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LOCAL CHARGE-COMPENSATION IN HYDROXYL-DEFICIENT UVITE

MATTHEW C. TAYLOR*, MARK A. COOPER AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structure of a sample of OH-deficient gem-quality uvite (tourmaline), $\square_{0.17}Na_{0.40}Ca_{0.43}[Mg_{1.70}Al_{1.28}Cr^{*}_{0.02}](Al_{5.16}Mg_{0.78}Cr^{*}_{0.06})Si_{5.998}O_6(BO_3)_3OH_{3.311}O_{0.689}$ [Cr^{*} = Cr + Ti + V + Fe] has been refined to an *R* index of 1.8% based on 1134 observed (5σ) reflections measured with Mo*K*α X-radiation. Unit-cell parameters are *a* 15.917(2), *c* 7.189(1) Å, *V* 1577.3(4) $Å^3$, *R*3*m*, *Z* = 3, D(calc) = 3.036 g cm^{-3}. The crystal used in the collection of the intensity data was analyzed by electron microprobe, and H_2O was determined by Karl Fischer titration. F was not detected. The OH content of 3.31 *apfu* (anions per formula unit) is significantly less than the ideal monovalent anion content of 4 *apfu*. The H atom associated with the O(3) (≡OH) anion was located on a difference-Fourier map, whereas no significant density was found in the vicinity of the O(1) site, in accord with the OH content determined by chemical analysis. There is significant Mg–Al disorder over the *Y* and *Z* sites, and site populations were determined from mean bond-length – constituent-cation-radius relations. The O(1) site-population is $O_{0.69}(OH)_{0.31}$, and of key importance is the mechanism by which short-range bond-valence requirements are satisfied around both O^{2-} and OH^- at this site. The O(1) site lies on a 3-fold axis, and the O(1) anion is bonded only to three *Y* cations. Where O(1) = O^{2-}, the anion is bonded to 2 Al + Mg; where O(1) = OH^-, the anion is bonded to 3 Mg. The individual bond-lengths needed for complete bond-valence satisfaction around O(1) average to give the observed *Y*–O(1) bond-length in this crystal, supporting these assignments.

Keywords: tourmaline, uvite, hydroxyl-deficient, ordering, short-range order, crystal structure.

SOMMAIRE

Nous avons affiné la structure d'un cristal d'uvite (tourmaline) gemme déficitaire en OH, $\square_{0.17}Na_{0.40}Ca_{0.43}[Mg_{1.70}Al_{1.28}Cr^{*}_{0.02}](Al_{5.16}Mg_{0.78}Cr^{*}_{0.06})Si_{5.998}O_6(BO_3)_3OH_{3.311}O_{0.689}$ [Cr^{*} = Cr + Ti + V + Fe] jusqu'à un résidu *R* de 1.8% en utilisant 1134 réflexions observées (5σ) et mesurées avec rayonnement Mo*K*α. Les paramètres réticulaires sont: *a* 15.917(2), *c* 7.189(1) Å, *V* 1577.3(4) $Å^3$, *R*3*m*, *Z* = 3, D(calc) = 3.036 g cm^{-3}. Nous avons analysé le même cristal avec une microsonde électronique, et déterminé sa teneur en eau par titration (méthode de Karl Fischer). Le fluor est sous le seuil de détection; la présence de 3.31 OH au lieu de 4 correspond à un déficit important. L'atome H associé avec l'anion O(3) (≡ OH) a été repéré sur la carte de différence Fourier; par contre, nous ne trouvons aucune densité d'électrons près du site O(1), en concordance avec la faible teneur en OH déterminée par analyse chimique. Il y a un désordre important impliquant Mg et Al sur les positions *Y* et *Z*; la proportion de cations à ces positions a été déterminée en utilisant les relations connues entre longueur moyenne de liaison et rayon du cation présent. Le site O(1) contient $O_{0.69}(OH)_{0.31}$. Il est important de comprendre le mécanisme de satisfaction des valences de liaison à courte échelle autour de O^{2-} et OH^- dans ce site. Le site O(1) est situé sur un axe de rotation 3, et l'anion O(1) est coordonné à seulement trois cations *Y*. Dans les cas où O(1) est en fait un atome O^{2-}, l'anion est en liaison avec 2 Al + Mg. Dans les cas où un groupe OH^- s'y trouve, l'anion est en liaison avec trois atomes de Mg. Les longueurs des liaisons individuelles requises pour assurer la satisfaction complète des valences de liaison autour de O(1) atteignent une moyenne valeur qui concorde très bien avec la longueur *Y*–O(1) observée dans ce cristal, ce qui étaye notre schéma de distribution des cations.

(Traduit par la Rédaction)

Mots-clés: tourmaline, uvite, déficit en hydroxyle, mise en ordre, ordre à courte échelle, structure cristalline.

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* Department of Earth Sciences, University of California, Riverside, California 92521, U.S.A.

INTRODUCTION

The general chemical formula of tourmaline may be written as $X\ Y_3\ Z_6\ (Si_6O_{18})\ (BO_3)_3\ W_4$ where X = Na,K,Ca,□, Y = Li,Mg,Fe^{2+},Mn^{2+},Al,Fe^{3+},Cr^{3+},V^{3+},(Ti^{4+}), Z = Al,Mg,Fe^{3+},Cr^{3+},V^{3+}, and W = OH,F,O.

Tourmaline is quite an intractable mineral to chemically analyze completely, as it is commonly strongly zoned, H, Li and Fe^{2+}/Fe^{3+} cannot be determined by electron microprobe, and the proportion of B cannot be established with sufficient accuracy by the electron microprobe to be useful in tourmaline studies. This problem of the behavior of light lithophile elements is of considerable significance for many rock-forming and important accessory minerals (*e.g.*, Hawthorne 1995); tourmaline is no exception. These difficulties are usually circumvented by making assumptions concerning the stoichiometry of these "difficult" components. In some cases, other techniques have shown that some of these assumptions *can be* valid for tourmaline (*e.g.*, Burns *et al.* 1994). However, evidence is accumulating (Povondra 1981, Povondra & Novák 1986, Henry & Dutrow 1990, Grice & Ercit 1993, Dyar *et al.* 1994) that some of these stoichiometric assumptions are not of general validity. It is often assumed that OH + F = 4 *apfu* (anions per formula unit), with the concomitant requirement that both the O(1) and O(3) sites of the tourmaline structure are occupied by monovalent anions; however, the analytical work of Povondra (1980), Povondra & Novák (1986) and Dyar *et al.* (1994) indicates that this assumption is not always justified. Here, we present structural results on a F-free OH-deficient uvite crystal and show how the structure responds to a monovalent-anion content less than the ideal value of 4 *apfu*.

TABLE 1. MISCELLANEOUS DATA FOR OH-DEFICIENT UVITE

a (Å)	15.917(2)	Crystal size	~0.20 mm
c	7.189(1)	Total reflections	1137
V (Å³)	1577.3(4)	Obs. reflections	1134
		R(azimuthal)%	1.4 → 1.1
Space Group	$R3m$	R(obs)%	1.8
		wR(obs)%	2.3

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

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

EXPERIMENTAL

Collection of X-ray data

The material used in this study was acquired from a gem dealer, and is from an unknown location in East Africa. The crystal used in the collection of the X-ray intensity data was ground to a sphere (approximately) and mounted on a Nicolet $R3m$ automated four-circle diffractometer. Forty reflections were centered using graphite-monochromated Mo$K\alpha$ X-radiation; the resulting cell dimensions are given in Table 1. A total of 1137 symmetry-independent reflections was measured ($3 \leq 2\theta \leq 60°$), with index ranges $0 \leq h \leq 19$, $0 \leq k \leq 19$, $-11 \leq l \leq 11$, according to the method described by Burns *et al.* (1994). The intensity data were corrected for absorption (psi-scan method), Lorentz, polarization and background effects, and reduced to structure factors. A reflection was considered observed if its magnitude exceeded that of five standard deviations above background, based on counting statistics.

TABLE 2. ATOMIC PARAMETERS FOR OH-DEFICIENT UVITE

	x	y	z	$^*U_{eq}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
X	0	0	0.8408	187(4)	178(5)	178(5)	204(7)	0	0	89(3)
Y	0.06148(3)	0.93852(3)	0.4269(3)	66(3)	48(3)	48(3)	90(4)	−18(1)	18(1)	15(3)
Z	0.26126(4)	0.29749(4)	0.4534(2)	68(2)	74(2)	73(2)	57(2)	1(2)	−5(2)	37(2)
Si	0.18986(3)	0.19175(3)	0.0640(2)	56(2)	57(2)	58(2)	52(2)	5(2)	8(2)	27(2)
B	0.8904(1)	0.1096(1)	0.6113(4)	74(7)	79(8)	79(8)	58(9)	−3(4)	3(4)	35(9)
O(1)	0	0	0.2929(4)	115(7)	129(9)	129(9)	85(14)	0	0	65(4)
O(2)	0.93958(7)	0.06042(7)	0.5795(3)	126(6)	129(6)	129(6)	158(9)	1(3)	−1(3)	93(7)
O(3)	0.13052(8)	0.86948(8)	0.5538(3)	148(6)	154(6)	154(6)	43(7)	2(4)	−2(4)	8(8)
O(4)	0.90697(7)	0.09303(7)	−0.0087(3)	119(5)	98(6)	98(6)	105(8)	11(4)	−11(4)	6(7)
O(5)	0.09146(7)	0.90854(7)	−0.0292(3)	115(5)	94(5)	94(5)	105(8)	4(3)	−4(3)	8(7)
O(6)	0.18417(9)	0.19430(9)	0.2874(6)	95(5)	114(6)	119(6)	63(5)	11(4)	20(4)	66(5)
O(7)	0.28499(8)	0.28554(9)	−0.0137(3)	97(4)	81(6)	92(5)	86(6)	17(4)	12(4)	20(5)
O(8)	0.26962(9)	0.20899(9)	0.6249(3)	104(5)	99(6)	65(6)	147(6)	−6(5)	−19(4)	40(5)
H	0.1264(14)	0.8736(14)	0.6876(15)	300						

* $U = \exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hkabU_{12} + 2hlacU_{13} + 2klbcU_{23})] \times 10^4$ Å²; U_{eq} is one-third of the trace of the orthogonalized U_{ij} tensor.

Refinement of the crystal structure

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used for this work.

The structure was refined in the space group *R*3*m* using positional coordinates of elbaite (Burns *et al.* 1994). The final cycles of refinement involved all variable positional parameters, anisotropic displacement parameters and site-scattering parameters for the *X*, *Y* and *Z* sites. The H-atom site was constrained to be approximately 0.98 Å from the O(3) site. The final *R* index is 1.8%. Final positional and displacement parameters are given in Table 2, selected interatomic distances and angles are given in Table 3, and the refined site-scattering values are given in Table 4 in *epfu* (electrons per formula unit). Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN OH-DEFICIENT UVITE

X–O(2)	x3	2.511(2)	O(2)–*X*–O(2)	x3	70.1(1)
X–O(4)	x3	2.784(1)	O(2)–*X*–O(4)	x3	71.3(1)
X–O(5)	x3	2.689(7)	O(2)–*X*–O(5)	x3	87.1(1)
<*X*–O>		2.661	O(4)–*X*–O(4)	x3	105.9(1)
			O(4)–*X*–O(5)	x6	55.5(1)
			<O–*X*–O>		74.5
Y–O(1)		1.949(2)	O(1)–*Y*–O(2)	x2	84.1(1)
Y–O(2)	x2	2.007(2)	O(1)–*Y*–O(6)	x2	100.5(1)
Y–O(3)		2.111(1)	O(2)–*Y*–O(2)		91.9(1)
Y–O(6)	x2	1.973(2)	O(2)–*Y*–O(3)	x2	98.7(1)
<*Y*–O>		2.003	O(2)–*Y*–O(6)	x2	89.3(1)
			O(3)–*Y*–O(6)	x2	76.7(1)
			O(6)–*Y*–O(6)		89.2(1)
			<O–O>		90.0
Z–O(3)		1.995(2)	O(3)–*Z*–O(6)		81.2(1)
Z–O(6)		1.901(2)	O(3)–*Z*–O(7)		96.3(1)
Z–O(7)		1.908(2)	O(3)–*Z*–O(8)		96.6(1)
Z–O(7′)		1.952(2)	O(3)–*Z*–O(8′)		90.0(1)
Z–O(8)		1.900(2)	O(6)–*Z*–O(7)		93.1(1)
Z–O(8′)		1.926(2)	O(6)–*Z*–O(8)		95.0(1)
<*Z*–O>		1.930	O(6)–*Z*–O(8′)		91.2(1)
			O(7)–*Z*–O(7′)		90.4(1)
			O(7)–*Z*–O(8)		95.9(1)
			O(7)–*Z*–O(8′)		78.1(1)
			O(7′)–*Z*–O(8)		77.6(1)
			O(7′)–*Z*–O(8′)		96.4(1)
			<O–*Z*–O>		90.1
Si–O(4)		1.628(1)	O(4)–Si–O(5)		102.3(1)
Si–O(5)		1.643(2)	O(4)–Si–O(6)		111.6(1)
Si–O(6)		1.610(3)	O(4)–Si–O(7)		110.4(1)
Si–O(7)		1.604(1)	O(5)–Si–O(6)		110.2(1)
<Si–O>		1.621	O(5)–Si–O(7)		110.7(1)
			O(6)–Si–O(7)		111.3(1)
			<O–Si–O>		109.4
B–O(2)		1.375(1)	O(2)–B–O(8)	x2	120.7(1)
B–O(8)	x2	1.374(2)	O(8)–B–O(8)		118.5(1)
<B–O>		1.374	<O–B–O>		120.0
O(3)–H		0.97(1)	H···O(5)		2.25(1)
			O(3)–H···O(5)		161.4(2)

TABLE 4. REFINED SITE-SCATTERING VALUES (*epfu*), SITE POPULATIONS AND CALCULATED SITE-SCATTERING VALUES FOR OH-DEFICIENT UVITE

	Site scattering	Site population	Calculated site scattering
X	13.9 e	0.43 Ca + 0.40 Na + 0.17 □	13.5 e
Y	37.4 e	1.70 Mg + 1.28 Al + 0.02 Cr*	37.5 e
Z	78.0 e	5.16 Al + 0.78 Mg + 0.06 Cr*	77.8 e

Cr* = Cr+Ti+V+Fe

Chemical analysis

The crystal used in the collection of the X-ray intensity data was mounted in epoxy, ground, polished, carbon coated and analyzed by electron microprobe with a CAMECA SX–50 instrument using the procedure described by Burns *et al.* (1994). The sample was powdered and "pre-dried" in a dessicating oven,

TABLE 5. ELECTRON-MICROPROBE DATA* AND UNIT FORMULA FOR OH-DEFICIENT UVITE

				(1)**	(2)**
SiO_2	37.22	wt %	Si	5.998	5.915
Al_2O_3	33.85		Al	–	0.085
TiO_2	0.25				
Cr_2O_3	0.33		Al^+	6.000	6.000
V_2O_3	0.06				
FeO	0.02		Al^+	0.429	0.255
MgO	10.14		Ti^{4+}	0.030	0.030
CaO	2.49		Cr^{3+}	0.042	0.041
Na_2O	1.28		V^{3+}	0.008	0.008
B_2O_3	(10.78)++		Fe^{2+}	0.003	0.003
H_2O	3.10		Mg	2.437	2.402
	99.52		Σ*Y*	2.948	2.698
			Ca	0.430	0.424
			Na	0.400	0.394
			Σ*X*	0.830	0.818
			OH	3.311	4

* K, F, Mn, Cu, Zn not detected

** (1): calculated on the basis of 31(O,OH);
(2): calculated on the basis of 31(O,OH) with OH=4 *apfu*

\+ This method of giving the Al content is not meant to infer that the *Z* site is completely occupied by Al.

++ calculated for B=3.0 *apfu*.

and analyzed for H_2O (in duplicate) using Karl Fischer titrimetry with a Mitsubishi Moisture Meter attached to a Mitsubishi Water Vaporizer operating at 1000°C. Two sample aliquots of 0.0512 and 0.0430 g gave H_2O values of 3.09 and 3.11 wt%, respectively. Background moisture introduced during sample exchange was measured (20 μg) in a series of blank runs and subtracted. Titration start and end rates were 0.01 and 0.03 μg H_2O s^{-1}, respectively, over run times of 15 minutes. The analytical data are summarized in Table 5. The structural formula was calculated on the basis of 31 anions using the transition-metal valence-states indicated in Table 5.

DISCUSSION

Chemical composition and chemical formula

The unit formula (Table 5) has a *Y*-site sum of 2.95 *apfu* (atoms per formula unit). The scattering values for the *Y* site calculated from the formula unit are 36.8 *epfu* for the *Y*-cation sum of 2.948 *apfu*, and 37.5 *epfu* if the *Y*-cation sum is normalized to 3.00 *apfu*. The latter value is in better agreement with the refined value of 37.4 *epfu* (Table 4), suggesting that the slightly low *Y*-site cation sum of 2.498 *apfu* in Table 5 is due to slight analytical inaccuracy. Several other aspects of the chemical composition and unit formula of this tourmaline warrant discussion, including the OH content and the influence of the OH content on the calculation of the unit formula.

OH content of the structure: A key aspect of this particular tourmaline crystal is the measured OH content: 3.3 OH *pfu*. This gives a monovalent anion content significantly less than the 4 anions *pfu* conventionally assigned to *most* tourmaline compositions. This value is supported by the fact that there is no sign of any electron density at the position expected for a H atom attached to the O(1) anion.

The influence of OH content on the calculation of the formula unit: H_2O is often not determined in tourmaline, and the unit formula is calculated with the assumption that OH + F = 4 anions *pfu*. This calculation is very sensitive to the H_2O content; Table 5 compares the results of normalization based on 31(O,OH,F) [formula(1)] and 31(O,OH,F) with OH + F = 4 anions *pfu* [formula(2)]. There is a significant deficiency in the *Y*-cation sum (~0.30 □ *pfu*) for the OH + F = 4 anions *pfu* calculation. If the amounts of all cations in the structure have been established by analysis, such a deficiency in the *Y*-cation sum is a good indicator of OH + F being less than 4 anions *pfu*; however, the amounts of Li and B are not normally determined. Burns *et al.* (1994) used the *Y*-cation sum difference from 3 *apfu* to estimate the Li content. These values were confirmed by the site-scattering refinement, which showed the scattering from the *Y* site (in *epfu*) to correspond exactly to the *Y*-cation contents of the unit formulae with Li calculated by difference. Thus their *assumption* of OH + F = 4 anions *pfu* is correct for the samples they examined. However, it is not correct for the tourmaline examined in this work. We can thus conclude that Li cannot be accurately estimated by difference unless H_2O has been determined *or* the X-ray scattering from the *Y* site has been measured accurately.

Site populations

The refined site-scattering values are compatible with small amounts of transition metals occurring at the *Y* and *Z* sites (Table 4). The principal problem to resolve is the relative ordering of Mg and Al over the *Y* and *Z* sites. Site-scattering refinement cannot effectively distinguish between Mg and Al, as they scatter X rays in a very similar fashion. However, Mg ($^{[6]}r$ = 0.72 Å; Shannon 1976) and Al ($^{[6]}r$ = 0.535 Å) are of different size, and this is reflected in the observed mean bond-lengths. Hence, using the mean bond-length – constituent-cation radius curves of Hawthorne *et al.* (1995), the Mg and Al may be quantitatively assigned to the *Y* and *Z* sites (Table 4). Note that significant Mg occurs at the *Z* site, and confirms that the general assumption that Al completely fills the *Z* site before occupying the *Y* site is not valid (Hawthorne *et al.* 1993, Grice & Ercit 1993).

Electron-microprobe analysis indicates that the *X* site is occupied by 0.43Ca + 0.40Na + 0.17□, in good agreement with the measured X-ray scattering at this site. The dominant chemical species at the *X* site is Ca, the dominant species at the *Y* site is Mg, and the dominant species at the *Z* site is Al; hence this tourmaline is a uvite.

Local bond-valence requirements at the O(1) anion

The bond-valence arrangement in this crystal of uvite is shown in Table 6; note that both H sites are included in the table, even though only H(3) is occupied. The O(2), O(4), O(5), O(6), O(7) and O(8) anions are all oxygen atoms, and the sums of the bond-valences incident at these anions are all close to the ideal value of 2 *vu* (valence units). The O(3) anion is an OH group, and the sum of the bond-valences incident from the *Y* and *Z* cations is 1.145 *vu*. The H(3) atom associated with O(3) forms a weak H-bond to the O(5) anion; the D(donor)–H and H...A(acceptor) bond-valences were thus assigned (Table 6). The resulting sum of the incident bond-valences around the O(3) *oxygen* anion is 2.045 *vu*, close to the ideal value of 2 *vu*. The O(1) anion is bonded to three *Y* cations (Fig. 1), and in the sample of uvite examined here, the resulting sum of the incident bond-valences is 1.365 *vu* (Table 6). Normally, this would lead one to assign the

TABLE 6. BOND-VALENCE* TABLE FOR OH-DEFICIENT UVITE

	X	*Y*	*Z*	Si	B	H(1)	H(3)	Σ
O(1)		$0.455^{\times 3}\rightarrow$				*		1.365
O(2)	$0.159^{\times 3}\downarrow$	$0.401^{\times 2}\downarrow\rightarrow$			1.009			1.970
O(3)		0.323	$0.411^{\times 2}\rightarrow$				0.90	2.045
O(4)	$0.095^{\times 3}\downarrow$			$0.984^{\times 2}\rightarrow$				2.063
O(5)	$0.113^{\times 2}\downarrow$			$0.946^{\times 2}\rightarrow$			0.10	2.105
O(6)		$0.432^{\times 2}\downarrow$	0.506	1.032				1.970
O(7)			0.498 0.452	1.049				1.999
O(8)			0.507 0.479		$1.012^{\times 2}\downarrow$			1.998
Σ	1.101	2.444	2.853	4.011	3.033		1.00	

* parameters from Brown (1981)

TABLE 7. BOND-VALENCE TABLE FOR F-BEARING UVITE*

	X	*Y*	*Z*	Si	B	H(1)	H(3)	Σ
O(1)		$0.291^{\times 3}\rightarrow$				–		0.873
O(2)	$0.248^{\times 3}\downarrow$	$0.372^{\times 2}\downarrow\rightarrow$			1.036			2.028
O(3)		0.314	$0.419^{\times 2}\rightarrow$				0.90	2.052
O(4)	$0.125^{\times 3}\downarrow$			$0.969^{\times 2}\rightarrow$				2.063
O(5)	$0.149^{\times 2}\downarrow$			$0.912^{\times 2}\rightarrow$			0.10	2.073
O(6)		$0.393^{\times 2}\downarrow$	0.533	1.063				1.989
O(7)			0.445 0.508	1.041				1.994
O(8)			0.481 0.514		$0.991^{\times 2}\downarrow$			1.986
Σ	1.566	2.135	2.900	3.985	3.018	–	1.00	

* data from T72 of MacDonald & Hawthorne (1995), bond-valence parameters from Brown (1981)

O(1) anion as an OH group in which the H atom forms a strong H bond to another anion in the structure; thus there would be an entry at the position marked by an asterisk in Table 6, such that the sum of the incident bond-valences at O(1) was ~2 *vu*. However, such an assignment requires $(OH)_4$ in the structure, which is inconsistent with the measured content of $(OH)_{3.3}$ (Table 4). The H(3) atom was easily detected in a difference-Fourier map, whereas H(1) was not, indicating that the H(3) position is occupied [*i.e.*, O(3) = OH] and the H(1) position corresponds to $\square_{0.7}H_{0.3}$ [*i.e.*, O(1) ≈ O^{2-}]. This presents an added complexity with respect to local bond-valence requirements of the O(1) position in this particular uvite.

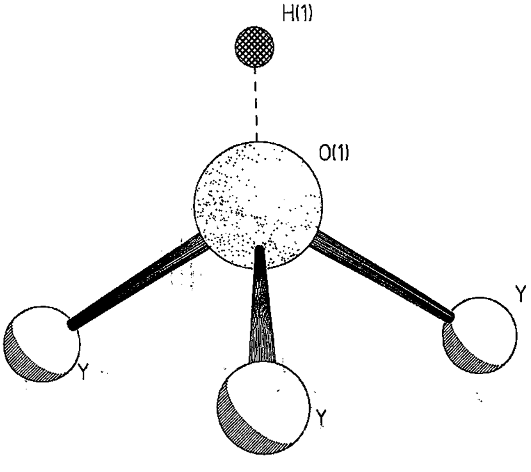

FIG. 1. Oblique view of the coordination of the O(1) site in tourmaline, *Z*-axis vertical. The O(1) atom (circle with random-dot shading) is bonded to three *Y* cations (highlighted circles), and the H(1) atom is shown by the small cross-hatched circle; the H(1) site is predominantly vacant in the uvite crystal refined here.

Table 7 shows the bond-valence arrangement in a crystal of F-bearing uvite in which O(1) ≈ F (MacDonald & Hawthorne 1995). All bond-valence sums are close to their ideal values. The sum around the O(1) anion, calculated using the curves for (Mg,Cr...)–F of Brown (1981), is somewhat lower than the ideal value of 1 *vu*, but is compatible with occupancy of O(1) by F, as indicated by the structure refinement. Grice & Ercit (1993) suggested that the variation in incident bond-valence at O(1) reflects variation in $O^{2-} \rightleftharpoons F^-$ substitution at this site, with $O^{2-} \rightleftharpoons OH^-$ and $F^- \rightleftharpoons OH^-$ substitutions being of lesser importance. If this proposal were correct, the valence-sum rule (Brown 1992, Hawthorne 1992, 1994) predicts that the incident bond-valence at O(1) should correspond to the aggregate charge of the anions at O(1). For the uvite crystal described in Table 6, this is not the case; the aggregate charge at O(1) is 1.69^-, which is not in accord with the incident bond-valence sum of 1.37 *vu*. The sum of the incident bond-valences around O(1) is a long-range (averaged) quantity. The bond-valence rule must be satisfied *locally* (*i.e.*, short-range) as well as in aggregate (*i.e.*, long-range), and it is here that another problem arises with this model. If the O(1) site is occupied by both monovalent (F^-, OH^-) and divalent (O^{2-}) anions, the local configurations involving F^- and OH^- must have incident bond-valence sums close to 1 *vu*, and the local configurations involving O^{2-} must have incident bond-valence sums close to 2 *vu*. As the O(1) anion is bonded only to three *Y* cations (Table 6, Fig. 1), such local arrangements must involve short-range order of the *Y* cations.

Short-range order around O(1)

For the crystal of uvite examined here, the *Y* site is occupied by 1.70 Mg + 1.30 Al* (=Al+Cr^{3+}...) *apfu*, and hence there is potential for short-range ordering of Mg and Al, with such local configurations as 3*Y* = Al–Al–Al, Al–Al–Mg, Al–Mg–Mg and Mg–Mg–Mg.

The sum of the short-range configurations over the crystal must give the (long-range) site populations. Hence the local configurations around O(1) must sum to the *Y* site-population of 1.70Mg + 1.30Al*. We cannot uniquely decompose the observed *Y* site-population into local configurations. However, we note that the *Y* site-population is compatible with the local arrangements 3*Y* = Al–Al–Mg and Mg–Mg–Mg in the ratio 0.65:0.35. Moreover, this closely matches the O^{2-}:OH ratio of 0.69:0.31 at the O(1) site. This suggests that O(1) = O^{2-} is locally associated with 3*Y* = Al–Al–Mg, and O(1) = O^{2-} is locally associated with 3*Y* = Mg–Mg–Mg. Can these local arrangements provide the necessary incident bond-valence at the associated anions? The arrangement (Mg–Mg–Mg)–OH with a *Y*–O(1) bond-length of 2.096 Å would give an incident bond-valence sum of 1.00 *vu* at the O(1) anion. The arrangement (Al–Al–Mg)–O with bond valences of Al–O(1) = 0.73 *vu* (≡1.745 Å) and Mg–O(1) = 0.54 *vu* (≡1.873 Å) give an incident bond-valence sum of 2.00 *vu* at O(1) and a <*Y*–O(1)> distance of 1.788 Å for the Al–Al–Mg configuration. Thus the local configurations Al–Al–Mg and Mg–Mg–Mg can accommodate the short-range bond-valence requirements of O^{2-} and OH^-, respectively, at the O(1) site. The calculated <*Y*–O> distance, summed over all the short-range-ordered configurations in the crystal, is 1.788 × 0.65 + 2.096 × 0.35 = 1.942 Å. The observed *Y*–O(1) distance in this uvite is 1.949 Å (Table 3), in excellent agreement with these calculations.

We are now in a better position to examine the relationship between the bond-valence sum at O(1) and the aggregate formal charge of the anions occupying this position. For this crystal of uvite, the aggregate charge at O(1) is 1.69^-, and the incident bond-valence is 1.365 *vu*, a significant difference. However, the calculations given above show that the short-range-ordered configurations consistent with the observed site-populations at the *Y* site can give an incident bond-valence sum at O(1) in accord with the observed aggregate formal charge and site-population at O(1): 1.65 *vu versus* 1.69^- and O(1) = $0.69O^{2-} + 0.31(OH)$. The grand <*Y*–O(1)> distance for these configurations is 1.942 Å, which, if used for bond-valence calculation, would give an incident bond-valence sum at O(1) of 1.39 *vu*, similar to the value in Table 6. The difference in the two values, 1.65 *vu versus* 1.39 *vu*, arises from the fact that the bond-valence curves are concave (Brown & Shannon 1973) and an averaged bond-length does not give an averaged bond-valence. Usually, this is not a significant issue; however, in the present case, there is a large difference between the shortest Al–O bond-length and the longest Mg–O bond-length, and this nonlinear effect becomes significant. Hence it seems unlikely that the method of estimating the OH content of tourmaline suggested by Grice & Ercit (1993) will give accurate results, although it may be possible to modify this approach to take into account this nonlinear bond-valence effect.

CONCLUSIONS

1. In OH(+F)-deficient tourmaline, the assumption of OH + F = 4 anions *pfu* can produce extensive *apparent* vacancies at the *Y* site.
2. There is considerable Mg–Al disorder over the *Y* and *Z* sites in this crystal of OH-deficient uvite.
3. The site population of the O(1) site is $O^{2-}{}_{0.69}(OH)^-{}_{0.31}$.
4. Where O(1) = O^{2-}, local bond-valence requirements can be satisfied by bonding to 2Al (*Y*–O^{2-} ≈ 1.745 Å) and Mg (*Y*–O^{2-} ≈ 1.873 Å), giving a bond-valence sum of 2.0 *vu* incident at O(1) = O^{2-}.
5. Where O(1) = OH, local bond-valence requirements can be satisfied by bonding to 3 Mg (*Y*–OH ≈ 2.096 Å), giving a bond-valence sum of 1.0 *vu* incident at O(1).
6. The grand <*Y*–O(1)> distance, averaged over all the local configurations in this crystal, is 1.942 Å, in excellent agreement with the observed value of 1.949 Å, supporting the proposed scheme of short-range order proposed here.

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