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Reinerite, $Zn_3(AsO_3)_2$: an arsenite with a novel type of Zn-tetrahedral double chain[1]

SUBRATA GHOSE, PAUL BOVING, WILLIAM A. LACHAPELLE AND CHE'NG WAN

Department of Geological Sciences, University of Washington
Seattle, Washington 98195

Abstract

Reinerite, $Zn_3(AsO_3)_2$ from Tsumeb, S. W. Africa, is orthorhombic, with cell dimensions a = 6.092(2), b = 14.407(2), c = 7.811(1)A, space group *Pbam* and Z = 4. The crystal structure has been determined by the symbolic addition method and difference Fourier synthesis and refined by the method of least squares to an R factor of 0.051 based on 1289 reflections, measured on an automatic single-crystal diffractometer. The standard deviation in Zn–O and As–O bond lengths is 0.003 and 0.004A and in O–Zn–O and O–As–O angles 0.02°.

The structure of reinerite contains a new type of Zn-tetrahedral double chain, $[Zn_4O_{10}]_\infty$, with two-tetrahedral repeat and four-membered rings; these double chains are cross-linked into a three-dimensional framework through corner-sharing of a new type of edge-sharing Zn-tetrahedral dimers and two types of trigonal pyramidal arsenite groups. The average Zn–O bond distances within the two independent Zn–O tetrahedra are 1.958 and 1.964A. Both the arsenite groups have the point symmetry m, with average As–O bond distances 1.776 and 1.771A and average O–As–O bond angles 98.4 and 96.8°.

Introduction

In the course of our investigation of the stereochemistry of copper and zinc (Ghose and Wan, 1974; Ghose *et al.*, 1974), we have now determined the crystal structure of reinerite, $Zn_3(AsO_3)_2$, from Tsumeb, S.W. Africa. At Tsumeb, it occurs at a depth of 800 m in a second oxidation zone of the lead–zinc–copper deposit, in association with smithsonite, hydrozincite, hemimorphite, willemite, adamite, and olivenite (Geier and Weber, 1958). In addition to the configuration of the arsenite group, the crystal structure of reinerite turned out to be of considerable interest, because it contains a new type of double chain consisting of corner-sharing ZnO_4 tetrahedra, reminiscent of the amphibole-type tetrahedral silicate double chains, and an edge-sharing Zn-tetrahedral dimer.

Experimental

Reinerite was reported to be orthorhombic with possible space group *Pmma* by Geier and Weber (1958). Precession photographs of a reinerite crystal from Tsumeb revealed extinction conditions as $0kl$, $k = 2n$ and $h0l$, $h = 2n$ present. Of the two possible space groups, *Pbam* and *Pba*2, the first proved to be correct on the basis of an $N(z)$-test of the measured X-ray diffraction intensities.

A single crystal of light blue transparent reinerite was checked for crystal perfection through a transmission Laue photograph and then ground to a sphere of diameter 0.225(2) mm. The single-crystal sphere was mounted on the syntex $P\bar{1}$ single-crystal diffractometer, and the unit-cell dimensions were refined by the least-squares method based on 15 reflections with measured 2θ values between 35 and 45°, using Mo$K\alpha$ radiation. The cell dimensions (Table 1) are in good agreement with those determined by Geier and Weber. All (hkl) reflections within 2θ = 65° were measured on the diffractometer by the 2θ–θ scan method, using Mo$K\alpha$ radiation monochromatized by reflection from a graphite "single" crystal, and scintillation counter. A variable scan rate was used, the minimum being 1°/min (50 kV, 15 mA). Out of a total of 1289 reflections, 239 were less than $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measured intensity as determined by the counting statistics. All the intensities were corrected for Lorentz, polarization, and absorption factors.

[1] Structural chemistry of copper and zinc minerals. Part III.

Table 1. Reinerite: crystal data

Reinerite, $Zn_3(AsO_3)_2$: Tsumeb, S. W. Africa, NMNH #115409	
Orthorhombic, *mmm*	
a: 6.092(2)Å	Cell content: $4[Zn_3(AsO_3)_2]$
b: 14.407(2)	D_m: 4.270 g cm^{-3}
c: 7.811(1)	D_c: 4.283 g cm^{-3}
Cell volume: 685.6(2)Å^3	μ(MoKα): 209.71 cm^{-1}
Space Group: *Pbcm*	

Determination and refinement of the structure

A three-dimensional Patterson synthesis was computed. However, due to the interaction of four heavy atoms, the interpretation of the Patterson map proved to be difficult. The four heavy-atom positions were determined directly by the symbolic addition method (Karle and Karle, 1966) using the computer program MULTAN (Germain *et al.*, 1971). The E values for all reflections were calculated. The signs of the following three reflections with large E values were chosen to define the origin:

h	k	l	E	Sign
1	9	2	2.94	+
3	6	2	2.75	+
1	7	7	2.41	−

In addition, the application of the Σ_1 relationship indicated the signs of two more reflections (0,0,10) and (18,2,0) with E values 1.90 and 1.65 respectively to be +, +. The following three reflections were assigned symbols:

h	k	l	E	Sign
0	16	5	3.24	e
1	11	5	2.54	f
4	1	2	2.53	g

Signs and symbols of 153 reflections with E > 1.60 were determined. Out of the eight possible E maps, one showed the correct structure in terms of the heavy atoms, namely 2 Zn and 2 As. The symbols e, f, g turned out to be −, +, −. A structure-factor calculation with the heavy atoms only yielded an R factor of 0.27.

The oxygen positions were determined from a three-dimensional difference Fourier synthesis. The R factor at this stage was 0.21. The structure was refined by the method of least squares using the program RFINE (Finger, 1969), first using isotropic and then anisotropic temperature factors for all atoms. The scattering factors were taken from Cromer and Mann (1968), corrected for anomalous dispersion (Cromer and Liberman, 1970). The observed structure factors F_o's were weighted by $1/\sigma^2(F_o)$, where $\sigma(F_o)$ is the standard deviation of F_o. A few strong low-angle reflections (*e.g.* 004, 121) were strongly affected by extinction. These reflections with $\Delta F >$ 10.0 were excluded from the refinement. The final R factor is 0.051 for all (1289) reflections and 0.046 excluding 18 reflections affected by extinction. The shift/error at this stage is 0.00. The atomic positional and thermal parameters are listed in Table 2 and a list of observed and calculated structure factors in Table 3.[2] The standard deviations in bond lengths and an-

[2] To obtain a copy of Table 3, order document AM-77-058 from the Business Office, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

Table 2. Reinerite, $Zn_3(AsO_3)_2$: atomic positional and thermal parameters (standard deviations in parentheses)

Atom	x	y	z	B eq.*	β_{11}†	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn(1)	0	0.5	0.31453(8)	1.10(1)	1251(17)	99(3)	252(9)	-6(6)	0	0
Zn(2)	0.56494(8)	0.77908(3)	0.78434(6)	1.04(1)	804(11)	124(2)	361(6)	2(4)	-58(8)	-9(3)
As(1)	0.91312(10)	0.87436(4)	0.5	0.94(1)	783(14)	113(2)	298(8)	-26(5)	0	0
As(2)	0.22305(10)	0.90126(4)	0	0.97(1)	847(15)	101(2)	335(8)	65(5)	0	0
O(1)	0.3304(8)	0.0608(3)	0.5	1.34(7)	1304(121)	149(18)	352(59)	158(41)	0	0
O(2)	0.3349(8)	0.2807(3)	0	1.16(6)	1103(108)	124(16)	338(58)	85(38)	0	0
O(3)	0.1519(5)	0.1997(2)	0.3262(4)	1.45(5)	840(70)	218(14)	534(45)	58(29)	53(50)	162(21)
O(4)	0.0904(5)	0.3965(2)	0.1736(4)	1.32(5)	1372(82)	98(11)	456(40)	-43(26)	353(51)	-42(18)

*Equivalent isotropic B, calculated from anisotropic temperature factors.

†Form of anisotropic temperature factor (x10^5): $\exp\{-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\}$

gles as well as in thermal ellipsoids were calculated using the ERROR program (Finger, personal communication, 1972). The bond lengths and angles are listed in Table 4, and the dimensions of the thermal ellipsoids in Table 5. The average standard deviation in Zn–O and As–O bond lengths are 0.003 and 0.004A, respectively, and in O–Zn–O and O–As–O angles 0.02°.

Description of the structure

The crystal structure of reinerite is a three-dimensional framework, consisting of three distinct structural components: (a) dimers of edge-sharing $Zn(1)O_4$ tetrahedra; (b) tetrahedral double chains, made up of corner-sharing $Zn(2)O_4$ tetrahedra; and (c) two isolated trigonal-pyramidal arsenite groups, $As(1)O_3$ and $As(2)O_3$.

Table 4. Reinerite, $Zn_3(AsO_3)_2$: interatomic distances (A) and angles (°) (standard deviations in parentheses)

The Zn(1) - Tetrahedron			
Zn(1) - O(1)(x2)	1.983(3)	O(1) - Zn(1) - O(1')	86.1(1)
Zn(1) - O(4)(x2)	1.933(3)	O(1) - Zn(1) - O(4)(x2)	127.4(2)
Mean	1.958	O(1) - Zn(1) - O(4')(x2)	102.9(1)
		O(4) - Zn(1) - O(4')	110.6(2)
O(1) - O(4)(x2)	3.512(4)	Mean	109.5
O(1) - O(4')(x2)	3.064(4)		
O(1) - O(1')	2.709(7)		
O(4) - O(4')	3.179(4)		
Mean	3.173		
The Zn(2) - Tetrahedron			
Zn(2) - O(2)	1.988(2)	O(2) - Zn(2) - O(3)	99.9(2)
Zn(2) - O(3)	1.953(3)	O(2) - Zn(2) - O(3')	109.2(2)
Zn(2) - O(3')	1.949(3)	O(2) - Zn(2) - O(4)	112.3(1)
Zn(2) - O(4)	1.966(3)	O(3) - An(2) - O(3')	119.6(1)
Mean	1.964	O(3) - Zn(2) - O(4)	111.4(1)
		O(3') - Zn(2) - O(4)	104.5(1)
O(2) - O(3)	3.016(4)	Mean	109.5
O(2) - O(4)	3.284(5)		
O(2) - O(3')	3.210(4)		
O(4) - O(3)	3.098(4)		
O(4) - O(3')	3.237(4)		
O(3) - O(3')	3.373(3)		
Mean	3.203		
The As(1)O_3 Trigonal Pyramid			
As(1) - O(1)	1.753(5)	O(1) - As(1) - O(3)(x2)	97.6(1)
As(1) - O(3)(x2)	1.772(3)	O(3) - As(1) - O(3')	100.0(1)
Mean	2.766	Mean	98.4
O(1) - O(3)(x2)	2.652(5)		
O(3) - O(3')	2.715(6)		
Mean	2.673		
The As(2)O_3 Trigonal Pyramid			
As(2) - O(2)	1.772(4)	O(2) - As(2) - O(4)(x2)	95.2(1)
As(2) - O(4)(x2)	1.771(3)	O(4) - As(2) - O(4')	100.0(1)
Mean	1.771	Mean	96.8
O(4) - O(2)(x2)	2.616(5)		
O(4) - O(4')	2.713(4)		
Mean	2.648		
Zn-Zn and Zn-As Distances		*Zn-O-Zn Angles*	
Zn(1) - Zn(1')	2.8974(9)	Zn(1) - O(1) - Zn(1')	93.9(2)
Zn(1) - Zn(2)	3.2990(7)	Zn(2) - O(2) - Zn(2')	115.9(2)
Zn(2) - Zn(2')	3.3590(8)	Zn(2) - O(3) - Zn(2')	108.1(1)
Zn(2) - Zn(2'')	3.3690(8)	Zn(1) - O(4) - Zn(2)	115.6(2)
Zn(1) - As(1)	3.4219(8)	*Zn-O-As Angles*	
An(1) - As(2)	3.3025(7)		
Zn(2) - As(1)	3.2673(7)	Zn(1) - O(1) - As(1)	132.5(2)
Zn(2) - As(1')	3.3640(8)	Zn(2) - O(2) - As(2)	119.1(1)
Zn(2) - As(2)	3.2054(8)	Zn(2) - O(3) - As(1)	129.1(2)
Zn(2) - As(2')	3.2429(8)	Zn(2') - O(3) - As(1)	122.8(2)
		Zn(1) - O(4) - As(2)	126.1(2)
		Zn(2) - O(4) - As(2)	118.0(2)

Table 5. Reinerite, $Zn_3(AsO_3)_2$: thermal ellipsoid parameters (standard deviations in parentheses)

Atom	Axis, r_i	rms amplitude (Å)	Angle (°) of r_i with respect to +a	+b	+c
Zn(1)	r1	0.088	90	90	90
	r2	0.102	89(1)	179(1)	90
	r3	0.153	179(1)	91(1)	90
Zn(2)	r1	0.103	107(3)	79(4)	20(4)
	r2	0.115	99(4)	167(4)	81(4)
	r3	0.125	161(4)	84(4)	108(3)
	r1	0.096	90	90	0
	r2	0.107	71(5)	161(5)	90
	r3	0.123	161(4)	109(4)	90
As(2)	r1	0.097	114(11)	156(11)	90
	r2	0.102	90	90	180
	r3	0.131	156(2)	66(2)	90
O(1)	r1	0.104	90	90	0
	r2	0.108	61(105)	29(105)	90
	r3	0.169	151(8)	61(8)	
O(2)	r1	0.102	90	90	0
	r2	0.107	112(71)	158(71)	90
	r3	0.149	158(11)	68(11)	90
O(3)	r1	0.099	95(12)	126(6)	36(4)
	r2	0.123	12(9)	83(9)	79(12)
	r3	0.173	101(6)	37(8)	55(7)
O(4)	r1	0.092	74(22)	49(25)	45(32)
	r2	0.105	114(34)	42(32)	112(45)
	r3	0.175	151(5)	98(3)	62(4)

(a) Tetrahedral edge-sharing dimer, $[Zn_2O_6]^{8-}$

Two $Zn(1)O_4$ tetrahedra share the O(1)–O(1′) edge across a mirror plane, forming a $[Zn_2O_6]^{8-}$ dimer (Figs. 1 and 2). This dimer is apparently of a new type. Because of the edge-sharing, the $Zn(1)O_4$ tetrahedron (av. Zn–O distance 1.958A) is highly distorted; the shared edge, O(1)–O(1′) (2.709A) is much shorter than the average tetrahedral edge distance (3.173A), and the O(1)–Zn(1)–O(1′) angle (86.1°) is much smaller than the average tetrahedral angle. The Zn(1)–Zn(1′) distance within the dimer is 2.897A. Although a similar edge-sharing tetrahedral silicate dimer would be very unlikely, a topologically comparable $[Be_2O_6]^{8-}$ dimer has been found in epididymite, $HNaBeSi_3O_8$ (Robinson and Fang, 1970).

(b) Tetrahedral double chains, $[Zn_4O_{10}]^{12-}_{\infty}$

A tetrahedral single chain running parallel to the *a* axis is formed by Zn(2)-tetrahedra sharing the oxygen corner, O(3). Two such single chains across a mirror plane share corners, to form double chains (Figs. 2, 3 and 4a). In Liebau's (1972) terminology

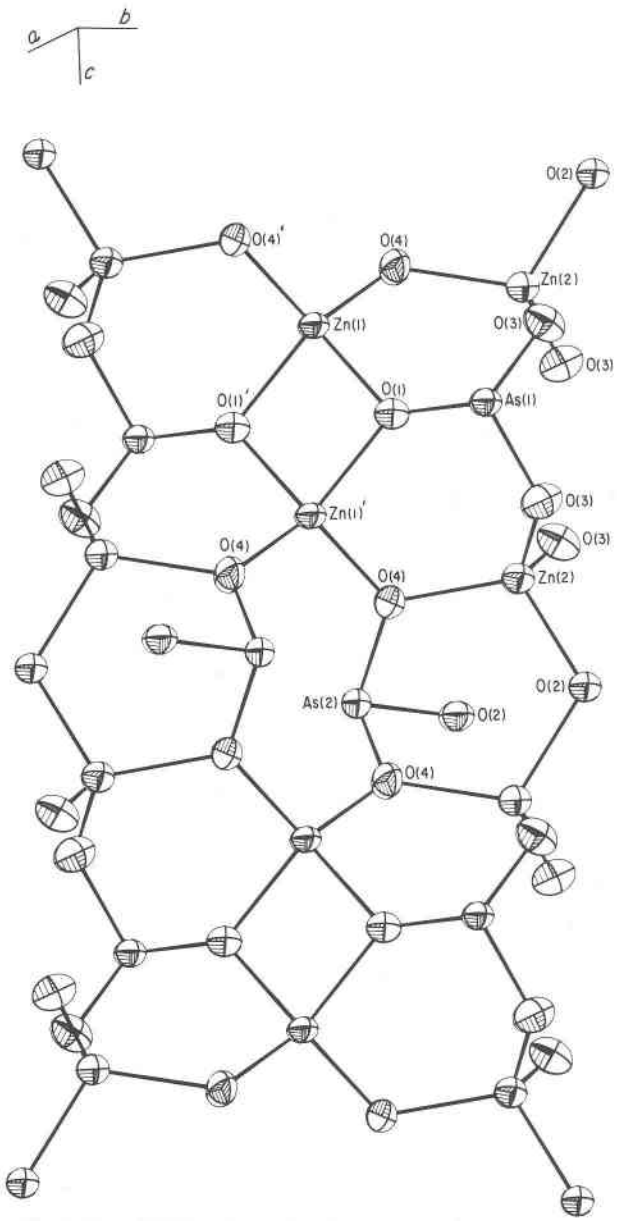

Fig. 1. A partial view of the reinerite structure, showing the atom nomenclature and the ellipsoids of thermal vibration.

this is a *Zweier-Doppelkette* or a double chain with two-tetrahedral repeat, accounting for the 6.09A *a* axis. These double chains are comparable to the amphibole-type silicate double chains. However, the double chains with the composition $[Zn_4O_{10}]$ in reinerite are characterized by four-membered rings, as opposed to six-membered rings in the $[Si_4O_{11}]$ double chains of amphiboles.

The $Zn(2)O_4$ tetrahedron (av. Zn–O distance 1.964A) shows considerable angular distortion, the O–Zn–O angle ranging from 99.9 to 119.6°.

(c) The arsenite groups

Both the AsO_3 groups are trigonal pyramids with point symmetry *m*, deviating significantly from the highest possible point symmetry 3*m*. The average As–O bond length and the pyramidal edge (O–O) distances are 1.769 and 2.661A respectively, and the average O–As–O angle is 97.6°. Other than the closest three oxygens, no oxygen atoms approach the relatively unshielded As^{3+} ion within 3.5A.

(d) The three-dimensional framework

The backbone of the reinerite structure is the tetrahedral double chain running parallel to the *a* axis. Such double chains are cross-linked through Zn-tetrahedral dimers by corner-sharing, giving rise to a second type of Zn-tetrahedral corrugated chain running parallel to the *c* axis (Fig. 4b). Such a framework is further strengthened by pyramidal arsenite groups sharing corners of two adjacent double chains with a corner of the Zn-tetrahedral dimer (Fig. 3). Each oxygen atom is being shared by two zinc and one arsenic atoms.

Discussion

Configuration of the arsenite group

The accurate configuration of the trigonal-pyramidal $As^{3+}O_3$ groups has been determined in relatively few minerals. In trippkeite, $CuAs_2O_4$, the As–O distances are: 1.89(×2), 1.69A (av. 1.82A), where the arsenite groups share corners to form chains (Zemann, 1951). In synadelphite, $Mn_9(OH)_9(H_2O)_2(AsO_3)(AsO_4)_2$ (Moore, 1970), asbecasite, $Ca_3Ti(As_3SiBeO_{10})_2$ (Canillo *et al.* 1969), and in finnemanite, $Pb_5Cl(AsO_3)_3$ (Gabrielson, 1956), the As–O distance within the isolated arsenite groups are 1.76, 1.797, and 1.81A respectively. The av. As^{3+}–O distance (1.769A) within the arsenite groups in reinerite is significantly shorter than all those mentioned above, except in synadelphite. It appears that the As^{3+}–O bond length is highly variable. However, some of the structures mentioned above, when refined by modern methods, may show much less variation in the As^{3+}–O bond length.

Crystal chemistry of the tetrahedral $[ZnO_4]^{6-}$ ion: a comparison with the crystal chemistry of silicates

The facility of the $[SiO_4]^{4-}$ ion to polymerize, giving rise to chains, rings, sheets, and framework structures, is well known. The tetrahedral $[ZnO_4]^{6-}$ ion is emerging in a similar rôle. Thus, a corner-sharing pyroxene-type $[ZnO_3]$ tetrahedral chain is found in

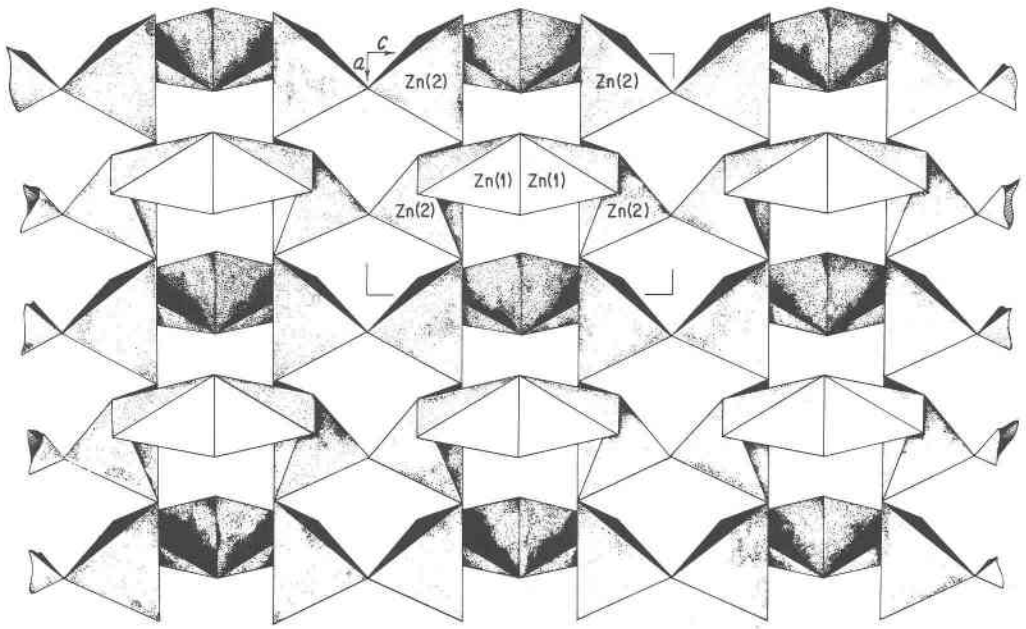

Fig. 2. A partial view of the reinerite structure down the *b* axis, showing the tetrahedral edge-sharing $[Zn_2O_6]$ dimers and tetrahedral corner-sharing $[Zn_4O_{10}]$ double chains.

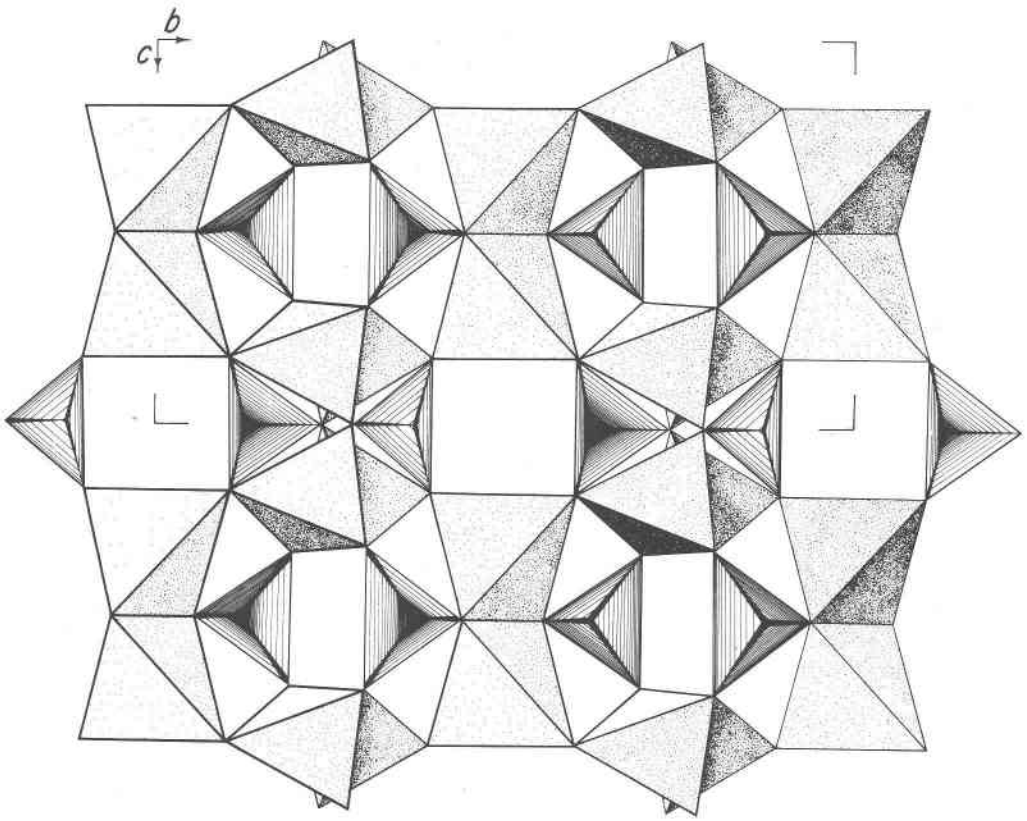

Fig. 3. A view of the reinerite structure down the *a* axis; the $[Zn_4O_{10}]$ double chains are projected end on.

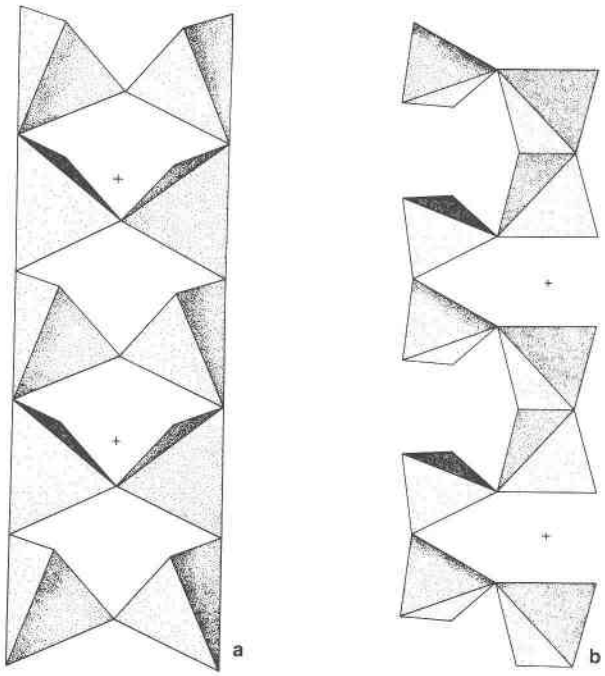

Fig. 4. (a) The $[Zn_4O_{10}]$ double chain in reinerite. (b) The corrugated tetrahedral chain with four-tetrahedral repeat in reinerite.

gerstmannite, $(Mn,Mg)Mg(OH)_2[ZnSiO_4]$ (Moore and Araki, 1977). The $[Zn_4O_{10}]_\infty$ double chain found in reinerite rivals the $[Si_4O_{11}]_\infty$ double chain in amphiboles; furthermore, the corrugated chain in reinerite is similar to the corrugated silicate chains found in alamosite, $Pb_{12}Si_{12}O_{36}$ (Boucher and Peacor, 1968), and in stokesite, $Ca_2Sn_2Si_6O_{18}$ (Vorma, 1963). However, the corrugated chain in reinerite is a *Vierer-Einfachkette*, whereas the silicate chains in alamosite and stokesite are *Zwölfer-Einfachkette* and *Sechser-Einfachkette* respectively.

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