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The Crystal Structure of Ludlamite

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The crystal structure of ludlamite, $Fe_3(PO_4)_2.4H_2O$, has been restudied by means of the double Fourier-series method. In the revised structure we may conceive an $Fe_3O_8(H_2O)_6$ group consisting of three octahedra of oxygen atoms and water molecules around an iron atom, joined by sharing the O–H_2O edges. Such groups are linked to each other in the directions of the a and b axes by phosphorus atoms situated at the centres of oxygen tetrahedra, and in the direction of the c axis by the shared water molecules. The difference in cohesive properties of vivianite, $Fe_3(PO_4)_2.8H_2O$, and ludlamite is explained in terms of their structures.

Introduction

Recently we have analysed the crystal structure of vivianite, $Fe_3(PO_4)_2.8H_2O$, and found that in it the H_2O–H_2O bonds, though weak enough to give rise to perfect cleavage across them, are well stabilized on account of the polarized state of the molecules (Mori & Ito, 1950). In ludlamite, whose structure, too, has been worked out (Ito, 1950, p. 168), the bonds responsible for the perfect cleavage appear to be quite different in spite of its similar chemical composition, $Fe_3(PO_4)_2.4H_2O$ (Wolfe, 1949). In order to compare the structures of these closely related minerals and to contribute to our knowledge of the function of water in crystals, we have decided to refine the atomic parameters of ludlamite by means of Fourier analysis. In our original analysis of this structure by the trial-and-error method we may not have attained the same degree of accuracy as in that of vivianite.

Experimental

The crystal constants redetermined on the specimens from Ashio, Japan (P_2O_5 32·22 %, As_2O_5 0·16 %, Fe_2O_3 0·66 %, FeO 50·81 %, MgO 0·12 %, CaO 0·10 %, H_2O 15·77 %, total 99·84 %; analysis by H. Minato) are as follows:

$$a = 10{\cdot}45 \pm 0{\cdot}02,\quad b = 4{\cdot}65 \pm 0{\cdot}01,\quad c = 9{\cdot}25 \pm 0{\cdot}02\ \text{A}.$$

(rotation photographs, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71$ A.);

$$\beta = 100^\circ\ 30' \pm 10'$$

(Weissenberg photographs, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71$ A.). There are two molecules of $Fe_3(PO_4)_2.4H_2O$ per cell. The specific gravity is 3·01, as measured by H. Minato and by T. Sameshima, compared with the calculated value 3·21. The space group is C_{2h}^5–$P2_1/a$.

We have re-examined the $a(0)$-, $b(0)$- and $b(1)$-Weissenberg–Buerger photographs (Mo $K\alpha$) used in the previous study. The intensities visually estimated were converted into a set of arbitrary numbers ((205)-reflexion = 1000) from which relative F values were derived by extracting the square roots and multiplying by the polarization, Lorentz and Debye–Waller ($B = 1$) factors. These relative F values were then reduced by multiplying by a proportionality factor (namely 8·80) which made the F values of the strong reflexions (denoted by an asterisk in Table 2) as a whole as near as possible to those calculated. In this way absolute values suitable for Fourier synthesis were obtained. In scaling the intensities we took advantage of the 5 : 1 intensity ratio of Mo $K\alpha$ and $K\beta$ radiations.

Fourier synthesis

We started the xz synthesis with the atomic parameters given in the previous paper (Ito, 1950, p. 168). Summation was made using the 175 ($h0l$) terms available and covering the unit cell at 60 × 60 evaluated points. Though the contour lines first obtained in (010) projection revealed that some of the peaks were somewhat widely displaced from those anticipated by the trial-and-error method, we were able, nevertheless, to apply the usual procedure of successive approximation, and obtained in the fifth synthesis a satisfactorily defined electron-density map, from which the final x and z parameters were read off. Further, we carried out the yz synthesis (65 ($0kl$) terms, 60 × 60 evaluated points per unit cell) after the y parameters had been so chosen that they, together with the x and z parameters now known, would give as regular a configuration as possible of oxygen atoms and water molecules around phosphorus and iron atoms. As this projection endorsed completely the y parameters thus determined, no further adjustment of atomic positions was necessary. The final parameters are given in Table 1. Table 2

Table 1. *Atomic co-ordinates*

Atom	No. of equiv. atoms in the unit cell	x/a	y/b	z/c
Fe_{I}	2	0	0	0
Fe_{II}	4	0·170	0·08	0·328
P	4	0·455	0·96	0·233
O_{I}	4	0·036	0·82	0·198
O_{II}	4	0·408	0·19	0·102
O_{III}	4	0·325	0·86	0·290
O_{IV}	4	0·035	0·38	0·360
$(H_2O)_{I}$	4	0·162	0·27	0·112
$(H_2O)_{II}$	4	0·332	0·38	0·446

Table 2. *Observed and calculated structure amplitudes*

hkl	F_o	F_c
004	10	9
005	17	−15
006	34	44
007	13	−8
008	—	3
009*	77	78
0,0,10	—	9
0,0,11	—	−9
0,0,12	25	30
0,0,13	—	12
0,0,14	—	−6
204	13	4
205*	124	149
206	13	−12
207	30	−47
208	55	61
209	18	21
2,0,10	—	−7
2,0,11	25	25
2,0,12	—	6
2,0,13	—	−1
2,0,14	23	27
401*	94	88
402	19	22
403	—	0
404*	111	93
405	45	39
406	13	9
407	12	6
408	—	−7
409	—	5
4,0,10	31	44
4,0,11	—	−1
4,0,12	—	−11
4,0,13	24	30
600*	108	114
601	21	−10
602	—	6
603	51	47
604	—	−5
605	24	20
606	49	55
607	—	−3
608	—	−12
609	31	42
6,0,10	—	13
6,0,11	—	−5
6,0,12	—	11
800	60	−38
801	9	7
802	57	62
803	24	−20
804	—	−22
805	63	68
806	—	9
807	—	−1
808	22	33
809	—	2
8,0,10	—	4
8,0,11	—	22
10,0,0	19	−17
10,0,1	40	41
10,0,2	23	22
10,0,3	—	3
10,0,4	23	29
10,0,5	—	−8
10,0,6	—	10
10,0,7	23	33
10,0,8	—	−5
10,0,9	—	−6
10,0,10	19	29
12,0,0	25	32
12,0,1	10	−7
12,0,2	25	22
12,0,3	31	41
12,0,4	—	−9
12,0,5	—	−10
12,0,6	20	27
12,0,7	—	9
12,0,8	—	−3
12,0,9	—	15
14,0,0	21	−14
14,0,1	—	−1
14,0,2	25	32
14,0,3	—	5
14,0,4	—	0
14,0,5	13	18
14,0,6	—	5
$20\bar{4}$*	96	108
$20\bar{5}$	—	7
$20\bar{6}$	18	−1
$20\bar{7}$	23	31
$20\bar{8}$	24	30
$20\bar{9}$	—	5
$2,0,\overline{10}$	25	31
$2,0,\overline{11}$	—	4
$2,0,\overline{12}$	—	1
$2,0,\overline{13}$	24	33
$2,0,\overline{14}$	—	1
$40\bar{1}$	25	−13
$40\bar{2}$	15	−1
$40\bar{3}$	15	23
$40\bar{4}$	12	4
$40\bar{5}$*	110	101
$40\bar{6}$	12	15
$40\bar{7}$	19	8
$40\bar{8}$	62	78
$40\bar{9}$	—	2
$4,0,\overline{10}$	25	−33
$4,0,\overline{11}$	25	34
$4,0,\overline{12}$	14	23
$4,0,\overline{13}$	14	−11
$60\bar{1}$	—	−23
$60\bar{2}$	17	−17
$60\bar{3}$*	116	112
$60\bar{4}$	27	16
$60\bar{5}$	58	−50
$60\bar{6}$	73	69
$60\bar{7}$	39	43
$60\bar{8}$	—	−12
$60\bar{9}$	23	35
$6,0,\overline{10}$	—	−3
$6,0,\overline{11}$	—	1
$6,0,\overline{12}$	25	37
$80\bar{1}$	66	66
$80\bar{2}$	60	45
$80\bar{3}$	23	26
$80\bar{4}$	52	56
$80\bar{5}$	—	−20
$80\bar{6}$	—	3
$80\bar{7}$	55	50
$80\bar{8}$	—	5
$80\bar{9}$	30	−26
$8,0,\overline{10}$	31	29
$8,0,\overline{11}$	18	23
$10,0,\bar{1}$	16	4
$10,0,\bar{2}$	63	59
$10,0,\bar{3}$	16	23
$10,0,\bar{4}$	28	−22
$10,0,\bar{5}$	29	31
$10,0,\bar{6}$	23	25
$10,0,\bar{7}$	—	10
$10,0,\bar{8}$	25	31
$10,0,\bar{9}$	—	−3
$10,0,\overline{10}$	—	−8
$12,0,\bar{1}$	21	9
$12,0,\bar{2}$	14	8
$12,0,\bar{3}$	24	36
$12,0,\bar{4}$	—	−8
$12,0,\bar{5}$	25	−24
$12,0,\bar{6}$	33	46
$12,0,\bar{7}$	23	26
$12,0,\bar{8}$	22	−18
$12,0,\bar{9}$	21	25
$14,0,\bar{1}$	25	38
$14,0,\bar{2}$	20	18
$14,0,\bar{3}$	14	−15
$14,0,\bar{4}$	—	21
$14,0,\bar{5}$	—	9
$14,0,\bar{6}$	—	3
013	87	−91
014	42	−41
015	28	35
016	18	25
017	—	−3
018	24	25
019	—	−2
0,1,10	17	−15
0,1,11	—	11
0,1,12	—	−3
020	65	51
021	19	−12
022	—	−10
023	86	72
024	54	57
025	21	34
026	32	34
027	—	2
028	—	13
029	31	35
0,2,10	—	−3
0,2,11	—	−10
0,2,12	19	25
031	34	−23
032	62	69
033	—	−14
034	22	−31
035	33	42
036	—	3
037	44	−49
038	17	12
039	—	10
0,3,10	13	−13
0,3,11	—	14
040	—	−2
041	32	47
042	21	21
043	19	−8
044	28	28
045	24	25
046	—	−6
047	—	10
048	19	29
049	—	9

* See text.

Table 2 (*cont.*)

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
114	50	−48	610	—	−13	$21\bar{5}$	16	22
115	49	36	611	18	−11	$21\bar{6}$	—	− 6
116	82	69	612	20	21	$21\bar{7}$	—	−12
117	15	12	613	26	−21	$21\bar{8}$	—	15
118	16	7	614	—	− 1	$21\bar{9}$	—	− 4
119	26	28	615	15	16	$2,1,\overline{10}$	—	−12
1,1,10	—	− 5	616	—	6	$2,1,\overline{11}$	—	16
1,1,11	18	23	617	—	−11			
			618	—	9	$31\bar{3}$	39	−42
213	62	−60	619	—	− 3	$31\bar{4}$	33	26
214	—	− 6				$31\bar{5}$	86	62
215	19	24	710	58	55	$31\bar{6}$	—	7
216	—	−17	711	38	−42	$31\bar{7}$	21	30
217	—	15	712	38	28	$31\bar{8}$	—	19
218	—	−13	713	61	70	$31\bar{9}$	19	20
219	—	−13	714	—	− 3	$3,1,\overline{10}$	41	41
2,1,10	—	15	715	15	21	$3,1,\overline{11}$	23	33
2,1,11	—	5	716	—	16			
			717	—	− 7	$41\bar{1}$	—	− 4
312	47	32	718	26	30	$41\bar{2}$	71	−56
313	19	9	719	19	27	$41\bar{3}$	—	1
314	48	48				$41\bar{4}$	—	−20
315	19	10	810	30	−32	$41\bar{5}$	36	−35
316	—	− 9	811	—	3	$41\bar{6}$	—	26
317	55	55	812	—	0	$41\bar{7}$	—	− 2
318	36	39	813	—	− 8	$41\bar{8}$	—	2
319	22	−25	814	17	24	$41\bar{9}$	16	18
3,1,10	22	19	815	—	9	$4,1,\overline{10}$	—	1
			816	—	− 7			
410	81	56	817	—	12	$51\bar{1}$	—	9
411	62	61	818	—	− 9	$51\bar{2}$	95	83
412	17	− 8				$51\bar{3}$	41	25
413	28	24	910	—	3	$51\bar{4}$	51	52
414	20	−17	911	36	34	$51\bar{5}$	65	67
415	21	−36	912	—	3	$51\bar{6}$	61	57
416	—	10	913	—	3	$51\bar{7}$	25	−21
417	16	16	914	41	49	$51\bar{8}$	—	0
418	22	−26	915	—	−22	$51\bar{9}$	58	45
419	—	7	916	—	−23	$5,1,\overline{10}$	—	8
4,1,10	—	18	917	—	17			
						$61\bar{1}$	20	31
510	86	58	$11\bar{4}$	70	70	$61\bar{2}$	20	−20
511	33	28	$11\bar{5}$	18	−22	$61\bar{3}$	—	−11
512	22	−26	$11\bar{6}$	64	72	$61\bar{4}$	23	11
513	67	59	$11\bar{7}$	53	59	$61\bar{5}$	—	− 3
514	64	69	$11\bar{8}$	39	−34	$61\bar{6}$	—	1
515	47	43	$11\bar{9}$	—	9	$61\bar{7}$	—	17
516	21	25	$1,1,\overline{10}$	50	43	$61\bar{8}$	28	−23
517	40	46	$1,1,\overline{11}$	—	3	$61\bar{9}$	—	0
518	—	1				$6,1,\overline{10}$	18	22
519	16	18	$21\bar{4}$	21	30			
5,1,10	—	15						

compares the observed F values with those calculated on the basis of the revised structure using the atomic f values given by Bragg & West (1928) with that for phosphorus derived by interpolation. The value of $R=\Sigma||F_o|-|F_c||\div\Sigma|F_o|$ is 0·36 for the 344 reflexions (both present and absent) considered.

The structure originally described is supported in its most essential features by the present revision, although the interpretation of the results has to be considerably modified owing principally to a change in the positions of phosphorus atoms.

The revised structure described

The revised structure of ludlamite, projected on (010) and on a plane normal to the a axis, is shown in Fig. 1. Fig. 2 gives the corresponding Fourier projections of electron density.

The structure consists of octahedra of oxygen and water around iron, and tetrahedra of oxygen around phosphorus. An Fe–O–H_2O octahedron is united with two others each sharing an O–H_2O edge (Fig. 3). This triple octahedral group, $Fe_3O_8(H_2O)_6$, is in its turn joined to the identical ones in the a and b directions by phosphorus atoms. In the c direction linkage is through water molecules, which are each shared by two of the groups at their extreme octahedral corners. The P–O tetrahedra and Fe–O–H_2O octahedra, it is to be further noted, share only the oxygen corners. In this arrangement the surroundings of oxygen atoms and water molecules are as follows: Each oxygen atom is between one phosphorus and one iron atom, or one phosphorus and two iron atoms, the former oxygen atom being further co-ordinated by one or two water molecules, the latter by one water molecule. Each water molecule is between two iron and one oxygen atoms, with one or two more oxygen atoms, as the second nearest neighbours, exerting a slight bond towards it. Shortening of the O–H_2O distances which occur along these bonds (as well as that of the shared O–H_2O edges of the Fe–O–H_2O octahedra) may be of some significance. The balance of valency is illustrated in Fig. 4 and the interatomic distances are given in Table 3.

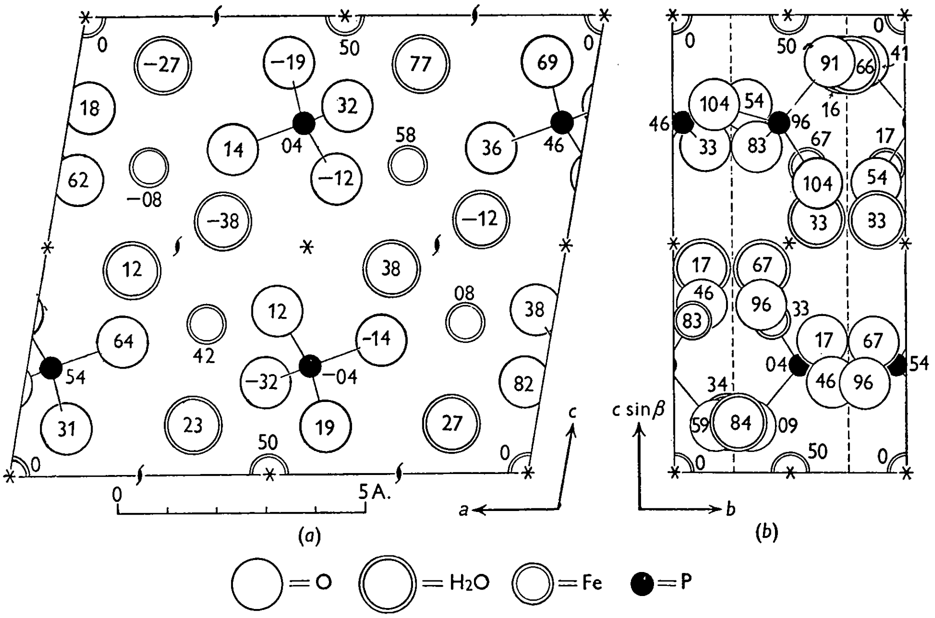

Fig. 1. The structure of ludlamite. (*a*) Projection on (010). Numbers give the height of each atom expressed as a percentage of the *b* translation (4·65 A.). (*b*) Projection on a plane perpendicular to the *a* axis. Numbers give the height of each atom (from $(100)_0$) expressed as a percentage of the *a* translation (10·45 A.).

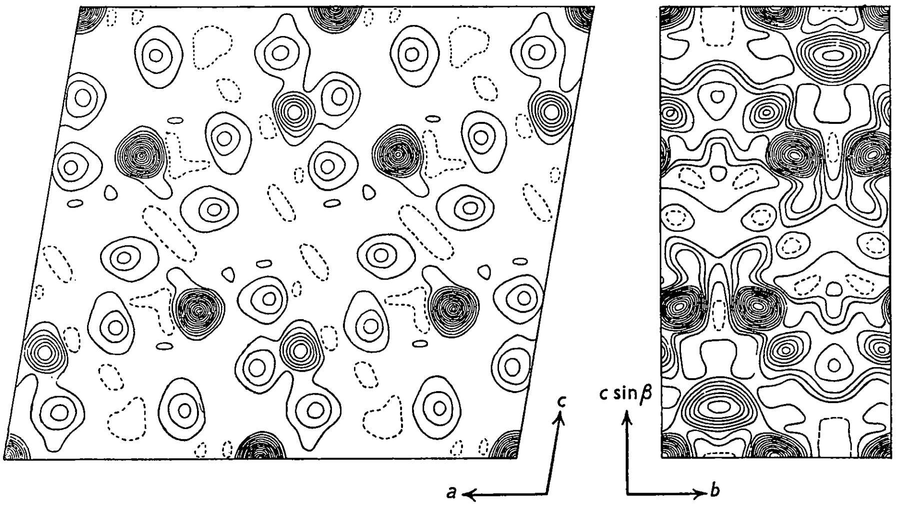

Fig. 2. Fourier projections of electron density corresponding to Fig. 1. Contours at intervals of 4 e.A.$^{-2}$, the zero-electron lines being broken.

Comparison with vivianite

The structures of vivianite and ludlamite are very similar, the co-ordination of oxygen atoms and water molecules around iron and phosphorus atoms being almost identical in shape and character. In vivianite there are separate single and double octahedral groups, $FeO_2(H_2O)_4$ and $Fe_2O_6(H_2O)_4$, and it is phosphorus atoms which unite them to build up a band. Likewise, in ludlamite, we can conceive of the triple octahedral groups that play a similar part in the structure passing into a band bound together by phosphorus. The concept of a band, however, is here rather artificially extended for comparison, for the parallel bands, as described above, are further linked to each other by the shared water molecules and not by such weak bonds as the H_2O–H_2O bonds in vivianite. The (001) cleavage of ludlamite, which presumably takes place through these water molecules and is a little less perfect than (010) cleavage of vivianite, seems therefore to be due to the mode of linkage of the phosphorus atoms; they exercise attractive forces in the *a* and *b* directions but not in the *c* direction, and are stronger in linkage than the water molecules. The difference in hardness between vivianite (H = 2·0) and ludlamite (H = 3·5) may also be accounted for similarly.

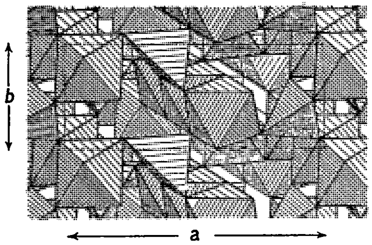

Fig. 3. The structure of ludlamite shown as linked polyhedra of oxygen atoms, or oxygen atoms and water molecules, around phosphorus and iron atoms, as viewed from a direction nearly parallel to the *c* axis. Note that Fe–O–H_2O octahedra are joined together to form a triple group, $Fe_3O_8(H_2O)_6$, which is linked to the neighbouring ones in the *a* and *b* directions by phosphorus atoms, situated at the centres of the oxygen tetrahedra, and in the *c* direction by the shared water molecules.

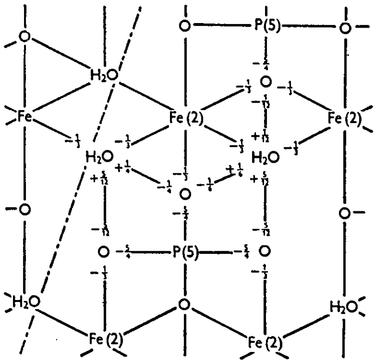

Fig. 4. The electrostatic balance in the structure of ludlamite. Note that some of the lines indicating bonds are referred to atoms above or below the ones designated. The broken line traces the plane on which the bonds presumably break to give rise to the perfect cleavage.

Table 3. *Interatomic distances*

Atom	Neighbour	Distance (A.)	Atom	Neighbour	Distance (A.)	Atom	Neighbour	Distance (A.)
$\mathrm{Fe_{I}}$	$\mathrm{O}_{\mathrm{I}}^{*}$ (2)	1·99	$\mathrm{O_{I}}$	$\mathrm{O_{II}}$	2·73	$\mathrm{O_{III}}$	$\mathrm{O_{IV}}$	2·49
	$\mathrm{O_{II}}$ (2)	2·10		$\mathrm{O}_{\mathrm{II}}^{*}$	2·74		$(\mathrm{H_2O})_{\mathrm{I'}}$	2·87
	$(\mathrm{H_2O})_{\mathrm{I}}$ (2)	2·17		$\mathrm{O_{III}}$	2·64		$(\mathrm{H_2O})_{\mathrm{II''}}$	2·72
$\mathrm{Fe_{II}}$	$\mathrm{O}_{\mathrm{I}}^{*}$	2·05		$\mathrm{O_{III'}}$	2·99		$(\mathrm{H_2O})_{\mathrm{II''}}^{*}$	2·65
	$\mathrm{O_{III}}$	2·01		$\mathrm{O_{IV}}$	2·54		$(\mathrm{H_2O})_{\mathrm{II'''}}$	3·14
	$\mathrm{O_{IV}}$	2·04		$\mathrm{O}_{\mathrm{IV}}^{*}$	3·00	$\mathrm{O_{IV}}$	$(\mathrm{H_2O})_{\mathrm{I}}$	2·87
	$(\mathrm{H_2O})_{\mathrm{I}}$	2·18		$(\mathrm{H_2O})_{\mathrm{I}}^{*}$	2·66		$(\mathrm{H_2O})_{\mathrm{II}}$	3·05
	$(\mathrm{H_2O})_{\mathrm{II}}$	2·30		$(\mathrm{H_2O})_{\mathrm{I}}$	3·04		$(\mathrm{H_2O})_{\mathrm{II'}}$	3·07
	$(\mathrm{H_2O})_{\mathrm{II'}}$	2·29		$(\mathrm{H_2O})_{\mathrm{II'}}$	3·21		$(\mathrm{H_2O})_{\mathrm{II'}}^{*}$	3·07
P	$\mathrm{O_{I}}$	1·61	$\mathrm{O_{II}}$	$\mathrm{O_{III}}$	2·56		$(\mathrm{H_2O})_{\mathrm{II''}}$	2·66
	$\mathrm{O}_{\mathrm{II}}^{*}$	1·60		$\mathrm{O_{IV}}$	2·53	$(\mathrm{H_2O})_{\mathrm{I}}$	$(\mathrm{H_2O})_{\mathrm{II}}$	3·26
	$\mathrm{O_{III}}$	1·60		$(\mathrm{H_2O})_{\mathrm{I}}$	2·67	$(\mathrm{H_2O})_{\mathrm{II}}$	$(\mathrm{H_2O})_{\mathrm{II'}}$	3·11
	$\mathrm{O}_{\mathrm{IV}}^{*}$	1·51		$(\mathrm{H_2O})_{\mathrm{I'}}$	3·45			
				$(\mathrm{H_2O})_{\mathrm{I}}^{*}$	2·75			
				$(\mathrm{H_2O})_{\mathrm{I''}}$	2·64			

Primes denote equivalent atoms and asterisks those in the neighbouring cell.

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