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The Hydrogen Positions in Scorodite

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Abstract. $FeAsO_4.2H_2O$; a=8·937 (1), b=10·278 (2), c=9·996 (2) Å; *Pcab*; R=5·7% for 1216 observed reflexions. Location of the H positions discounts previous suggestions that scorodite and its isotypes contain the hydroxonium ion (H_3O^+).

Introduction. The refinement of the crystal structure of scorodite was undertaken in order to locate the H positions, as several workers (Mooney-Slater, 1961; Tarte & Paques-Ledent, 1968; Paques-Ledent & Tarte, 1968) have postulated the presence of the hydroxonium ion (H_3O^+) in scorodite and its isotypes. After this work was completed, a refinement of the scorodite structure was presented by Kitahama, Kiriyama & Baba (1975); however this study did not locate the H positions although on the basis of the H_2O–O distances, they assumed that the H atoms were present as H_2O molecules.

Single-crystal precession photographs confirmed the space group *Pcab* assigned by Kiriyama & Sakurai (1949). Cell dimensions were obtained by least-squares refinement of 15 reflexions automatically aligned on a four-circle diffractometer; the resultant cell volume agrees with that derived from a Type I stability diagram (Shannon & Prewitt, 1970) for the orthorhombic $M^{3+}AsO_4.2H_2O$ phases. 1521 intensities were collected according to the experimental method of Hawthorne & Ferguson (1975); standard data-reduction procedures (including absorption corrections) resulted in 1216 (4σ) observed reflexions.

With scattering factors for neutral atoms (Cromer & Mann, 1968) and anomalous dispersion corrections from Cromer & Liberman (1970), the refinement converged to R=5·9 and R_w=6·3%. Difference Fourier maps revealed two small maxima in the vicinity of each of the O*W* atoms; these were inserted as H positions (with isotropic temperature factors fixed at 1·5 Å^2) and refinement of all possible variables resulted in convergence at R and R_w values of 5·7 and 6·1% (observed) and 6·7 and 6·6% (all data). Final parameters are given in Table 1 and interatomic distances and angles are in Table 2.*

Discussion. It is well known that H positions derived from X-ray data contain a strong systematic error because of the delocalization of density along the O–H bond. Thus in the bond-strength table of scorodite (see Table 3), hydrogen-bond strengths were calculated by assigning sufficient bond strength to the acceptor anion to bring its sum to the ideal value of 2, with the remainder assigned to the donor anion. Hydrogen-bond strengths were calculated both for O*W*(1)=OH, O*W*(2)=H_3O^+ and for O*W*(1)=H_2O, O*W*(2)=H_2O; for the former model, the acceptor anions were those indicated by Mooney-Slater (1961), while for the second model O(1) was considered as an acceptor for O*W*(1). As is apparent from Table 3, the anion sums around O*W*(1) and O*W*(2) for the hydroxonium model are completely unsatisfactory (1·23 and 2·98) whereas those for the water model (2·10 and 2·10) correspond closely to the ideal value of 2·0. This confirms the result of the present refinement, *i.e.* that H is present as water molecules in scorodite, and further indicates that the presence of hydroxonium in the isotypes of scorodite is impossible. The IR spectra of the $M^{3+}X^{5+}O_4.2H_2O$ phases isotypic with scorodite (Tarte & Paques-Ledent, 1968; Paques-Ledent & Tarte, 1968)

Table 1. *Atomic parameters for scorodite* ($\beta_{ij}\times 10^4$)

	x	y	z	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0·1468 (1)	0·1269 (1)	0·1823 (1)	1·59 (2)	52 (1)	35 (1)	41 (1)	1 (1)	2 (1)	1 (1)
As	0·4646 (1)	0·1516 (1)	0·3636 (1)	1·42 (2)	45 (1)	32 (1)	37 (1)	0 (1)	1 (1)	1 (1)
O(1)	0·4955 (7)	0·3012 (6)	0·3044 (6)	1·83 (9)	64 (7)	34 (4)	50 (5)	−3 (5)	2 (5)	6 (4)
O(2)	0·5831 (7)	0·0508 (6)	0·2830 (6)	1·83 (9)	66 (7)	38 (5)	45 (5)	−2 (5)	16 (5)	0 (4)
O(3)	0·2859 (6)	0·1102 (6)	0·3329 (6)	2·02 (9)	45 (7)	62 (6)	51 (6)	−11 (5)	−8 (5)	3 (5)
O(4)	0·4951 (7)	0·1426 (6)	0·5293 (6)	1·84 (9)	54 (7)	52 (5)	41 (5)	3 (5)	−2 (5)	2 (4)
O*W*(1)	0·3282 (8)	0·5543 (7)	0·4305 (7)	2·35 (10)	81 (9)	60 (6)	48 (6)	5 (6)	−2 (6)	10 (5)
O*W*(2)	0·2277 (7)	0·8006 (6)	0·3836 (7)	1·98 (9)	53 (7)	44 (5)	60 (6)	0 (5)	−8 (5)	−1 (5)
H(1)	0·377 (12)	0·476 (11)	0·397 (11)	1·5						
H(2)	0·301 (12)	0·534 (11)	0·501 (12)	1·5						
H(3)	0·157 (12)	0·854 (10)	0·297 (11)	1·5						
H(4)	0·310 (12)	0·810 (11)	0·418 (11)	1·5						

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31830 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for scorodite*

As-O(1)	1·671 (6)	Fe-O(1)	1·965 (6)
As-O(2)	1·686 (6)	Fe-O(2)	1·944 (6)
As-O(3)	1·681 (6)	Fe-O(3)	1·960 (6)
As-O(4)	1·681 (6)	Fe-O(4)	1·993 (6)
Mean	1·680	Fe-O*W*(1)	2·111 (7)
		Fe-O*W*(2)	2·035 (6)
		Mean	2·001
As tetrahedron			
O(1)-O(2)	2·698 (8)	O(1)-As-O(2)	107·0 (3)
O(1)-O(3)	2·728 (8)	O(1)-As-O(3)	109·0 (3)
O(1)-O(4)	2·777 (8)	O(1)-As-O(4)	111·9 (3)
O(2)-O(3)	2·771 (8)	O(2)-As-O(3)	110·7 (3)
O(2)-O(4)	2·752 (8)	O(2)-As-O(4)	109·6 (3)
O(3)-O(4)	2·731 (8)	O(3)-As-O(4)	108·7 (3)
Mean	2·743	Mean	109·5
Fe octahedron			
O(1)—O(2)	2·820 (8)	O(1)—Fe-O(2)	92·3 (2)
O(1)—O(3)	2·765 (9)	O(1)—Fe-O(3)	89·5 (3)
O(1)—O(4)	2·811 (8)	O(1)—Fe-O(4)	90·5 (3)
O(1)—O*W*(2)	2·988 (9)	O(1)—Fe-O*W*(2)	96·6 (3)
O(2)—O(3)	2·714 (8)	O(2)—Fe-O(3)	88·1 (3)
O(2)—O(4)	2·821 (8)	O(2)—Fe-O(4)	91·5 (3)
O(2)—O*W*(1)	2·853 (9)	O(2)—Fe-O*W*(1)	89·3 (3)
O(3)—O*W*(1)	2·721 (9)	O(3)—Fe-O*W*(1)	83·8 (3)
O(3)—O*W*(2)	2·963 (9)	O(3)—Fe-O*W*(2)	95·7 (3)
O(4)—O*W*(1)	3·055 (9)	O(4)—Fe-O*W*(1)	96·2 (3)
O(4)—O*W*(2)	2·712 (8)	O(4)—Fe-O*W*(2)	84·7 (3)
O*W*(1)-O*W*(2)	2·726 (9)	O*W*(1)-Fe-O*W*(2)	82·2 (3)
Mean	2·829	Mean	90·0
Hydrogen bonds			
O*W*(1)-H(1)	0·97 (11)	O*W*(2)-H(3)	1·20 (11)
O*W*(1)-H(2)	0·77 (12)	O*W*(2)-H(4)	0·82 (11)
H(1)—H(2)	1·37 (15)	H(3)—H(4)	1·88 (14)
H(1)—O(1)	2·28 (12)	H(3)—O(2)	1·43 (11)
H(2)—O(3)	2·00 (12)	H(4)—O(4)	1·89 (11)
O*W*(1)-O(1)	3·255 (9)	O*W*(2)-O(2)	2·603 (9)
O*W*(1)-O(3)	2·639 (9)	O*W*(2)-O(4)	2·691 (9)
H(1)—O*W*(1)-H(2)	103 (10)	H(3)—O*W*(2)-H(4)	136 (9)
O*W*(1)-H(1)—O(1)	175 (9)	O*W*(2)-H(3)—O(2)	164 (9)
O*W*(1)-H(2)—O(3)	140 (12)	O*W*(2)-H(4)—O(4)	168 (11)

are characterized by a narrow absorption at ~3560 cm^{-1}, a rather wide diffuse band centred around 3000 cm^{-1} and a diffuse band between 1500 and 1700 cm^{-1}; these were interpreted respectively as an OH valence band, the symmetric and antisymmetric H_3O^+ valence bands and the H_3O antisymmetric deformation. As indicated above, the H is present as $2H_2O$ and this assignment is obviously incorrect. In scorodite and its isotypes, the symmetry of the water molecules is 1, and in particular O*W*(1) shows a large departure from the 2*mm* symmetry of free water. Thus the use of the conventional internal coordinates of H_2O becomes less useful, and it is much more convenient to use the internal coordinates outlined by Wallace (1975) for a triatomic molecule. Because the mass of the H atom is small when compared to that of O, coupling is small and it is possible to associate a specific IR peak with a specific bond stretching. On the basis of the structure presented here, the IR spectra may be interpreted more satisfactorily as follows:

(i) 3650 cm^{-1}:	O*W*(1)-H(1) stretching band;
(ii) 2900–3400 cm^{-1}:	overlap of O*W*(1)-H(2), O*W*(2)-H(3) and O*W*(2)-H(4) stretching bands;
(iii) 1500–1700 cm^{-1}:	overlap of H_2O bending modes from both molecules.

This is more satisfactory than the previous assignment as there is no peak at ~1100 cm^{-1} corresponding to the prominent H_3O parallel bending vibration (Ferrisco & Hornig, 1955).

Table 3. *Bond-strength table for scorodite*

The upper entries correspond to O*W*(1)=OH, O*W*(2)=H_3O; the lower entries correspond to O*W*(1)=H_2O, O*W*(2)=H_2O.

	Fe*	As*	H(1)	H(2)	H(3)	H(4)	Σ
O(1)	0·569	1·304	0·127 0·127				2·000
O(2)	0·601	1·236			0·163 0·163		2·000
O(3)	0·577	1·258		0·165 0·165			2·000
O(4)	0·529	1·258				0·123 0·123	2·000
O*W*(1)	0·394		— 0·873	0·835 0·835			1·229 2·102
O*W*(2)	0·476		0·873 —		0·837 0·837	0·787 0·787	2·976 2·100

* Bond strengths calculated from the universal curves of Brown & Shannon (1973).

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