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PARAKHINITE, $Cu_3^{2+}PbTe^{6+}O_6(OH)_2$: CRYSTAL STRUCTURE AND REVISION OF CHEMICAL FORMULA

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ABSTRACT

The crystal structure of parakhinite, $Cu_3^{2+}PbTe^{6+}O_6(OH)_2$, trigonal, a 5.765(2), c 18.001(9) Å, V 518.0(4) Å^3, $Z = 3$, space group $P3_2$, has been solved by direct methods and refined by least-squares methods to an R index of 8.1% and a wR index of 7.7% using 744 unique observed [$I \geq 2.5\sigma(I)$] reflections collected on a twinned crystal. The chemical formula of parakhinite has been revised as a result of this determination of the crystal structure. Parakhinite contains one Pb position; the Pb is coordinated by six oxygen anions and two hydroxyl groups. The single Te^{6+} position is octahedrally coordinated by six oxygen anions. There are three unique Cu^{2+} positions, each of which is coordinated by a (4 + 2)-distorted octahedral arrangement of anions, the distortion being due to the Jahn–Teller effect. Cu(1) and Cu(2) are coordinated by four oxygen anions and two hydroxyl groups, and Cu(3) is coordinated by six oxygen anions. Parakhinite contains corrugated sheets of octahedra parallel to (001). These sheets are linked *via* interstitial Pb atoms bonded to four anions in each adjacent sheet, and *via* hydrogen bonds. The parakhinite structure is approximately compatible with $P6_2$ symmetry. The group–subgroup relationships and optical characteristics suggest that parakhinite goes through a series of phase transitions on cooling.

Keywords: parakhinite, crystal structure, tellurate, copper oxysalt, Tombstone, Arizona.

SOMMAIRE

Nous avons affiné la structure cristalline de la parakhinite, $Cu_3^{2+}PbTe^{6+}O_6(OH)_2$, trigonale, a 5.765(2), c 18.001(9) Å, V 518.0(4) Å^3, $Z = 3$, groupe spatial $P3_2$, par méthodes directes et par moindres carrés jusqu'à un résidu R de 8.1% ($wR = 7.7\%$) en utilisant 744 réflexions uniques observées [$I \geq 2.5\sigma(I)$] à l'examen d'un cristal maclé. La formule chimique de cette espèce a été révisée à la suite de l'ébauche de la structure cristalline. La parakhinite contient une position occupée par le Pb, qui s'y trouve en coordinence avec six anions d'oxygène et deux groupes hydroxyle. Le Te^{6+}, qui occupe une seule position, est entouré de six anions d'oxygène. Par contre, le Cu^{2+} occupe trois positions uniques, et dans chaque cas la coordinence octaédrique implique un agencement difforme (4 + 2) d'anions dû à l'effet de Jahn–Teller. Cu(1) et Cu(2) sont entourés par quatre anions d'oxygène et deux groupes hydroxyles, tandis que le Cu(3) est entouré de six anions d'oxygène. La structure comprend des feuillets ondulés d'octaèdres parallèles à (001). Ces feuillets sont liés par les atomes de Pb interstitiels, dont les liaisons impliquent quatre anions dans chaque paire de feuillets adjacents, et par des liaisons hydrogène. La structure est approximativement compatible avec la symétrie $P6_2$. Les relations groupe – sous-groupe et les caractéristiques optiques font penser que la parakhinite subit une série de transitions en refroidissant.

(Traduit par la Rédaction)

Mots-clés: parakhinite, structure cristalline, tellurate, oxysel de cuivre, Tombstone, Arizona.

INTRODUCTION

Parakhinite was described as a new mineral species by Williams (1978). It was found in the dumps of the Emerald mine, Tombstone, Arizona, where it occurs in vugs in massive vein quartz. Parakhinite [originally described as $Cu_3^{2+}PbTe^{6+}O_4(OH)_6$] may alter to dugganite [$Pb_3(Zn,Cu^{2+})_3(Te^{6+}O_6)(AsO_4)(OH)_3$], and it is associated with xocomecatlite [$Cu_3^{2+}(Te^{6+}O_4)(OH)_4$], bromargyrite [AgBr] and various unknown tellurates and tellurites. Parakhinite is dimorphous with khinite, which is orthorhombic (Williams 1978). As part of our general interest in Cu^{2+} oxysalt minerals (Burns 1994, Eby & Hawthorne 1993), we have solved the structure of parakhinite, and present the results here.

EXPERIMENTAL

The parakhinite used in this study is from the 400 level of the Empire mine, Tombstone, and was graciously provided for study by Mr. William Pinch of Rochester, New York. Parakhinite occurs in the

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sample as euhedral hexagonal prisms, and rarely as hexagonal pyramids terminated by a basal pinacoid. The crystals readily cleave parallel to {001}, yielding tabular plates. In cross-polarized light, these hexagonal plates show a pronounced sectoral twinning; in addition, there are further signs of twinning within each sector. Viewed down the *c* axis, the crystals are birefringent, indicating that they are biaxial. However, owing to the complex twinning, we were unable to obtain an interference figure. In no case did we observe uniaxial behavior.

A small hexagonal plate was mounted on a Nicolet *R*3*m* automated four-circle diffractometer. Thirty reflections were centered using graphite-monochromated Mo*K*α X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the thirty automatically aligned reflections by least-squares techniques. Data were collected using the θ–2θ scan method, with a scan range of 2.2°. A variable scan-rate inversely proportional to the peak intensity was used, with maximum and minimum scan-rates of 29.3° 2θ/min and 2.9° 2θ/min, respectively. A total of 1299 reflections was measured over the range $4° \leq 2\theta \leq 60°$, with index ranges $0 \leq h \leq 9$, $0 \leq k \leq 9$, $-26 \leq l \leq 26$. Two standard reflections were measured every fifty-eight reflections; no significant changes in their intensities occurred during data collection. An empirical absorption correction was applied, on the basis of 36 psi-scans of each of 10 reflections over the range $8 \leq 2\theta \leq 48°$, and the crystal was modeled as a {001} plate. The absorption correction reduced *R*(azimuthal) from 11.5 to 3.2%. Reflections with a plate-glancing angle less than 11° were discarded; the value of 11° was determined by using a range of glancing angles between 5 and 20°, and determining where the effect of varying the glancing angle produced no improvement in the refinement; 380 reflections had a plate-glancing angle less than 11°, and were discarded. The remaining data were corrected for Lorentz, polarization and background effects; of the 919 reflections remaining after the absorption correction, there were 744 unique observed reflections $[I \geq 2.5\sigma(I)]$.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. *R* indices are of the form given in Table 1 and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study.

Williams (1978) reported that the space group of parakhinite is $P6_222$ or $P6_422$ on the basis of Weissenberg and rotation photographs. We were unable to solve the structure in either of these space groups, and reflection statistics indicate trigonal symmetry. A structure solution was obtained in the space group $P3_2$ by direct methods, which gave the coordinates of the Pb, Te and three Cu positions. Subsequent cycles of least-squares refinement followed by calculation of difference-Fourier maps gave eight oxygen positions. Least-squares refinement of the positional parameters and an isotropic displacement model gave an *R* index of 8.3% and a *wR* index of 9.0%. Conversion of the cation displacement parameters to an anisotropic form, together with refinement of all variable parameters, gave an *R* index of 8.1% an a *wR* index of 8.8%. An isotropic extinction correction was then included in the final stage of refinement; it refined to a non-zero value, and this model gave an *R* index of 8.1% and a *wR* index of 7.7%. Final positional parameters and equivalent isotropic-displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3, and a bond-valence analysis in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 1. MISCELLANEOUS INFORMATION FOR PARAKHINITE

Space group	$P3_2$	Crystal size (mm)	0.08 x 0.06 x 0.025
a (Å)	5.765(2)	Total Ref.*	919
c (Å)	18.001(9)	$\lvert I \rvert \geq 2.5\sigma \lvert I \rvert$	744
V (Å³)	518.0(4)	Final *R*	8.1%
		Final *wR*	7.7%
μ	37.8 cm^{-1}		
D_{calc}	6.302 g/cm^3	F(000)	861
Unit-cell contents	$3[Cu_3PbTeO_6(OH)_2]$		

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

$wR = [\Sigma w(|F_o| - |F_o|)^2/\Sigma wF_o^2]^{½}$, $w = 1/\sigma^2(F)$

*Total Ref. is the total number of reflections collected minus the number of reflections omitted during absorption correction.

TABLE 2. ATOMIC PARAMETERS AND ISOTROPIC DISPLACEMENT PARAMETERS (x 10⁴) FOR PARAKHINITE

	x	*y*	*z*	**U*
Pb	0.3331(4)	0.1659(4)	0.1883	95(9)
Te	0.3296(8)	0.1661(6)	−0.0167(3)	3(1)
Cu(1)	0.833(2)	0.659(2)	−0.2733(6)	12(3)
Cu(2)	0.326(2)	0.660(2)	0.0592(4)	6(2)
Cu(3)	−0.177(2)	0.660(2)	−0.0155(4)	5(2)
O(1)	0.575(6)	0.413(6)	−0.082(3)	10(7)
O(2)	0.080(7)	0.909(7)	−0.084(4)	27(8)
O(3)	0.497(8)	0.980(8)	−0.012(4)	36(8)
O(4)	0.576(5)	0.412(6)	0.059(2)	6(5)
O(5)	0.118(6)	0.364(9)	−0.015(3)	86(8)
O(6)	0.076(6)	0.911(6)	0.058(3)	10(6)
OH(7)	0.561(6)	0.916(6)	0.134(3)	15(7)
OH(8)	0.081(7)	0.413(7)	0.132(3)	19(7)

* *U* is *U* x 10⁴

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR PARAKHINITE

Pb–O(4)	2.72(4)	Cu(2)–O(3)	2.04(5)
Pb–OH(8)	2.69(5)	Cu(2)–O(4)	2.49(4)
Pb–O(1)a	2.77(3)	Cu(2)–O(5)	2.02(5)
Pb–O(2)b	2.74(4)	Cu(2)–O(6)	2.50(4)
Pb–O(3)c	2.94(6)	Cu(2)–OH(7)	1.96(4)
Pb–O(5)d	2.75(5)	Cu(2)–OH(8)	1.93(4)
Pb–O(6)e	2.77(4)	<Cu(2)–O>	2.16
Pb–OH(7)e	2.57(5)	<Cu(2)–O$_{eq}$>	1.99
<Pb–O>	2.74		
		Cu(3)–O(2)	1.91(5)
Te–O(1)	1.84(3)	Cu(3)–O(6)	1.96(4)
Te–O(4)	1.97(3)	Cu(3)–O(1)k	1.86(4)
Te–O(5)	2.05(6)	Cu(3)–O(4)k	1.96(3)
Te–O(2)e	1.90(5)	Cu(3)–O(5)	2.95(7)
Te–O(3)e	1.77(5)	Cu(3)–O(3)k	3.23(6)
Te–O(6)e	1.98(4)	<Cu(3)–O>	2.31
<Te–O>	1.92	<Cu(3)–O$_{eq}$>	1.92
Cu(1)–O(3)f	2.09(6)		
Cu(1)–O(4)g	2.47(3)		
Cu(1)–O(5)h	2.01(6)		
Cu(1)–O(6)i	2.52(3)		
Cu(1)–OH(7)j	2.00(5)		
Cu(1)–OH(8)h	1.94(5)		
<Cu(1)–O>	2.17		
<Cu(1)–O$_{eq}$>	2.01		
Pb polyhedron			
O(4)–OH(8)	3.15(6)	O(4)–Pb–OH(8)	71(1)
O(4)–O(1)a	3.77(6)	O(4)–Pb–O(1)a	87(1)
O(4)–O(6)e	2.88(3)	O(4)–Pb–O(6)e	63.3(9)
O(4)–OH(7)e	3.12(6)	O(4)–Pb–OH(7)e	72(1)
OH(8)–O(2)b	3.23(7)	OH(8)–Pb–O(2)b	73(1)
OH(8)–O(3)c	4.01(8)	OH(8)–Pb–O(3)c	91(1)
OH(8)–O(6)e	3.17(6)	OH(8)–Pb–O(6)e	71(1)
O(1)a–O(3)e	2.63(6)	O(1)a–Pb–O(3)e	54.7(9)
O(1)a–O(5)d	3.49(7)	O(1)a–Pb–O(5)d	78(1)
O(1)a–OH(7)e	3.31(6)	O(1)a–Pb–OH(7)a	76.4(9)
O(2)b–O(3)e	3.81(7)	O(2)b–Pb–O(3)e	84(1)
O(2)b–O(5)d	2.81(7)	O(2)b–Pb–O(5)d	61(1)
O(2)b–O(6)e	3.73(7)	O(2)b–Pb–O(6)e	85(1)
O(3)e–O(5)d	3.13(6)	O(3)e–Pb–O(5)d	67(1)
O(5)–OH(7)e	3.73(8)	O(5)d–Pb–OH(7)e	89(1)
O(6)e–OH(7)e	3.10(5)	O(6)e–Pb–OH(7)e	71(1)
<O–O>	3.32	<O–Pb–O>	74.6
Te octahedron			
O(1)–O(4)	2.53(6)	O(1)–Te–O(4)	83(2)
O(1)–O(5)	2.78(7)	O(1)–Te–O(5)	91(2)
O(1)–O(2)e	2.88(4)	O(1)–Te–O(2)e	101(2)
O(1)–O(3)e	2.63(6)	O(1)–Te–O(3)e	93(2)
O(4)–O(5)	2.85(7)	O(4)–Te–O(5)	90(2)
O(4)–O(3)e	2.62(6)	O(4)–Te–O(3)e	89(2)
O(4)–O(6)e	2.88(3)	O(4)–Te–O(6)e	94(2)
O(5)–O(2)e	2.81(7)	O(5)–Te–O(2)e	91(2)
O(5)–O(6)e	2.82(7)	O(5)–Te–O(6)e	89(2)
O(2)e–O(3)e	2.59(7)	O(2)e–Te–O(3)e	90(2)
O(2)e–O(8)e	2.56(8)	O(2)e–Te–O(6)e	82(2)
O(3)e–O(6)e	2.58(7)	O(3)e–Te–O(6)e	86(2)
<O–O>	2.71	<O–Te–O>	89.9
Cu(1) octahedron			
O(3)f–O(4)g	2.62(6)	O(3)f–Cu(1)–O(4)g	70(1)
O(3)f–O(5)h	3.13(6)	O(3)f–Cu(1)–O(5)h	99(2)
O(3)f–O(6)i	3.77(7)	O(3)f–Cu(1)–O(6)i	109(1)
O(3)f–OH(7)j	2.70(8)	O(3)f–Cu(1)–OH(7)j	82(2)
O(4)g–O(5)h	2.53(8)	O(4)g–Cu(1)–O(5)h	104(2)
O(4)g–OH(7)j	3.12(6)	O(4)g–Cu(1)–OH(7)j	88(1)
O(4)g–OH(8)h	3.19(6)	O(4)g–Cu(1)–OH(8)h	92(1)
O(5)h–O(6)i	2.82(7)	O(5)h–Cu(1)–O(6)i	76(2)
O(5)h–OH(8)h	2.69(8)	O(5)h–Cu(1)–OH(8)h	86(2)
O(6)i–OH(7)j	3.29(6)	O(6)i–Cu(1)–OH(7)j	92(1)
O(6)i–OH(8)h	3.17(6)	O(6)i–Cu(1)–OH(8)h	90(1)
OH(7)j–OH(8)h	2.93(4)	OH(7)j–Cu(1)–OH(8)h	96(2)
<O–O>	3.00	<O–Cu(1)–O>	90.3
Cu(2) octahedron			
O(3)–O(4)	3.75(6)	O(3)–Cu(2)–O(4)	111(2)
O(3)–O(5)	3.10(5)	O(3)–Cu(2)–O(5)	99(2)
O(3)–O(6)	2.58(6)	O(3)–Cu(2)–O(6)	68(2)
O(3)–OH(7)	2.70(8)	O(3)–Cu(2)–OH(7)	85(2)
O(4)–O(5)	2.85(7)	O(4)–Cu(2)–O(5)	78(2)
O(4)–OH(7)	3.25(6)	O(4)–Cu(2)–OH(7)	93(2)
O(4)–OH(8)	3.15(6)	O(4)–Cu(2)–OH(8)	90(2)
O(5)–O(6)	3.53(7)	O(5)–Cu(2)–O(6)	102(2)
O(5)–OH(8)	2.69(8)	O(5)–Cu(2)–OH(8)	86(2)
O(6)–OH(7)	3.10(6)	O(6)–Cu(2)–OH(7)	87(2)
O(6)–OH(8)	3.19(6)	O(6)–Cu(2)–OH(8)	91(2)
OH(7)–OH(8)	2.84(4)	OH(7)–Cu(2)–OH(8)	93(2)
<O–O>	3.06	<O–Cu(2)–O>	90.2
Cu(3) octahedron			
O(2)–O(3)k	3.81(7)	O(2)–Cu(3)–O(3)k	92(2)
O(2)–O(5)	3.49(8)	O(2)–Cu(3)–O(5)	89(2)
O(2)–O(6)	2.56(8)	O(2)–Cu(3)–O(6)	83(2)
O(2)–O(1)k	2.89(4)	O(2)–Cu(3)–O(1)k	100(2)
O(3)k–O(6)	3.77(7)	O(3)k–Cu(3)–O(6)	90(2)
O(3)k–O(1)k	3.73(6)	O(3)k–Cu(3)–O(1)k	90(2)
O(3)k–O(4)k	3.75(6)	O(3)k–Cu(3)–O(4)k	89(2)
O(5)–O(6)	3.53(7)	O(5)–Cu(3)–O(6)	90(2)
O(5)–O(1)k	3.49(7)	O(5)–Cu(3)–O(1)k	90(2)
O(5)–O(4)k	3.53(7)	O(5)–Cu(3)–O(4)k	90(2)
O(6)–O(4)k	2.88(3)	O(6)–Cu(3)–O(4)k	94(2)
O(1)k–O(4)k	2.53(6)	O(1)k–Cu(3)–O(4)k	83(2)
<O–O>	3.33	<O–Cu(3)–O>	90.0

a = $\bar{x}+y+1, \bar{x}+1, z+\frac{1}{3}$; b = $\bar{x}+y-1, \bar{x}, z+\frac{1}{3}$; c = $\bar{x}+y, \bar{x}+1, z+\frac{1}{3}$; d = $\bar{x}+y, \bar{x}, z+\frac{1}{3}$; e = $x, y-1, z$; f = $\bar{y}+2, x-y+1, z-\frac{1}{3}$; g = $\bar{y}+1, x-y, z-\frac{1}{3}$; h = $\bar{y}+1, x-y+1, z-\frac{1}{3}$; i = $\bar{y}+2, x-y+2, z-\frac{1}{3}$; j = $\bar{y}+x, x-y+1, z-\frac{1}{3}$; k = $x-1, y, z$

TABLE 4. BOND-VALENCE* ANALYSIS (v.u.) FOR PARAKHINITE

	Pb	Te	Cu(1)	Cu(2)	Cu(3)	H(1)	H(2)	Σ
O(1)	0.17	1.23			0.61		0.1	2.11
O(2)	0.18	1.05			0.54	0.1		1.87
O(3)	0.11	1.49	0.33	0.38	0.02			2.33
O(4)	0.19	0.87	0.12	0.11	0.47			1.76
O(5)	0.17	0.70	0.41	0.40	0.03			1.71
O(6)	0.17	0.82	0.10	0.11	0.47			1.67
OH(7)	0.29		0.42	0.47		0.9		2.08
OH(8)	0.21		0.49	0.51			0.9	2.11
Σ	1.49	6.16	1.87	1.98	2.14			

* parameters from Brown & Altermatt (1985)

CHEMICAL FORMULA

Williams (1978) gave the chemical formula of parakhinite as $Cu^{2+}_3PbTe^{6+}O_4(OH)_6$, $Z = 3$, which gives a calculated density of 6.69 g/cm^3, a value within the range 6.5 to 7.0 g/cm^3 estimated by Williams (1978). The structure refinement reported here shows that all atoms are on general positions in the space group $P3_2$, and that there are three Cu atoms, one Pb atom, one Te atom and eight anions in the asymmetric unit. Bond-valence arguments (Table 4) and the electroneutrality principle indicate that two of these anions are OH groups. Thus the correct formula for parakhinite is $Cu^{2+}_3PbTe^{6+}O_6(OH)_2$, $Z = 3$, which gives a calculated density of 6.302 g/cm^3.

DESCRIPTION OF THE STRUCTURE

Pbϕ$_8$ polyhedron

There is one unique Pb position in the structure of parakhinite. The Pb atom bonds to six oxygen anions and two hydroxyl groups, forming an irregular $PbO_6(OH)_2$ polyhedron (Fig. 1). The <Pb–O> distance is 2.74 Å, with individual Pb–ϕ (ϕ: unspecified ligand) bond-lengths ranging from 2.57(5) to 2.94(6) Å, indicating that the Pb^{2+} is not significantly lone-pair stereoactive.

Teϕ$_6$ octahedron

Parakhinite contains one unique Te position, which is octahedrally coordinated by six oxygen anions. The octahedral coordination indicates that the tellurium is present as Te^{6+}, and the bond-valence analysis (Table 4) is consistent with this conclusion. About twenty Te^{6+}-bearing minerals have been described to date, but the structures are known for only two of these. Effenberger *et al.* (1978) reported the structure of carlfriesite, $CaTe_3O_8$, and showed that it contains one Te^{4+} position and one Te^{6+} position. The Te^{6+} cation is octahedrally coordinated by six oxygen atoms, and the <Te^{6+}–O> distance is 1.933 Å. Jarosch & Zemann (1989) reported the garnet-type structure of yafsoanite, $Ca_3Te_2Zn_3O_{12}$. The structure contains a single Te^{6+} site, which is octahedrally coordinated by six oxygen anions, with a <Te^{6+}–O> distance of 1.929 Å. The <Te^{6+}–O> distance in parakhinite is 1.92 Å, a value similar to the observed <Te^{6+}–O> distances in carlfriesite and yafsoanite, as well as in various synthetic materials.

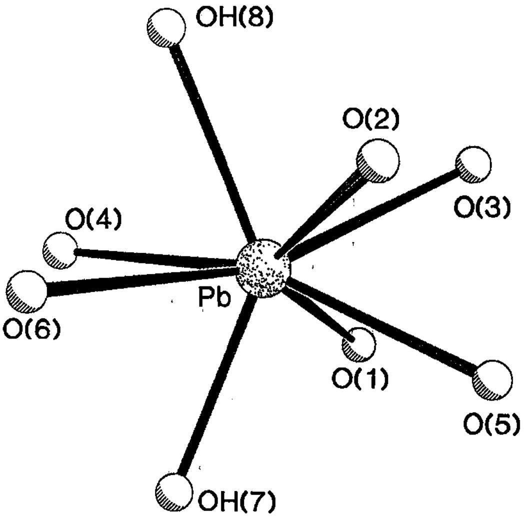

FIG. 1. The Pbϕ$_8$ polyhedron in parakhinite, showing the coordination of the Pb atom.

Cu octahedra

The structure of parakhinite contains three unique Cu positions, each of which is in a general position. Cu(1) and Cu(2) are both octahedrally coordinated by four oxygen atoms and two hydroxyl groups in a *cis* arrangement. Both the Cu(1)ϕ$_6$ and Cu(2)ϕ$_6$ octahedra are strongly distorted owing to the Jahn–Teller effect associated with a d^9 cation in an octahedral ligand-field. The octahedra are typically (4 + 2)-distorted; both octahedra have four short equatorial Cu–ϕ bond-lengths at ~2.0 Å, and there are two long apical bond-lengths of ~2.5 Å. The Cu(1)ϕ$_6$ and Cu(2)ϕ$_6$ octahedra have <Cu–ϕ> distances of 2.17 and 2.16 Å, respectively, and <Cu–ϕ$_{equatorial}$> distances of 2.01 and 1.99 Å, respectively.

Cu(3) bonds to four oxygen anions with Cu–O distances of ~1.92 Å, giving an essentially square-planar coordination, with a <Cu(3)–ϕ$_{equatorial}$> distance of 1.92 Å. The bond-valence analysis (Table 4) indicates that these oxygen atoms provide sufficient bond-valence to satisfy the requirements of the central Cu position. However, there are two additional atoms of oxygen in the positions that correspond to apical oxygen atoms of a (4 + 2)-distorted octahedron. The apical oxygen atoms are 2.95 and 3.23 Å from Cu(3); examination of the bond angles (Table 3) verifies that these oxygen anions are the apical ligands of a very strongly (4 + 2)-distorted octahedron. Cu^{2+}ϕ$_6$ octahedra commonly show such extreme distortion (Burns 1994), and the Cu(3)ϕ$_6$ octahedral geometry in parakhinite is consistent with the existence of a complete series of geometries between (4 + 2)-distorted octahedral and square-planar arrangements.

Hydrogen bonding

The bond-valence analysis (Table 4) indicates that two of the eight anion positions in the asymmetric unit

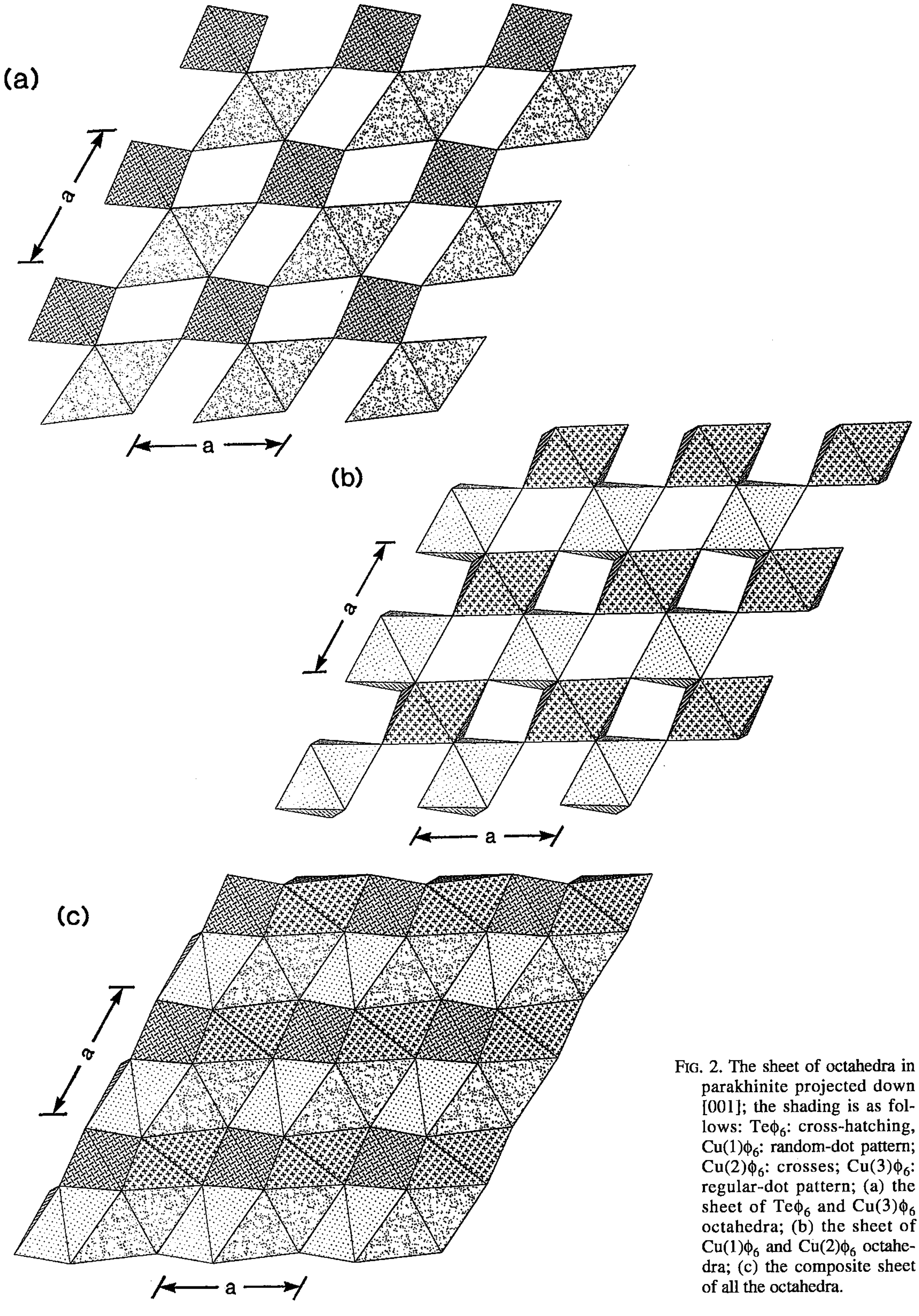

FIG. 2. The sheet of octahedra in parakhinite projected down [001]; the shading is as follows: Teϕ_6: cross-hatching, Cu(1)ϕ_6: random-dot pattern; Cu(2)ϕ_6: crosses; Cu(3)ϕ_6: regular-dot pattern; (a) the sheet of Teϕ_6 and Cu(3)ϕ_6 octahedra; (b) the sheet of Cu(1)ϕ_6 and Cu(2)ϕ_6 octahedra; (c) the composite sheet of all the octahedra.

are hydroxyl groups, and this is in accord with the electroneutrality principle. Difference-Fourier maps calculated around the OH(7) and OH(8) positions did not reveal the locations of the H atoms. However, for both hydroxyl groups, there is only one plausible acceptor anion for the hydrogen bond. In both cases, the acceptor anion is about 2.6 Å from the donor anion. The locations of the two hydrogen atoms were estimated by assuming that they will be located about 0.98 Å along the line connecting the donor and acceptor anions.

Structure connectivity

The Teϕ_6 and Cu(3)ϕ_6 octahedra share *trans* edges to form rutile-like [$M\phi_4$] chains that extend parallel to [110]. These [$M\phi_4$] chains link by octahedra sharing corners to form a [$M\phi_3$] sheet of composition TeCuϕ_6 in the (100) plane (Fig. 2a). The Cu(1)ϕ_6 and Cu(2)ϕ_6 octahedra link in a similar fashion (Fig. 2b) to form a CuCuϕ_6 sheet. These two sheets then link by octahedra sharing edges, the octahedra of one sheet matching to the interstices of the other sheet to form an uninterrupted [$M\phi_2$] sheet (Fig. 2c) of composition TeCu$_3\phi_8$. These sheets are repeated along the *c* axis through the 3_2 screw operator, and there is an interesting difference in appearance with viewing direction (Fig. 3).

Interstitial linkage between adjacent sheets is provided by Pb atoms, which link to four anions in each of the adjacent sheets, and by hydrogen bonds. The OH(7)–H(1)...O(2) and OH(8)–H(2)...O(1) linkages (Fig. 3) bridge between anions of adjacent sheets of octahedra. However, bonding between the sheets is significantly weaker than bonding within the sheets, accounting for the excellent {001} cleavage in parakhinite.

Twinning and phase transitions

As mentioned above, optical examination shows biaxial behavior and extensive twinning. The parakhinite structure was refined in the space group $P3_2$, but the structure is compatible with $P6_2$ symmetry (which refined to an *R* index of 14.4%). However, the biaxial optical behavior indicates the true symmetry to be lower than hexagonal (trigonal). Taking the $P6_2$ structure as the parent, the cell-conserving isotropy subgroups are $P3_2$, $P2$ and $P1$, and the results of this work suggest a series of transitions beginning with $P6_2 \rightarrow P3_2$. The $P6_2 \rightarrow P3_2$ transition still retains the uniaxial nature of the crystal and cannot give rise to biaxial behavior. Nevertheless, the adequate structure-refinement in $P3_2$ suggests that parakhinite had this symmetry prior to becoming biaxial. Khinite is dimorphous with parakhinite, and is orthorhombic, *Fddd*,

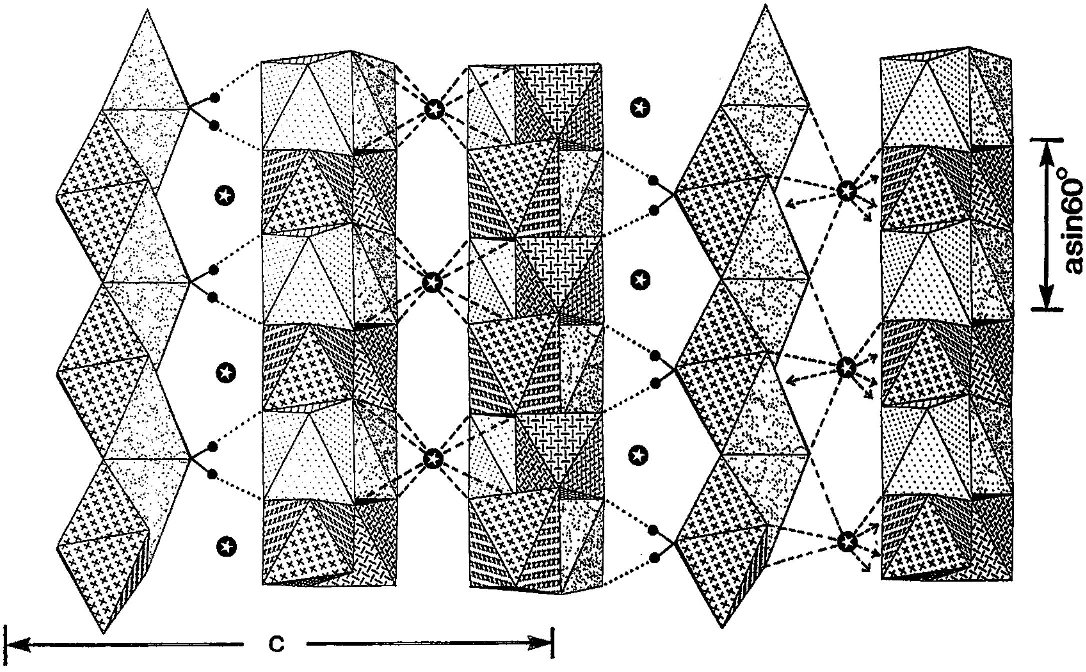

FIG. 3. The parakhinite structure projected down [100]. Legend as in Fig. 2, Pb atoms are shown as starred circles, Pb–O bonds are shown as broken lines, H atoms are shown as solid circles, hydrogen bonds are shown as dotted lines.

a 5.740, *b* 9.983, *c* 23.960 Å (Williams 1978). The *a* and *b* dimensions of khinite correspond to the C-centered orthorhombic equivalent of the trigonal parakhinite cell, and the *c* dimension is $\sim\frac{3}{2}$ times the *c* dimension of parakhinite. It seems reasonable to suppose that khinite is a lower-temperature equivalent of parakhinite, with single crystals of khinite forming below the trigonal → orthorhombic transition.

Graphical isomerism

The sheet that constitutes the structural unit in parakhinite has the general form $[M\phi_2]$. This is a very common stoichiometry for polyhedral sheets in minerals. However, none of the known Cu^{2+} oxysalt structures (Eby & Hawthorne 1993) or other mineral structures based on $[M\phi_2]$ sheets have arrangements graphically similar to the $[M\phi_2]$ sheet in parakhinite.

Consider a rutile-like $[M\phi_4]$ chain (Fig. 4a). There are two distinct ways in which such $[M\phi_4]$ chains can link together (in a stereochemically reasonable fashion) by sharing edges; these are shown in Figures 4b and 4c. Continuation of the linkage in Figure 4b produces a trioctahedral brucite-like sheet that is a common structural unit (or part of one) in hydroxides and sheet silicates. Continuation of the linkage in Figure 4c produces the $[M\phi_2]$ sheet in parakhinite. This is most easily seen by considering the pattern of shared edges in the different types of sheets. In the brucite sheet, the shared edges form a circuit around the prototype octahedron (Fig. 4b). In the parakhinite sheet, the shared edges form the pattern shown in Figure 4c. Thus although the structural unit in parakhinite seems unique, it is a member of a small family of graphically isomeric $[M\phi_2]$ sheets. Figure 5 shows a $[TeCu_3O_6(OH)_2]$ planar sheet of edge-sharing octahedra; this sheet and the parakhinite sheet are graphical isomers. Why does the parakhinite sheet occur and the sheet in Figure 5 does not? In parakhinite, half of the anions in the sheet are [4]-coordinated, and half are 2-coordinated by cations of the sheet (Table 4), whereas in the sheet of Figure 5, all anions are [3]-coordinated. Can we see a preference for which graphical isomer is stable based on bond-valence requirements? If we postulate a (4 + 2) distortion of the $Cu^{2+}\phi_6$ octahedra in the sheet of Figure 5, a result of Jahn–Teller relaxation, we expect equatorial and apical bond-valences of ~0.4 and 0.2 v.u., respectively. With equatorial and apical Te^{6+}–O bond-valences of 1.1 and 0.9 v.u., respectively, this leads to sums of 1.7 and 1.0 v.u., respectively, around the oxygen and hydroxyl anions of the sheet (Fig. 5), with the additional bond-valence requirements to be satisfied by the interstitial Pb^{2+} cations. This is a more homogeneous distribution of bond valences than occurs for the analogous sheet in parakhinite, and so it seems that we cannot assign instability of the $[TeCu_3O_6(OH)_2]$ sheet in Figure 5 to a poor arrangement of bond valences. A simple reason for the relative stability of these two geometrical isomers is not apparent.

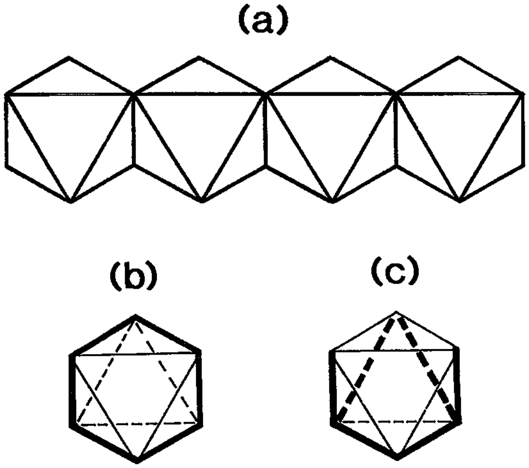

FIG. 4. The $[M\phi_4]$ rutile-type chain and some ways of linking such chains together: (a) the $[M\phi_4]$ chain; (b) pattern of shared edges in an octahedron of the brucite-type sheet; (c) pattern of shared edges in an octahedron of the parakhinite sheet; in (b) and (c), shared edges are denoted by heavy lines.

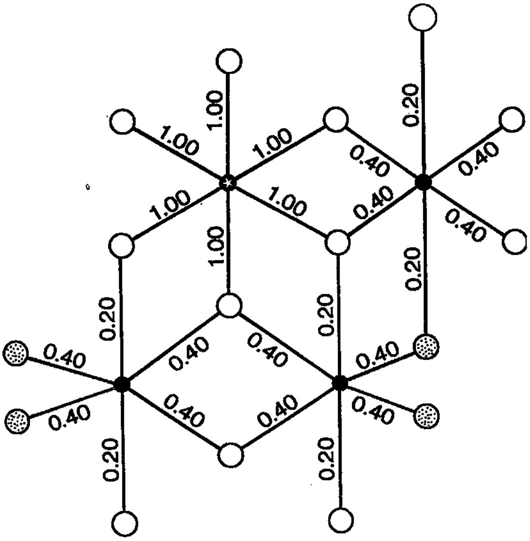

FIG. 5. A brucite-type sheet of composition $TeCu_3O_6(OH)_2$ showing an idealized arrangement of bond valences (in v.u.); Te atoms are shown as starred circles, Cu atoms as solid circles, simple O atoms as open circles, and OH groups as stippled circles.

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