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HYDROGEN BONDING IN TUNELLITE

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ABSTRACT

The crystal structure of tunellite, $SrB_6O_9(OH)_2(H_2O)_3$, monoclinic, *a* 14.415(3), *b* 8.213(1), *c* 9.951(2) Å, β 114.05(1)°, *V* 1075.8(4) $Å^3$, Z = 4, space group $P2_1/a$, has been refined by full-matrix least-squares methods to an *R* index of 5.1% and a *wR* index of 3.7% for 2680 unique observed [$F \geq 5\sigma(F)$] reflections measured with Mo*K*α X-radiation. The H positions were located on difference-Fourier maps and were refined using the "soft" constraint that H–O distances are approximately 0.96 Å. The 6:(3Δ + 3*T*) hexaborate fundamental building block (*FBB*) of the tunellite structure contains three $(B\phi_4)$ tetrahedra (ϕ: unspecified ligand) and three $(B\phi_3)$ triangles. All three $(B\phi_4)$ tetrahedra share a central oxygen position, and the $(B\phi_3)$ triangles each attach to two $(B\phi_4)$ tetrahedra, forming three three-membered rings of the form (1Δ + 2*T*). The *FBB*s polymerize to form sheets parallel to (100) by sharing four ligands with adjacent *FBB*s, and the irregular $SrO_6(H_2O)_4$ polyhedron occurs in voids within the heteropolyhedral sheet. Bonding between the sheets takes place *via* one Sr–OW–Sr bond and by a network of hydrogen bonds. There are eight hydrogen positions in the structure; five form bonds that bridge between adjacent heteropolyhedral sheets, two form bonds within the heteropolyhedral sheet, and one does not participate in a hydrogen bond.

Keywords: tunellite, borate, crystal structure, hydrogen bonding.

SOMMAIRE

Nous avons affiné la structure cristalline de la tunellite, $SrB_6O_9(OH)_2(H_2O)_3$, monoclinique, *a* 14.415(3), *b* 8.213(1), *c* 9.951(2) Å, β 114.05(1)°, *V* 1075.8(4) $Å^3$, Z = 4, groupe spatial $P2_1/a$, par moindres carrés sur matrice entière, jusqu'à un résidu *R* de 5.1% (*wR* = 3.7%) en utilisant 2680 réflexions uniques observées [$F \geq 5\sigma(F)$] et mesurées avec rayonnement Mo*K*α. La position des atomes d'hydrogène a été localisée sur des projections par différence-Fourier et affinée au moyen d'une contrainte "molle" que les distances H–O soient d'une longueur d'environ 0.96 Å. Les blocs structuraux fondamentaux sont des agencements hexaboratés 6:(3Δ + 3*T*), avec trois tétraèdres $B\phi_4$ (ϕ: ligand non spécifié) et trois triangles $B\phi_3$. Les trois tétraèdres $B\phi_4$ partagent un atome central d'oxygène, et les trois triangles $B\phi_3$ se rattachent chacun à deux tétraèdres, pour former trois anneaux à trois membres ayant la formule (1Δ + 2*T*). Ces blocs fondamentaux sont polymérisés en feuillets parallèles à (100) par partage de quatre ligands avec des blocs semblables adjacents. Le polyèdre irrégulier $SrO_6(H_2O)_4$ occupe une cavité au sein du feuillet hétéropolyédrique. Les liaisons entre les feuillets dépendent d'une liaison Sr–OW–Sr et d'un réseau de liaisons hydrogène. Il y a huit atomes d'hydrogène distincts dans la structure; cinq forment des liaisons entre feuillets adjacents, deux assurent des liaisons à l'intérieur d'un seul feuillet, et un seul ne participe pas à une liaison hydrogène.

Mots-clés: tunellite, borate, structure cristalline, liaison hydrogène.

INTRODUCTION

Tunellite, $SrB_6O_9(OH)_2(H_2O)_3$, is a secondary mineral found in the open pits at Kramer, California; it also occurs at Furnace Creek, Death Valley, California and in the borate deposits at Sarikaya, Eskiçehir, Turkey. The crystal structure of tunellite from the Kramer district, based on photographic X-ray data, was reported by Clark (1964). The refinement converged to an *R* index of 11%, and the quality of the data precluded the direct determination of the hydrogen positions. However, Clark (1964) reasoned that only four of the eight crystallographically distinct hydrogen atoms participate in hydrogen bonds, and that only two of these bridge between adjacent heteropolyhedral sheets.

We are currently studying the infrared spectra of borate minerals in the OH-stretching region (Burns & Hawthorne 1994a) to ascertain the different roles of OH and H_2O (Hawthorne 1992). Here we report a refinement of the structure of tunellite, including a description of the hydrogen bonding, which will be necessary in the interpretation of the infrared spectrum of this mineral.

EXPERIMENTAL

The tunellite used in this study is from California and was provided by the Canadian Museum of Nature (number 57614). We first selected a small single-crystal fragment for data collection, but the refinement converged to an *R* index of ~11%. A second data-collection was done for another fragment from the same specimen, with no improvement in the *R* index. Refinement of an extinction correction seemed to confirm our suspicion that extinction was the problem. The data collection was repeated for the second crystal after it was shocked by repeatedly immersing it in liquid nitrogen, which has the effect of increasing the mosaic spread in the crystal. These data resulted in a spectacular improvement of the refinement results, and here we report the details of that collection of data.

A (100) cleaved plate of tunellite was shocked in nitrogen and mounted on a Nicolet *R*3*m* automated four-circle diffractometer. Fifty reflections over the range $8° \leq 2\theta \leq 35°$ were centered using graphite-monochromated Mo*K*α X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the fifty automatically aligned reflections by least-squares techniques. Data were collected in the θ–2θ scan mode, with a scan range of 2.2°. A variable scan-rate set to be inversely proportional to the peak intensity was used, with maximum and minimum scan-rates of 29.3°2θ/min and 4°2θ/min. A total of 5164 reflections was measured over the range $4° \leq 2\theta \leq 70°$, with index ranges $0 \leq h \leq 23$, $0 \leq k \leq 13$, $-16 \leq l \leq 14$. Two standard reflections were measured every fifty reflections; no significant changes in their intensities occurred during data collection. An empirical absorption correction based on 36 psi-scans collected for each of ten reflections over the range $8° \leq 2\theta \leq 56°$ was applied, which reduced *R*(azimuthal) from 3.9% to 1.8%. The data were corrected for Lorentz, polarization and background effects; of the 5164 reflections measured, there were 2680 unique observed reflections $[|F_o| \leq 5\theta|F_o|]$.

TABLE 1. MISCELLANEOUS INFORMATION FOR TUNELLITE

Space group	$P2_1/a$	Crystal size (mm)	0.26 x 0.16 x 0.08
a (Å)	14.415(3)		
b (Å)	8.213(1)	Total ref.	5164
c (Å)	9.951(2)	$[F \geq 5\sigma(F)]$	2680
β (°)	114.05(1)	Final *R*	5.1%
V (Å³)	1075.8(4)	Final *wR*	3.7%
		GOF*	1.69
F(000)	752		

Unit cell contents $4\{SrB_6O_9(OH)_2(H_2O)_3\}$

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

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

*GOF = Goodness of fit

STRUCTURE REFINEMENT

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

Refinement of the structure was done in the space group $P2_1/a$, with the atomic positional parameters given by Clark (1964) as the starting model. Refinement of the positional parameters and an isotropic displacement model gave an *R* index of 8.9%. Conversion to an anisotropic-displacement model, together with the refinement of all parameters, gave an *R* index of 5.0% and a *wR* index of 5.9%. At this stage of the refinement, a difference-Fourier map was calculated, and the positions of all eight of the hydrogen atoms were obtained. Refinement of this structure model resulted in unreasonably short donor–hydrogen bond-lengths, a problem that is common in refinements of hydrogen positions using X-ray data. The soft constraint that O–H bond-lengths are ~0.96 Å was imposed by adding additional weighted

TABLE 2. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR TUNELLITE

	x	*y*	*z*	*U_{eq}
Sr	0.16216(3)	0.05603(5)	0.19511(5)	126(1)
B(1)	0.1925(4)	0.1548(6)	0.8474(5)	91(16)
B(2)	0.1923(4)	0.1590(6)	0.5854(5)	96(16)
B(3)	0.0432(4)	0.2489(6)	0.6286(5)	134(17)
B(4)	0.1909(3)	0.4530(7)	0.2190(4)	102(15)
B(5)	0.2537(4)	0.3916(6)	0.4832(5)	109(17)
B(6)	0.2521(4)	0.3881(6)	0.0227(5)	95(16)
O(1)	0.1933(2)	0.0287(3)	0.9513(3)	134(11)
O(2)	0.2011(2)	0.0413(4)	0.4814(3)	145(11)
OH(3)	0.0513(3)	0.6818(5)	0.4274(3)	286(14)
OW(4)	0.9996(3)	0.1712(5)	0.2355(4)	348(16)
OH(5)	0.0943(2)	0.5346(4)	0.1759(4)	201(13)
O(6)	0.2427(2)	0.8011(3)	0.3995(3)	137(12)
O(7)	0.2085(2)	0.3405(4)	0.3409(3)	147(12)
O(8)	0.2381(2)	0.7884(4)	0.0797(3)	138(12)
O(9)	0.1947(2)	0.3512(4)	0.0993(3)	134(12)
O(10)	0.0895(2)	0.2126(4)	0.7740(3)	132(11)
O(11)	0.0866(2)	0.2093(4)	0.5338(3)	151(11)
OW(12)	0.0221(3)	0.8404(4)	0.0693(4)	244(15)
OW(13)	0.1410(3)	0.5794(5)	0.7144(3)	295(14)
O(14)	0.2259(2)	0.0794(3)	0.7357(3)	86(9)
H(1)	0.057(4)	0.659(7)	0.337(3)	⁺570(68)
H(2)	0.95(4)	0.077(4)	0.204(6)	570(68)
H(3)	0.022(4)	0.165(7)	0.340(1)	570(68)
H(4)	0.038(3)	0.461(5)	0.139(6)	570(68)
H(5)	0.045(4)	0.730(2)	0.084(6)	570(68)
H(6)	−0.013(4)	0.832(7)	0.132(5)	570(68)
H(7)	0.111(4)	0.630(6)	0.774(5)	570(68)
H(8)	0.105(4)	0.604(7)	0.612(2)	570(68)

* $U_{eq} = U_{eq} \times 10^4$

⁺ a single U_{eq} was refined for all H positions observational equations to the least-squares matrix. Only the O–H distance is constrained, and each H position is free to refine around the oxygen atom. Neutron-diffraction studies (*i.e.*, Hamilton & Ibers 1968) of structures containing hydrogen bonds have shown that donor–hydrogen bond lengths do vary somewhat with the hydrogen–acceptor bond length. However, the donor–hydrogen bond lengths obtained *via* unconstrained refinement of X-ray data normally fall well outside the range found using neutron data, and this makes the hydrogen bonding in the structure difficult or impossible to interpret. Neutron-diffraction studies of borate minerals are limited owing to extreme absorption effects. Therefore, the most appropriate way to obtain information on hydrogen bonding is *via* constrained refinement of X-ray data, and we have found that this method gives reasonable hydrogen bonding for several borate minerals (Burns & Hawthorne 1993a, b, 1994b, c). Refinement of this structure model gave an R index of 4.7% and a wR index of 5.5%. An isotropic-extinction correction was then added to the refinement, and although the crystal had been repeatedly shocked in liquid nitrogen, the extinction parameter refined to a non-zero value and gave an R index of 5.1% and a wR index of 3.7%. A refinable weighting scheme of structure factors was tried, but it did not lead to an improvement in the refinement. Final positional parameters and equivalent isotropic-displacement parameters are given in Table 2, anisotropic-displacement parameters in Table 3, selected interatomic distances and angles in Table 4, and a bond-valence analysis in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS FOR TUNELLITE

	*U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	199(2)	121(2)	84(2)	−8(3)	85(1)	−8(2)
B(1)	99(24)	94(21)	87(20)	10(19)	46(18)	−7(18)
B(2)	133(25)	91(21)	73(21)	−13(20)	53(19)	−15(8)
B(3)	155(27)	144(23)	102(23)	−7(21)	53(20)	−1(20)
B(4)	170(23)	94(19)	65(19)	−27(23)	72(17)	11(22)
B(5)	163(26)	109(21)	82(23)	31(19)	78(20)	27(18)
B(6)	82(23)	110(21)	79(23)	23(19)	17(19)	7(18)
O(1)	199(17)	129(17)	110(14)	44(13)	100(13)	55(11)
O(2)	260(18)	103(16)	83(13)	32(14)	81(13)	−1(12)
OH(3)	202(19)	492(25)	169(18)	158(18)	82(15)	118(18)
OW(4)	327(24)	476(26)	168(19)	9(20)	27(18)	−91(19)
OH(5)	140(17)	190(19)	279(19)	8(14)	91(15)	−14(15)
O(6)	225(18)	100(15)	103(15)	19(14)	84(14)	−16(12)
O(7)	265(20)	96(15)	64(15)	−55(14)	79(14)	−6(12)
O(8)	205(18)	128(15)	121(15)	17(13)	107(14)	47(12)
O(9)	213(18)	113(14)	112(15)	−39(14)	101(14)	−57(12)
O(10)	143(16)	192(17)	88(14)	74(14)	71(13)	34(13)
O(11)	172(17)	212(17)	68(14)	60(14)	48(13)	24(13)
OW(12)	328(22)	214(19)	289(20)	11(17)	228(17)	27(16)
OW(13)	291(21)	385(23)	183(18)	100(19)	69(15)	79(19)
O(14)	163(14)	77(14)	38(12)	2(13)	61(11)	6(11)

* U_{ij} = Å^2 x 10^4

STRUCTURE DESCRIPTION

Borate fundamental building block

The borate fundamental building block (*FBB*) contains six boron atoms (Fig. 1). There are three $B\phi_4$ (ϕ: unspecified anion) tetrahedra and three $B\phi_3$ triangles in the *FBB*. The $B(1)O_4$, $B(2)O_4$ and $B(4)O_3(OH)$ tetrahedra have <B–O> distances of 1.469, 1.474 and 1.473 Å, respectively, and the $B(3)O_2(OH)$, $B(5)O_3$ and $B(6)O_3$ triangles have <B–O> distances of 1.364, 1.366 and 1.363 Å, respectively, values within the typical ranges of <$^{[4]}$B–O> and <$^{[3]}$B–O> observed in minerals.

The *FBB* contains three tetrahedra, all of which share the central O(14) anion (Fig. 1). The *FBB* also has three three-membered rings that contain two tetrahedra and one triangle ($1\Delta + 2T$). In each ring, the tetrahedra are also members of the adjacent three-membered rings, forming a hexaborate $B_6\phi_{13}$ polyanion (Fig. 1). Using the notation proposed by Christ & Clark (1977), this *FBB* may be written $6{:}(3\Delta + 3T)$. It occurs as an isolated cluster in aksaite {$Mg[B_6O_7(OH)_6]{\cdot}2H_2O$}, mcallisterite {$Mg_2[B_6O_7(OH)_6]_2{\cdot}9H_2O$} and rivadavite {$Na_6Mg[B_6O_7(OH)_6]_4{\cdot}10H_2O$}; it is polymerized into chains in aristarainite {$Na_2Mg[B_6O_8(OH)_4]_2{\cdot}4H_2O$}, and into sheets in strontioginorite {$SrCaB_{14}O_{23}{\cdot}8H_2O$}, tunellite {$Sr[B_6O_9(OH)_2](H_2O)_3$} and nobleite {$Ca[B_6O_9(OH)_2](H_2O)_3$}, the Ca analogue of tunellite.

Sr polyhedron

The single Sr position in tunellite is coordinated by six oxygen anions and four H_2O groups. The <Sr–ϕ> distance is 2.734 Å, and the Sr–ϕ bond lengths range from 2.592(3) to 3.001(2) Å. The Sr–OW(12)d bond length is longer than the rest of the Sr–ϕ bonds, but the bond-valence analysis of the Sr cation (Table 5) indicates that this bond is significant, providing 0.09 v.u. toward the bond-valence requirements of the cation.

Structural connectivity

The borate *FBB*s in tunellite polymerize to form sheets parallel to (100) (Fig. 2). Each borate *FBB* shares anions with four others, and each of these *FBB*s point in the opposite direction from the central *FBB*. This arrangement results in sheets that contain alternating rows of *FBB*s, with all *FBB*s pointing either up (as in Fig. 1) or down (Fig. 2). Each hexaborate polyanion shares two tetrahedron vertices with two *FBB*s on one side, and two triangle vertices with two *FBB*s on the other side. This leaves vertices of one tetrahedron and one triangle that do not bridge between borate polyhedra; the anions at these non-bridging vertices are (OH) groups.

The polymerization of the hexaborate *FBB*s into

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR TUNELLITE

Sr–O(2)	2.672(3)	B(3)–O(10)	1.357(8)
Sr–O(7)	2.687(3)	B(3)–O(11)	1.368(7)
Sr–O(9)	2.715(3)	B(3)–OH(3)f	1.368(6)
Sr–O(1)a	2.650(4)	<B(3)–O>	1.364
Sr–OW(4)b	2.705(5)		
Sr–O(6)c	2.819(3)	B(4)–OH(5)	1.445(6)
Sr–O(8)a	2.894(3)	B(4)–O(7)	1.463(6)
Sr–OW(12)c	2.592(3)	B(4)–O(9)	1.474(6)
Sr–OW(12)d	3.001(3)	B(4)–O(14)e	1.510(6)
Sr–OW(13)e	2.610(4)	<B(4)–O>	1.473
<Sr–O>	2.734		
		B(5)–O(7)	1.362(6)
B(1)–O(1)	1.460(6)	B(5)–O(2)e	1.369(6)
B(1)–O(10)	1.442(5)	B(5)–O(6)e	1.367(6)
B(1)–O(14)	1.512(7)	<B(5)–O>	1.366
B(1)–O(8)e	1.463(5)		
<B(1)–O>	1.469	B(6)–O(9)	1.368(7)
		B(6)–O(1)e	1.362(6)
B(2)–O(2)	1.456(6)	B(6)–O(8)g	1.356(6)
B(2)–O(11)	1.456(6)	<B(6)–O>	1.363
B(2)–O(14)	1.519(5)		
B(2)–O(6)e	1.465(6)		
<B(2)–O>	1.474		
Hydrogen bonding			
OH(3)–H(1)	0.96(5)	H(1)···OH(5)	2.13(5)
OH(3)–OH(5)	3.061(6)	OH(3)–H(3)–OH(5)	164(4)
OW(4)–H(2)	0.96(4)	H(2)···O(1)h	2.26(4)
OW(4)–O(1)h	3.109(6)	OW(4)–H(2)–O(1)h	147(3)
OW(4)–H(3)	0.95(2)	H(3)···O(11)i	1.81(2)
OW(4)–O(11)i	2.729(5)	OW(4)–H(3)–O(11)i	162(6)
H(2)–H(3)	1.46(6)	H(2)–OW(4)–H(3)	102(5)
OH(5)–H(4)	0.95(4)		
OW(12)–H(5)	0.95(2)	H(5)···OH(5)	1.84(3)
OW(12)–OH(5)	2.759(5)	OW(12)–H(5)–OH(5)	160(5)
OW(12)–H(6)	0.95(6)	H(6)···O(10)f	1.75(6)
OW(12)–O(10)f	2.693(6)	OW(12)–H(6)–O(10)f	170(4)
H(5)–H(6)	1.40(6)	H(5)–OW(12)–H(6)	94(6)
OW(13)–H(7)	0.96(6)	H(7)···OW(4)j	2.26(5)
OW(13)–OW(4)j	3.052(6)	OW(13)–H(7)–OW(4)j	140(4)
OW(13)–H(8)	0.95(2)	H(8)···OH(3)	1.80(3)
OW(13)–OH(3)	2.743(5)	OW(13)–H(8)–OH(3)	170(5)
H(7)–H(8)	1.59(6)	H(7)–OW(13)–H(8)	112(4)

TABLE 4. continued

B(1) tetrahedron			
O(1)–O(10)	2.341(4)	O(1)–B(1)–O(10)	107.6(4)
O(1)–O(14)	2.412(5)	O(1)–B(1)–O(14)	108.5(3)
O(1)–O(8)e	2.423(4)	O(1)–B(1)–O(8)e	112.0(3)
O(10)–O(14)	2.412(5)	O(10)–B(1)–O(14)	109.5(3)
O(10)–O(8)e	2.394(4)	O(10)–B(1)–O(8)e	111.0(4)
O(14)–O(8)e	2.411(4)	O(14)–B(1)–O(8)e	108.2(4)
<O–O>	2.399	<O–B(1)–O>	109.5
B(2) tetrahedron			
O(2)–O(11)	2.367(5)	O(2)–B(2)–O(11)	108.8(3)
O(2)–O(14)	2.426(4)	O(2)–B(2)–O(14)	109.2(3)
O(2)–O(6)e	2.414(4)	O(2)–B(2)–O(6)e	111.3(4)
O(11)–O(14)	2.433(3)	O(11)–B(2)–O(14)	109.7(4)
O(11)–O(6)e	2.394(5)	O(11)–B(2)–O(6)e	110.1(4)
O(14)–O(6)e	2.413(4)	O(14)–B(2)–O(6)e	107.9(3)
<O–O>	2.408	<O–B(2)–O>	109.5
B(3) triangle			
O(10)–O(11)	2.375(5)	O(10)–B(3)–O(11)	121.3(4)
O(10)–OH(3)f	2.361(4)	O(10)–B(3)–OH(3)f	120.1(5)
O(11)–OH(3)f	2.351(5)	O(11)–B(3)–OH(3)f	118.5(4)
<O–O>	2.362	<O–B(3)–O>	120.0
B(4) tetrahedron			
OH(5)–O(7)	2.397(4)	OH(5)–B(4)–O(7)	111.0(4)
OH(5)–O(9)	2.416(5)	OH(5)–B(4)–O(9)	111.9(3)
OH(5)–O(14)e	2.402(4)	OH(5)–B(4)–O(14)e	108.8(4)
O(7)–O(9)	2.332(5)	O(7)–B(4)–O(9)	105.2(4)
O(7)–O(14)e	2.432(5)	O(7)–B(4)–O(14)e	109.8(3)
O(9)–O(14)e	2.446(4)	O(9)–B(4)–O(14)e	110.2(4)
<O–O>	2.404	<O–B(4)–O>	109.5
B(5) triangle			
O(7)–O(2)e	2.380(4)	O(7)–B(5)–O(2)e	121.3(4)
O(7)–O(6)e	2.407(4)	O(7)–B(5)–O(6)e	123.8(4)
O(2)–O(6)e	2.306(5)	O(2)e–B(5)–O(6)e	114.9(4)
<O–O>	2.364	<O–B(5)–O>	120.0
B(6) triangle			
O(9)–O(1)e	2.377(5)	O(9)–B(6)–O(1)e	121.1(4)
O(9)–O(8)g	2.405(5)	O(9)–B(6)–O(8)g	123.8(4)
O(1)e–O(8)g	2.296(4)	O(9)e–B(6)–O(8)g	115.1(5)
<O–O>	2.359	<O–B(6)–O>	120.0

a = x, y, z−1; b = x−1, y, z; c = x, y−1, z; d = $\bar{x}, \bar{y}+1, \bar{z}$; e = $\bar{x}+½, \bar{y}-½, \bar{z}+1$; f = $\bar{x}, \bar{y}+1, \bar{z}+1$; g = $\bar{x}+½, y-½, \bar{z}$; h = $\bar{x}+1, \bar{y}, \bar{z}+1$; i = x+1, y, z; j = $\bar{x}+1, \bar{y}+1, \bar{z}+1$

TABLE 5. BOND-VALENCE* ANALYSIS (v.u.) FOR TUNELLITE

	Sr	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	Σ
O(1)	0.237	0.786					1.025		0.10							2.148
O(2)	0.224		0.790			1.005		0.90							0.15	2.019
OH(3)				1.008					0.90	0.85				0.10		2.058
OW(4)	0.205							0.10			1.00	0.15				2.055
OH(5)					0.819											2.069
O(6)	0.151				0.780	1.011										1.938
O(7)	0.215				0.780	1.025										2.020
O(8)	0.123	0.780					1.036									1.939
O(9)	0.199				0.759		1.008									1.966
O(10)		0.825		1.039									0.15			2.014
O(11)			0.795	1.008						0.15						1.953
OW(12)	0.278 0.092											0.85	0.85			2.070
OW(13)	0.265													0.90	0.85	2.015
O(14)		0.883	0.670		0.687											2.040
Σ	1.989	3.074	3.031	3.055	3.045	3.041	3.069	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

* parameters from Brown & Altermatt (1985)

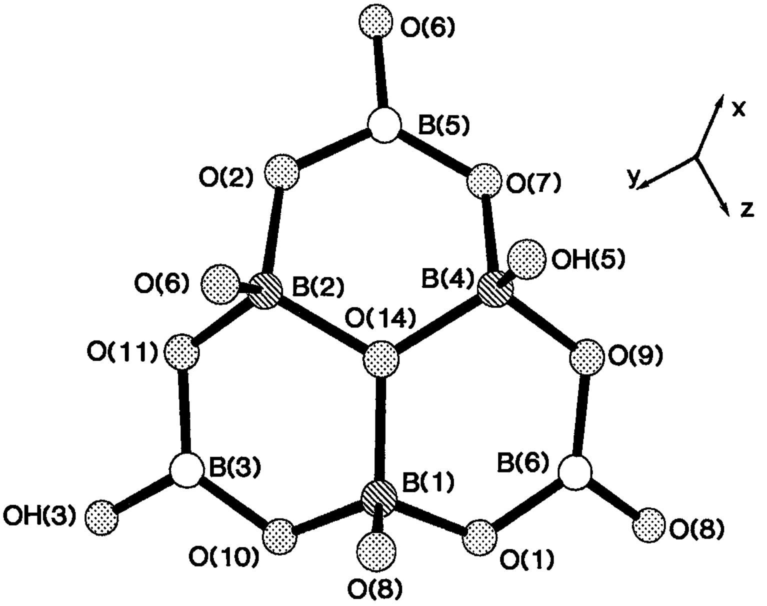

FIG. 1. The hexaborate fundamental building block in tunellite; $^{[3]}B$ atoms are unshaded circles, $^{[4]}B$ atoms are line-shaded circles, and anions are dot-shaded circles.

sheets leaves large, irregular voids within the sheets. The Sr positions occur within these voids, where they share edges and corners with the four surrounding borate *FBB*s, forming complex heteropolyhedral sheets. The heteropolyhedral sheets are joined along [100] by one Sr–OW(12)–Sr bond (Fig. 3), where the bridging bond-length is 3.001(3) Å, and *via* a network of hydrogen bonds. Thus, intersheet bonding is quite weak, consistent with the perfect (100) cleavage observed in tunellite.

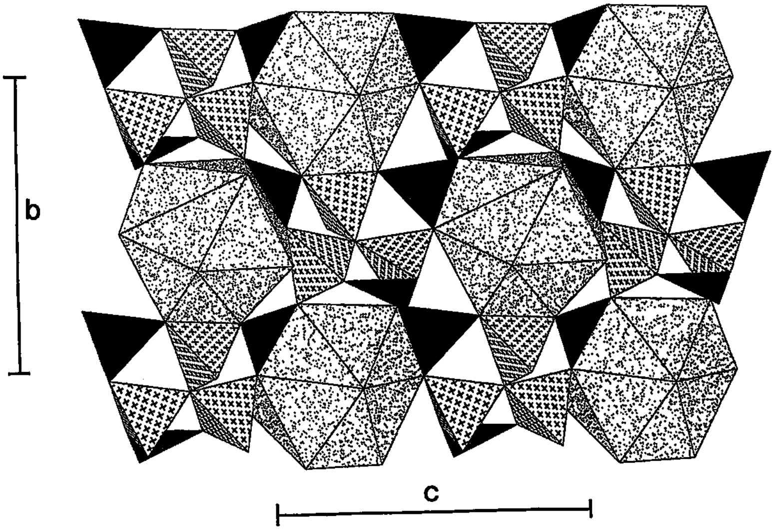

FIG. 2. The heteropolyhedral sheets in tunellite projected onto (100). Borate tetrahedra are shaded with crosses, borate triangles are given as solid triangles, and $Sr\phi_{10}$ polyhedra are shaded with a random-dot pattern.

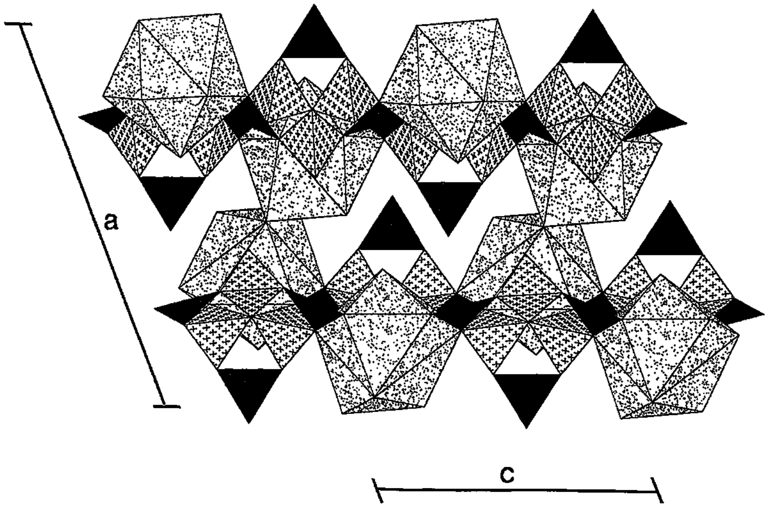

FIG. 3. The structure of tunellite projected onto (010). Legend as in Figure 2.

HYDROGEN BONDING

The hydrogen positions obtained *via* constrained least-squares refinement of the X-ray data are realistic in terms of bond lengths and angles (Table 4) and the bond-valence requirements of both donor and acceptor anions (Table 5). There are eight hydrogen positions in tunellite; five provide linkage between the heteropolyhedral sheets, and two bond within the heteropolyhedral sheets. The H(4) position does not form a hydrogen bond (Fig. 4), as the closest possible acceptor anion is O(4), at a distance of 2.69(5) Å, which is too long for a significant bond to occur.

Hydrogen bonds between the heteropolyhedral sheets

A total of five hydrogen positions provide bonding that bridges between adjacent heteropolyhedral sheets: OH(3)–H(1)...OH(5), OW(4)–H(2)...O(1), OW(12)–H(6)...O(10), OW(13)–H(7)...OW(4), and OW(13)–H(8)...OH(3). Acceptor distances, O...H, range from 1.75 Å (strong) to 2.26 Å (weak).

The OH(3)–H(1)...OH(5) bond has an acceptor distance of 2.13(5) Å, and is thus of intermediate strength. The OH(3) anion bonds to B(3) and also accepts the H(8) bond. The OH(3)–H(1)...OH(5) bond bridges between the OH(3) anion and the OH(5) anion of an adjacent heteropolyhedral sheet. The OH(5) anion bonds to B(4); it is a donor anion to H(4), and an acceptor anion for the H(5) hydrogen.

The OW(4) anion bonds to Sr, and it accepts the H(7) hydrogen bond. The OW(4) position donates two hydrogen bonds, H(2) and H(3), only one of which bridges between anions of adjacent heteropolyhedral sheets. The bridging OW(4)–H(2)...O(1) bond has an acceptor distance of 2.26(4) Å, and thus the bond is quite weak. The O(1) oxygen bonds to Sr, B(1) and B(6), which satisfy most of its bond-valence requirements (Table 5).

The OW(12) anion is bonded to two Sr cations in adjacent heteropolyhedral sheets. However, the OW(12) anion is considerably closer to one sheet, giving Sr–OW(12) distances of 2.593(3) and 3.001(3) Å, respectively. The OW(12) anion donates two hydrogen bonds, one of which bridges to an anion of the nearest heteropolyhedral sheet (this bond is considered below), whereas the OW(12)–H(6)...O(10) bond bridges to the further sheet (this bond is included here as an intersheet bond). The OW(12)–H(6)...O(10) bond is strong, as indicated by the short distance to the acceptor, 1.75(6) Å. The O(10) anion bonds to B(2) and B(3).

The OW(13) anion bonds to Sr and is the donor of two hydrogen bonds, both of which bridge to the adjacent heteropolyhedral sheet. The OW(13)–H(7)...OW(4) bond is weak, as indicated by a long distance to the acceptor, 2.26(6) Å. The OW(13)–H(8)...OH(3) bond is strong, with an acceptor distance of 1.80(3) Å.

Hydrogen bonds within the heteropolyhedral sheet

The OW(4) and OW(12) anions both bond to Sr, and each donates a hydrogen bond to an anion of the same heteropolyhedral sheet (Fig. 4). The OW(4)–H(3)...O(11) and OW(12)–H(5)...OH(5) bonds are strong, as indicated by acceptor distances of 1.81(2) and 1.84(3) Å, respectively. Both bonds are directed to anions that belong to borate *FBB*s; the OH(5) anion bonds to B(4), and the O(11) anion bonds to B(2) and B(3).

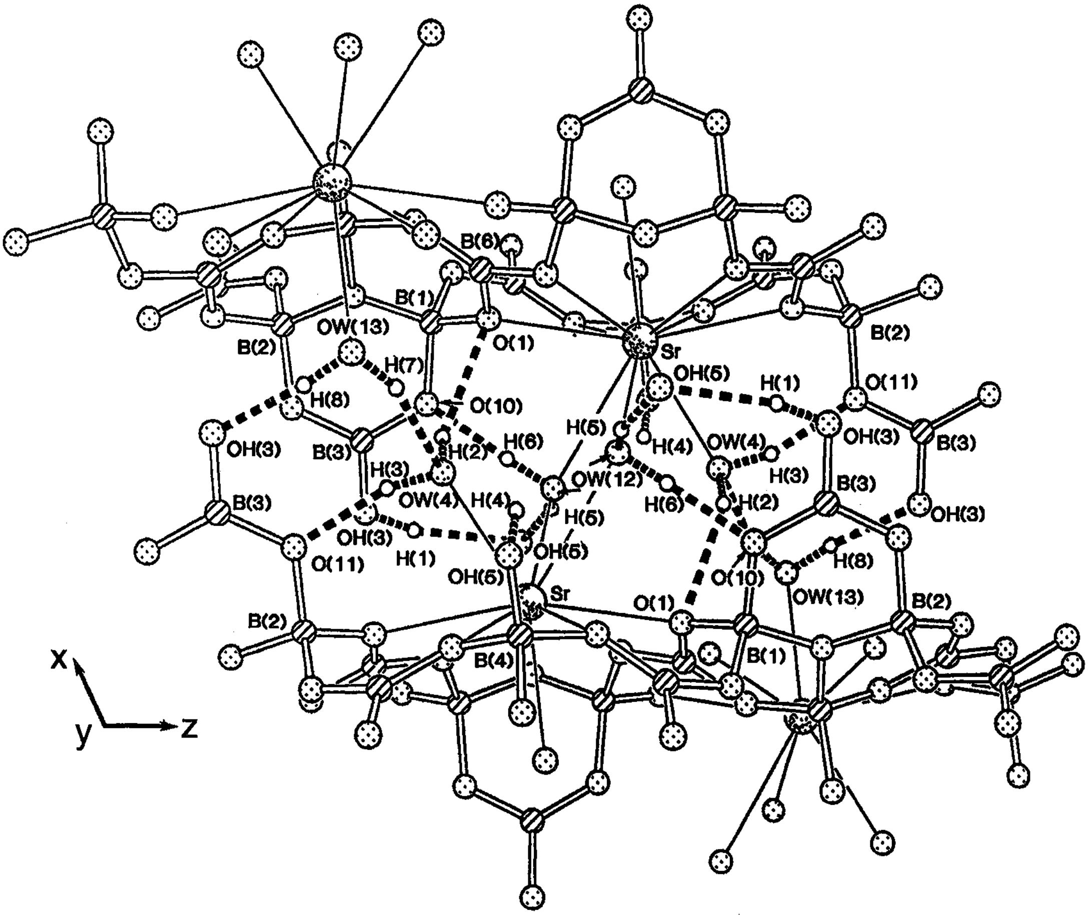

FIG. 4. The structure of tunellite projected onto (010). Boron atoms are circles shaded with parallel lines, strontium atoms are circles shaded with a random-dot pattern, oxygen atoms are circles shaded with a regular-dot pattern, and hydrogen atoms are given as small, open circles. Donor–hydrogen and hydrogen–acceptor bonds are shown as heavy broken lines.

CONCLUSIONS

This work has directly located all of the hydrogen positions in tunellite, and shows that seven of the hydrogen atoms form hydrogen bonds, although only four are strong bonds; one is of intermediate strength, and two are weak. Five hydrogen bonds bridge between adjacent heteropolyhedral sheets, and only the H(4) atom does not participate in a hydrogen bond.

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