1891–1898

— *Mann JB* (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Cryst A24: 321–324

Fehlmann M, Ghose S, Finney JJ (1964) Direct determination of the crystal structure of cornetite, $Cu_3PO_4(OH)_3$, by the Monte Carlo method. J Chem Phys 41: 1910–1924

Groat LA, Hawthorne FC (1987) Refinement of the crystal structure of papagoite. Tschermaks Min Petr Mitt 37: 87–96

Hawthorne FC (1983) Graphical enumeration of polyhedral clusters. Acta Cryst A39: 724–736

— (1985a) Refinement of the crystal structure of botallackite. Mineral Mag 49: 87–89

— (1985b) The crystal structure of stringhamite. Tschermaks Min Petr Mitt 34: 15–34

— (1985c) Towards a structural classification of minerals: the $[VI]M[IV]T_2\varphi_n$ minerals. Amer Mineral 70: 455–473

— (1986a) Lammerite, a modulated close-packed structure. Amer Mineral 71: 206–209

— (1986b) Structural hierarchy in $[VI]M_x[III]T_y\varphi_z$ minerals. Can Mineral 24: 625–642

— *Eby RK* (1985) Refinement of the crystal structure of lindgrenite. N Jb Min Mh 1985: 234–240

— *Groat LA* (1985) The crystal structure of wroewolfeite, a mineral with $[Cu_4(OH)_6(SO_4)(H_2O)]$ sheets. Amer Mineral 70: 1050–1055

— (1986) The crystal structure and chemical composition of cumengeite. Mineral Mag 50: 157–162

Hutchinson A, Macgregor AM (1913) A crystalline basic copper phosphate from Rhodesia. Nature 92: 364

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