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The Structure of Vivianite and Symplesite

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The crystal structure of vivianite, $Fe_3(PO_4)_2.8H_2O$, and symplesite, $Fe_3(AsO_4).8H_2O$, has been determined using Weissenberg and oscillation photographs (Mo $K\alpha$, $\lambda = 0{\cdot}710$ A.). The unit cells have dimensions:

Vivianite $a = 10{\cdot}08$, $b = 13{\cdot}43$, $c = 4{\cdot}70$ A., $\beta = 104°\ 30'$,

Symplesite $a = 10{\cdot}25$, $b = 13{\cdot}48$, $c = 4{\cdot}71$ A., $\beta = 103°\ 50'$,

with two molecules in each cell. The space group is C_2^3h–$C2/m$. The structure is built up of single and double octahedral groups of oxygen and H_2O around Fe. The double group, $Fe_2O_6(H_2O)_4$, is linked to two neighbouring similar groups and four other single groups, $FeO_2(H_2O)_4$, by P (or As) which is in the middle of a tetrahedron of oxygen, forming a complex band extended parallel to (010). Parallel bands are held to each other by H_2O molecules which, lying on both sides of the band, are again grouped together tetrahedrally. The electrostatic balance of the component atoms and atom groups are almost ideally maintained.

Introduction

Vivianite and symplesite belong to the group of minerals whose chemical composition is expressed by the formula $A_3(XO_4)_2.8H_2O$, where A is Mg, Zn, Ni, Co or Fe and X is P or As. They are all similar crystallographically, but isomorphous replacement is rather rare. We present in the following the result of a study undertaken to find the structural type of this well-defined mineral family.

Experimental

The vivianite and symplesite crystals used were respectively from Ashio and Kiura, Japan. They were both slender prisms about 5 mm. in length. A number of Weissenberg–Buerger as well as oscillation photographs were taken (Mo $K\alpha$, $\lambda = 0{\cdot}710$ A.). In view of strong absorption care was taken in estimating intensities of reflexions, comparing visually only adjacent spots in the photographs.

Unit cell and space group

The dimensions of the unit cells measured in the photographs are as follows:

	a	b	c	β
Vivianite	10·08 A.	13·43 A.	4·70 A.	104° 30′
Symplesite	10·25 A.	13·48 A.	4·71 A.	103° 50′

There are two molecules respectively of $Fe_3(PO_4)_2.8H_2O$ and $Fe_3(AsO_4)_2.8H_2O$ in the cell.

The space group C_2^3h–$C2/m$ of vivianite has been determined by Barth (1937) and by Takané & Omori (1936*a*, *b*). We have found the same group also for symplesite.

Analysis

The general trends of X-ray spectra of the two minerals are, except for minor differences, very similar and suggest that their structures may be based on the same general plan. We have observed, further, regularities of spectra which provided a clue to their structure, certain strong or weak reflexions occurring invariably in pairs. $(3n.k.0)$ reflexions $(n = 0, 2, 4, \ldots)$ are strong when $k = 8m$ or $8m+2$, and weak when $k = 8m+4$ or $8m+6$ $(m = 0, 1, 2, \ldots)$; and $(3n.k.0)$ reflexions $(n = 1, 3, 5, \ldots)$ are strong when $k = 8m+3$ or $8m+5$, and weak when $k = 8m+1$ or $8m+7$ $(m = 0, 1, 2, \ldots)$ (see Table 2). This would be roughly explained by placing one of the heavy atoms, say A, at $\frac{1}{3}, 0, z$ and the other, say B, at $0, \frac{2}{3}, 0$. Similar regularities found regarding $(hk1)$ and $(hk\bar{1})$ reflexions further narrow down the range of the z parameter of A atom to around $\frac{1}{3}$.

Out of six Fe in the cell we may accordingly place two at the centres of symmetry, 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, 0$, and the remaining four Fe and four P (or As) either in the A or B positions. A preliminary calculation indicated

Table 1. *Co-ordinates of atoms in symplesite*

(These co-ordinates are applicable also to the structure of vivianite to a first approximation.)

Atom	No. of equiv. points	x/a	y/b	z/c
Fe_I	2	0	0	0
Fe_{II}	4	0	0·390	0
As (or P)	4	0·315	0	0·410
O_I	4	0·155	0	0·350
O_{II}	4	0·400	0	0·750
O_{III}	8	0·365	0·100	0·245
$(H_2O)_I$	8	0·085	0·110	0·820
$(H_2O)_{II}$	8	0·400	0·220	0·750

Table 2. *Intensity of X-ray spectra of vivianite and symplesite*

Intensities were estimated visually in Weissenberg–Buerger photographs (Mo $K\alpha$ radiation; camera radius 34·1 mm.; coupling 1 mm. to 1°). $Q=(4\sin^2\theta)/\lambda^2$, where θ is Bragg angle and $\lambda=0{\cdot}710$ A. Q values are given only for symplesite.

(*a*) Symplesite and vivianite. Rotation axis [001]; zero level

	Symplesite			Vivianite	
hkl	$Q\times10^4$	$I_{obs.}$	$F_{calc.}$	$I_{obs.}$	$F_{calc.}$
060	1981	*m*	56	—	−3
080	3522	*vvs*	230	*vs*	177
0.10.0	5503	*vs*	218	*vs*	174
0.12.0	7924	*mw*	76	*w*	37
0.14.0	10786	*w*	45	—	9
0.16.0	14088	*ms*	71	*w*	38
0.18.0	17830	*ms*	129	*m*	98
0.20.0	22012	*w*	82	*w*	54
150	1477	—	21	*m*	47
170	2797	—	26	*mw*	47
190	4558	*m*	−75	*mw*	−56
1.11.0	6759	—	−10	—	6
1.13.0	9401	—	24	*vw*	25
1.15.0	12483	—	26	*w*	40
260	2384	*mw*	−81	*w*	−41
280	3925	—	27	*m*	61
2.10.0	5906	—	30	*mw*	60
2.12.0	8328	*vw*	−47	*vw*	−21
2.14.0	11189	*vw*	−65	*w*	−41
2.16.0	14491	—	−18	—	4
330	1403	*s*	134	*s*	72
350	2284	*s*	153	*s*	98
370	3605	*mw*	78	*vw*	31
390	5366	*w*	53	—	12
3.11.0	7567	*mw*	77	*w*	40
3.13.0	10208	*m*	117	*m*	84
3.15.0	13290	*w*	87	*w*	55
400	1613	*w*	−47	*w*	−42
420	1833	—	23	*w*	27
440	2495	—	−36	*vw*	−32
460	3594	—	14	—	16
480	5135	—	30	*vw*	31
4.10.0	7116	—	16	—	19
4.12.0	9537	—	−5	—	−4
510	2575	*s*	−117	*m*	−68
530	3015	—	−4	*m*	44
550	3896	*mw*	64	*s*	108
570	5217	*w*	−67	*vw*	−27
590	6977	*w*	−64	*w*	−34
5.11.0	9179	*vw*	−46	—	−13
5.13.0	11820	—	30	*w*	61
5.15.0	14902	—	−3	—	25
600	3629	*s*	110	*s*	72
620	3849	*s*	124	*s*	87
640	4509	—	42	—	6
660	5610	*mw*	73	—	39
680	7151	*m*	108	*m*	73
6.10.0	9132	*mw*	97	*m*	70
6.12.0	11553	—	61	*w*	35
6.14.0	14415	—	26	—	1
710	4994	—	−7	—	−19
730	5435	*m*	101	*ms*	88
750	6315	*ms*	146	*s*	124
770	7636	—	46	*w*	35
790	9397	—	5	—	−5
7.11.0	11598	—	25	—	15
7.13.0	14249	*w*	88	*mw*	80
7.15.0	17321	*vw*	67	*w*	58

Table 2(*a*) (*cont.*)

	Symplesite			Vivianite	
hkl	$Q \times 10^4$	$I_{obs.}$	$F_{calc.}$	$I_{obs.}$	$F_{calc.}$
800	6451	—	29	*m*	70
820	6671	—	−33	—	7
840	7332	*mw*	−90	*w*	−49
860	8432	*w*	−75	*vw*	−36
880	9973	—	−1	*vw*	32
8.10.0	11954	—	8	*w*	42
8.12.0	13110	*vw*	−47	—	−15
910	8220	—	2	—	−18
930	8660	*w*	77	*w*	58
950	9541	*w*	85	*vw*	65
970	10861	*vw*	49	—	31
990	12622	—	−12	—	−30
9.11.0	14823	*vw*	34	—	17
9.13.0	17465	*vw*	70	*vw*	55
10.0.0	10080	*m*	124	*ms*	103
10.2.0	10300	*vw*	58	*vw*	34
10.4.0	11680	—	22	—	1
10.6.0	12781	—	28	—	8
10.8.0	14322	*w*	87	*mw*	68
10.10.0	16303	*vw*	86	*w*	68
11.1.0	12252	*vw*	−61	—	−27
11.3.0	12692	—	−23	—	10
11.5.0	13573	—	−25	—	7
11.7.0	14893	—	−37	—	−6
11.9.0	16654	*w*	−87	*vw*	−57
11.11.0	18855	—	−32	—	−1
12.0.0	14515	*w*	58	*w*	52
12.2.0	14735	*vw*	37	—	31
13.1.0	17090	—	43	—	18
13.3.0	17531	*w*	79	*w*	54

(*b*) Symplesite. Rotation axis [001]; 1st level

hkl	$Q \times 10^4$	$I_{obs.}$	$F_{calc.}$	*hkl*	$Q \times 10^4$	$I_{obs.}$	$F_{calc.}$
061	2459	*ms*	−129	481	6033	—	42
081	4000	*w*	7	4.10.1	8014	—	36
0.10.1	5981	—	12	4.12.1	10435	—	−22
0.12.1	8402	*m*	−58				
0.14.1	11264	*m*	−81	531	4018	*s*	141
0.16.1	14566	—	−27	551	4899	*s*	146
				571	6220	*m*	92
151	2060	*m*	59	591	7980	*w*	60
171	3380	*vw*	24	5.11.1	10182	*mw*	80
191	5141	*vw*	−28	5.13.1	12823	*mw*	120
1.11.1	7342	—	−15				
1.13.1	9984	*w*	39	661	6788	*vw*	−32
1.15.1	13066	—	43	681	8329	*w*	34
241	1972	*m*	−73	$\bar{1}51$	1850	*vs*	172
261	3072	*w*	−5	$\bar{1}71$	3170	*s*	89
281	4613	*s*	155	$\bar{1}91$	4931	*w*	32
2.10.1	6594	*ms*	153	$\bar{1}.11.1$	7132	*s*	83
2.12.1	9016	*vw*	63	$\bar{1}.13.1$	9774	*s*	121
2.14.1	11877	*vw*	1	$\bar{1}.15.1$	12856	*mw*	80
2.16.1	15179	*m*	70				
2.18.1	18921	*m*	95	$\bar{2}61$	2652	*w*	60
				$\bar{2}81$	4193	*mw*	96
331	2196	—	3	$\bar{2}.10.1$	6174	*w*	79
351	3077	*w*	28	$\bar{2}.12.1$	8096	—	8
371	4398	—	12				
391	6159	—	29	$\bar{3}31$	1566	—	8
3.11.1	8360	—	28	$\bar{3}51$	2447	—	40
3.13.1	11001	—	16	$\bar{3}71$	3768	*w*	−85
3.15.1	14083	—	18	$\bar{3}91$	5529	*ms*	−130
				$\bar{3}.11.1$	7730	—	−42
441	3391	*mw*	−86	$\bar{3}.13.1$	10371	—	24
461	4492	—	−55				

Table 2 (*b*) (*cont.*)

hkl	$Q \times 10^4$	$I_{obs.}$	$F_{calc.}$	*hkl*	$Q \times 10^4$	$I_{obs.}$	$F_{calc.}$
$\bar{4}01$	1671	*vs*	162	$\bar{6}61$	5459	*m*	−121
$\bar{4}21$	1891	*s*	85	$\bar{6}81$	7000	—	−19
$\bar{4}41$	2551	*ms*	80	$\bar{6}.10.1$	8981	—	−4
$\bar{4}61$	3652	*w*	49	$\bar{6}.12.1$	11402	*vw*	−55
$\bar{4}81$	5193	*ms*	102				
$\bar{4}.10.1$	7174	*m*	100	$\bar{7}11$	4738	*w*	26
$\bar{4}.12.1$	9595	*vw*	44	$\bar{7}31$	5179	*m*	72
				$\bar{7}51$	6059	*m*	102
$\bar{5}11$	2528	*w*	−34	$\bar{7}71$	7380	*vw*	59
$\bar{5}31$	2968	*ms*	117	$\bar{7}91$	9141	—	8
$\bar{5}51$	3849	*s*	164	$\bar{7}.11.1$	11342	—	13
$\bar{5}71$	5170	—	47				
$\bar{5}91$	6930	—	−25	$\bar{8}01$	6090	*m*	126
$\bar{5}.11.1$	9032	—	27	$\bar{8}21$	6310	*w*	108
$\bar{5}.13.1$	11773	*w*	98	$\bar{8}41$	6971	—	8
				$\bar{8}61$	8071	—	27
$\bar{6}01$	3478	—	−11	$\bar{8}81$	9612	*w*	111
$\bar{6}21$	3698	*vw*	−39	$\bar{8}.10.1$	11593	*vw*	103
$\bar{6}41$	4358	*s*	−141				

(*c*) Symplesite. Rotation axis [102]; zero level

hkl	$Q \times 10^4$	$I_{obs.}$	$F_{calc.}$	*hkl*	$Q \times 10^4$	$I_{obs.}$	$F_{calc.}$
$\bar{2}41$	1553	*s*	134	$\bar{6}03$	6054	*mw*	68
$\bar{2}61$	2654	*w*	75	$\bar{6}23$	6274	—	2
$\bar{2}81$	4195	*m*	90	$\bar{6}43$	6935	—	38
$\bar{2}.10.1$	6176	—	76	$\bar{6}63$	8035	—	19
				$\bar{6}83$	9576	*vw*	41
$\bar{4}02$	2692	*s*	100	$\bar{6}.10.3$	11557	—	28
$\bar{4}22$	2912	—	24				
$\bar{4}42$	3573	*s*	78	$\bar{8}04$	10768	*m*	120
$\bar{4}62$	4673	*m*	78	$\bar{8}24$	10998	*mw*	76
$\bar{4}82$	6214	—	18	$\bar{8}44$	11649	—	32
$\bar{4}.10.2$	8195	—	32	$\bar{8}64$	12749	—	40
$\bar{4}.12.2$	10616	*vw*	45	$\bar{8}84$	14290	*w*	91

Table 3. *Interatomic distances in symplesite*

Atom	Neighbour		Distance (A.)
Fe_I	O_I	(2)	2·00
	(H_2O)	(4)	2·01
Fe_{II}	O_{II}	(2)	2·02
	O_{III}	(2)	2·01
	$(H_2O)_{II}$	(2)	2·02
As	O_I		1·60
	O_{II}		1·63
	O_{III}	(2)	1·69
P	O_I		1·57
	O_{II}		1·62
(vivianite)	O_{III}	(2)	1·68
O_I	O_{II}		2·75
	O_{III}	(2)	2·69
	$(H_2O)_I$	(2)	2·84
	$(H_2O)_I$	(2)	2·82
	$(H_2O)_I$	(2)	2·89
O_{II}	O_{III}	(2)	2·69
	O_{III}	(2)	2·75
	O_{III}	(2)	2·78
	O_{II}	(2)	2·79
	$(H_2O)_{II}$	(2)	2·96
	$(H_2O)_I$	(2)	3·64
O_{III}	O_{III}		2·69
	$(H_2O)_I$		2·73
	$(H_2O)_{II}$		2·89
	$(H_2O)_{II}$		2·92
	$(H_2O)_{II}$		2·84
	$(H_2O)_{II}$		3·53
$(H_2O)_I$	$(H_2O)_I$		2·96
	$(H_2O)_I$		3·09
H_2O tetrahedron:			
$(H_2O)_I$	$(H_2O)_{I'}$		2·71
	$(H_2O)_{II}$		3·00
	$(H_2O)_{II'}$		3·04
$(H_2O)_{I'}$	$(H_2O)_{II}$		3·04
	$(H_2O)_{II'}$		3·00
$(H_2O)_{II}$	$(H_2O)_{II'}$		2·72

that Fe in the *B* and P (or As) in the *A* positions furnish a more adequate explanation of experimental data than conversely Fe in the *A* and P (or As) in the *B* positions.

The final positions of atoms (Table 1) have been determined by trial and error, guided as usual by the possibilities that P (or As) may be surrounded tetrahedrally by four oxygen and Fe octahedrally by six oxygen (or H_2O). We have obtained the parameters using the intensity data of symplesite and tested them later on those of vivianite. The agreement between experiment and calculation, as shown in Table 2, is satisfactory, accounting simultaneously for the differences as well as similarities that exist between the

observed spectra of vivianite and symplesite. The effect of replacement of As by P appears to be not so much on the parameters of atoms as on the lattice dimensions.

regular tetrahedron formed of four oxygen. The linkage repeats indefinitely, making up a complex band extended parallel with (010) (Fig. 2). A band is joined to a similar band only by the weak H_2O–H_2O bonds. It is

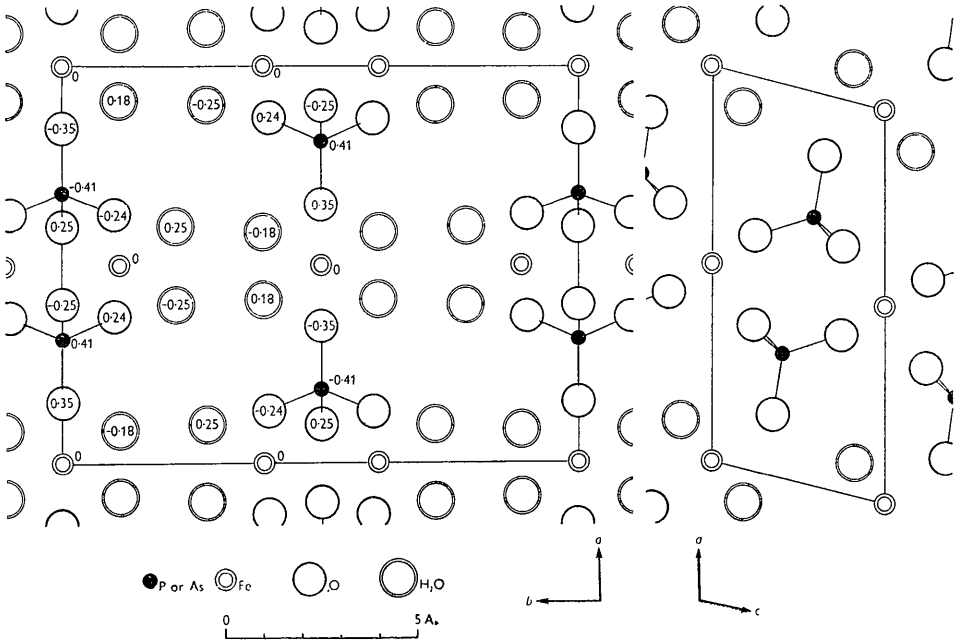

Fig. 1. The structure of vivianite and symplesite, projected along the c direction on to (001). Numbers give in decimal fractions of c the height of atoms from (001). The accompanying projection on (010) shows only half the b length of the cell.

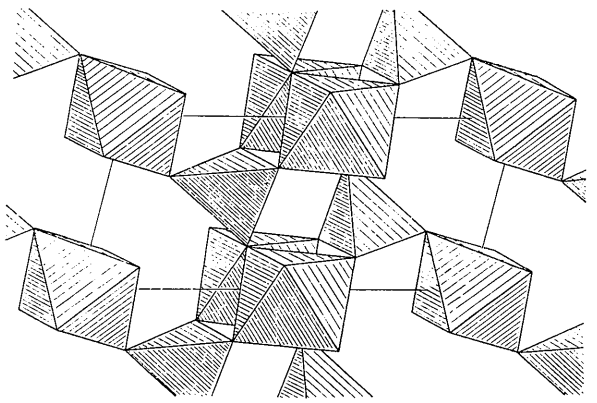

Fig. 2. The structure of vivianite and symplesite shown as linked polyhedra of O or O and H_2O around P (or As) or Fe, as viewed from the b direction. Two O–H_2O octahedra are joined together to form a double group with the composition $Fe_2O_6(H_2O)_4$, while the single octahedral group has the composition $FeO_2(H_2O)_4$.

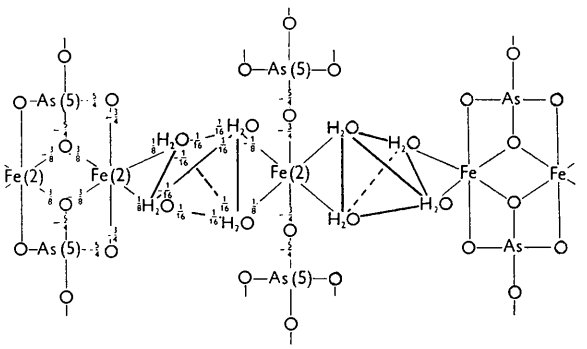

Fig. 3. The electrostatic balance around the tetrahedra formed of H_2O, which link the single octahedral group to the double octahedral group. Note that two H_2O molecules of a tetrahedron are equally but oppositely polarized to the other two.

Description of the structure

The bulk of the structure (Fig. 1) is built up, as expected, of the octahedral groups of oxygen and H_2O around Fe. Of these, two identical ones are grouped together holding an O–O edge in common. Such a double group, $Fe_2O_6(H_2O)_4$, is linked to two neighbouring similar groups and to four other single octahedral groups, $FeO_2(H_2O)_4$, by P (or As) which is at the centre of a

to be noted that four H_2O are combined to form a nearly regular tetrahedron. Two constituent H_2O of the tetrahedron each form part of the single octahedral group and the other two each of the double octahedral group. The balance of valency is such that the former two H_2O are to match each a residual bond of $\frac{1}{8}$ and the latter each a bond of $-\frac{1}{8}$, making them equally but oppositely polarized (Fig. 3). The grouping in tetra-

hedra of H_2O molecules in the structure seems to be well stabilized. The extremely perfect (010) cleavage of vivianite and symplesite may presumably take place across these H_2O–H_2O bonds. Interatomic distances calculated are given in Table 3.

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The Hydrogen Bond in Crystals. VIII. The Isotope Effect in KH_2AsO_4

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The axial lengths of tetragonal KH_2AsO_4 are found to be $a = 7{\cdot}609 \pm 0{\cdot}001$, $c = 7{\cdot}148 \pm 0{\cdot}001$ kX. at 18° C. X-ray measurements on KH_2AsO_4 show that the isotope effect when deuterium is substituted for hydrogen involves a lattice expansion in the direction of the short hydrogen bonds. On the basis of certain assumptions, the isotope effect (D for H) involves an expansion of 0·0080 kX. in KH_2AsO_4 which compares with 0·0097 kX. in KH_2PO_4 and 0·0100 kX. in $(NH_4)H_2PO_4$.

Various evidence indicates that the protons are less strongly bonded to the AsO_4 complex than to the PO_4 complex. Experiments are described which show (*a*) that, unlike KD_2PO_4, KD_2AsO_4 shows no evidence of a tendency to crystallize spontaneously in a monoclinic form; and (*b*) that, when heated, KH_2AsO_4 loses water fairly readily to form $KAsO_3$. When $KAsO_3$ is dissolved in water it undergoes the reaction $KAsO_3 + H_2O \rightarrow KH_2AsO_4$ practically instantaneously. On the other hand, KH_2PO_4 is much more resistant to heat. When the KPO_3 is dissolved in water, the PO_3' is at first largely polymerized and hydrates only with difficulty.

The free energies of transfer and heats of transfer of the proton in the reactions

$$2H_2PO_4' \rightleftharpoons H_3PO_4 + HPO_4'', \quad \Delta G = 6{\cdot}5, \quad \Delta H = 3{\cdot}8 \text{ Cal. mole}^{-1},$$
$$2H_2AsO_4' \rightleftharpoons H_3AsO_4 + HAsO_4'', \quad \Delta G = 5{\cdot}2, \quad \Delta H = 2{\cdot}2 \text{ Cal. mole}^{-1},$$

are briefly discussed in relation to the theory of the hydrogen bond in these crystals.

Introduction

From the isomorphism and from recent determinations of crystal structure (Helmholz & Levine, 1942), it may be inferred that KH_2AsO_4 contains short hydrogen bonds similar to those in KH_2PO_4 and in a number of other crystals. KH_2AsO_4 also shows a continuous transition to the ferro-electric state, analogous to that in KH_2PO_4, but at 95·6° K. instead of at 122° K. (Stephenson & Zettlemoyer, 1944). It was of particular interest to study the isotope effect in KH_2AsO_4 in view of these similarities, and also in view of the fact that KD_2PO_4 crystallizes spontaneously in a structure distinct from KH_2PO_4 (Ubbelohde, 1939*b*). In the course of experiments on the isotope effect, significant differences between H_2AsO_4' and H_2PO_4' were observed, which were further investigated because of their bearing on the behaviour of hydrogen bonds in crystals.

So far as the evidence goes, the hydrogen bonds in crystals of KH_2AsO_4 appear to be somewhat weaker than in KH_2PO_4. The origin of this difference may be tentatively related with the ionic sizes of the H_2AsO_4' and H_2PO_4' complexes.

Experimental procedure

Preparation of KH_2AsO_4

KH_2AsO_4 was prepared by neutralizing ignited K_2CO_3 ('Analar' grade) with the equivalent amount of As_2O_5 in hot distilled water according to the equation

$$K_2CO_3 + As_2O_5 + 2H_2O \rightarrow 2KH_2AsO_4 + CO_2 \qquad \text{(i)}$$

Owing to impurities of silicate in the As_2O_5 the solution had to be filtered; the amounts of As_2O_5 corresponding to the weight of insoluble residue were then added in a second neutralization. The KH_2AsO_4 was recrystallized three times. In the final sample, analysis of the arsenic content by precipitation as $Mg(NH_4)AsO_4 \cdot 6H_2O$ and ignition to $Mg_2As_2O_7$ gave 41·48 % as the mean of four observations (theory 41·61 %). When the crystals were dehydrated at 400° C. according to the reaction

$$KH_2AsO_4 \rightarrow KAsO_3 + H_2O, \qquad \text{(ii)}$$

the yield of potassium metarsenate was 99·7 % of theory, which gave a further check on the purity.

Preparation of KD_2AsO_4

As is detailed below, special tests showed that the reaction

$$AsO_3' + D_2O \rightarrow D_2AsO_4' \qquad \text{(iii)}$$