American Mineralogist, Volume 59, pages 573–581, 1974

Structural Chemistry of Copper and Zinc Minerals. Part I. Veszelyite, $(Cu,Zn)_2ZnPO_4(OH)_3 \cdot 2\,H_2O$: A Novel Type of Sheet Structure and Crystal Chemistry of Copper-Zinc Substitution

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Abstract

To elucidate the crystal-chemical role of copper and zinc in mixed copper-zinc minerals, the crystal structure of veszelyite from Arakawa Mine, Japan, (Cu/Zn ratio 1.43) has been determined. The cell dimensions are: $a_o = 9.828(3)$, $b_o = 10.224(3)$, $c_o = 7.532(2)$ Å, $\beta = 103.18(2)°$; space group: $P2_1/a$, $Z = 4$. The structure had been refined to an R-factor of 0.044 using 1691 reflections collected on an automatic single crystal diffractometer. Both Cu(1) and Cu(2) have tetragonally distorted octahedral coordination. Cu(1) has 4 (OH) ions in a square plane (Cu–OH av. 1.98 Å), while O(3) and $H_2O(2)$ at distances of 2.47 and 2.62 Å complete the octahedron. Cu(2) has 3 (OH) and one O in a square plane (Cu–O, OH av. 2.00 Å), while $H_2O(1)$ and $H_2O(2)$ occur at 2.47 and 2.35 Å respectively. The $ZnO_3(OH)$ and PO_4 ions are nearly regular tetrahedra, with average Zn–O 1.95 Å and P–O 1.54 Å.

The Cu(1) and Cu(2) octahedra share edges to form a novel type of open octahedral sheet containing eight-membered octahedral rings. Zinc and phosphorus tetrahedra share corners to form a tetrahedral sheet which has four- and eight-membered rings. In each ring, half the tetrahedra point up, the apices sharing corners with the octahedral sheet above, while the other half of the tetrahedra point down, the apices sharing corners with the octahedral sheet below. The tetrahedral sheet is comparable to the silicate sheet formed of four- and eight-membered rings in a number of framework silicates, *e.g.*, paracelsian, $BaAl_2Si_2O_8$. Both sheet structures are parallel to the (001) plane. Further substitution of copper by zinc is possible at Cu(1) and Cu(2) sites, resulting in more regular octahedra.

Introduction

Stereochemistry of the divalent copper (d^9) ion is of great interest, because d^9 ions cause distortions in regular octahedral or tetrahedral coordination according to the Jahn-Teller effect. In addition to the distorted octahedral or tetrahedral coordination, Cu^{2+} can also adopt square planar, trigonal bipyramidal, and square pyramidal coordinations. Due to this variety of coordination which can be adopted by divalent copper, the structural chemistry of copper minerals is very complex (Zemann, 1961, 1972; Ghose, 1966).

The Zn^{2+} ion, on the other hand, has a filled d^{10} shell and is very similar to Mg^{2+} ion in many respects. However, in addition to the regular octahedral coordination, Zn^{2+} ion has a strong tendency to adopt regular tetrahedral coordination. Zinc in mixed coordination is found in a number of zinc minerals. Zinc sometimes also adopts the trigonal bipyramidal or square pyramidal coordination. As a result, the structural chemistry of zinc minerals is also rather complex (Brehler, 1969).

In spite of the stereochemical differences between Cu^{2+} and Zn^{2+} ions, zinc is known to replace copper in a number of basic copper minerals. The crystal chemistry of the copper-zinc substitution cannot be understood, unless details of these mineral structures are known. In this series of papers we plan to examine the details of the structural chemistry of copper and zinc minerals including the mixed varieties. In Part I of this series, we present the crystal structure of a mixed copper zinc phosphate mineral, namely, veszelyite, $(Cu, Zn)_3\,PO_4\,(OH)_3 \cdot 2\,H_2O$.

Crystal Data and Experimental

Bluish green veszelyite crystals from Arakawa Mine, Japan (varietal name, arakawaite) $Cu_{1.77}\ Zn_{1.24}\ PO_4(OH)_3 \cdot 2\,H_2O$ (Wakabayashi and Komada, 1921; in Palache, Berman, and Frondel, 1951) were used for the structure determination. The cell dimensions have been determined and refined by the method of least squares using 15 high angle reflections measured on an automatic single crystal diffractometer.

The crystal data are: monoclinic, $2/m$; space group,

$P2_1/a$; a_o = 9.8275 (22), b_o = 10.2244 (30), c_o = 7.5322 (28) Å, β = 103.18 (2)°; cell content, 4[$Cu_{1.77}$ $Zn_{1.24}$ $PO_4(OH)_3 \cdot 2\ H_2O$]; density, g/cm^3, 3.4 (meas), 3.42 (calc); μ for Mo$K\alpha$, 95.86 cm^{-1}; cleavage, {001}. The foregoing cell dimensions are in good agreement with those measured by Berry (1948) for crystals from Moravička.

A crystal sphere (0.297 mm in diameter) was prepared using a Bond type sphere grinder (Bond, 1951) and mounted on a Syntex P$\bar{1}$ automatic single crystal diffractometer in an arbitrary orientation. The orientation matrix was found automatically. A total of 1691 reflections were collected by the 2θ:θ method within a sphere of 2θ = 60°, using Mo$K\alpha$ radiation, graphite monochromator, and a solid state detection system. The scan rate was variable, the minimum rate being 1°/min. The intensity data have been corrected for Lorentz, polarization, and absorption factors (μR = 1.42). The infrared spectrum of veszelyite has been recorded on a Perkin Elmer (model 13) spectrometer with CaF_2 prism using a Nujol mull technique.

Determination and Refinement of the Structure

A three dimensional Patterson synthesis (*Puvw*) showed Patterson peaks concentrated in sections at v = 0, 1/6, 1/3, and 1/2. Three minimum function (*M*2) maps (Buerger, 1959) were prepared using these sections and three peaks presumably of the type $2x$, $2y$, $2z$ as points of superposition. These three peaks were chosen on the basis of their consistency with the Harker section at v = 1/2 and Harker line at 1/2 v0. Structure factor calculations using the three sets of heavy atom positions obtained from the *M*2 maps yielded *R* factors of 0.56, 0.58, and 0.36. The set of heavy atom positions giving the lowest *R*-factor apparently was correct. Three dimensional Fourier and difference-Fourier syntheses, based on the phases determined by these heavy atom positions, revealed the locations of phosphorus and all the oxygen atoms. The refinement of the structure was carried out using the full matrix least squares program RFINE (Finger, 1969) on a CDC 6400 computer. The observed structure factors (Fo's) were weighted by $1/\sigma^2$(Fo), where σ(Fo) is the standard deviation based on counting statistics. The scattering factors for Cu, Zn, P, and O were taken from Cromer and Mann (1968). Corrections for anomalous dispersion have been made (Cromer, 1965). Copper and zinc were assigned on the basis of site geometry at the heavy atom locations. No attempt was made to refine the site occupancies at the Cu(1) and Cu(2) sites, although about 10 percent of the copper is thought to be replaced by zinc at these positions according to the chemical analysis (Wakabayashi and Komada, 1921; cited in Palache, Berman, and Frondel, 1951). For the least squares refinement, these two positions were considered to be completely filled by copper. Three cycles of least square refinement using anisotropic temperature factors reduced the *R* factor to 0.052 (weighted) and 0.044 (unweighted) for all reflections. The final atomic parameters with standard deviations are listed in Table 1. The r.m.s. displacements and the orientation of thermal ellipsoids are listed in Table 2. The interatomic distances and angles with

TABLE 1. Atomic Parameters for Veszelyite

Atom	x	y	z	B eq.	β_{11}*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	.12991(8)	.07328(7)	.49115(10)	.982(15)	318(8)	172(7)	583(14)	-70(6)	224(8)	-78(7)
Cu(2)	.35837(8)	.25318(8)	.45957(9)	.946(14)	321(8)	165(6)	527(13)	-62(6)	211(8)	-39(8)
Zn	.21036(7)	.07612(7)	.06936(9)	.990(14)	308(8)	184(7)	534(13)	-20(5)	149(7)	-40(7)
P	.41433(16)	.29884(15)	.06551(21)	.835(24)	273(15)	155(13)	451(25)	2(11)	166(16)	21(15)
O(1)	.03230(45)	.15904(45)	.97475(60)	1.209(71)	324(45)	322(42)	553(78)	120(36)	168(47)	17(47)
O(2)	.35754(46)	.16623(44)	.98344(60)	1.237(73)	466(49)	152(39)	712(82)	-88(35)	253(52)	-69(46)
O(3)	.46803(44)	.28632(43)	.27424(57)	1.076(70)	434(49)	237(41)	352(72)	-56(35)	176(47)	-21(43)
O(4)	.29531(46)	.39994(43)	.02472(64)	1.315(74)	365(46)	190(40)	904(90)	91(37)	231(51)	179(49)
OH(1)	.26853(45)	.08673(42)	.33723(57)	1.030(68)	424(46)	189(39)	450(73)	-14(35)	270(48)	-13(43)
OH(2)	.23522(43)	.21782(42)	.62330(57)	1.008(69)	332(44)	220(41)	487(74)	-75(34)	211(47)	-41(43)
OH(3)	.46392(41)	.40724(40)	.60096(56)	.853(64)	210(40)	161(38)	563(75)	-27(33)	149(44)	-26(43)
OH_2(1)	.03710(49)	.38414(51)	.65793(71)	1.929(87)	395(50)	373(49)	1254(106)	4(40)	107(58)	-19(57)
OH_2(2)	.19138(50)	.40815(51)	.31930(65)	1.815(85)	569(56)	450(51)	780(92)	34(42)	301(57)	1(53)

*$\beta ij \times 10^{-5}$; form of temperature factor, $\exp \{\sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j \beta_{ij}\}$

standard errors (including the errors in cell dimensions) have been calculated using the ERROR program (Finger, private communication) and are listed in Table 3. Observed and calculated structure factors are listed in Table 4.

Description of the Structure

Stereochemistry of the Cupric Ions

Both Cu(1) and Cu(2) have tetragonally distorted, octahedral coordination (Fig. 1). Cu(1) is surrounded by four (OH) ions, roughly in a square planar arrangement at distances of 1.99, 1.94, 2.00, and 1.98 Å; one oxygen, O(3), and a water molecule, $H_2O(2)$, complete the octahedron at distances of 2.47 and 2.62 Å. Likewise, the Cu(2) ion is bonded to one oxygen and three (OH) ions in a square plane at distances of 1.98, 2.05, 1.95, and 2.04 Å; two water molecules, $H_2O(1)$ and $H_2O(2)$, at distances of 2.47 and 2.35 Å, respectively, complete the octahedron.

TABLE 2. Magnitudes and Orientations of Thermal Ellipsoids for Veszelyite

Atom	Axis	rms amplitude (Å)	angles (°) of r_i with a	b	c
Cu(1)	1	.086	59.2(10.5)	35.2(6.5)	81.8(9.1)
	2	.094	58.4(10.5)	110.2(9.4)	50.3(11.7)
	3	.145	46.8(2.4)	113.5(1.7)	138.6(3.0)
Cu(2)	1	.085	60.2(5.8)	38.4(3.6)	75.5(5.7)
	2	.099	62.5(6.1)	113.4(5.6)	48.2(6.9)
	3	.137	37.5(3.3)	110.2(1.8)	132.0(4.0)
Zn	1	.096	88.4(5.1)	15.0(5.5)	104.8(5.8)
	2	.109	48.8(8.8)	84.1(6.5)	54.9(8.8)
	3	.128	45.9(5.8)	107.1(3.5)	142.8(6.8)
P	1	.088	67.4(29.5)	43.7(27.7)	61.9(30.7)
	2	.095	56.6(38.1)	120.8(30.8)	58.9(36.9)
	3	.123	37.0(10.6)	84.2(6.2)	139.4(10.9)
O (1)	1	.094	46.8(12.0)	118.3(10.6)	67.5(16.5)
	2	.122	92.4(17.6)	66.4(23.1)	25.7(21.5)
	3	.149	50.5(13.1)	39.5(13.1)	98.5(14.6)
O (2)	1	.082	75.3(9.1)	14.7(8.7)	92.5(11.0)
	2	.122	57.8(17.0)	94.3(10.2)	45.6(17.2)
	3	.159	30.9(16.4)	108.2(7.8)	126.4(22.0)
O (3)	1	.089	108.7(19.2)	92.8(20.6)	148.0(19.7)
	2	.108	105.4(13.5)	164.5(15.7)	84.2(25.7)
	3	.146	19.4(11.6)	108.8(12.0)	97.8(8.5)
O (4)	1	.083	103.8(12.8)	18.8(13.6)	74.6(11.6)
	2	.121	140.2(14.7)	95.7(11.9)	116.1(14.6)
	3	.168	72.6(8.6)	65.1(8.9)	154.4(9.8)
OH (1)	1	.085	118.4(30.6)	89.2(27.6)	138.4(30.6)
	2	.100	93.7(20.8)	176.3(18.4)	89.5(31.7)
	3	.148	15.2(11.4)	94.5(9.7)	117.6(11.6)
OH (2)	1	.090	127.2(51.4)	113.3(26.2)	122.4(53.5)
	2	.104	85.4(43.9)	139.1(53.8)	52.1(57.1)
	3	.140	36.5(15.3)	119.4(14.0)	120.7(17.4)
OH (3)	1	.086	46.3(70.5)	53.4(58.7)	76.1(48.2)
	2	.095	57.3(67.5)	131.6(70.4)	67.7(55.8)
	3	.127	72.9(14.9)	100.8(14.4)	168.4(16.2)
OH_2 (1)	1	.135	14.0(36.0)	96.9(81.2)	91.0(9.0)
	2	.140	95.9(78.4)	173.9(70.2)	87.0(12.8)
	3	.188	103.0(7.5)	92.6(7.3)	153.7(7.5)
OH_2 (2)	1	.128	120.7(17.4)	83.6(12.3)	135.5(17.7)
	2	.154	83.5(21.4)	165.8(20.8)	103.8(21.8)
	3	.170	24.3(30.1)	72.3(26.0)	118.5(28.5)

TABLE 3. Interatomic Distances and Bond Angles in Veszelyite

Bond Lengths (Å)		Bond Angles (°)	
Cu(1) Octahedron			
Cu(1) - OH(1)	1.985(4)	OH(1) - Cu(1) - OH(2)	87.7(2)
Cu(1) - OH(2)	1.943(4)	OH(2) - Cu(1) - OH(3)	95.8(2)
Cu(1) - OH(3)	2.000(4)	OH(3) - Cu(1) - OH(3)'	82.6(2)
Cu(1) - OH(3)'	1.980(4)	OH(3)'- Cu(1) - OH(1)	100.4(2)
Cu(1) - O(3)	2.465(4)	O(3) - Cu(1) - OH(1)	89.9(2)
OH(2) - OH(3)	2.927(6)	O(3) - Cu(1) - OH(2)	94.9(2)
OH(3) - OH(3)'	2.628(8)	O(3) - Cu(1) - OH(3)	75.7(2)
OH(3)'- OH(1)	3.045(6)	O(3) - Cu(1) - OH(3)'	95.1(2)
OH(1) - OH(2)	2.624(6)	OH_2(2) - Cu(1) - OH(1)	84.2(2)
OH_2(2)- OH(2)	2.962(7)	OH_2(2) - Cu(1) - OH(2)	89.9(2)
OH_2(2)- OH(3)	3.014(6)	OH_2(2) - Cu(1) - OH(3)	110.4(2)
OH_2(2)- OH(3)'	3.013(6)	OH_2(2) - Cu(1) - OH(3)'	80.7(2)
OH_2(2)- OH(1)	3.118(6)	O(3) - Cu(1) - OH_2(2)	171.9(2)
O (3) OH(2)	3.266(6)		
O (3)- OH(3)	2.763(6)		
O (3)- OH(3)'	3.296(6)		
O (3)- OH(1)	2.942(6)		
Cu(2) Octahedron			
Cu(2) - OH(1)	2.038(4)	OH(1) - Cu(2) - O(3)	94.2(2)
Cu(2) - OH(2)	1.949(4)	OH(2) - Cu(2) - OH(1)	82.2(2)
Cu(2) - OH(3)	2.047(5)	OH(3) - Cu(2) - OH(2)	97.3(2)
Cu(2) - O(3)	1.978(4)	O(3) - Cu(2) - OH(3)	86.7(2)
Cu(2) -OH_2(1)	2.468(5)	OH_2(1) - Cu(2) - OH(1)	88.5(2)
Cu(2) -OH_2(2)	2.352(5)	OH_2(1) - Cu(2) - O(3)	95.6(2)
OH(3) - OH(2)	2.927(6)	OH_2(1) - Cu(2) - OH(3)	85.2(2)
OH(2) - OH(1)	2.621(6)	OH_2(1) - Cu(2) - OH(2)	88.3(2)
OH(1) - O(3)	2.942(6)	OH_2(2) - Cu(2) - OH(1)	100.0(2)
O(3) - OH(3)	2.763(6)	OH_2(2) - Cu(2) - O(3)	90.2(2)
OH_2(1) - OH(3)	3.072(7)	OH_2(2) - Cu(2) - OH(3)	86.2(2)
OH_2(1) - OH(2)	2.642(7)	OH_2(2) - Cu(2) - OH(2)	86.5(2)
OH_2(1) - OH(1)	2.812(6)	OH_2(2) - Cu(2) - OH_2(1)	169.3(2)
OH_2(1) - O(3)	3.311(7)		
OH_2(2) - OH(3)	3.014(6)		
OH_2(2) - OH(2)	2.962(7)		
OH_2(2) - OH(1)	3.118(6)		
OH_2(2) - O(3)	2.923(7)		
Zn - Tetrahedron			
Zn - OH(1)	1.971(4)	OH(1) - Zn - O(1)	112.4(2)
Zn - O(1)	1.929(4)	O(1) - Zn - O(2)	110.4(2)
Zn - O(2)	1.946(4)	O(2) - Zn -OH(1)	104.5(2)
Zn - O(4)	1.932(4)	O(4) - Zn -OH(1)	113.9(2)
O(4) - O(1)	2.516(6)	O(4) - Zn - O(1)	109.1(2)
O(1) - O(2)	2.489(6)	O(4) - Zn - O(2)	106.3(2)
O(2) - O(4)	2.503(6)		
OH(1) - O(4)	3.271(6)		
OH(1) - O(2)	3.098(6)		
OH(1) - O(1)	3.241(6)		
P - Tetrahedron			
P - O(1)	1.536(5)	O(1) - P - O(3)	111.0(2)
P - O(2)	1.541(5)	O(3) - P - O(4)	109.1(3)
P - O(3)	1.546(3)	O(4) - P - O(1)	109.8(2)
P - O(4)	1.539(4)	O(2) - P - O(1)	108.1(3)
O(4) - O(2)	2.503(6)	O(2) - P - O(3)	110.1(2)
O(2) - O(1)	2.489(6)	O(2) - P - O(4)	108.8(3)
O(1) - O(4)	2.516(6)		
O(3) - O(4)	2.512(6)		
O(3) - O(2)	2.530(6)		
O(3) - O(1)	2.540(6)		

The $[Cu(1)(OH)_4O(H_2O)]^{4-}$ octahedron shares one edge, OH(3)-(OH)(3)', with a centrosymmetrically related Cu(1) octahedron, and the opposite edge, (OH)(1)-(OH)(2), with a Cu(2) octahedron. Furthermore, it shares two edges, namely O(3)-(OH)(3) and OH(3)-(OH)(2), with two centrosymmetrically related Cu(2)-octahedra (Fig. 2).

The $[Cu(2)O(OH)_3(H_2O)_2]^{3-}$ octahedron shares two adjacent edges, namely O(3)-(OH)(3) and O(3)-OH_2(2), with two Cu(1)-octahedra on the one side and one

TABLE 4. Observed and Calculated Structure Factors for Veszelyite*

k	h	F_{obs}	F_{calc}
		l = 0	
0	2	93.010	145.312
0	4	46.947	58.963
0	6	27.044	28.408
0	8	47.707	52.326
0	10	13.867	14.858
0	12	63.131	78.296
1	1	130.802	121.598
1	2	96.456	94.837
1	3	87.297	94.209
1	4	27.845	29.477
1	5	21.491	22.738
1	6	63.927	71.249
1	7	14.560	17.461
1	8	37.681	40.826
1	9	46.295	52.536
1	10	17.795	20.660
1	11	32.382	36.227
1	12	19.004	20.222
2	0	54.488	51.682
2	1	134.953	128.816
2	2	83.542	73.131
2	3	61.829	57.045
2	4	66.346	63.551
2	5	52.408	49.535
2	6	9.686	9.532
2	7	46.029	45.957
2	8	20.199	20.659
2	9	30.355	30.366
2	10	41.026	43.620
2	11	27.939	28.663
2	12	33.602	37.375
3	1	36.093	34.561
3	2	284.999	257.211
3	3	59.298	50.227
3	4	82.083	75.619
3	5	5.659	6.432
3	6	62.783	58.384
3	7	28.864	27.628
3	8	9.998	8.146
3	9	4.274 *	3.508
3	10	59.968	58.781
3	11	18.077	17.179
3	12	26.907	28.126
4	0	37.497	28.843
4	1	136.637	133.960
4	2	5.699	7.747
4	3	22.201	28.841
4	4	93.521	83.113
4	5	27.184	24.688
4	6	14.641	13.169
4	7	50.921	47.876
4	8	34.671	33.822
4	9	10.879	11.833
4	10	38.544	35.778
4	11	30.838	28.619
5	1	6.783	3.290
5	2	9.392	10.345
5	3	89.486	80.107
5	4	57.095	51.098
5	5	32.969	31.506
5	6	25.872	22.594
5	7	15.139	12.878
5	8	67.916	64.453
5	9	36.484	35.221
5	10	18.158	16.161
5	11	35.600	33.507
6	0	262.446	256.039
6	1	47.213	43.370
6	2	118.945	115.263
6	3	51.031	47.654
6	4	47.711	46.310
6	5	11.189	7.614
6	6	37.443	33.645
6	7	5.412 *	4.327
6	8	46.288	42.255
6	9	22.209	20.420
6	10	8.993	6.121
6	11	18.150	17.423
7	1	110.801	109.097
7	2	31.920	31.774
7	3	97.889	93.966
7	4	21.976	22.137
7	5	3.109 *	3.577
7	6	33.499	29.430
7	7	12.654	13.330
7	8	46.353	42.693
7	9	45.749	41.594
7	10	22.858	22.293
8	0	67.551	66.125
8	1	33.758	31.996
8	2	32.046	30.793
8	3	59.970	57.540
8	4	12.924	12.172
8	5	10.356	9.725
8	6	40.533	38.224
8	7	41.814	39.844
8	8	10.365	9.114
8	9	3.689 *	1.592
9	1	6.966	6.371
9	2	93.872	92.056
9	3	14.836	13.699
9	4	87.871	88.221
9	5	9.287	8.126
9	6	43.988	42.576
9	7	4.571 *	1.489
9	8	13.096	8.904
9	9	15.521	12.609
10	0	6.064 *	4.630
10	1	93.933	96.064
10	2	8.796	9.860
10	3	9.480	9.376
10	4	53.436	50.866
10	5	23.716	23.861
10	6	46.071	45.661
10	7	5.472 *	4.216
10	8	39.173	37.799
11	1	14.744	15.545
11	2	30.754	31.155
11	3	6.551 *	7.397
11	4	3.830 *	2.980
11	5	3.710 *	1.802
11	6	32.454	33.679
12	0	91.033	95.294
12	1	46.683	48.276
12	2	49.430	50.801
12	3	5.322 *	5.362
12	4	33.261	34.652
12	5	7.699 *	6.665
13	1	30.357	31.658
13	2	35.657	38.223
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0	-4	87.948	95.653
0	-2	57.736	60.023
0	0	72.669	70.836
0	2	12.976	14.098
0	4	192.151	204.136
0	6	70.086	80.894
0	8	76.942	88.651
0	10	79.186	88.676
0	12	7.474 *	8.582
1	-12	19.134	16.790
1	-11	39.084	38.190
1	-10	20.336	20.018
1	-9	24.534	24.613
1	-8	47.865	48.181
1	-7	120.578	123.836
1	-6	13.734	12.476
1	-5	152.738	155.713
1	-4	24.164	27.796
1	-3	16.257	16.513
1	-2	30.050	31.535
1	-1	13.931	14.141
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1	1	56.923	62.122
1	2	12.798	8.004
1	3	21.913	24.261
1	4	66.210	69.274
1	5	82.849	86.270
1	6	23.656	22.709
1	7	186.818	115.663
1	8	34.812	36.812
1	9	11.394	12.363
1	10	29.744	34.017
1	11	9.118	6.128
1	12	19.188	20.942
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2	-9	29.537	28.137
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2	-7	84.605	88.119
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2	-5	61.358	61.465
2	-4	19.856	18.159
2	-3	54.288	58.785
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2	-1	35.175	26.468
2	0	38.939	41.681
2	1	32.226	32.365
2	2	179.552	166.661
2	3	51.953	55.769
2	4	34.364	32.651
2	5	50.986	51.421
2	6	19.265	19.541
2	7	53.649	54.915
2	8	3.866 *	1.058
2	9	10.624	9.612
2	10	22.615	23.055
2	11	15.588	15.426
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3	2	270.687	245.459
3	3	33.087	29.594
3	4	52.170	48.985
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3	6	148.536	145.628
3	7	14.898	14.788
3	8	105.074	101.858
3	9	4.393 *	4.209
3	10	5.682 *	6.300
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4	-4	49.599	50.766
4	-3	57.616	56.225
4	-2	26.613	26.451
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4	2	113.170	105.383
4	3	107.630	101.553
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4	5	123.464	115.819
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4	8	16.929	15.902
4	9	65.290	61.975
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7	2	40.625	39.611
7	3	22.332	21.170
7	4	31.347	29.423
7	5	58.387	55.998
7	6	31.450	28.395
7	7	97.862	90.595
7	8	26.568	25.781
7	9	19.665	19.926
7	10	8.335	7.072
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8	-8	18.602	18.475
8	-7	38.510	39.918
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8	-5	12.422	14.222
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13	-1	14.143	15.218
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1	-6	114.760	115.970
1	-5	17.613	16.486
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1	-2	67.970	70.318
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1	2	65.601	67.007
1	3	25.928	25.534
1	4	68.993	72.127
1	5	32.611	31.982
1	6	6.719	3.140
1	7	17.276	14.273
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1	9	60.195	65.943
1	10	42.466	46.725
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2	-11	41.020	38.409
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2	-9	9.742	8.227
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2	-7	71.204	72.797
2	-6	38.595	38.017
2	-5	101.799	103.141
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2	-3	104.807	101.409
2	-2	32.623	34.210
2	-1	73.217	73.910
2	0	16.733	17.389
2	1	121.318	124.187
2	2	9.631	8.769
2	3	29.926	31.634
2	4	47.245	46.136
2	5	14.557	14.320
2	6	51.211	52.137
2	7	50.764	54.397
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2	9	50.477	56.937
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3	-1	2.538 *	4.234
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3	1	22.789	23.147
3	2	159.450	162.403
3	3	59.906	57.870
3	4	48.595	49.071
3	5	13.620	11.750
3	6	40.413	40.566
3	7	20.781	19.898
3	8	11.343	12.098
3	9	15.197	15.487
3	10	44.619	48.869
3	11	17.486	17.676
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4	-7	.717	7.197
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4	3	12.180	9.692
4	4	41.436	40.804
4	5	38.239	35.567
4	6	42.713	42.612
4	7	62.109	65.285
4	8	14.892	13.880
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5	-9	19.081	21.933
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5	-7	3.579 *	.711
5	-6	36.522	37.871
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5	1	31.570	30.782
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5	3	55.206	52.805
5	4	36.520	34.465
5	5	50.899	49.538
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5	7	10.802	9.324
5	8	52.462	54.101
5	9	69.612	72.429
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6	3	19.806	18.893
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6	6	6.639	4.709
6	7	23.430	23.100
6	8	64.423	63.999
6	9	27.490	27.166
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7	3	44.928	45.072
7	4	59.131	58.164
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7	7	17.334	16.789
7	8	48.086	48.048
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8	-9	18.156	18.049
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9	1	6.937	5.860
9	2	61.264	62.205
9	3	3.333 *	1.833
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9	5	12.422	12.341
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3	-11	4.599 *	3.843
3	-10	109.280	107.832
3	-9	22.463	24.013
3	-8	12.360	10.715
3	-7	10.043	10.206
3	-6	129.912	134.499
3	-5	6.847	10.066
3	-4	56.923	57.997
3	-3	3.865 *	3.185
3	-2	26.733	27.145
3	-1	21.946	22.318
3	0	26.506	25.941
3	1	54.766	56.094
3	2	183.721	189.301
3	3	20.401	19.917
3	4	110.771	107.784
3	5	5.363 *	1.889
3	6	77.879	72.548
3	7	20.038	18.441
3	8	49.769	46.185
3	9	9.601	7.098
3	10	3.712 *	3.631
4	-12	41.554	39.277
4	-11	21.223	20.403
4	-10	3.465 *	2.243
4	-9	94.991	95.256
4	-8	5.526 *	4.832
4	-7	45.230	44.929
4	-6	14.296	13.854
4	-5	21.104	19.679
4	-4	43.215	42.768
4	-3	8.669	7.931
4	-2	56.738	57.031
4	-1	61.507	63.540
4	0	92.963	92.540
4	1	50.883	50.852
4	2	86.645	86.975
4	3	93.181	92.938
4	4	17.141	17.056
4	5	136.792	127.238
4	6	49.895	46.499
4	7	23.491	20.408
4	8	3.416 *	1.514
4	9	11.849	10.932
4	10	32.147	28.782
5	-11	29.705	29.101
5	-10	8.006	10.273
5	-9	39.939	37.496
5	-8	11.961	12.718
5	-7	29.617	29.116
5	-6	24.797	25.611
5	-5	56.449	55.531
5	-4	10.064	9.979
5	-3	9.545	9.560
5	-2	57.007	58.901
5	-1	39.100	38.329
5	0	103.535	104.179
5	1	131.487	130.999
5	2	40.308	39.278
5	3	11.389	11.647
5	4	63.410	60.224
5	5	9.448	8.862
5	6	19.345	18.121
5	7	9.504	7.264
5	8	10.942	8.796
5	9	12.188	9.803
6	-11	12.425	11.677
6	-10	61.292	60.608
6	-9	13.882	13.697
6	-8	128.412	125.540
6	-7	36.353	35.848
6	-6	41.389	41.070
6	-5	37.452	35.818
6	-4	123.019	123.768
6	-3	13.969	12.692
6	-2	29.699	29.449
6	-1	21.710	22.557
6	0	72.583	71.865
6	1	25.274	24.888
6	2	29.594	29.909
6	3	47.681	47.741
6	4	121.618	114.479
6	5	3.204 *	2.750
6	6	99.789	93.064
6	7	6.142 *	3.588
6	8	15.515	13.775
6	9	3.736 *	.418
7	-10	21.332	20.423
7	-9	6.414 *	7.042
7	-8	5.569 *	5.585
7	-7	26.729	26.817
7	-6	63.906	64.299
7	-5	46.408	46.201
7	-4	11.485	11.983
7	-3	3.210 *	1.542
7	-2	83.697	84.477
7	-1	18.929	17.833
7	0	38.851	39.375
7	1	71.568	70.379
7	2	17.248	15.963
7	3	74.292	72.581
7	4	39.329	39.291
7	5	17.632	15.438
7	6	4.036 *	.741
7	7	67.798	64.026
7	8	40.393	36.165
8	-10	35.361	35.298
8	-9	30.173	30.602
8	-8	5.858 *	5.494
8	-7	22.694	21.970
8	-6	11.764	10.772
8	-5	10.345	8.314
8	-4	53.202	54.666
8	-3	3.318 *	4.102
8	-2	31.278	31.572
8	-1	33.960	34.643
8	0	11.718	11.183
8	1	3.206 *	1.785
8	2	60.940	61.460
8	3	81.999	81.979
8	4	60.073	59.031
8	5	24.001	23.196
8	6	4.382 *	5.144
8	7	30.933	28.295
8	8	18.152	16.112
9	-9	27.669	27.680
9	-8	4.965 *	1.853
9	-7	30.280	31.341
9	-6	95.716	95.310
9	-5	17.841	15.984
9	-4	30.815	31.310
9	-3	11.042	8.959
9	-2	46.387	46.957
9	-1	18.351	18.676
9	0	32.744	32.073
9	1	44.915	45.589
9	2	99.567	99.613
9	3	40.115	40.135
9	4	24.591	21.949
9	5	16.454	17.060
9	6	17.671	17.353
9	7	3.777 *	1.932
10	-8	48.093	49.398
10	-7	55.166	56.287
10	-6	5.519 *	2.278
10	-5	7.819	6.151
10	-4	38.299	38.507
10	-3	6.178 *	3.872
10	-2	3.534 *	4.230
10	-1	30.409	30.429
10	0	58.157	60.493
10	1	6.869 *	5.604
10	2	28.982	30.537
10	3	54.925	54.405
10	4	5.470 *	4.222
10	5	68.000	68.207
10	6	15.300	16.264
11	-6	4.616 *	1.286
11	-5	10.997	10.178
11	-4	7.352 *	8.784
11	-3	11.107	9.093
11	-2	38.803	39.115
11	-1	22.680	22.576
11	0	48.176	50.047
11	1	30.754	31.877
11	2	41.805	41.755
11	3	18.038	18.238
11	4	3.787 *	2.004
12	-4	44.233	46.091
12	-3	3.873 *	2.507
12	-2	8.026	1.329
12	-1	3.845 *	2.088
12	0	32.887	33.884
12	1	3.809 *	1.866
12	2	20.029	19.894
		l = 4	
0	-12	70.848	69.662
0	-10	5.296 *	.930
0	-8	66.131	63.387
0	-6	64.506	63.643
0	-4	278.354	285.299
0	-2	64.011	66.200
0	0	97.308	102.287
0	2	27.626	30.868
0	4	9.412	8.356
0	6	32.102	33.727
0	8	46.677	48.835
0	10	39.544	39.801
1	-12	7.680 *	6.419
1	-11	10.827	6.933
1	-10	69.219	68.029
1	-9	6.590 *	2.814
1	-8	47.149	48.725
1	-7	43.988	43.340
1	-6	56.073	56.909
1	-5	6.283	4.260
1	-4	45.567	46.866
1	-3	117.200	120.526
1	-2	9.710	7.316
1	-1	88.092	92.218
1	0	10.287	9.400
1	1	6.669	5.576
1	2	39.278	39.783
1	3	27.578	27.814
1	4	79.894	85.125
1	5	43.501	45.763
1	6	50.811	52.847
1	7	25.001	24.598
1	8	46.123	45.846
1	9	26.637	25.094
1	10	38.715	38.512
2	-12	31.345	31.306
2	-11	10.980	11.792
2	-10	9.116	9.442
2	-9	27.355	27.235
2	-8	58.904	58.986
2	-7	56.172	57.519
2	-6	60.560	62.890
2	-5	84.560	85.395
2	-4	8.673	7.170
2	-3	102.239	102.803
2	-2	45.237	46.490
2	-1	10.828	9.764
2	0	19.868	18.730
2	1	53.526	54.708
2	2	10.173	9.317
2	3	51.301	54.133
2	4	22.446	22.361
2	5	3.303 *	1.625
2	6	80.845	81.978
2	7	50.715	49.726
2	8	62.017	60.724
2	9	48.966	47.162
3	-12	13.827	14.136
3	-11	3.753 *	1.314
3	-10	53.700	53.469
3	-9	12.519	12.659
3	-8	48.063	48.592
3	-7	11.137	11.466
3	-6	120.974	120.848
3	-5	3.453 *	2.383
3	-4	19.023	18.362
3	-3	15.497	13.291
3	-2	218.167	225.603
3	-1	23.164	23.021
3	0	119.121	124.424
3	1	29.849	29.805
3	2	12.772	15.453
3	3	45.939	45.457
3	4	11.987	13.970
3	5	30.248	31.002
3	6	31.692	30.224
3	7	13.077	13.810
3	8	29.516	27.515
3	9	17.493	16.737
4	-11	33.241	31.678
4	-10	5.899 *	7.895
4	-9	29.136	27.714
4	-8	53.213	53.550
4	-7	14.469	11.973
4	-6	30.669	29.602
4	-5	118.741	119.185
4	-4	8.613	8.677
4	-3	68.378	70.116
4	-2	59.187	60.611
4	-1	40.698	43.902
4	0	16.980	18.408
4	1	13.590	15.237
4	2	26.533	26.964
4	3	22.055	21.222
4	4	6.126 *	4.394
4	5	38.520	38.842
4	6	51.028	49.551
4	7	41.838	39.639
4	8	39.975	37.781
4	9	45.984	43.834
5	-11	3.779 *	6.215
5	-10	34.018	34.836
5	-9	12.787	10.161
5	-8	43.787	42.823
5	-7	8.214	7.643
5	-6	7.459	5.857
5	-5	26.699	26.523
5	-4	82.201	82.334
5	-3	62.090	61.575
5	-2	37.140	36.618
5	-1	66.749	65.994
5	0	8.613	5.621

* Please note that the *h* and *k* columns are not in their usual order.

TABLE 4, Continued

k	h	F_{obs}	F_{calc}
5	1	24.315	24.623
5	2	8.013	6.688
5	3	34.314	35.188
5	4	78.175	75.622
5	5	56.915	55.725
5	6	47.559	44.864
5	7	28.212	18.988
5	8	33.651	31.025
5	9	42.142	39.120
6	-11	16.944	16.269
6	-10	3.693 *	1.260
6	-9	17.834	17.844
6	-8	33.280	31.814
6	-7	19.401	19.718
6	-6	43.252	43.727
6	-5	27.785	29.170
6	-4	152.053	151.486
6	-3	14.484	14.874
6	-2	58.573	59.241
6	-1	19.167	18.752
6	0	44.861	44.007
6	1	23.300	22.163
6	2	65.961	65.956
6	3	7.264	5.531
6	4	23.519	23.439
6	5	30.900	31.440
6	6	3.440 *	1.955
6	7	40.147	37.799
6	8	49.589	45.997
7	-10	38.117	30.235
7	-9	6.759 *	4.331
7	-8	16.145	16.599
7	-7	64.017	63.325
7	-6	12.227	12.026
7	-5	28.538	28.881
7	-4	48.387	48.515
7	-3	115.189	116.244
7	-2	5.564 *	5.152
7	-1	72.075	72.284
7	0	29.299	29.430
7	1	7.628	5.407
7	2	37.331	38.692
7	3	26.334	24.997
7	4	60.676	60.233
7	5	34.920	34.221
7	6	3.549 *	2.019
7	7	28.220	25.532
7	8	28.986	25.659
8	-9	10.090	9.758
8	-8	16.090	16.383
8	-7	33.179	33.570
8	-6	72.358	72.777
8	-5	44.175	44.435
8	-4	51.563	50.694
8	-3	21.150	21.319
8	-2	27.882	26.714
8	-1	35.098	35.235
8	0	10.071	10.763
8	1	12.637	11.207
8	2	54.511	54.552
8	3	33.701	32.643
8	4	7.283	6.582
8	5	3.607 *	2.330
8	6	55.509	52.931
8	7	42.194	41.152
9	-8	32.186	32.265
9	-7	13.633	12.585
9	-6	52.644	52.733
9	-5	3.584 *	1.947
9	-4	3.534 *	.466
9	-3	19.349	18.968
9	-2	93.299	95.790
9	-1	20.066	21.420
9	0	108.254	110.010
9	1	7.648	6.431
9	2	17.948	16.688
9	3	6.560 *	6.602
9	4	5.802 *	2.266
9	5	28.550	27.812
9	6	43.986	42.600
10	-7	11.794	12.707
10	-6	11.924	12.550
10	-5	65.867	66.922
10	-4	12.755	11.157
10	-3	63.187	64.507
10	-2	52.917	53.820
10	-1	29.136	30.755
10	0	36.288	37.077
10	1	33.066	32.713
10	2	47.112	48.383
10	3	4.792 *	.406
10	4	24.621	24.341
10	5	3.856 *	5.316
11	-5	10.543	10.858
11	-4	48.061	48.354
11	-3	37.758	38.972
11	-2	41.965	43.792
11	-1	3.764 *	2.213
11	0	28.299	27.559
11	1	3.762 *	4.707
11	2	17.045	18.453
11	3	11.285	11.691
12	-2	43.027	43.745
12	-1	21.499	22.680
12	0	37.745	38.878
		l = 5	
0	-12	39.413	39.028
0	-10	20.025	19.125
0	-8	96.325	91.194
0	-6	55.760	64.481
0	-4	23.994	23.126
0	-2	5.672 *	4.038
0	0	103.707	112.535
0	2	64.963	79.607
0	4	82.824	88.498
0	6	50.215	51.187
0	8	17.815	16.617
1	-12	13.839	10.824
1	-11	56.116	54.881

k	h	F_{obs}	F_{calc}
1	-10	4.549 *	4.659
1	-9	52.350	52.209
1	-8	14.742	14.778
1	-7	25.224	24.177
1	-6	3.172 *	3.933
1	-5	10.931	10.607
1	-4	84.796	86.377
1	-3	34.662	35.633
1	-2	6.202	3.621
1	-1	4.427 *	6.034
1	0	121.777	128.084
1	1	68.051	71.046
1	2	28.679	29.940
1	3	81.864	86.913
1	4	16.765	13.740
1	5	22.772	25.398
1	6	5.371 *	2.444
1	7	12.819	9.817
1	8	14.345	14.826
1	9	11.573	10.958
2	-12	3.848 *	1.564
2	-11	20.021	21.080
2	-10	24.695	23.677
2	-9	56.777	55.500
2	-8	14.051	12.679
2	-7	61.588	62.524
2	-6	20.943	20.353
2	-5	11.133	9.369
2	-4	17.476	17.338
2	-3	81.268	81.680
2	-2	145.708	151.029
2	-1	83.328	87.302
2	0	36.531	37.580
2	1	22.812	21.811
2	2	51.473	52.367
2	3	50.872	53.318
2	4	15.163	15.481
2	5	34.293	35.759
2	6	12.322	11.228
2	7	18.851	19.686
2	8	15.991	14.274
2	9	17.465	15.242
3	-11	19.281	17.706
3	-10	109.372	108.347
3	-9	9.073	10.764
3	-8	41.095	40.487
3	-7	5.824 *	6.227
3	-6	20.705	17.631
3	-5	6.746	6.175
3	-4	20.903	20.530
3	-3	36.112	36.929
3	-2	92.008	93.850
3	-1	25.100	25.546
3	0	21.600	20.198
3	1	26.162	26.234
3	2	126.665	129.391
3	3	21.883	23.696
3	4	74.946	75.471
3	5	21.716	22.777
3	6	3.380 *	2.978
3	7	3.534 *	4.585
3	8	20.452	19.395
4	-11	6.657 *	2.217
4	-10	12.341	11.998
4	-9	65.270	64.549
4	-8	20.503	21.180
4	-7	46.020	44.502
4	-6	19.019	18.782
4	-5	50.676	52.036
4	-4	25.939	27.517
4	-3	17.082	16.380
4	-2	103.969	108.068
4	-1	93.538	95.067
4	0	7.957	7.702
4	1	90.862	92.381
4	2	44.162	44.998
4	3	57.818	58.694
4	4	6.386 *	7.561
4	5	52.606	52.216
4	6	30.212	29.812
4	7	4.292 *	5.761
4	8	14.158	13.552
5	-11	41.237	40.057
5	-10	8.141	6.000
5	-9	52.700	52.962
5	-8	16.148	14.673
5	-7	16.418	15.932
5	-6	34.192	34.671
5	-5	3.283 *	2.120
5	-4	52.080	51.974
5	-3	61.253	63.795
5	-2	8.021	4.872
5	-1	47.932	48.539
5	0	108.269	102.822
5	1	43.003	41.818
5	2	54.438	56.430
5	3	15.246	14.899
5	4	20.746	20.169
5	5	7.431	6.677
5	6	15.177	16.112
5	7	10.388	7.820
5	8	26.076	24.930
6	-10	20.152	19.032
6	-9	17.190	16.250
6	-8	98.057	98.721
6	-7	17.210	15.544
6	-6	46.119	45.697
6	-5	32.699	33.539
6	-4	46.297	46.293
6	-3	6.137 *	5.957
6	-2	22.806	24.226
6	-1	46.524	47.098
6	0	93.403	94.508
6	1	29.883	30.637
6	2	44.196	43.906
6	3	3.313 *	1.761
6	4	38.445	37.979
6	5	16.585	15.761
6	6	65.052	62.205
6	7	10.888	10.001
7	-9	27.299	26.270
7	-8	8.201	10.686
7	-7	4.573 *	2.647

k	h	F_{obs}	F_{calc}
7	-6	67.463	69.336
7	-5	9.262	11.036
7	-4	21.364	21.740
7	-3	3.395 *	3.728
7	-2	14.298	12.385
7	-1	11.845	12.264
7	0	54.897	55.806
7	1	74.298	76.591
7	2	14.081	13.358
7	3	65.820	67.935
7	4	34.276	34.452
7	5	9.922	6.564
7	6	9.194	6.500
8	-9	37.922	38.428
8	-8	3.764 *	1.834
8	-7	30.229	29.575
8	-6	4.268 *	6.676
8	-5	10.895	11.093
8	-4	47.258	47.708
8	-3	24.971	26.246
8	-2	66.373	68.288
8	-1	62.537	65.029
8	0	58.678	58.553
8	1	3.455 *	6.735
8	2	27.495	27.746
8	3	28.134	29.739
8	4	56.745	57.786
8	5	26.888	25.652
8	6	19.868	18.450
9	-8	20.311	21.692
9	-7	6.017 *	2.392
9	-6	42.527	43.159
9	-5	3.691 *	3.685
9	-4	3.905 *	3.080
9	-3	39.761	41.249
9	-2	44.078	44.945
9	-1	7.778	9.358
9	0	18.913	19.345
9	1	34.449	35.615
9	2	49.346	50.312
9	3	26.986	26.731
9	4	48.816	50.567
9	5	4.682 *	6.599
10	-6	7.524 *	9.434
10	-5	13.772	14.734
10	-4	29.865	30.006
10	-3	22.959	23.826
10	-2	10.865	11.262
10	-1	55.024	57.259
10	0	4.985 *	3.865
10	1	35.516	35.753
10	2	24.881	25.271
10	3	24.997	25.966
11	-4	30.149	32.190
11	-3	15.819	16.380
11	-2	3.869 *	.936
11	-1	9.732	10.486
11	0	30.297	29.687
11	1	15.482	16.419
		l = 6	
0	-10	21.478	20.688
0	-8	105.440	103.622
0	-6	20.997	21.861
0	-4	114.683	111.293
0	-2	42.406	44.565
0	0	12.695	11.455
0	2	18.002	20.391
0	4	15.761	14.939
0	6	28.739	28.137
0	8	19.051	16.524
1	-11	5.388 *	1.485
1	-10	63.637	63.466
1	-9	24.518	24.032
1	-8	71.386	71.016
1	-7	99.870	97.703
1	-6	25.458	25.459
1	-5	50.612	50.087
1	-4	9.938	10.254
1	-3	33.567	33.976
1	-2	31.072	31.152
1	-1	9.474	9.704
1	0	62.178	65.862
1	1	7.555	7.525
1	2	22.984	22.731
1	3	21.920	21.273
1	4	67.288	69.236
1	5	59.381	61.315
1	6	46.179	46.216
1	7	36.175	35.492
2	-11	31.487	32.233
2	-10	34.678	32.887
2	-9	44.537	43.411
2	-8	37.482	37.166
2	-7	4.530 *	4.620
2	-6	56.142	53.319
2	-5	53.033	52.988
2	-4	21.032	21.714
2	-3	97.248	100.312
2	-2	26.160	24.751
2	-1	9.939 *	9.920
2	0	22.205	22.350
2	1	3.781 *	4.901
2	2	59.549	63.371
2	3	38.915	38.857
2	4	46.778	48.443
2	5	9.315	6.371
2	6	48.899	48.321
2	7	44.986	45.421
3	-11	4.603 *	.234
3	-10	33.967	34.167
3	-9	9.519	11.502
3	-8	54.254	51.787
3	-7	6.613 *	1.975
3	-6	113.827	110.321
3	-5	15.903	13.966
3	-4	33.617	32.976
3	-3	3.255 *	4.153
3	-2	76.238	75.812
3	-1	43.239	42.517
3	0	60.573	61.321

k	h	F_{obs}	F_{calc}
3	1	10.090	10.444
3	2	26.231	27.755
3	3	10.877	9.798
3	4	21.843	21.931
3	5	26.297	26.422
3	6	37.700	36.914
3	7	12.654	10.531
4	-10	27.770	26.489
4	-9	56.882	56.154
4	-8	36.597	34.881
4	-7	3.794 *	2.849
4	-6	39.027	38.770
4	-5	105.591	104.737
4	-4	3.378 *	4.265
4	-3	39.932	40.205
4	-2	40.979	40.614
4	-1	15.199	16.353
4	0	24.694	25.294
4	1	28.078	28.460
4	2	50.162	52.584
4	3	22.888	22.766
4	4	19.988	20.667
4	5	9.150	6.063
4	6	30.162	28.771
4	7	33.632	32.273
5	-10	32.007	31.991
5	-9	25.263	25.930
5	-8	71.152	70.445
5	-7	39.874	39.075
5	-6	38.033	38.913
5	-5	39.168	39.365
5	-4	41.726	41.780
5	-3	17.311	17.882
5	-2	20.678	19.885
5	-1	41.664	43.185
5	0	36.660	36.857
5	1	4.066 *	.704
5	2	19.909	20.024
5	3	3.395 *	4.236
5	4	55.678	54.937
5	5	72.049	70.854
5	6	58.322	56.502
6	-9	3.882 *	1.622
6	-8	56.239	56.809
6	-7	7.850	7.492
6	-6	6.616 *	1.505
6	-5	5.208 *	6.968
6	-4	73.257	71.762
6	-3	33.922	33.033
6	-2	53.372	53.532
6	-1	13.873	12.606
6	0	8.079	6.763
6	1	13.856	15.037
6	2	22.504	20.251
6	3	33.941	35.018
6	4	31.374	31.047
6	5	16.731	13.912
6	6	3.800 *	5.187
7	-9	7.716 *	10.120
7	-8	46.571	46.310
7	-7	105.147	107.372
7	-6	8.759	7.114
7	-5	46.284	46.037
7	-4	40.333	41.647
7	-3	29.744	29.367
7	-2	6.455 *	1.563
7	-1	5.478 *	5.262
7	0	41.190	41.217
7	1	9.976	10.329
7	2	8.214	8.125
7	3	9.890	10.592
7	4	38.651	37.631
7	5	44.383	43.827
8	-8	14.242	12.609
8	-7	9.991	9.401
8	-6	71.088	71.499
8	-5	16.843	17.401
8	-4	43.185	43.979
8	-3	37.359	37.735
8	-2	34.580	34.886
8	-1	3.905 *	2.774
8	0	10.751	11.540
8	1	10.328	8.560
8	2	48.187	48.830
8	3	29.563	29.161
8	4	26.400	27.469
9	-6	59.994	60.902
9	-5	4.759 *	6.957
9	-4	53.247	54.328
9	-3	12.819	13.260
9	-2	48.902	49.738
9	-1	23.871	25.172
9	0	48.803	47.542
9	1	17.581	18.568
9	2	8.253	7.891
9	3	19.590	20.749
10	-4	27.873	28.844
10	-3	53.363	54.510
10	-2	58.666	60.206
10	-1	3.832 *	2.127
10	0	18.590	19.340
10	1	3.882 *	1.210
		l = 7	
0	-10	43.001	42.538
0	-8	41.144	40.125
0	-6	44.689	45.288
0	-4	9.633	7.578
0	-2	15.618	17.004
0	0	90.971	93.692
0	2	65.009	66.748
0	4	13.285	12.820
0	6	19.366	19.720
1	-10	26.686	24.397
1	-9	29.051	26.859
1	-8	46.222	46.068
1	-7	15.948	15.589
1	-6	15.897	15.319
1	-5	11.401	11.611
1	-4	84.888	85.719

k	h	F_{obs}	F_{calc}
1	-3	66.605	66.804
1	-2	5.695 *	2.613
1	-1	27.115	28.161
1	0	65.287	63.547
1	1	36.799	37.850
1	2	49.174	49.162
1	3	51.331	51.555
1	4	3.494 *	1.803
1	5	3.616 *	1.754
1	6	5.377 *	2.940
2	-10	22.042	21.328
2	-9	18.527	17.346
2	-8	3.822 *	2.908
2	-7	3.560 *	1.655
2	-6	81.530	80.282
2	-5	24.671	23.877
2	-4	9.978	7.996
2	-3	46.393	47.706
2	-2	84.132	83.189
2	-1	78.551	79.695
2	0	50.237	49.714
2	1	39.385	40.303
2	2	21.525	21.910
2	3	14.117	14.143
2	4	16.892	16.371
2	5	3.637 *	1.413
2	6	11.107	9.374
3	-10	63.425	60.502
3	-9	3.601 *	.872
3	-8	60.612	59.755
3	-7	7.901	7.232
3	-6	4.869 *	6.141
3	-5	29.495	30.047
3	-4	9.618	9.694
3	-3	11.892	11.282
3	-2	64.646	62.656
3	-1	9.199	8.613
3	0	8.081	7.287
3	1	9.011	7.344
3	2	55.208	55.574
3	3	11.654	10.406
3	4	45.295	44.768
3	5	13.188	11.745
3	6	15.388	15.504
4	-9	9.714	7.617
4	-8	12.551	11.519
4	-7	12.500	12.559
4	-6	67.024	66.541
4	-5	12.444	12.792
4	-4	22.152	23.577
4	-3	19.604	19.413
4	-2	57.987	57.571
4	-1	94.248	95.153
4	0	24.905	24.168
4	1	64.655	62.341
4	2	28.679	28.809
4	3	3.541 *	3.079
4	4	19.542	19.740
4	5	10.098	8.198
5	-9	12.914	12.423
5	-8	25.469	25.939
5	-7	32.647	31.701
5	-6	23.924	25.020
5	-5	43.722	42.545
5	-4	68.730	68.312
5	-3	49.599	48.273
5	-2	36.263	36.114
5	-1	3.448 *	1.934
5	0	65.230	66.147
5	1	14.543	15.279
5	2	49.221	48.679
5	3	13.440	15.384
5	4	9.877	7.851
5	5	18.892	9.886
6	-8	43.735	42.678
6	-7	13.532	12.262
6	-6	18.941	18.344
6	-5	17.100	15.411
6	-4	14.941	13.526
6	-3	25.617	27.239
6	-2	16.971	16.411
6	-1	20.332	19.748
6	0	63.352	63.577
6	1	12.452	12.068
6	2	56.661	55.420
6	3	6.832 *	1.678
6	4	9.058	9.393
7	-7	9.043	9.869
7	-6	32.336	31.838
7	-5	3.745 *	2.382
7	-4	23.630	23.589
7	-3	47.198	47.740
7	-2	8.285	5.444
7	-1	26.699	25.818
7	0	57.208	56.249
7	1	46.408	45.275
7	2	31.969	31.151
7	3	43.458	42.269
8	-6	25.591	24.888
8	-5	4.289 *	4.595
8	-4	6.066 *	5.482
8	-3	21.868	22.144
8	-2	67.307	69.607
8	-1	56.496	58.527
8	0	69.847	67.717
8	1	21.665	21.353
8	2	13.622	12.102
9	-4	6.626 *	7.251
9	-3	26.765	27.265
9	-2	20.619	19.273
9	-1	13.131	13.847
		l = 8	
0	-8	81.678	76.992
0	-6	17.439	17.588
0	-4	21.750	22.283
0	-2	44.659	45.045
0	0	29.572	29.660
0	2	10.328	12.037
0	4	17.562	17.958

k	h	F_{obs}	F_{calc}
1	-9	15.251	16.998
1	-8	36.563	35.362
1	-7	62.296	59.708
1	-6	29.443	28.533
1	-5	34.952	33.803
1	-4	17.034	18.163
1	-3	6.038 *	4.296
1	-2	19.489	19.722
1	-1	20.781	19.591
1	0	54.462	53.400
1	1	37.930	38.124
1	2	43.619	41.964
1	3	3.663 *	3.968
1	4	44.645	43.420
2	-9	32.130	29.945
2	-8	17.836	15.976
2	-7	18.924	17.951
2	-6	44.192	43.899
2	-5	35.608	36.088
2	-4	35.361	34.608
2	-3	54.775	52.046
2	-2	20.023	19.426
2	-1	23.488	21.867
2	0	20.012	18.324
2	1	18.913	17.819
2	2	64.579	62.574
2	3	39.580	39.372
2	4	66.893	65.091
3	-8	32.295	30.508
3	-7	16.508	16.329
3	-6	77.851	76.560
3	-5	20.941	20.415
3	-4	64.710	64.190
3	-3	3.558 *	4.256
3	-2	16.671	18.454
3	-1	17.276	15.446
3	0	3.566 *	4.293
3	1	14.152	13.067
3	2	15.010	13.357
3	3	9.998	10.246
3	4	4.910 *	1.686
4	-8	4.616 *	6.571
4	-7	7.305 *	5.474
4	-6	40.597	40.136
4	-5	46.689	46.099
4	-4	14.306	15.354
4	-3	18.225	18.130
4	-2	20.437	19.969
4	-1	10.738	11.462
4	0	13.583	12.979
4	1	37.809	37.439
4	2	44.544	44.193
4	3	30.870	30.344
5	-7	43.578	42.571
5	-6	46.998	46.438
5	-5	40.245	40.016
5	-4	25.890	26.164
5	-3	4.905 *	1.038
5	-2	9.182	8.974
5	-1	5.365 *	2.914
5	0	43.421	42.104
5	1	44.237	44.498
5	2	44.252	42.895
6	-6	19.920	20.682
6	-5	5.337 *	6.722
6	-4	21.347	21.265
6	-3	7.120 *	4.167
6	-2	42.136	42.635
6	-1	15.399	12.641
6	0	18.914	19.477
6	1	17.663	17.739
7	-5	25.169	25.678
7	-4	31.038	31.099
7	-3	9.000	7.701
7	-2	6.041 *	6.572
7	-1	18.042	17.194
7	0	25.540	24.907
		l = 9	
0	-6	16.815	16.451
0	-4	33.394	33.542
0	-2	18.583	18.250
0	0	41.979	41.266
0	2	16.776	16.299
1	-7	9.152	9.603
1	-6	3.832 *	1.730
1	-5	28.381	28.043
1	-4	75.380	75.033
1	-3	59.728	58.907
1	-2	25.739	25.540
1	-1	45.906	45.313
1	0	3.745 *	3.987
1	1	20.720	18.641
1	2	21.141	19.276
2	-7	28.010	28.293
2	-6	71.856	70.067
2	-5	38.612	38.736
2	-4	32.173	31.224
2	-3	16.448	15.849
2	-2	37.465	36.587
2	-1	33.186	30.777
2	0	29.621	27.597
2	1	23.018	22.601
3	-6	12.551	9.772
3	-5	10.523	10.718
3	-4	8.090	10.392
3	-3	9.034	7.368
3	-2	45.174	44.272
3	-1	12.504	12.103
3	0	21.594	20.827
3	1	9.405	8.856
4	-5	42.821	41.625
4	-4	17.780	18.198
4	-3	29.364	29.130
4	-2	28.091	27.602
4	-1	56.148	53.132
4	0	16.971	15.363
5	-3	36.958	35.500
5	-2	56.603	55.694

edge, OH(1)-(OH)(2), with another Cu(1) octahedron on the opposite side. This type of edge-sharing results in an open octahedral sheet structure (Fig. 3). The Cu(1)-Cu(1) distance is 2.99 Å, while the closest Cu(1)-Cu(2) distance is 2.95 Å. Further Cu(1)-Cu(2) distances are 3.17 and 3.29 Å.

The $[ZnO_3(OH)]^{5-}$ and $[PO_4]^{3-}$ Ions

The $[ZnO_3(OH)]$ ion is a fairly regular tetrahedron, with an average Zn-O distance of 1.95 Å. The Zn-OH(1) distance, 1.97 Å, is significantly longer than the Zn-O distances. The O-Zn-O (or OH) angles vary from 106.3° to 113.8°. Tetrahedral corners, O(1), O(2) and O(4) are shared with PO_4 tetrahedra, while OH(1) is shared with Cu(1) and Cu(2) octahedra (Fig. 2).

The PO_4 ion is also a nearly regular tetrahedron, with average P-O distance of 1.54 Å. The O-P-O angles vary from 107.9° to 111.0°. Three corners of the tetrahedra are shared by Zn-tetrahedra, while the

fourth corner, O(3) is shared by Cu(1) and Cu(2) octahedra (Fig. 2).

The Complex Sheet Structure

The structure of veszelyite can be considered to consist of two types of connected sheets parallel to (001): (a) an octahedral sheet formed of edge-sharing $[Cu(1)(OH)_4O(H_2O)]$ and $[Cu(2)O(OH)_3(H_2O)_2]$ octahedra, and (b) a mixed tetrahedral sheet formed of $[ZnO_3(OH)]$ and $[PO_4]$ tetrahedra sharing corners.

(*a*) *Octahedral Sheet*

The open octahedral sheet is a novel type (Fig. 3) that consists of eight-membered rings of alternating Cu(1) and Cu(2) octahedra. The eight-membered octahedral ring is stretched and is oriented the same way as the eight-membered tetrahedral ring (Fig. 4). Open channels pass through these eight-membered rings to accommodate the water molecules, which are thus somewhat zeolitic in character, though they are definitely bonded, albeit loosely, to the cupric ions. Consistent with this environment, the water molecules show large thermal vibration (Table 2).

(*b*) *Mixed Tetrahedral Sheet*

The tetrahedral sheet is composed of tetrahedral chains with alternating $[PO_4]$ and $[ZnO_3(OH)]$ tetrahedra running parallel to the *a* axis. Tetrahedra in alternate chains point up and down. These chains share corners to form a sheet parallel to (001) (Fig. 4). The interconnection of the chains results in the formation of four- and eight-membered rings. In each ring, half the tetrahedra are pointing up and the other half pointing down. Such a sheet formed of four- and eight-membered rings is common in silicate structures, particularly framework silicates, namely feldspars and zeolites (Smith and Rinaldi, 1962). Such a silicate sheet has recently been found in the vanadium silicate, cavansite (Evans, 1973). A zincate-phosphate sheet of this type has not been encountered before, though a comparable beryllate-phosphate sheet has been found in hurlbutite, $CaBe_2(PO_4)_2$ (Bakakin and Belov, 1960).

The tetrahedral sheets are connected to the octahedral sheets by sharing apical oxygens of Zn- and P-tetrahedra, namely OH(1) and O(3), with Cu-octahedra. The tetrahedra pointing up are connected to the octahedral sheet above, while those pointing down are connected to the octahedral sheet below (Fig. 2). The good {001} cleavage is easily explained by the sheet structure parallel to the (001) plane.

Hydrogen Bonding

An infra-red spectrum of veszelyite from Moravičza shows (in the 3μ region) the following peaks due to O-H stretching vibration: 3530 cm^{-1} (sharp), 3270

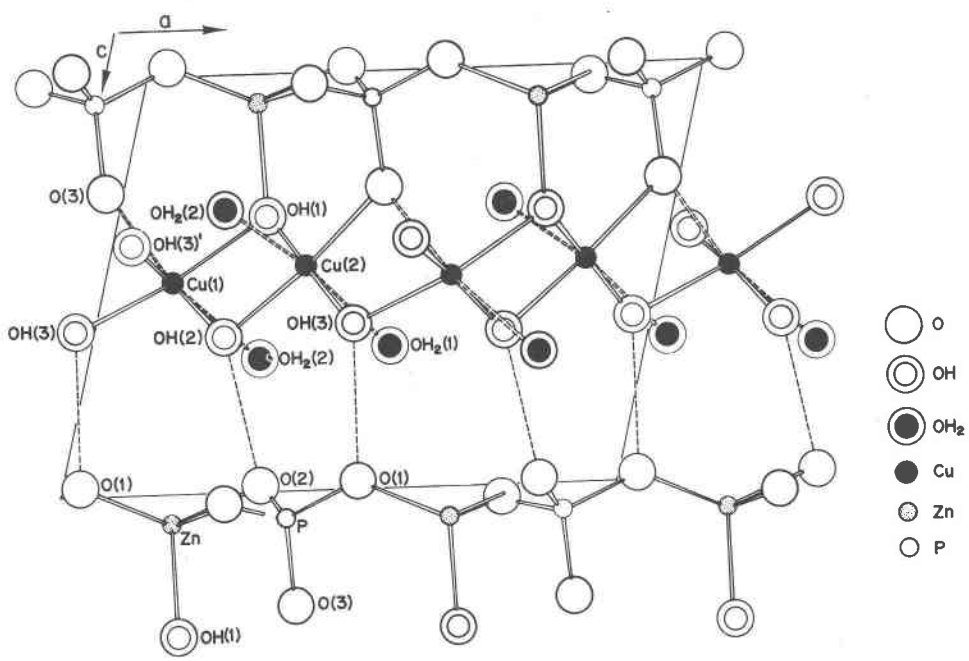

FIG. 1. Partial projection of the veszelyite structure down the *b* axis.

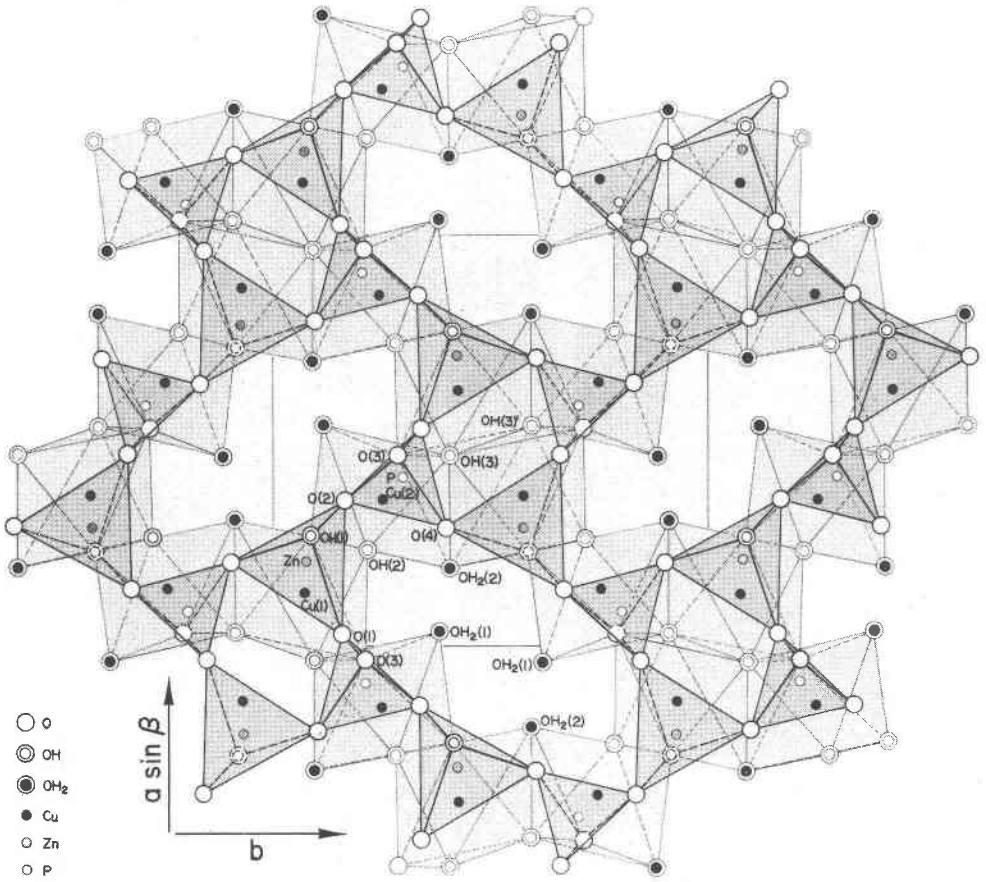

FIG. 2. A view of the veszelyite structure down the *c* axis, showing interconnection of the octahedral and tetrahedral sheets.

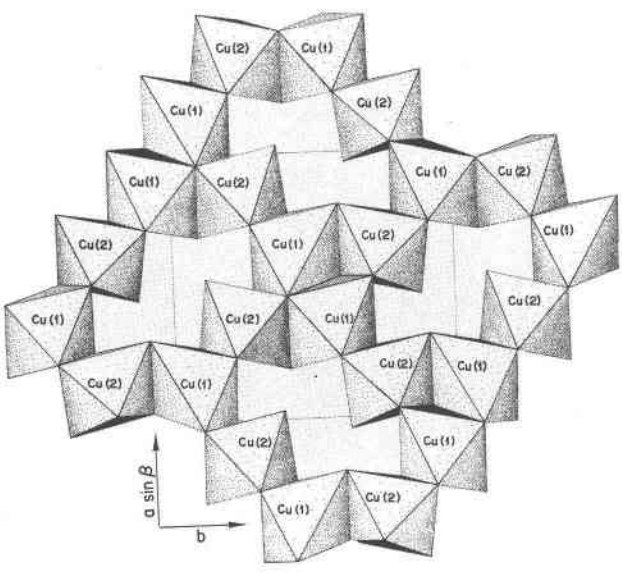

FIG. 3. Copper octahedral sheet in the veszelyite structure viewed down the *c* axis.

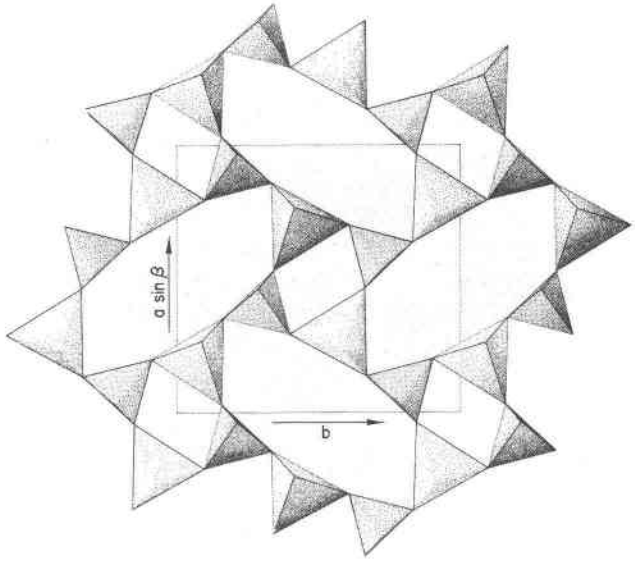

FIG. 4. Mixed tetrahedral sheet in the veszelyite structure viewed down the *c* axis. Larger tetrahedra: $ZnO_3(OH)$; smaller tetrahedra: PO_4.

cm^{-1} (broad) with broad shoulders on either side at 3350 cm^{-1} and 3170 cm^{-1}. The sharp peak at 3530 cm^{-1} indicates O-H radicals virtually free of hydrogen bonding, while the other broad peaks indicate hydrogen bonds of variable strength for OH and H_2O.

OH(1) is bonded to Zn, Cu(1), and Cu(2), located at the corners of a triangle. The O-H bond is presumably pointing away from this triangle and does not appear to be hydrogen bonded. OH(2) and OH(3) are bonded to two copper ions each. OH(2)-O(2) distance is 2.77 Å, while OH(3)-O distance is 2.84 Å. These distances indicate that hydrogen bonds connect the octahedral sheet to the tetrahedral sheet (Fig. 1). These hydrogen bonds are also stereochemically reasonable, assuming a tetrahedral (sp^3) charge distribution around the oxygen. The hydrogen bonding of the water molecules is not very clear. $H_2O(1)$ is bonded only to Cu(2). It shows two close approaches, one to OH(2) at 2.64 Å and the other to OH(1) at 2.82 Å, that may indicate hydrogen bonds, though stereochemically they are not very favorable. $H_2O(2)$ is bonded to both Cu(1) and Cu(2). Its close approach to O(4)—namely, 2.65 Å—probably indicates a strong hydrogen bond. The other hydrogen seems to be free.

Crystal Chemistry of Copper-Zinc Substitution

Veszelyite is known to have variable Cu/Zn ratio, which is reported to be 1.43 (Arakawa Mine, Japan), 1.44–1.38 (Moravičza), 1.27 (Kipushi), and 0.96 (Kamioka Mine, Japan) (Guillemin, 1955). The composition of the Arakawa specimen is close to $Cu_2ZnPO_4(OH)_3 \cdot 2\,H_2O$, which is presumably an end member composition. Substitution of copper by zinc at Cu(1) and Cu(2) positions is possible, which would involve movement of apical oxygen atoms, namely O(3), $H_2O(1)$, and $H_2O(2)$. From the stereochemistry of Cu(1) and Cu(2) atoms, it appears that Cu(2), which is less distorted, would be more amenable to replacement by zinc than Cu(1), since this would involve movement of two water molecules only and would cause least structural distortion. Progressive replacement of copper by zinc would result in more regular octahedra.

Veszelyite: A New Structure Type

The octahedral sheet found in veszelyite is unique, since it is formed of eight-membered octahedral rings, which are topologically difficult to construct using regular octahedra. This difficulty probably explains why complete substitution of copper by zinc at the Cu(1) and Cu(2) sites does not take place.

Because the copper coordination octahedra are so highly distorted, it is topologically impossible to form a regular hexagonally close-packed brucite-type sheet using copper octahedra. Instead, a variety of octahedral sheets have been found in basic copper compounds, whose building block is the tetragonally distorted copper octahedron. Thus, a corrugated sheet structure has been found in $Cu(OH)_2$ (Jaggi and Oswald, 1961) and serpierite, $Ca(Cu, Zn)_4(OH)_6(SO_4)_2 \cdot 3\,H_2O$ (Sabelli and Zanazzi, 1968). The octahedral sheet found in brochantite, $Cu_4(OH)_6SO_4$ (Cocco and Mazzi, 1959), and a number of other basic copper compounds is formed of two types of octahedral chains; one chain is formed by copper octahedra sharing edges of the square plane, and the other formed by the octahedra sharing the bipyramidal edges. Pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ shows yet another type of octahedral sheet with holes, above which occur the phosphate groups (Ghose, 1963). The pseudomalachite type sheet is formed of two types of octahedral chains: one chain is formed of one Cu(1) and two Cu(2) octahedra, each kind sharing four and three edges alternately; the other chain is formed of Cu(3) octahedra sharing edges of the square plane. Spangolite, $Cu_6Al(SO_4)(OH)_{12}Cl \cdot 3\,H_2O$ has an octahedral layer structure, containing cations in the proportion Cu_6Al (Rosenzweig *et al*, 1971). Although the copper octahedra show the usual tetragonal distortion, the octahedral layer is very similar to that found in kaolinite, and the Cu and Al atoms lie within 0.1 Å of the average plane drawn through them.

Analogs of mixed tetrahedral sheet are common in silicate structures as mentioned earlier. Replacement of cations in the tetrahedral sheet should be possible, provided the valence balance is maintained. The following compounds conceivably would have the veszelyite structure:

$Cu_2AlSiO_4(OH)_3 \cdot 2H_2O$;
$Cu_2BSiO_4(OH)_3 \cdot 2H_2O$;
$Cu_2BePO_4(OH)_3 \cdot 2H_2O$;
$Cu_2BeAsO_4(OH)_3 \cdot 2H_2O$;
$Cu_2ZnAsO_4(OH)_3 \cdot 2H_2O$;
$Cu_2ZnVO_4(OH)_3 \cdot 2H_2O$.

Acknowledgments

We are indebted to the following for donation of veszelyite samples: Dr. M. Bunno, Mineralogical Institute, Tokyo; Professor H. Strunz, Technische Universität, Berlin; and Mr. J. S. White, Smithsonian Institution, Washington, D. C. Marguerite Stroh prepared the diagrams.

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Manuscript received, August 31, 1973; accepted for publication, January 18, 1974.