Canadian Mineralogist
Vol. 28, pp. 709-718 (1990)

THE CRYSTAL STRUCTURE OF SZYMAŃSKIITE, A PARTLY DISORDERED[1] $(Hg{-}Hg)^{2+}$, $(Ni,Mg)^{2+}$ HYDRONIUM-CARBONATE-HYDROXIDE-HYDRATE

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ABSTRACT

The crystal structure of the new mineral *szymańskiite* has been resolved and refined to an *R* index of 3.49% using absorption-corrected Mo$K\alpha$ X-ray-diffraction data, averaged from a sphere of reflections collected to $2\theta = 60°$. The cell is hexagonal, space group $P6_3$, with *a* 17.3984(7), *c* 6.0078(4) Å. The structure contains Hg^{1+} in its expected near-linear coordination of –O–Hg–Hg–O–, as well as a second chain containing Hg^{1+} atoms and trios of oxygen atoms in a face-sharing column of the form $-Hg-O_3-Hg-Hg-O_3-Hg-$. The ordered part of the structure contains these mercury coordination chains, as well as (Ni,Mg)–O distorted octahedra, held together by carbonate groups. Between the clearly defined tubular walls of the structure, there are very large tunnels (over 13 Å across), within which the remaining portion of the structure is disordered. A planar triangular group with bond lengths corresponding to a carbonate is clearly visible, though partly positionally disordered; there are three other partially occupied oxygen sites within the tunnel. A tunnel remains of some 7 Å in diameter within which *no* atom sites were found. The structure can be regarded as a non-silicate zeolite. With a balancing of charges and summation of the disordered atomic site-occupancies, the contents of the unit cell can be written: $(Hg_2)_8 \cdot (Ni,Mg)_6 \cdot (CO_3)_{12} \cdot (OH)_{12} \cdot (H_3O)_8 \cdot (H_2O)x$, where *x* is about 3.

Keywords: szymańskiite, disordered structure, Hg^{1+} and (Ni,Mg) cations, zeolite-like tunnels, Clear Creek claim, San Benito County, California.

SOMMAIRE

La structure cristalline de la *szymańskiite,* nouvelle espèce minérale, a été résolue et affinée jusqu'à un résidu de 3.49% à l'aide d'une sphère complète de données d'intensité de diffraction des rayons X (Mo$K\alpha$), mesurées jusqu'à $2\theta = 60°$ et corrigées pour l'absorption. La maille est hexagonale, groupe spatial $P6_3$, *a* 17.3984(7) et *c* 6.0078(4) Å. La structure contient des ensembles -O-Hg-Hg-O- où l'ion Hg^{1+} adopte la coordination quasi-linéaire habituelle, ainsi qu'une seconde chaîne $-Hg-O_3-Hg-Hg-O_3-Hg-$ où les ions Hg^{1+} et les trios d'atomes d'oxygène sont disposés en colonne avec partage de faces. La partie ordonnée de la structure contient ces chaînes de mercure(I) de même que les octaèdres déformés (Ni,Mg)-O maintenus ensemble par des groupes carbonates. Entre les arrangements tubulaires de la structure se trouvent de larges canaux (plus de 13 Å de diamètre) dans lesquels le reste de la structure est désordonné. Un groupe plan triangulaire avec des longueurs de liaison correspondant à celles d'un carbonate est clairement visible, bien que partiellement désordonné; on trouve également dans ce tunnel trois sites partiellement occupés par des atomes d'oxygène. Finalement, on y observe aussi un tunnel d'environ 7 Å de diamètre à l'intérieur duquel aucun atome n'a été trouvé. La structure s'apparente à celle d'une zéolite sans silicate. En équilibrant les charges et en tenant compte des sites atomiques partiellement occupés, le contenu de la maille élémentaire s'établit comme suit: $(Hg_2)_8 \cdot (Ni,Mg)_6 \cdot (CO_3)_{12} \cdot (OH)_{12} \cdot (H_3O)_8 \cdot (H_2O)x$, où *x* est environ égal à 3.

Mots-clés: szymańskiite, nouvelle espèce minérale, structure désordonnée, cations Hg^{1+} et (Ni,Mg), canaux de type zéolite, concession de Clear Creek, comté de San Benito, Californie.

INTRODUCTION

Szymańskiite has been described recently by Roberts *et al.* (1990). Although the metal cations in the mineral were clearly defined in the electron-microprobe analyses, the nature of the anions was unclear, particularly in the early stages of study, before the presence of carbon could be confirmed. The mineral shows no effervescence in dilute HCl, and very little with *concentrated* HCl. The presence of some carbon was eventually confirmed by the microprobe, and results of an infrared-absorption analysis were found to be compatible with the presence of some carbonate, but in the presence of about 70 wt.% mercury, and significant amounts of nickel and magnesium, the analytical results for carbon are semiquantitative at best. In view of the extreme scarcity of material, it was not possible to perform a quantitative wet-chemical analysis, and so a combination of electron-microprobe analyses and X-ray single-crystal structural analysis was used to determine the composition and to help resolve the enigmatic chemistry of this mineral. Three separate data-sets were collected in successive attempts to resolve the apparent disorder found within this structure. In the end, some aspects of this structural work still remain unclear because of the partially dis-

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[1] Geological Survey of Canada contribution number 45689.

TABLE 1. SZYMAŃSKIITE, CRYSTAL DATA

Szymańskiite, $(Hg_2)_8(Ni_{4.08}Mg_{1.92})_{\Sigma=6}(CO_3)_{12}(OH)_{12}(H_3O)_8 \cdot 3H_2O$

Source: Clear Creek Claim, San Benito County, California, U.S.A.

Crystal system: hexagonal

Space group: $P6_3/m$ or $P6_3$ from systematic absences, $P6_3$ from structure determination.

Cell dimensions: a 17.3984(7), c 6.0078(4) Å. Refined from 98 reflections measured for $\pm hkl$ at $\pm 2\theta$.

Density: D_{calc} = 4.86g/cm^3, D_{obs} not measured.

Linear absorption coefficient: $\mu(MoK\alpha)$=418cm^{-1}, $\mu(CuK\alpha)$= 754cm^{-1}.

Crystal dimensions: elongate [0001], 0.09mm between {0001}, hexagonal cross-section, 0.03mm between {$10\bar{1}0$}

X-ray data: Whole sphere of data collected to $2\theta=60°$ using Mo$K\alpha$ radiation [$\lambda(K\alpha_1)$=0.70930 Å], absorption corrected and averaged to give 3031 (2155 obs.) reflections, including Friedel pairs. Residual: R = 3.49%, R_w = 3.88%.

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ordered nature of the structure, and the mineral must be reported in the category of "This is the best we can achieve". Better definition of the structure must await future technical advances.

EXPERIMENTAL

Two crystals, extracted from small vugs on one of the holotype specimens, were used in the structure determinations. The first crystal was significantly smaller than the second crystal, and with Mo$K\alpha$ radiation, the scattering from it proved to be insufficient at high diffraction-angles to resolve what turned out to be a major problem of structural disorder. The ordered part of the structure was determined without problem from this first crystal.

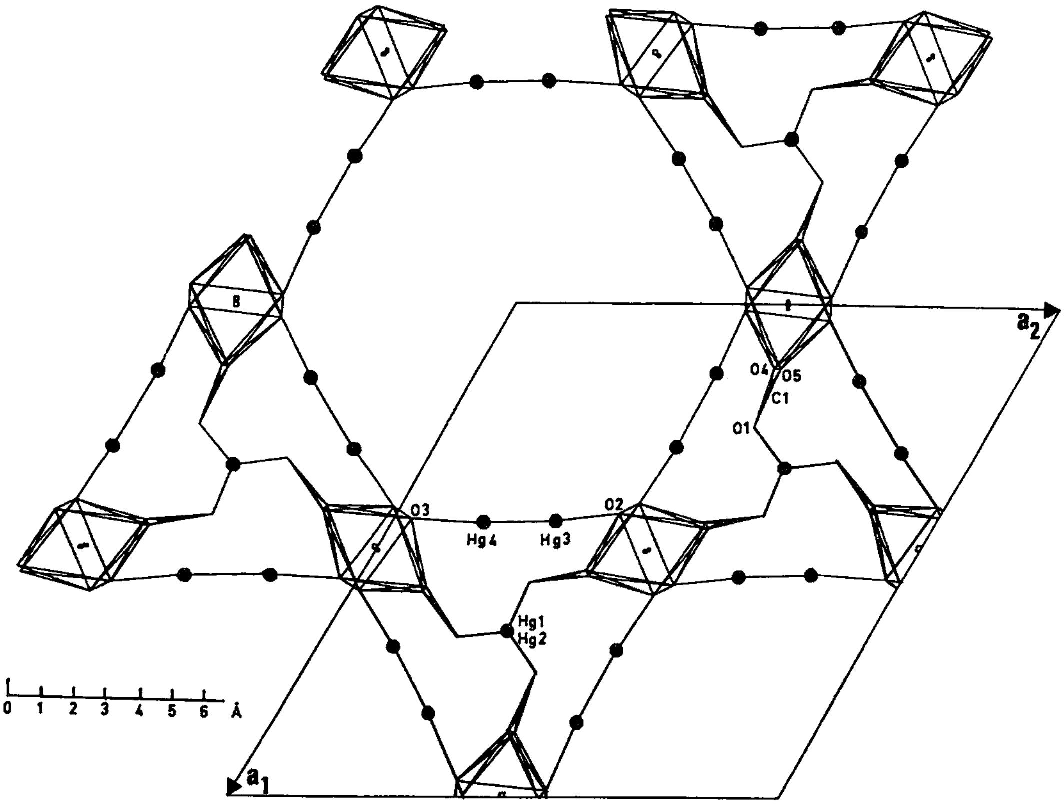

FIG. 1. The ordered part of the szymańskiite structure, projected on the x-y plane; octahedrally coordinated (Ni,Mg) cations are stacked *via* edge-sharing into columns along z and centered on 0,½,z. They are coordinated *via* carbonate groups to a column of pairs of mercury atoms separated by triangles of oxygen atoms, centered on 1/3,2/3,z and 2/3,1/3,z, the crystallographic 6_3 axes. A second, nearly linear, di-mercury atom chain links two other vertices of the (Ni,Mg) octahedra *via* O2–Hg3–Hg4–O3. On the structural scale, the result is trigonal prisms extending in z and corner-shared to produce a honeycomb structure. The nearly hexagonal "voids" within this are about 13.6 Å across, and contain the disordered part of the structure shown in Figure 2.

However, little of the disordered part was resolved. This led to the search for and ultimately the finding of a second, larger crystal, with which it was hoped to improve the counting statistics, and hence resolve the disorder. Some aspects of the disorder (but not all) were resolved using Mo*K*α data with this second crystal. Ultimately, a third data-set was collected on this second crystal, this time using Cu*K*α data to $2\theta = 124°$ and ¼°/min scans in 2θ. The stronger scattering of the copper radiation, the slower scan-speed used and the shape of the Lorentz-polarization correction curve all contributed to the greater number of counts, in some cases as much as thirty times more for a given reflection than with molybdenum radiation. Using the stronger but more limited data-set generated with copper radiation ($\sin\theta/\lambda = 0.573$ rather than 0.705), additional minor peaks were identified, and the structure refined to $R = 3.1\%$. These peaks were then accepted and refined with the more extensive data-set generated with Mo radiation into the picture that is presented here. The cell data given below are based on the second crystal studied with molybdenum radiation. These cell dimensions differ slightly from those presented in Roberts *et al.* (1990), which were refined from X-ray powder-diffraction data.

The lattice symmetry is hexagonal, with *a* 17.3984(7) and *c* 6.0078(4) Å. The crystal used is hexagonal in cross section, showing forms $\{10\bar{1}0\}$ and $\{0001\}$. It is elongate [0001], measuring 0.09 mm in length and 0.03 mm between $\{10\bar{1}0\}$ faces. A full sphere of diffraction data to $2\theta = 60°$ was collected using the θ–2θ mode and a scan speed of about 1°/min in 2θ. The Friedel pairs were kept separate in view of the uncertainty of whether the space group would be $P6_3/m$ (centrosymmetric) or $P6_3$ (noncentrosymmetric, polar). This resulted in 1652 unique reflections (1181 observed) if only the *hkl* values are considered, and 3031 (2155 observed) if the Friedel pairs are included. The criterion for an "observed" reflection was that I_{obs} exceeds $2.5\sigma(I_{obs})$. Gaussian absorption corrections using a grid of $10 \times 10 \times 10$ points were applied to the intensity data prior to averaging, and gave an agreement factor *R* between equivalent intensities of 3.1%. The cell dimensions were refined by least squares using 98 reflections in the range $20 < 2\theta < 48°$. The relevant details of this structure determination are summarized in Table 1.

STRUCTURE SOLUTION AND REFINEMENT

The software used for all crystallographic calculations was the PC version of the NRCVAX package (Gabe *et al.* 1989). The structure was solved initially by direct methods in space group $P6_3/m$ (centrosymmetric). This revealed the distribution within the unit cell of mercury atoms with some of the coordinating oxygen atoms, and the (Ni,Mg) atom with its coordination octahedron. Difference Fourier and least-squares refinement revealed the rest of the ordered part of the structure, which includes a carbonate group. The structure is shown in Figure 1 in a view down the *c* axis. Once the agreement factor had converged to 5.1%, refinement was tried in the noncentrosymmetric space group $P6_3$, and this improved the refinement in that it showed more clearly some of the disordered atoms. Statistically, the improvement is very significant (Hamilton 1965) and shows that the structure is noncentric, but approximately centric. This is particularly true of the disordered part of the structure. The final agreement-factor *R* is 3.49% for the parameters listed in Table 2 (atomic coordinates) and Table 3 (thermal parameters). Tables 4 and 5 give the interatomic bond-lengths and bond angles, respectively. The structure factors (Table 6) have been deposited and

TABLE 2. SZYMAŃSKIITE, ATOMIC COORDINATES

Atom	pos.	pop.	x	y	z	B_{iso}
Hg1	2*b*	1.0	2/3	1/3	.0440(3)	2.39(5)
Hg2	2*b*	1.0	1/3	2/3	-.0408(3)	2.33(5)
Hg3	6*c*	1.0	.44218(6)	.29903(5)	1/4[‡]	1.91(8)
Hg4	6*c*	1.0	.44636(5)	.15674(5)	.2545(7)	1.67(7)
NiMg	6*c*	1.02(1)	.0049 (6)	.5019 (8)	-.0093(15)	0.59(14)
O1	6*c*	1.0	.2495 (7)	.5667 (7)	.241 (8)	1.06(19)
O2	6*c*	1.0	.4274 (8)	.4141 (7)	.237 (7)	1.12(20)
O3	6*c*	1.0	.4387 (7)	.0325 (7)	.258 (7)	1.02(21)
C1	6*c*	1.0	.1683 (11)	.5547 (11)	.246 (14)	1.16(23)
O4	6*c*	1.0	.1316 (10)	.5428 (10)	.062 (3)	1.19(23)
O5	6*c*	1.0	.1322 (10)	.5550 (10)	.442 (3)	1.31(24)
C2	6*c*	1.0	.0426 (13)	.2461 (13)	.221 (6)	1.7 (4)
O6	6*c*	1.0	.0742 (17)	.3328 (17)	.297 (5)	4.9 (7)
O7	6*c*	.76(12)	.228 (5)	.040 (5)	.313 (19)	15.8 (45)
O8	6*c*	.36(7)	.111 (4)	.230 (4)	.207 (18)	5.1 (24)
O9	6*c*	.72(6)	.2685 (15)	.4075 (15)	.219 (7)	2.7 (7)
O10	6*c*	.35(7)	.240 (5)	.339 (5)	.22 (3)	6.4 (30)
O11	6*c*	.73(10)	.234 (4)	.198 (4)	.351 (12)	10.5 (28)

[‡] Coordinate fixed to define origin of polar space group. B_{iso} is the mean of the principal axes of the thermal ellipsoid. "Pos." is a combination of multiplicity and Wyckoff letter. The cell content of a given atom is the multiplicity times the population parameter. E.S.D. refers to the last digit(s) printed. The Table is divided into the ordered part of the structure (upper) and the disordered part (lower).

TABLE 3. SZYMAŃSKIITE, THERMAL PARAMETERS ($Å^2$x100)

Atom	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg1	4.44(6)	4.308	0.30(6)	2.154	-	-
Hg2	3.92(6)	3.791	1.12(7)	1.896	-	-
Hg3	3.39(4)	1.43 (3)	2.90(4)	1.55(3)	0.60(14)	-.64(12)
Hg4	3.09(4)	1.33 (3)	2.29(4)	1.39(3)	0.46(13)	-.09(12)
NiMg	0.30(18)	1.22 (13)	0.61(14)	0.29(14)	0.31(11)	.30(11)
O1	1.34(34)					
O2	1.4 (3)					
O3	1.3 (3)					
C1	1.5 (3)					
O4	1.5 (3)					
O5	1.7 (3)					
C2	2.2 (5)					
O6	6.2 (8)					
O7	20.0 (57)					
O8	6.4 (30)					
O9	3.4 (8)					
O10	8.1 (37)					
O11	13.2 (35)					

E.S.D. refers to the last digit(s) printed.

Anisotropic temperature-factors are of the form:-

Temp = $-2\pi^2*(h^2*U_{11}*astar^2 + \ldots + 2*h*k*U_{12}*astar*bstar + \ldots)$

are available for a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0S2.

DESCRIPTION OF STRUCTURE

The structure is best considered in terms of its two separate components: the ordered part (Fig. 1) and the disordered part (Fig. 2).

The ordered component is made up of four distinct elements:

(a) Octahedrally coordinated (Ni,Mg) cations, bonded to oxygen atoms 2 × O2, 2 × O3, O4 and O5 at distances that vary between 1.99(3) and 2.16(3) Å, are connected to symmetry-related octahedra, adjacent in z, by means of O2-O3 edge-sharing hydroxyl groups (Fig. 3). The bond lengths within these octahedra are quite normal and do not merit further discussion; they are found in Table 4.

(b) A second link between adjacent octahedra is found in the form of an ordered carbonate group [C1,O1,O4,O5, with C–O bond distances 1.32(2), 1.24(8), 1.34(8) Å; angles 115(6), 119(2), 125(2)°]. This group spans from oxygen O4 of one octahedron to oxygen O5 of the adjacent octahedron. In this way, each octahedron is linked to the one immediately above it, and by a second O5–C1–O4 bridge to the octahedron immediately below it in the z direction. These first two elements are illustrated in Figure 3. This ordered carbonate group (Fig. 4a) has what appears at first sight to be a somewhat distorted geometry, but this is within about 1σ of the expected values of both the bonds and angles for this anion. The largest angle, 125(2)°, is all the more reasonable when one considers that this bidentate ligand has to expand its bite to accommodate the O4...O5 distance in adjacent octahedra. The carbonate group is perfectly planar: the sum of the angles around carbon atom C1 is 359.99°.

TABLE 4. SZYMAŃSKIITE, BOND LENGTHS

The unique-atom coordinates are listed in Table 2. The symmetry equivalent positions are designated as follows:-

Name	x	y	z	Name	x	y	z
a	1+x-y	x	1/2 +z	i	y	1-x+y	-1/2 +z
b	1+x-y	x	-1/2 +z	j	-x	1-y	1/2 +z
c	1 -x	1-y	-1/2 +z	k	-x	1-y	-1/2 +z
d	y	-x+y	-1/2 +z	l	-y	x-y	z
e	x-y	x	-1/2 +z	m	x-y	x	1/2 +z
f	1 -y	1+x-y	z	n	-x+y	-x	z
g	-x+y	1-x	z	o	1-x+y	1-x	z
h	y	-x+y	1/2 +z	p	1 -y	x-y	z

Bond distances (Å)

Bond	Distance	Bond	Distance
Hg1 - Hg2(a)	2.494(3)	NiMg- O5(k)	2.096(18)
Hg1 - O1(b)	2.44(4)	O1 - Hg1(m)	2.44(4)
Hg1 - O1(c)	2.44(4)	O1 - C1	1.321(19)
Hg1 - O1(d)	2.44(4)	O2 - NiMg(f)	2.05(3)
Hg2 - Hg1(e)	2.494(3)	O2 - NiMg(h)	2.05(3)
Hg2 - O1	2.34(4)	O3 - NiMg(a)	1.99(4)
Hg2 - O1(f)	2.34(4)	O3 - NiMg(n)	2.16(4)
Hg2 - O1(g)	2.34(4)	C1 - O4	1.24(8)
Hg3 - Hg4	2.5131(10)	C1 - O5	1.34(8)
Hg3 - O2	2.144(11)	O5 - NiMg(j)	2.096(18)
Hg4 - O3	2.099(11)	C2 - O6	1.40(3)
NiMg- O2(e)	2.05(4)	C2 - O7(l)	1.39(6)
NiMg- O2(g)	2.05(4)	C2 - O8	1.36(7)
NiMg- O3(l)	2.16(4)	O7 - C2(n)	1.39(9)
NiMg- O3(i)	1.99(4)	O9 - O10	1.04(8)
NiMg- O4	1.996(18)		

Non-bonded contacts:

a) metal...metal		b) ...continued	
Hg3 - NiMg(f)	3.537(23)	O2 - O5(f)	2.97(4)
Hg3 - NiMg(h)	3.385(22)	O2 - O5(d)	2.79(4)
Hg4 - NiMg(a)	3.545(23)	O3 - O2(p)	2.75(3)
NiMg- Hg3(g)	3.537(23)	O3 - O4(a)	2.94(3)
NiMg- Hg3(e)	3.385(22)	O3 - O4(o)	2.90(3)
NiMg- Hg4(i)	3.545(23)	O3 - O5(b)	2.87(3)
NiMg- NiMg(j)	3.0076(10)	O3 - O5(n)	2.95(3)
NiMg- NiMg(k)	3.0076(10)	O4 - O3(l)	2.896(23)
		O4 - O5	2.289(24)
b) O...O in NiMg octahedra			
O2 - O3(o)	2.746(15)**	c) O...O between Hg1 & Hg2	
O2 - O3(e)	2.96(6)	O1 - O1(f)	2.801(17)
O2 - O4(h)	2.82(4)	O1 - O1(g)	2.801(17)
** edge-sharing contact		O1(f)-O1(g)	2.801(17)

E.S.D. refers to the last digit(s) printed.

TABLE 5. SZYMANSKIITE, BOND ANGLES (°)

The unique-atom coordinates are listed in Table 2. The symmetry equivalent positions are listed in Table 4.

Angle	Value	Angle	Value
Hg2(a) -Hg1- O1(b)	138.4(9)	Hg4(i) -NiMg-O5(k)	121.1(6)
Hg2(a) -Hg1- O1(c)	138.4(8)	NiMg(j)-NiMg-NiMg(k)	174.3(4)
Hg2(a) -Hg1- O1(d)	138.4(9)	NiMg(j)-NiMg-O2(e)	138.5(11)
O1(b) -Hg1- O1(c)	70.2(9)	NiMg(j)-NiMg-O2(g)	42.9(10)
O1(b) -Hg1- O1(d)	70.2(12)	NiMg(j)-NiMg-O3(l)	41.5(9)
O1(c) -Hg1- O1(d)	70.2(9)	NiMg(j)-NiMg-O3(i)	135.0(12)
Hg1(e) -Hg2- O1	136.3(9)	NiMg(j)-NiMg-O4	80.4(6)
Hg1(e) -Hg2- O1(f)	136.3(9)	NiMg(j)-NiMg-O5(k)	95.2(6)
Hg1(e) -Hg2- O1(g)	136.3(9)	NiMg(k)-NiMg-O2(e)	42.7(10)
O1 -Hg2- O1(f)	73.5(10)	NiMg(k)-NiMg-O2(g)	135.3(11)
O1 -Hg2- O1(g)	73.5(10)	NiMg(k)-NiMg-O3(l)	137.0(10)
O1(f) -Hg2- O1(g)	73.5(12)	NiMg(k)-NiMg-O3(i)	46.0(10)
Hg4 -Hg3- NiMg(f)	149.8(3)	NiMg(k)-NiMg-O4	105.3(6)
Hg4 -Hg3- NiMg(h)	148.5(4)	NiMg(k)-NiMg-O5(k)	79.1(6)
Hg4 -Hg3- O2	175.2(4)	O2(e) -NiMg-O2(g)	175.6(11)
NiMg(f)-Hg3- NiMg(h)	51.4(3)	O2(e) -NiMg-O3(l)	98.8(13)
NiMg(f)-Hg3- O2	31.6(9)	O2(e) -NiMg-O3(i)	85.4(13)
NiMg(h)-Hg3- O2	35.4(9)	O2(e) -NiMg-O4	88.3(9)
Hg3 -Hg4- NiMg(a)	153.41(18)	O2(e) -NiMg-O5(k)	91.2(9)
Hg3 -Hg4- O3	175.4(3)	O2(g) -NiMg-O3(l)	81.4(12)
NiMg(a)-Hg4- O3	29.2(10)	O2(g) -NiMg-O3(i)	94.2(14)
Hg3(e) -NiMg-Hg3(g)	178.2(4)	O2(g) -NiMg-O4	96.0(9)
Hg3(e) -NiMg-Hg4(i)	82.10(20)	O2(g) -NiMg-O5(k)	84.5(8)
Hg3(e) -NiMg-NiMg(j)	117.5(4)	O3(l) -NiMg-O3(i)	174.9(14)
Hg3(e) -NiMg-NiMg(k)	66.9(3)	O3(l) -NiMg-O4	88.1(8)
Hg3(e) -NiMg-O2(e)	37.2(7)	O3(l) -NiMg-O5(k)	84.7(7)
Hg3(e) -NiMg-O2(g)	147.2(8)	O3(i) -NiMg-O4	94.9(8)
Hg3(e) -NiMg-O3(l)	93.8(9)	O3(i) -NiMg-O5(k)	92.4(8)
Hg3(e) -NiMg-O3(i)	91.3(9)	O4 -NiMg-O5(k)	172.6(9)
Hg3(e) -NiMg-O4	51.2(5)	Hg1(m) -O1- Hg2	94.7(4)
Hg3(e) -NiMg-O5(k)	127.6(6)	Hg1(m) -O1- C1	107(4)
Hg3(g) -NiMg-Hg4(i)	99.6(3)	Hg2 -O1- C1	110(4)
Hg3(g) -NiMg-NiMg(j)	61.7(3)	Hg3 -O2- NiMg(f)	115.2(15)
Hg3(g) -NiMg-NiMg(k)	113.9(4)	Hg3 -O2- NiMg(h)	107.4(14)
Hg3(g) -NiMg-O2(e)	142.4(8)	NiMg(f)-O2- NiMg(h)	94.3(6)
Hg3(g) -NiMg-O2(g)	33.3(7)	Hg4 -O3- NiMg(a)	120.0(15)
Hg3(g) -NiMg-O3(l)	84.6(9)	Hg4 -O3- NiMg(n)	120.3(16)
Hg3(g) -NiMg-O3(i)	90.3(10)	NiMg(a)-O3- NiMg(n)	92.6(9)
Hg3(g) -NiMg-O4	129.3(6)	O1 -C1- O4	115(6)
Hg3(g) -NiMg-O5(k)	51.6(5)	O1 -C1- O5	119(6)
Hg4(i) -NiMg-NiMg(j)	115.3(4)	O4 -C1- O5	125.5(16)
Hg4(i) -NiMg-NiMg(k)	68.1(3)	NiMg -O4- C1	129.6(22)
Hg4(i) -NiMg-O2(e)	95.5(6)	NiMg(j)-O5- C1	123.3(19)
Hg4(i) -NiMg-O2(g)	86.2(6)	O6 -C2- O7(l)	111(8)
Hg4(i) -NiMg-O3(l)	150.1(7)	O6 -C2- O8	109(3)
Hg4(i) -NiMg-O3(i)	30.8(6)	O7(l) -C2- O8	124(9)
Hg4(i) -NiMg-O4	66.2(5)		

E.S.D. refers to the last digit(s) printed

(c) The third oxygen atom (O1) of the carbonate group is involved in a most *unusual* Hg^{1+} chain. The two atoms Hg1 and Hg2 overlap in the z-projection (2.494 Å apart on the 6_3 axis), and the pairs of Hg atoms are separated from each other by a face of three O1 oxygen atoms, represented here

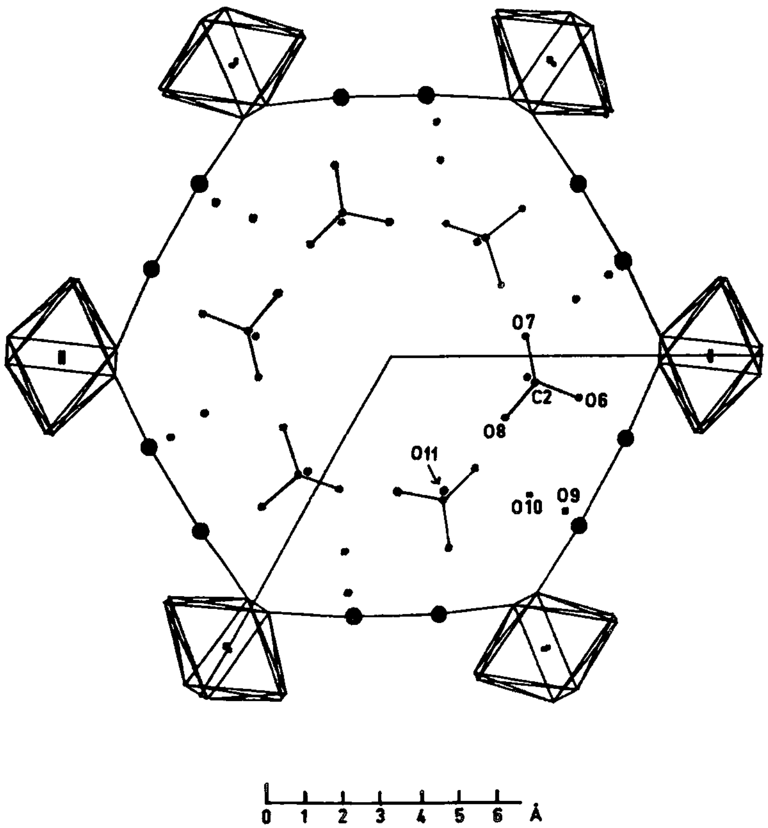

FIG. 2. The nearly hexagonal "tunnel walls" enclosing the disordered part of the szymańskiite structure, drawn in the same orientation as Figure 1. The disordered carbonate group (C2,O6,O7,O8) is indicated, as well as the "either/or" pair of oxygen atoms (O9,O10) 1 Å apart. The least-well defined oxygen atom O11 is 2.23(8) Å above the carbonate group.

as $(O1)_3$. An infinite chain is formed from these three oxygen atoms, and the pair of fourfold coordinated Hg^{1+} atoms: $-Hg2-(O1)_3-Hg1-Hg2-(O1)_3-Hg1-$ (Fig. 5). However, the Hg1–Hg2 bond length [2.494(3) Å] is typical of the $[Hg-Hg]^{2+}$ dimer, and the bond lengths to oxygen atoms [Hg1–O1 = 2.44(4) Å; Hg2–O1 = 2.34(4) Å] are sufficiently longer than found for single Hg^{1+}–O bonds, that bond-valence considerations are roughly satisfied for all the atoms involved (Table 7). A related multi-oxygen coordination for Hg^{1+} was found in magnolite (Grice 1989), though the chain is not infinite, but limited to $(O)_4-Hg-Hg-(O)_4$.

(d) The (Ni,Mg)–O octahedra are cross-linked in the x-y plane by means of a $[Hg-Hg]^{2+}$ bridge, which extends from oxygen O2 of the interoctahedral edge of one column to oxygen O3 of an equivalent edge of another column. In this way, near-linear chains are formed: O2–Hg3–Hg4–O3, with bond distances 2.144(11), 2.513(10), 2.099(11) Å, and bond angles of approximately 175° at mercury atoms Hg3 and Hg4 (Fig. 6). This is the more common form of $[Hg-Hg]^{2+}$ dimer coordination.

The ordered block of the structure is centered on the crystallographic 6_3 axes at $2/3,1/3,z$ and $1/3,2/3,z$ and appears in Figure 1 as trigonal prisms with the (Ni,Mg) octahedra at the vertices. As indicated above, there is very strong bonding in the z direction within these prisms: the (Ni,Mg) octahedra edge-share to adjacent octahedra; the carbonate cation (C1,O1,O4,O5) bridges two octahedra in z; the two tetrahedrally coordinated mercury atoms link carbonate groups adjacent in z; finally, the trigonal prismatic blocks themselves share edges (columns of octahedra) along z. A framework structure of very rigid tubes is thus formed, with the tubes strongly held together.

The *disordered* component of this structure is centered on the line $0,0,z$, and consists of enormous hexagon-shaped tunnels about 13.6 Å across

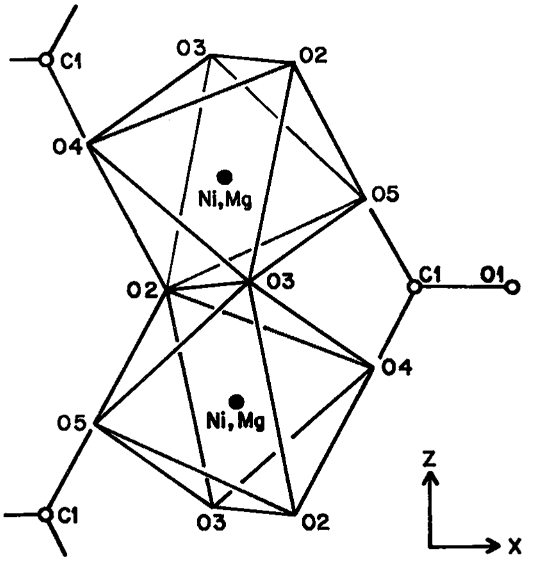

FIG. 3. The (Ni,Mg) octahedra, edge-sharing *via* O2–O3, with oxygen atoms O4 and O5 being part of a carbonate group that cross-links to the Hg1–Hg2 mercury atom pairs.

(Fig. 2). Even if the radius of the Hg atoms is included to decrease the apparent size of these tunnels, they are still over 10.4 Å across. No ordered cation is found within this region. A number of atomic sites were, however, identified within this cavity using the Cu$K\alpha$ data (and later refined using the Mo$K\alpha$ data), but most of these are disordered. Closest to the hexagon's wall (and to the mercury Hg3 atom) are oxygen O6 and carbon C2 atoms, which are part of what appears to be a second carbonate group. These two atoms were located from the original (weaker) Mo$K\alpha$ data set (though not "accepted" at the time) and are reasonably well defined; the remaining atoms required the Cu$K\alpha$ and the second Mo$K\alpha$ data sets, and refinement in the noncentrosymmetric space group $P6_3$ in order to be identified and accepted. Oxygen atoms O6, O7 and O8 are in a triangle around a lighter atom (identified as carbon atom C2). The scattering from this lighter atom is about 3/4 of that of an oxygen atom (a value obtained by least-squares refinement of its population parameter while treating it as an oxygen atom), and hence corresponds well to its assigned identity as a carbon atom. The other two oxygen atoms of this carbonate group (O8, and *particularly* O7) appear to be smeared out, with large thermal parameters, which suggests that the group is disordered as a result of a rotational disorder about the O6–C2 bond. Both the O7 and O8 oxygen atoms refine to fractional site-occupancies. The refined positions given in Table 2 represent only one set of a number of possible orientations of this carbonate anion. The bond lengths within this disordered molecule (Fig. 4b) are somewhat longer than expected for a carbonate group, but bearing in mind the positional disorder in the oxygen atoms O7 and O8, and the fact that C2 is clearly a carbon atom, we are forced to conclude that this is indeed a carbonate group. Chemically, there appears to be no other possibility, with the possible exception of a bicarbonate anion. The O6 and O7 oxygen atoms of this disordered carbonate group are located 3.20 and 3.31 Å from mercury atoms Hg3 and Hg4, respec-

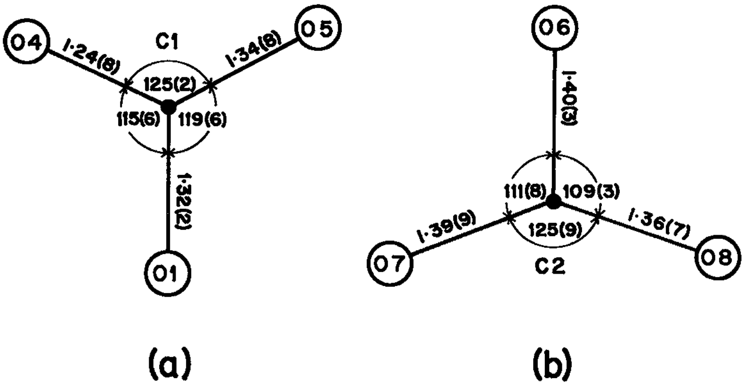

FIG. 4. (a) The ordered carbonate group, perfectly planar, with the O4–C–O5 angle expanded to accommodate the span of two (Ni,Mg) octahedra, and (b) the partly disordered carbonate group. Oxygen atom O6 and carbon atom C2 appear ordered, whereas oxygen atoms O7 and O8 are disordered, with large thermal parameters, probably as a result of rotation about O6–C2. The bonds are somewhat longer than expected for a carbonate group.

tively. This is farther than expected bonding distances, but certainly less than van der Waals interaction. Three more partially occupied oxygen atom sites also were identified: oxygen atoms O9 and O10 refined with large thermal parameters and site occupancies of 0.73, 0.34 (σ = 0.10), respectively, and a separation of 1.04(0.1) Å. These can be interpreted as an "either/or" disorder, *i.e., either* oxygen atom O9 is present *or* oxygen atom O10 is present, *but not both,* within a given pair of adjacent sites in the same unit cell. The last disordered oxygen atom, O11, is within hydrogen-bonding distance of oxygen atoms O7, O8 and O10. It also has a large thermal parameter and a site occupancy of 0.72(14). We could not identify any other atomic sites within a tunnel of about 7 Å diameter, centered on the line 0,0,*z*.

Electron-microprobe analyses of a number of crystals of szymańskiite show that the ratio Ni:Mg is somewhat variable, but consistent with solid solution at the same crystallographic site, *i.e.,* (Ni + Mg) is about constant. In the structure determination, no site other than the (Ni,Mg) site could be identified as a separate cation location. In the least-squares refinement, a composite scattering curve of (0.68 Ni + 0.32 Mg) was created to represent the (Ni,Mg) atom, since this was the mean proportion found in the electron-microprobe analyses. The real $\Delta f'$ and the imaginary $\Delta f''$ components of the anomalous scattering were also adjusted for this proportion. In the final stages of refinement of the structure, the population parameter of this site was refined, and gave a value of 1.025(12), indicating that the proportion of Ni to Mg in the actual crystal used may have been slightly higher than the assumed ratio (0.68:0.32).

CHEMICAL COMPOSITION

A bond-valence analysis was carried out (Table 7); though the results are not as clear-cut as usually found with ordered and complete structures, they indicate that oxygen atoms O2 and O3, which form part of the coordination octahedron around (Ni,Mg), are hydroxyl groups. The angles about these two oxygen atoms also are consistent with the presence of a hydrogen atom attached to each of them. Including, for the time being, the second (partly disordered) carbonate group, the composition of the ordered part of the unit cell is thus: $(Hg_2)^{2+}_8 \cdot (Ni,Mg^{2+})_6 \cdot (CO_3^{2-})_{12} \cdot (OH^{1-})_{12}$. Summation of charges shows an excess of −8. Charge balance has to be achieved by accepting the protonation of some of the water molecules, represented by oxygen atoms O9, O10 or possibly O11, to the hydronium state (H_3O^{1+}). The total site-occupancy of these three six-fold sites is 1.80(39), or a total of 10.80(2.34) oxygen atoms per unit cell; charge balance requires a hydronium content of 8 ions per unit cell, or 8/6 = 1.33 for the three six-fold sites taken together. This leaves approximately three water molecules in the

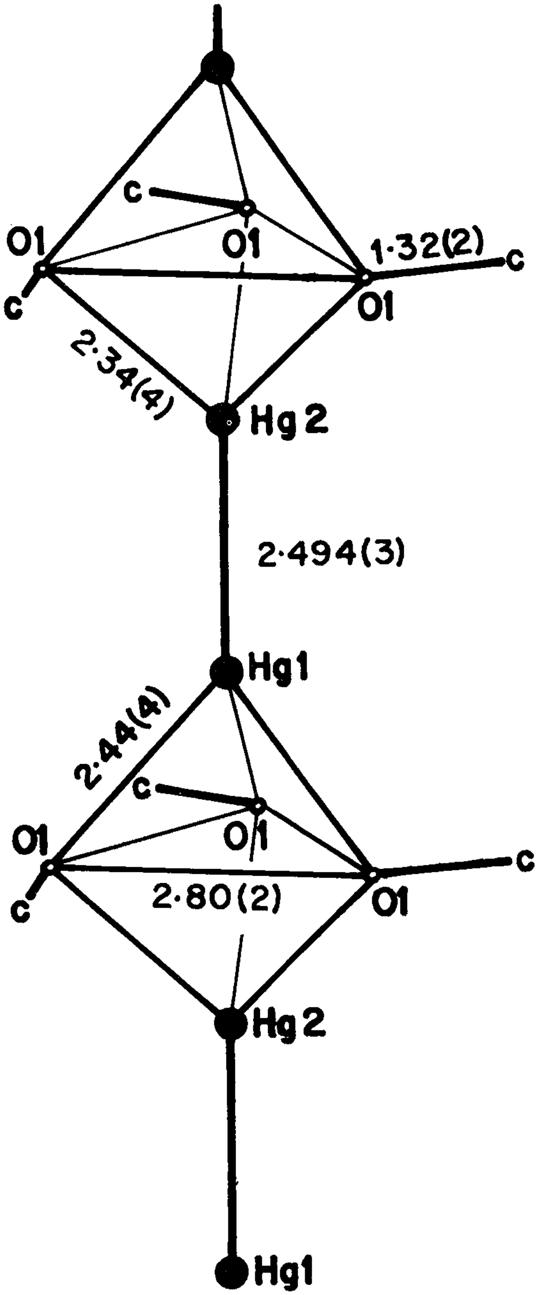

FIG. 5. A column of $[Hg\text{–}Hg]^{2+}$ atom pairs, separated by a triangle of carbonate-forming oxygen atoms (O1). The view is at 15° to the *x–y* plane, with the 6_3 crystallographic axis along the Hg1–Hg2 direction. Some bond lengths and contact distances (Å) are shown.

TABLE 7. SZYMAŃSKIITE, BOND-VALENCE SUMMATION FOR THE ORDERED PART OF THE STRUCTURE

	To Hg1		To Hg2		To Hg3		To Hg4		To (Ni,Mg)		To C1		Sum for oxygen
	d(Å)	s	d(Å)	s	d(Å)	s	d(Å)	s	d(Å)	s	d(Å)	s	
O1	2.4351	.2632	2.3414	.3396							1.3208	1.1882	1.791
	2.4351	.2632	2.3414	.3396									
	2.4351	.2632	2.3414	.3396									
O2					2.1437	.6026			2.0543	.3385			1.286
									2.0467	.3456			
O3							2.0986	.6918	2.1639	.2607			1.345
									1.9947	.3923			
O4									1.9962	.3908	1.2381	1.5451	1.936
O5									2.0953	.3064	1.3360	1.1341	1.441
O6					3.1953	.0454							
O7							3.3076	.0360					
Total	0.790		1.019		0.648		0.728		2.034		3.693		

The parameters used are: for Hg, R_1=1.983Å, N=6.5; for Ni, R_1=1.670Å, N=5.4; for Mg, R_1=1.622Å, N=4.29 (Ni/Mg contributions scaled in proportion 0.68/0.32); for C, R_1=1.378Å, N=4.065 (Brown & Wu 1976).

structure. The contents of the unit cell can be written as: $(Hg_2)_8^{2+}\cdot(Ni,Mg^{2+})_6\cdot(CO_3^{2-})_{12}\cdot(OH^{1-})_{12}\cdot(H_3O^{1+})_8\cdot(H_2O)_x$, where $x \approx 2.8$ or rounded off to 3. The disorder precludes the placement of the hydrogen atoms, which undoubtedly must be present. The largest peaks (about 2e/Å^3) observed in the final difference-synthesis were two series-termination peaks within about 1 Å of a Hg atom site, *i.e.*, their height was about 1/4 of an oxygen atom, but their position was found to be impossible for real atoms. Excluding these, the next highest peak is about half this height, and close to (Ni,Mg), *i.e.*, nowhere near a possible site for a hydrogen atom. The whole volume within 3.5 Å of the line 0,0,*z* is totally devoid of peaks. There is an apparently increasing degree of disorder with distance from the ordered triangular prisms that make up the ordered portion of the structure. This is strongly reminiscent of the increase of disorder within coordinating water molecules around macromolecular structures: the first coordination shell is generally visible with good data; the second coordination shell is seen as a diffuse layer one can only guess at; the third is totally invisible. In the present case, no peaks were observed closer to the origin than the disordered oxygen atom O11. The result is a system of tunnels along *z* through the structure, and is somewhat reminiscent of a zeolite, though, of course, this mineral is not a silicate.

The weakness in the above proposition, concerning the composition of this mineral, rests on the nature of the partly disordered "carbonate" group made up of atoms C2,O6,O7,O8 (Fig. 4b). What is seen in the electron-density map is a triangular set of four atoms, with the lightest one in the middle. The distances from the central atom to the other three atoms are larger than expected for a carbonate group: C2–O6 = 1.40(3), C2–O7 = 1.39(6), C2–O8 = 1.36(7) Å. However, as already mentioned, there appears to be rotational disorder in the molecule, with oxygen atom O6 and carbon atom C2 reasonably well defined, and diffuse elongate regions of electron density designated as oxygen atoms O7 and O8. The disorder in the two oxygen atoms O7 and O8 has been "taken up" in the least-squares refinement in two different ways: atom O7 has refined to a very large isotropic thermal parameter [U = 20(6) × 10^{-2} Å^2], and a somewhat decreased population-parameter [pop. = 0.76(12)]; atom O8 refined to a reasonable isotropic thermal parameter [U = 6.4(3.0) × 10^{-2} Å^2], but a much smaller population parameter [pop. = 0.36(7)]. Attempts to refine these two atoms anisotropically were not successful, the resulting "ellipsoids" being nonpositive-definite. It is probable that the standard deviations of the atomic positions in this molecule are *underestimated;* the model description is simply inadequate to account

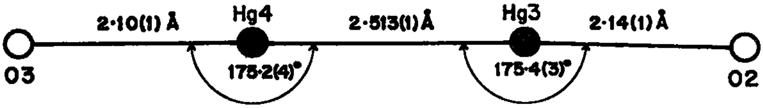

FIG. 6. The more usual $[Hg–Hg]^{2+}$ atom coordination. The angles at atoms Hg3 and Hg4 are about equal, with a dihedral angle of about 11° between the two planes.

for what is happening within the structure. We cannot conceive of any other chemical grouping that would simulate what we have called a disordered carbonate group, with the possible exception of the very unlikely bicarbonate group. When the proposal for szymańskiite as new mineral species and mineral name was put forward to the Commission on New Minerals and Mineral Names, I.M.A., one objection raised was that infrared-absorption studies should be conducted in order to resolve the nature of the carbonate–bicarbonate ambiguity. This suggestion does not take into account the paucity of the material at hand for any further spectral analysis. Analysis already carried out is consistent with some low-symmetry carbonate grouping, and it is doubtful whether the spectrum could be resolved to the point of identifying any *bicarbonate* in the presence of *carbonate* in the small proportion that carbonate is present in the mineral. Furthermore, we are not convinced that infrared-absorption spectral evidence is definitive in this matter; the first author was once asked to solve the structure of the mineral hydrodresserite (Szymański 1982), previously considered to be a bicarbonate on the basis of its IR absorption spectrum (Farrell 1978). A structural analysis showed that the C–O frequency shifts attributed to the proposed bicarbonate group were in fact caused by very strong hydrogen bonding to the C–O group from hydroxyl groups: $-O-H...O=C$. In the present structure, whether the disordered group is a carbonate or a bicarbonate will not be determined by X-ray diffraction, because the very disorder one is trying to resolve precludes the strong high-angle diffraction one needs to achieve the necessary resolution. The elucidation of this problem will have to await other techniques yet to be developed. In the meantime, it is proposed to consider this disordered group a carbonate, despite the longer bond-lengths found.

Finally, it has been reported (Roberts *et al.* 1990) that the mineral changes color over a prolonged period of time; the discovery crystals resemble stibnite in color (black). All crystals examined in this study were extracted from a freshly opened vug, and were bright blue in color. Within the two months that each of the two crystals examined was being used for data collection, there was no change of color. We presume that the slow color change is related to the break-up of the dimeric mercury^{1+} part of the structure over a prolonged period of time; it does NOT relate to the disorder found in fresh crystals of this mineral.

DISCUSSION

In a disordered structure of this type, it is difficult, if not impossible, to be definitive about the oxidation state of oxygen atoms (some of them disordered) in the presence of so much scattering from the heavy metals. In szymańskiite, the simultaneous existence of both the hydroxyl ion (OH^{1-}) and the hydronium ion (H_3O^{1+}) in the structure is proposed. This may be unusual, but it is not unique; hydronium jarosite (Ripmeester *et al.* 1986) has been shown to have just such a configuration within its structure.

It was pointed out to the authors by one of the referees of this paper, Prof. Paul Moore, that although this type of disordered tunnel structure is unusual, it is not new. Cacoxenite [kakoxen] (Moore & Shen 1983), a highly hydrated basic ferric oxyphosphate, has disordered tunnels some 14.2 Å in diameter between the ordered building blocks of the structure in a hexagonal cell. The space group of cacoxenite ($P6_3/m$) is closely related to the space group of szymańskiite ($P6_3$). Both minerals exhibit fine acicular habit, with the tunnel direction parallel to the needle axis.

The (Ni,Mg)–O,(OH) octahedra have a close parallel in the structure of kambaldaite (Engelhardt *et al.* 1985), a hydrated sodium nickel hydroxycarbonate. In this structure, there are chains of Ni–O octahedra joined *via* edge-sharing of hydroxyl and carbonate oxygen atoms. In this case, though, carbonate groups form inter- rather than intra-octahedral bridges. This structure is noteworthy in that having the same space group as szymańskiite, it also has tunnels parallel to *c*, but in this case, the very large tunnels are filled with a polymeric $Na_2(H_2O)_6$ chain, which is weakly bonded to the walls of the "honeycomb". It was reported that in kambaldaite, the "impurity element" (Mg^{2+}) is believed to occupy the same site as Na^{1+}, rather than the Ni^{2+} site as found in szymańskiite.

ACKNOWLEDGEMENTS

Our grateful thanks are extended to Mr. R.C. Erd, U.S. Geological Survey, Menlo Park, California, for supplying the holotype specimen from which the crystals for structure analysis were extracted. We thank Dr. Yvon Le Page, of the National Research Council of Canada, Ottawa, for collecting the Cu*K*α data on their diffractometer, for the reduction of these data, and for assistance with the preparation of Figure 1. Finally, we are greatly indebted to Prof. Paul Moore, University of Chicago, whose review of this manuscript contributed many insights into bonding in similar disordered structures. His suggestions for improvements of the text are much appreciated.

REFERENCES

BROWN, I.D. & WU, KANG KUN (1976): Empirical parameters for calculating cation–oxygen bond valences. *Acta Crystallogr.* **B32**, 1957-1959.

Engelhardt, L.M., Hall, S.R. & White, A.H. (1985): Crystal structure of kambaldaite, $Na_2Ni_8(CO_3)_6(OH)_6 \cdot 6H_2O$. *Am. Mineral.* **70**, 423-427.

Farrell, D.M. (1977): Infrared investigation of basic double-carbonate hydrate minerals. *Can. Mineral.* **15**, 408-413.

Gabe, E.J., Le Page, Y., Charland, J.-P., Lee, F.L. & White, P.S. (1989): NRCVAX – an interactive program system for structure analysis. *J. Appl. Crystallogr.* **A22**, 384-387.

Grice, J.D. (1989): The crystal structure of magnolite, $Hg_2^{1+}Te^{4+}O_3$. *Can. Mineral.* **27**, 133-136.

Hamilton, W.C. (1965): Significance tests on the crystallographic *R* factor. *Acta Crystallogr.* **18**, 502-510.

Moore, P.B. & Shen, J. (1983): An X-ray study of cacoxenite, a mineral phosphate. *Nature* **306**, 356-358.

Ripmeester, J.A., Ratcliffe, C.I., Dutrizac, J.E. & Jambor, J.L. (1986): Hydronium ion in the alunite–jarosite group. *Can. Mineral.* **24**, 435-447.

Roberts, A.C., Ercit, T.S., Erd, R.C. & Oscarson, R.L. (1990): Szymańskiite, $(Hg_2^{1+})_8(Ni,Mg)_6(CO_3)_{12}(OH)_{12}(H_3O)_8^{1+} \cdot 3H_2O$, a new mineral species from the Clear Creek Claim, San Benito County, California. *Can. Mineral.* **28**, 703-707.

Szymański, J.T. (1982): The crystal structure of hydrodresserite, $BaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$. *Can. Mineral.* **20**, 253-262.

Received February 26, 1990, revised manuscript accepted June 15, 1990.