The Canadian Mineralogist
Vol. 54, pp. 707-713 (2016)
DOI: 10.3749/canmin.1500102

REFINEMENT OF THE CRYSTAL STRUCTURE OF SCHNEIDERHÖHNITE

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ABSTRACT

The crystal structure of schneiderhöhnite, $Fe^{2+}Fe^{3+}{}_3As^{3+}{}_5O_{13}$, triclinic $P\bar{1}$, *a* 8.945(3), *b* 10.022(3), *c* 9.161(4) Å, α 62.942(5), β 116.072(6), γ 81.722(6)°, has been refined to an *R*1 value of 1.4%. The structure is very close to that reported by Hawthorne (1985), but detailed examination of the structural connectivity shows that schneiderhöhnite is better described as a sheet structure than as a framework structure. Zig-zag chains of edge-sharing *Fe*(1), *Fe*(2), *Fe*(3) (= Fe^{3+}) octahedra extend parallel to the **c** axis, and these chains are cross-linked into a corrugated sheet by tetramers of edge-sharing *Fe*(4) (= Fe^{3+}) and *Fe*(5) (= Fe^{2+}) octahedra. ($As^{3+}O_3$) triangular pyramids decorate the surface of this sheet of octahedra as single (AsO_3) groups, with all three short bonds linked to anion vertices of the octahedra, and as two crystallographically distinct [As_2O_5] dimers with four short bonds (two from each As^{3+}) to octahedron vertices. The sheets are connected along [100] *via* the bridging anion of one of the two [As_2O_5] dimers that bonds to an Fe^{2+} octahedron of the adjacent sheet, imparting a strong sheet-like character to the structure and accounting for the perfect (100) cleavage.

Keywords: schneiderhöhnite, crystal-structure refinement, Tsumeb, Namibia.

INTRODUCTION

During investigation of a sample from Ariakas, Usakos, Namibia, purchased from a dealer, black crystals of possible schneiderhöhnite were examined. Preliminary unit-cell fitting to the diffraction data confirmed the mineral's identity as schneiderhöhnite. However, there was a difference between the original unit cell reported by Ottemann *et al*. (1973): *a* 8.940, *b* 9.998, *c* 9.145 Å, α 63.00, β 116.20, γ 81.79°, and that from the crystal-structure solution and refinement of Hawthorne (1985): *a* 8.924, *b* 10.016, *c* 9.103 Å, α 59.91, β 112.41, γ 81.69°, where the α and β angles differ by ~3 and 4°, respectively. We presumed that this difference was due to a difference in vector selection, but decided to collect a full intensity data set and refine the structure to be sure. We were able to reproduce the original structure results of Hawthorne (1985), and also refined the analogous structure on the original cell setting of Ottemann *et al*. (1973). Structure drawings for each setting revealed a better correspondence between structural connectivity and the axial vectors corresponding to the cell setting of Ottemann *et al*. (1973). More importantly, we realized that the schneiderhöhnite structure is better represented as a sheet structure, rather than as a framework structure. Here, we report a more precisely refined schneiderhöhnite structure based on the original cell setting of Ottemann *et al*. (1973), and present the structural connectivity with an emphasis on its sheet-like character.

EXPERIMENTAL

A crystal was attached to a tapered glass fiber and X-ray diffraction data were collected with Mo*K*α X-radiation using a Bruker APEX II ULTRA three-circle diffractometer equipped with a rotating-anode generator (Mo*K*α), multilayer optics, and an APEX II 4K CCD detector. The intensities of 23177 reflections (6942 in the Ewald sphere) were collected to 60° 2θ using 16 s per 0.3° frame with a crystal-to-detector distance of 5 cm. An empirical absorption correction (SADABS, Sheldrick 2008) was applied, and the data were corrected for Lorentz, polarization, and background effects. The refined unit-cell parameters were obtained from 4048 reflections with $I > 10\sigma I$, and are given in Table 1, together with other information

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TABLE 1. MISCELLANEOUS INFORMATION FOR SCHNEIDERHÖHNITE

a (Å)	8.945(3)	Crystal size (μm)	25 × 30 × 5
b	10.022(3)	Total reflections	23177
c	9.161(4)	No. in Ewald sphere	6942
α (°)	62.942(5)	No. unique reflections	3475
β	116.072(6)	R_{merge} %	1.1
γ	81.722(6)	R_1	1.4
V (Å^3)	593.2(6)	wR_2	3.5
Space group	$P\bar{1}$	No. with $F_o > 4\sigma F$	3226
		A,B weights	0.0162, 0.51

pertaining to the data collection and structure refinement.

The structure was refined in space group $P\bar{1}$, with the SHELXTL version 5.1 system of programs (Bruker 1997), using the general site-labelling scheme of Hawthorne (1985) in which the *Fe*(1), *Fe*(2), *Fe*(3), and *Fe*(4) sites are occupied by Fe^{3+} and the *Fe*(5) site is occupied by Fe^{2+}. The refinement converged at an R_1 index of 1.4 %. Final atom parameters are given in Table 2, selected interatomic distances and angles in Table 3, and bond valences, calculated with the parameters of Brese & O'Keeffe (1991), in Table 4. A .cif file may be obtained from The Depository of Unpublished Data on the MAC website [document schneiderhöhnite CM_54-3_10.3749/canmin.1500102]. The refined positions and resulting interatomic distanc-

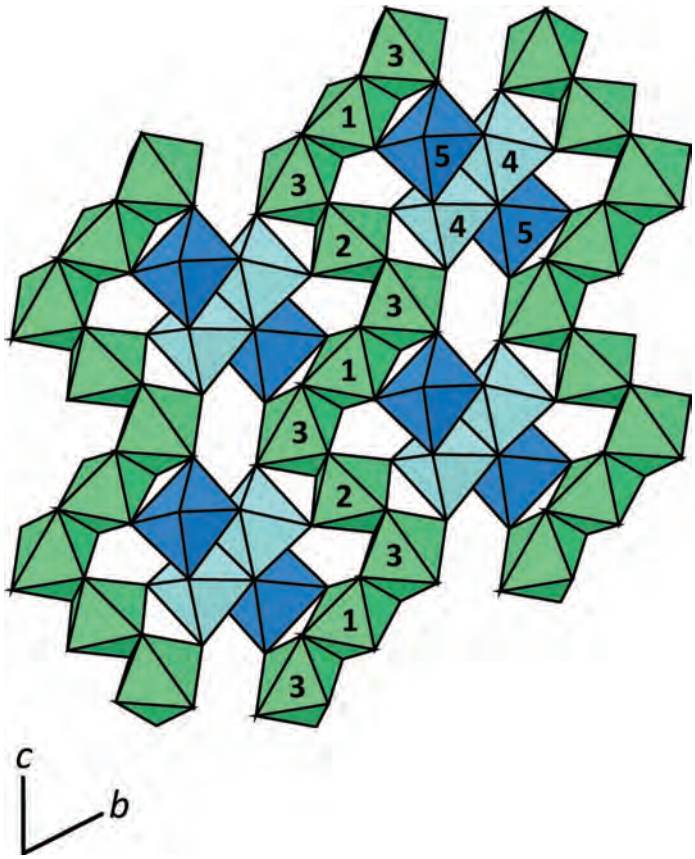

FIG. 1. The sheet of Fe polyhedra in schneiderhöhnite projected onto (100). Green shading: *Fe*(1), *Fe*(2), and *Fe*(3) polyhedra; light blue: *Fe*(4) polyhedra; dark blue: *Fe*(5) polyhedra.

TABLE 2. ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR SCHNEIDERHÖHNITE

Site	*x*	*y*	*z*	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U^{eq}
As(1)	0.69195(3)	0.20543(2)	0.49402(3)	0.00820(9)	0.00957(9)	0.00744(9)	–0.00490(8)	0.00360(8)	–0.00351(7)	0.00891(5)
As(2)	0.32490(3)	–0.16350(2)	0.99449(3)	0.00818(9)	0.00940(9)	0.00722(9)	–0.00463(7)	0.00409(8)	–0.00375(7)	0.00854(4)
As(3)	0.78094(3)	0.43238(2)	0.66523(3)	0.00930(10)	0.00804(9)	0.00867(9)	–0.00473(7)	0.00571(8)	–0.00347(7)	0.00851(4)
As(4)	0.37493(3)	0.09540(2)	0.64275(3)	0.00816(9)	0.01006(9)	0.00841(9)	–0.00560(7)	0.00514(8)	–0.00455(7)	0.00848(4)
As(5)	0.74312(3)	0.55039(3)	–0.01233(3)	0.01093(10)	0.00961(9)	0.00835(9)	–0.00553(8)	0.00485(8)	–0.00507(8)	0.00972(5)
Fe(1)	0	0	0	0.00976(19)	0.00942(18)	0.00821(17)	–0.00588(15)	0.00575(16)	–0.00485(15)	0.00834(8)
Fe(2)	0	0	½	0.00986(19)	0.00902(18)	0.00777(17)	–0.00508(15)	0.00590(15)	–0.00488(15)	0.00825(8)
Fe(3)	0.06750(4)	0.20118(3)	0.18122(4)	0.00973(13)	0.00832(12)	0.00738(12)	–0.00487(10)	0.00554(11)	–0.00445(10)	0.00793(6)
Fe(4)	0.96572(4)	0.38308(3)	0.42012(4)	0.00980(14)	0.00809(13)	0.00811(13)	–0.00436(10)	0.00504(11)	–0.00407(10)	0.00887(6)
Fe(5)	0.24986(4)	0.21934(4)	0.88613(4)	0.01030(14)	0.00833(13)	0.00977(13)	–0.00538(11)	0.00513(11)	–0.00422(11)	0.00968(6)
O(1)	0.9798(2)	0.39755(18)	0.1832(2)	0.0121(7)	0.0104(7)	0.0107(7)	–0.0064(6)	0.0061(6)	–0.0036(6)	0.0114(3)
O(2)	0.4501(2)	–0.08308(18)	0.8830(2)	0.0082(7)	0.0114(7)	0.0088(6)	–0.0039(6)	0.0047(6)	–0.0029(5)	0.0108(3)
O(3)	0.2321(2)	0.24402(18)	0.6315(2)	0.0117(7)	0.0104(7)	0.0096(6)	–0.0063(6)	0.0055(6)	–0.0028(6)	0.0109(3)
O(4)	0.6486(2)	0.36880(19)	0.5234(2)	0.0103(7)	0.0131(7)	0.0143(7)	–0.0097(6)	0.0057(6)	–0.0046(6)	0.0124(3)
O(5)	0.1993(2)	0.01929(18)	0.9511(2)	0.0133(7)	0.0118(7)	0.0152(7)	–0.0097(6)	0.0107(6)	–0.0078(6)	0.0108(3)
O(6)	0.8271(2)	0.03162(17)	0.7471(2)	0.0116(7)	0.0098(6)	0.0077(6)	–0.0053(5)	0.0062(6)	–0.0047(5)	0.0092(3)
O(7)	0.7236(2)	0.56365(15)	0.1673(2)	0.0111(7)	0.0111(7)	0.0087(6)	–0.0058(5)	0.0056(6)	–0.0042(6)	0.0104(3)
O(8)	0.9038(2)	0.23991(18)	0.9083(2)	0.0126(7)	0.0105(7)	0.0075(6)	–0.0048(5)	0.0056(6)	–0.0050(6)	0.0105(3)
O(9)	0.1983(2)	0.06590(18)	0.4853(2)	0.0106(7)	0.0117(7)	0.0084(6)	–0.0062(6)	0.0055(6)	–0.0059(6)	0.0098(3)
O(10)	0.7699(2)	0.73640(18)	–0.1084(2)	0.0145(7)	0.0101(7)	0.0146(7)	–0.0063(6)	0.0102(6)	–0.0060(6)	0.0125(3)
O(11)	0.1437(2)	–0.14935(18)	0.7941(2)	0.0105(7)	0.0128(7)	0.0076(6)	–0.0065(5)	0.0051(6)	–0.0063(6)	0.0099(3)
O(12)	0.9605(2)	0.41206(18)	0.6260(2)	0.0111(7)	0.0105(6)	0.0113(7)	–0.0068(6)	0.0082(6)	–0.0056(5)	0.0097(3)
O(13)	0.8859(2)	0.20660(17)	0.4793(2)	0.0137(7)	0.0103(7)	0.0123(7)	–0.0070(6)	0.0099(6)	–0.0068(6)	0.0104(3)

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN SCHNEIDERHÖHNITE

As(1)–O(4)	1.7926(16)	*As*(3)–O(4)	1.7648(15)
As(1)–O(6)	1.7680(15)	*As*(3)–O(8)	1.7936(15)
As(1)–O(13)	1.7997(16)	*As*(3)–O(12)	1.7968(15)
As(1)–O(9)	2.6447(16)	<*As*(3)–O_{py}>	1.785
<*As*(1)–O_{py}>	1.787		
		As(4)–O(2)	1.8075(16)
As(2)–O(2)	1.8610(15)	*As*(4)–O(3)	1.7485(15)
As(2)–O(5)	1.7689(16)	*As*(4)–O(9)	1.7844(15)
As(2)–O(11)	1.7608(15)	<*As*(4)–O_{py}>	1.780
As(2)–O(8)	2.6450(16)		
<*As*(2)–O_{py}>	1.797	*As*(5)–O(1)	1.8095(16)
		As(5)–O(7)	1.7893(16)
Fe(1)–O(5)	2.0343(15)	*As*(5)–O(10)	1.7687(15)
Fe(1)–O(6)	1.9756(16)	<*As*(5)–O_{py}>	1.789
Fe(1)–O(8)	2.0392(16)		
<*Fe*(1)–O>	2.016	*Fe*(4)–O(1)	2.1700(17)
		Fe(4)–O(3)	1.9757(16)
Fe(2)–O(9)	2.0161(15)	*Fe*(4)–O(7)	1.9949(16)
Fe(2)–O(11)	1.9706(16)	*Fe*(4)–O(12)	2.0537(16)
Fe(2)–O(13)	2.0563(15)	*Fe*(4)–O(12)	2.1623(15)
<*Fe*(2)–O>	2.014	*Fe*(4)–O(13)	1.9398(15)
		<*Fe*(4)–O>	2.049
Fe(3)–O(1)	2.0219(16)		
Fe(3)–O(6)	2.0473(16)	*Fe*(5)–O(2)	2.2066(16)
Fe(3)–O(8)	2.0695(17)	*Fe*(5)–O(3)	2.1601(18)
Fe(3)–O(9)	2.0520(17)	*Fe*(5)–O(5)	1.9976(15)
Fe(3)–O(10)	1.9203(16)	*Fe*(5)–O(7)	2.0759(16)
Fe(3)–O(11)	2.1072(16)	*Fe*(5)–O(10)	2.3427(18)
<*Fe*(3)–O>	2.036	*Fe*(5)–O(12)	2.2495(16)
		<*Fe*(5)–O>	2.172

es are in close agreement with those of Hawthorne (1985), the current refinement offering greater precision, *i.e.*, smaller standard deviations for refined site positions and improved atom-displacement parameters.

Structure Description

(AsO_3) groups

Each of the five *As* sites is occupied by As^{3+} which forms three short bonds to oxygen atoms (~1.8 Å, Table 3); for *As*(1) and *As*(2), there is an additional oxygen atom at ~2.64 Å with a bond valence of ~0.10 *vu* (Tables 3 and 4). All other oxygen atoms are more than 3.08 Å away from the As^{3+} atoms and have calculated bond-valence interactions of ≤0.03 *vu*.

Bond topology

Zig-zag chains of edge-sharing *Fe*(1), *Fe*(2), and *Fe*(3) (= Fe^{3+}) octahedra extend parallel to the **c** axis, and these chains are cross-linked into a corrugated sheet by tetramers of edge-sharing *Fe*(4) (= Fe^{3+}) and *Fe*(5) (= Fe^{2+}) octahedra (Fig. 1). The ($As^{3+}O_3$) triangular pyramids attach to the surface of this sheet of octahedra in two distinct ways (Fig. 2): (1) as single (AsO_3) groups [*As*(5)] with all three short bonds linked to anion vertices of the octahedra; (2) as [As_2O_5] dimers, [As(1)As(3)O_5] and [As(2)As(4)O_5], each with four short bonds (two from each As^{3+}) to octahedron vertices below, and the third bond bridging the As^{3+} cations of the [As_2O_5] group (Fig. 2). The O(4) anion that bridges the [*As*(1)*As*(3)O_5] dimer is a [2]-coordinated oxygen atom, whereas the O(2) anion that bridges the [*As*(2)*As*(4)O_5] dimer is a [3]-coordinated oxygen atom, as O(2) forms an additional bond with Fe^{2+} at *Fe*(5) (Table 4). The O(2) anion (red

TABLE 4. BOND-VALENCE VALUES FOR SCHNEIDERHÖHNITE

	As(1)	*As*(2)	*As*(3)	*As*(4)	*As*(5)	*Fe*(1)	*Fe*(2)	*Fe*(3)	*Fe*(4)	*Fe*(5)	Σ
O(1)					0.95			0.49	0.33		1.77
O(2)		0.82		0.95						0.28	2.05
O(3)				1.12					0.56	0.32	2.00
O(4)	0.99		1.07								2.06
O(5)		1.00				0.48↓^{x2}				0.49	1.97
O(6)	1.06					0.56↓^{x2}		0.46			2.08
O(7)					1.00				0.53	0.40	1.93
O(8)		0.10	0.99			0.47↓^{x2}		0.43			1.99
O(9)	0.10			1.01			0.50↓^{x2}	0.45			2.06
O(10)					1.06			0.65		0.19	1.90
O(11)		1.08					0.56↓^{x2}	0.39			2.03
O(12)			0.98						0.45	0.25	2.02
									0.34		
O(13)	0.97						0.45↓^{x2}		0.61		2.03
Σ	3.12	3.00	3.04	3.08	3.01	3.02	3.02	2.87	2.82	1.93	

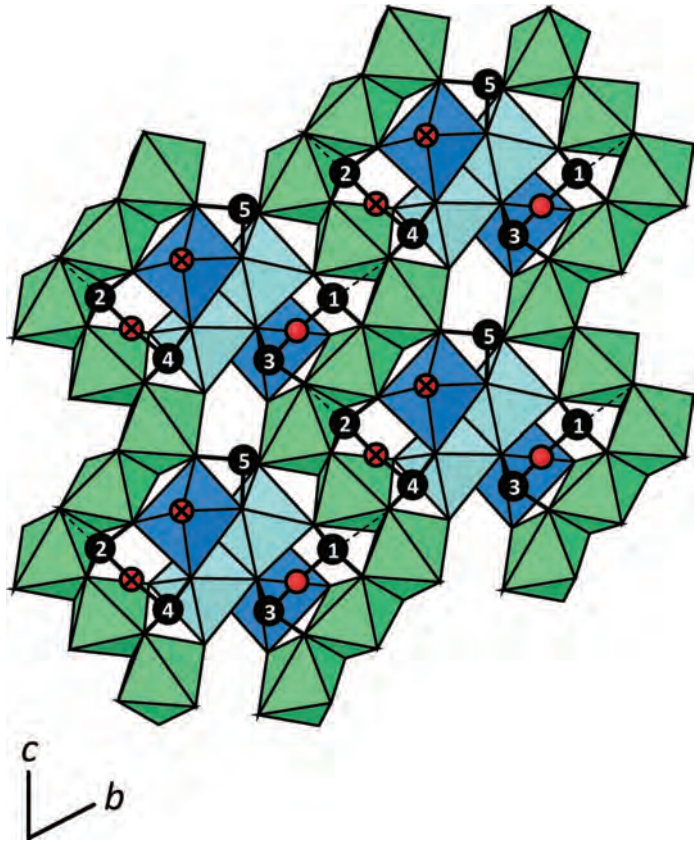

FIG. 2. The AsO_3 groups and As_2O_5 dimers decorating the upper surface of the Fe polyhedra in schneiderhöhnite, projected onto (100). Legend as in Figure 1; black circles: As^{3+} atoms; red circles: O(4) oxygen atoms; red circle with **X**: O(2) oxygen atoms; thick black line: short As^{3+}–O bonds; thin dashed black line: longer As^{3+}–O contacts.

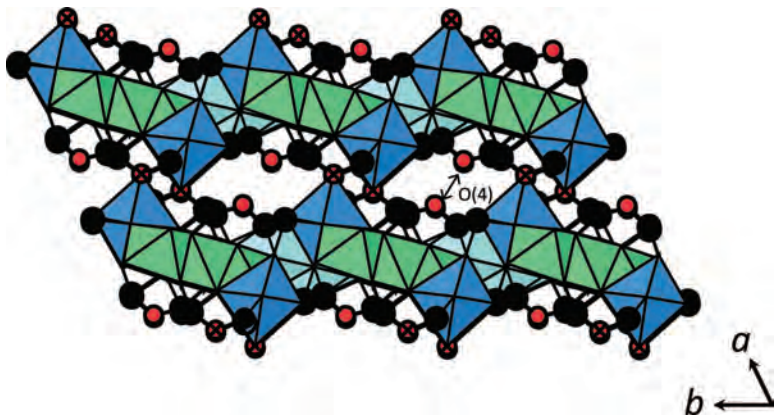

FIG. 3. The schneiderhöhnite structure projected down [001]. Legend as in Figure 2.

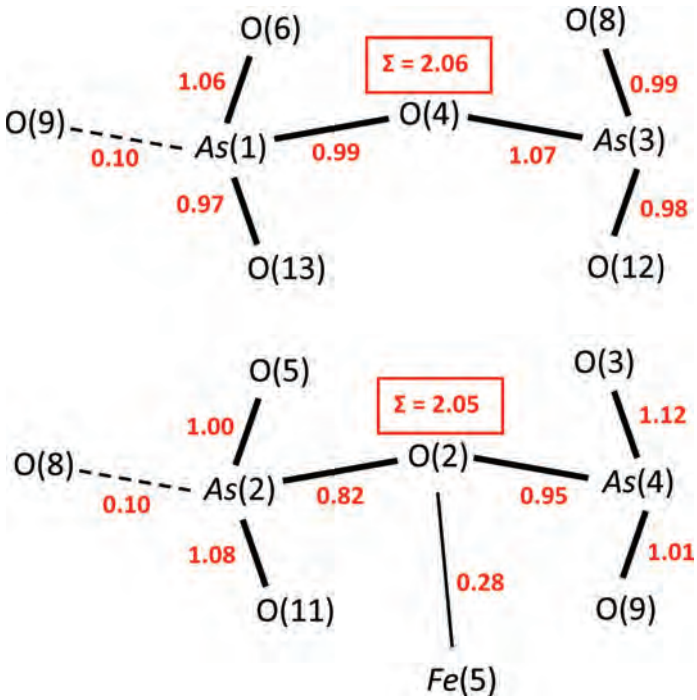

FIG. 4. Sketches of the two $[As_2O_5]$ groups in schneiderhöhnite, showing the environments around the the bridging oxygen atoms. Bond valences (*vu*) in red.

circle with X in Figs. 2, 3) is the only linkage between the sheets in the [100] direction, giving rise to the perfect cleavage parallel to (100) (Ottemann *et al.* 1973). There is a close approach of the O(4) anions in adjacent sheets (Fig. 3, see arrow), but no attractive interaction involving other cations.

It is noteworthy that O(2) and O(4) are both bridging anions in similar $[As_2O_5]$ groups, but play quite different roles in terms of structural connectivity, and a closer examination of their different roles is warranted in terms of understanding structural variability associated with polymerization involving $(As^{3+}O_3)$ groups. The general configurations of the two $[As_2O_5]$ dimers are shown in Figure 4, with bond valences indicated in red. The incident bond-valence sums at the bridging anions O(2) and O(4) are similar, 2.05 and 2.06 *vu*, and accord with the valence-sum rule, despite the difference in their coordination numbers. The longer As–O(bridging) bonds involved in the $[As(2)As(4)O_5]$ dimer compensate for the additional incident bond-valence from Fe^{2+}, the additional coordinating cation. Examination of the

TABLE 5. THIRD LIGAND TO O_{BR} IN POLYMERIZED As^{3+} OXIDE MINERALS

Mineral	Polymerized unit	O_{BR}	Third cation to O_{BR}	b.v. (*vu*)*	Ref.
paulmooreite	$[As_2O_5]$ dimer	O(3)	Pb	0.11	[1]
trippkeite	$[As_2O_4]$ chains	O(1)	Cu^{2+}	0.12	[2]
ludlockite	$[As_5O_{11}]$ cluster	O(14)	Pb	0.17	[3]
		O(20)	Pb	0.20	
stenhuggarite	$[As_4O_8]$ ring	O(7)	Ca	0.23	[4]
schneiderhöhnite	$[As_2O_5]$ dimer	O(2)	Fe^{2+}	0.28	[5]

* From Brese & O'Keeffe (1991)

References: [1] Araki *et al.* (1980); [2] Pertlik (1975); [3] Cooper & Hawthorne (1996); [4] Coda *et al.* (1977); [5] this work.

bridging distances and corresponding bond-valence values in minerals (Table 5) shows that the bond-valence contribution of 0.28 *vu* to the bridging oxygen atom in schneiderhöhnite is the largest known for the As^{3+}-oxide minerals.

As is apparent from Figure 3, the schneiderhöhnite structure is a sheet structure. Sheets of edge- and corner-sharing ($Fe^{2+}O_6$) and ($Fe^{3+}O_6$) octahedra are decorated on both surfaces by ($As^{3+}O_3$) triangular pyramids, and linkage between the sheets in the [100] direction involves only a small number of Fe^{2+}–O bonds.

Acknowledgments

We thank the reviewers for their comments on this paper. This work was supported by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada, and by Canada Foundation for Innovation Grants, to FCH.

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Received November 23, 2015. Revised manuscript accepted January 19, 2016.