

Structures of Fluoroarsenates $\text{KAsF}_{6-n}(\text{OH})_n$, $n = 0, 1, 2$: Application of the Heavy-Atom Method for Modulated Structures

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Abstract

Structures of $\text{KAsF}_{6-n}(\text{OH})_n$, $n = 0, 1, 2$, have been determined from single-crystal X-ray diffraction data. Potassium hexafluoroarsenate, KAsF_6 , has a standard structure, potassium hydroxopentafluoroarsenate, $\text{KAsF}_5(\text{OH})$, has a superstructure, and potassium dihydroxotetrafluoroarsenate, $\text{KAsF}_4(\text{OH})_2$, has an incommensurate modulated structure. The superstructure has been solved both in the supercell by standard methods and in the basic cell as a commensurate modulated structure, giving the same results in both cases. The heavy-atom method for modulated structures has been developed and applied to identify a good starting point for the refinement of strongly modulated $\text{KAsF}_4(\text{OH})_2$. Moreover, the influence of hydrogen bonding on a regular disturbance of simple translation symmetry of the structure is discussed.

1. Introduction

The tendency of the fluoroarsenates to form complicated structures increases with the number of hydroxyl groups (OH) that participate in hydrogen bonds. The network of hydrogen bonds affects the structure in two contradictory ways: it attracts the $\text{AsF}_{6-n}(\text{OH})_n$ anions to shorter distances but, at the same time, makes their close packing difficult because they can no longer move independently. The necessity to fulfill such inconsistent conditions leads to commensurate and incommensurate modulation for $\text{KAsF}_5(\text{OH})$ and $\text{KAsF}_4(\text{OH})_2$, respectively. On the other hand, KAsF_6 , without any hydrogen bond, is a simple, highly symmetrical structure.

The structures of $\text{KAsF}_5(\text{OH})$ and $\text{KAsF}_4(\text{OH})_2$ were originally published by Dunken *et al.* (1967*a,b*). They found that the diffraction spots on the rotation photographs can be divided into two parallel systems of weak and strong intensities. The common cell was unusually large and, moreover, the number of observable reflections, due to limited experimental possibilities at that time, was too low to make a full crystal structure determination. This was the reason why the authors just used dominating reflections, which led to a smaller

'pseudocell'. As the structure analysis of aperiodic structures has undergone substantial development in the past 20 years, it was reasonable to perform a new structure determination based on a full data set, including weak reflections. Besides $\text{KAsF}_5(\text{OH})$ and $\text{KAsF}_4(\text{OH})_2$, the already known KAsF_6 structure (Gafner, 1974) was also redetermined in order to use comparable data sets for the whole group $\text{KAsF}_{6-n}(\text{OH})_n$.

In this paper we report structure determinations of $\text{KAsF}_{6-n}(\text{OH})_n$, $n = 0, 1, 2$, and their comparison. The crystal structure of $\text{KAsF}_4(\text{OH})_2$ has been solved using the heavy-atom method for modulated structures (Petříček, 1994*a*), which allows the discovery of a better starting point for the refinement of the modulation function of the heavy atom from the shape of relevant Patterson maxima. The interpretation of the (3 + 1)-dimensional Patterson function follows from superspace theory (de Wolff *et al.*, 1981) and has already been described (Steurer, 1987). This method, however, gives the initial modulations of the light atoms from the subsequent Fourier synthesis and therefore can be used in a similar way as the heavy-atom method for standard structures.

2. Experimental

2.1. Syntheses

KAsF_6 was obtained by ion exchange from a 1 M solution of LiAsF_6 . $\text{KAsF}_5(\text{OH})$ and $\text{KAsF}_4(\text{OH})_2$ were prepared by dissolving $\text{KH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$ in hot 40% HF in the ratios 1:10 and 1:4, respectively. The resulting crystals were hygroscopic and were kept under oil (Nujol).

2.2. Data collection

The data collection was performed on a Hilger & Watts diffractometer with Ag $K\alpha$ radiation, using the $\omega/2\theta$ technique. The absorption of the samples was neglected as the shape of the crystals did not allow indexing of the crystal planes and the absorption based on the sphere approximation did not improve the

Table 1. *Experimental details*

	KAsF ₆	KAsF ₅ (OH)	KAsF ₄ (OH) ₂
Crystal data			
Chemical formula	KAsF ₆	KAsF ₅ (OH)	KAsF ₄ (OH) ₂
Chemical formula weight	228.008	226.02	224.024
Cell setting	Trigonal	Orthorhombic	Monoclinic
Space group	$R\bar{3}$	$Pnab$	$C2/c$
a (Å)	7.348 (1)	9.391 (2)	4.818 (1)
b (Å)	—	11.336 (3)	16.001 (4)
c (Å)	7.274 (8)	28.173 (8)	6.374 (2)
β (°)	—	—	99.36 (2)
V (Å ³)	340.1 (1)	2999.2 (1)	484.8 (2)
Z	3	24	4
D_x (Mg m ⁻³)	3.33900	3.002	3.068 (2)
D_m (Mg m ⁻³)	3.289 (5)	2.951 (6)	2.994 (3)
Density measured by	Flotation	Flotation	Flotation
Radiation type	Ag $K\alpha$	Ag $K\alpha$	Ag $K\alpha$
Wavelength (Å)	0.5609	0.5609	0.5609
No. of reflections for cell parameters	45	33	39
θ range (°)	7–16	7–21	6.5–18
μ (mm ⁻¹)	4.45	4.02	4.13
Temperature (K)	291	291	291
Crystal form	Prism	Prism	Irregular
Crystal size (mm)	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.2 (average size)
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Hilger & Watts	Hilger & Watts	Hilger & Watts
Data collection method	ω - 2θ scans	ω - 2θ scans	ω - 2θ scans
Absorption correction	None	None	None
No. of measured reflections	1359	5377	8556
No. of independent reflections	456	5363	4351
No. of observed reflections	453	3711	2727
Criterion for observed reflections	$F > 3.0\sigma(F)$	$F > 3.0\sigma(F)$	$F > 3.0\sigma(F)$
R_{int}	5.54	—	9.3
θ_{max} (°)	30	25.4	31
Range of h, k, l	-13 → h → 13 -13 → k → 13 0 → l → 12	0 → h → 14 0 → k → 17 0 → l → 42	-7 → h → 7 0 → k → 24 -11 → l → 11
No. of standard reflections	3	9	4
Frequency of standard reflections	Every 30 reflections	Every 30 reflections	Every 30 reflections
Intensity decay (%)	11	11	28
Refinement			
Refinement on	F	F	F
R	0.024	0.047	0.054
wR	0.031	0.077	0.071
S	1.82	1.55	1.6
No. of reflections used in refinement	453	3711	2727
No. of parameters used	15	219	182
H-atom treatment	Only coordinates of H atoms refined	Only coordinates of H atoms refined	Not found
Weighting scheme	$w = 1/[\sigma^2(F) + 0.003F^2]$	$w = 1/[\sigma^2(F) + 0.003F^2]$	$w = 1/[\sigma^2(F) + 0.003F^2]$
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001	0.001
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.3	1.54	1.37
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-1.67	-1.24	-1.94
Extinction method	B–C type 2 isotropic	B–C type 2 isotropic	None
Extinction coefficient	$140(12) \times 10^1$	$53(12) \times 10^1$	—
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.2B)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.2B)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.2B)
Computer programs			
Data collection	HW (Petříček, 1994b)	HW (Petříček, 1994b)	HW (Petříček, 1994b)
Cell refinement	HW (Petříček, 1994b)	HW (Petříček, 1994b)	HW (Petříček, 1994b)

Table 1 (*cont.*)

	KAsF ₆	KAsF ₅ (OH)	KAsF ₄ (OH) ₂
Data reduction	JANA96 (Petříček & Dušek, 1996)	JANA96 (Petříček & Dušek, 1996)	JANA96 (Petříček & Dušek, 1996)
Structure solution	JANA96 (Petříček & Dušek, 1996)	JANA96 (Petříček & Dušek, 1996)	JANA96 (Petříček & Dušek, 1996)
Structure refinement	JANA96 (Petříček & Dušek, 1996)	JANA96 (Petříček & Dušek, 1996)	JANA96 (Petříček & Dušek, 1996)
Preparation of material for publication	JANA96 (Petříček & Dušek, 1996); <i>PICTUR</i> (Dušek, 1994)	JANA96 (Petříček & Dušek, 1996); <i>PICTUR</i> (Dušek, 1994)	JANA96 (Petříček & Dušek, 1996); <i>PICTUR</i> (Dušek, 1994)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
KAsF₆				
K	1/3	2/3	0.16667	0.0705 (4)
As	0	0	0	0.0457 (2)
F	0.1292 (2)	0.2165 (2)	0.1381 (2)	0.0893 (9)
KAsF₅(OH)				
<i>Ka</i>	1/4	0.3420 (2)	0	0.0395 (5)
<i>Kb</i>	0.2304 (1)	0.3383 (1)	0.16589 (4)	0.0327 (3)
<i>Kc</i>	0.2512 (1)	0.3227 (1)	0.33167 (4)	0.0317 (3)
<i>Kd</i>	1/4	0.3185 (1)	1/2	0.0304 (4)
<i>As1a</i>	0.07660 (4)	0.10448 (4)	0.08083 (1)	0.0209 (1)
<i>F1a</i>	−0.0962 (3)	0.0503 (3)	0.0801 (1)	0.0473 (11)
<i>O2a</i>	0.2443 (4)	0.1693 (3)	0.0815 (1)	0.0362 (11)
<i>F3a</i>	0.0174 (3)	0.2034 (3)	0.1230 (1)	0.0462 (10)
<i>F4a</i>	0.1167 (4)	0.0032 (3)	0.1243 (1)	0.0501 (11)
<i>F5a</i>	0.0222 (3)	0.2030 (3)	0.0375 (1)	0.0433 (10)
<i>F6a</i>	0.1201 (4)	0.0033 (3)	0.0382 (1)	0.0509 (11)
<i>As2b</i>	0.10687 (5)	0.09384 (4)	0.41583 (1)	0.0235 (1)
<i>F1b</i>	0.1286 (5)	0.2453 (3)	0.4136 (1)	0.0579 (14)
<i>O2b</i>	0.0942 (5)	−0.0585 (3)	0.4189 (1)	0.0461 (13)
<i>F4b</i>	−0.0554 (5)	0.1106 (4)	0.3901 (2)	0.0867 (20)
<i>F5b</i>	0.0315 (5)	0.1156 (3)	0.4705 (1)	0.0647 (14)
<i>F6b</i>	0.2717 (4)	0.0864 (4)	0.4431 (2)	0.0718 (16)
<i>F3b</i>	0.1886 (5)	0.0851 (3)	0.3617 (1)	0.0712 (16)
<i>As1c</i>	0.08279 (4)	0.10744 (4)	0.75732 (2)	0.0224 (1)
<i>F1c</i>	−0.0926 (3)	0.0578 (3)	0.7593 (1)	0.0495 (11)
<i>O2c</i>	0.2524 (3)	0.1678 (3)	0.7551 (1)	0.0384 (11)
<i>F3c</i>	0.0294 (4)	0.2147 (3)	0.7967 (1)	0.0624 (13)
<i>F4c</i>	0.1211 (4)	0.0157 (4)	0.8033 (2)	0.0829 (18)
<i>F5c</i>	0.0308 (4)	0.1964 (5)	0.7117 (1)	0.0789 (17)
<i>F6c</i>	0.1216 (4)	−0.0046 (4)	0.7189 (2)	0.0887 (19)

results. The recording conditions are summarized in Table 1. The modulated crystal of KAsF₄(OH)₂ was measured directly with four indices using the local controlling program *HW* (Petříček, 1994*a,b*).

3. Structure determination

Crystal data and refinement results are summarized in Table 1. The refined positional and temperature parameters are given in Tables 2 [KAsF₆ and KAsF₅(OH)], 3 and 4 [KAsF₄(OH)₂]. Selected bond distances and angles are listed in Table 5†.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: SH0109). Services for accessing these data are described at the back of the journal.

Table 3. KAsF₄(OH)₂: final values for coordinates and Fourier amplitudes of the displacive modulation functions

The modulations of positions are expressed as $\mathbf{r}^v(x_4) = \mathbf{r}_0^v + \sum_n [\mathbf{u}_{s,n}^v \sin(2\pi n x_4) + \mathbf{u}_{c,n}^v \cos(2\pi n x_4)]$, where *v* represents the independent atoms, $\mathbf{u}_{s,n}^v = (A_{xs,n}^v, A_{ys,n}^v, A_{zs,n}^v)$, $\mathbf{u}_{c,n}^v = (A_{xc,n}^v, A_{yc,n}^v, A_{zc,n}^v)$.

Atom	Wave	<i>x</i>	<i>y</i>	<i>z</i>
As		0	0.63103 (2)	1/4
	<i>s,1</i>	−0.0111 (1)	0	−0.02638 (9)
	<i>c,1</i>	0	0.01390 (3)	0
K	<i>s,2</i>	−0.0014 (2)	0	0.0039 (1)
	<i>c,2</i>	0	0.00140 (4)	0
		1/2	0.59091 (7)	3/4
F1	<i>s,1</i>	0.0082 (3)	0	−0.0133 (2)
	<i>c,1</i>	0	0.01728 (9)	0
	<i>s,2</i>	−0.0122 (4)	0	−0.0070 (2)
F2	<i>c,2</i>	0	−0.0032 (1)	0
	<i>s,1</i>	−0.0994 (5)	0.6272 (1)	0.4993 (3)
	<i>c,1</i>	−0.0133 (6)	0.0149 (2)	−0.0249 (4)
F3	<i>s,2</i>	−0.0132 (5)	0.0098 (2)	0.0026 (4)
	<i>c,2</i>	0.0045 (7)	0.0008 (2)	0.0058 (5)
	<i>s,1</i>	0.0088 (7)	0.0012 (2)	0.0015 (5)
F4	<i>c,2</i>	0.2376 (5)	0.5519 (1)	0.3314 (4)
	<i>s,1</i>	−0.0045 (6)	0.0136 (2)	0.0088 (4)
	<i>c,1</i>	−0.0292 (6)	−0.0137 (2)	−0.0084 (4)
F5	<i>s,2</i>	−0.0043 (8)	−0.0015 (2)	−0.0068 (6)
	<i>c,2</i>	−0.0025 (8)	−0.0006 (2)	0.0030 (5)
	<i>s,1</i>	0.2594 (6)	0.7042 (2)	0.3346 (5)
O3	<i>c,1</i>	0.0017 (8)	0.0121 (3)	0.0149 (7)
	<i>s,2</i>	0.0492 (7)	−0.0178 (2)	0.0606 (6)
	<i>c,2</i>	0.007 (1)	−0.0027 (3)	0.0003 (8)
		−0.004 (1)	−0.0025 (3)	0.0040 (8)

3.1. KAsF₄(OH)₂

The average structure of KAsF₄(OH)₂ was solved by the heavy-atom method. The modulation waves were then refined from arbitrary small starting values. This method, however, turned out to be difficult and tedious. It was more efficient to estimate the parameters of the first harmonic modulation wave of the As atom from the shape of the Patterson maximum (0,2*y*,¹/₂), which corresponds to the distances between arsenic in the basic position *x*₁, *x*₂, *x*₃, *x*₄ and that expanded by the glide plane *x*₁, −*x*₂, ¹/₂ + *x*₃, *x*₄.

Fig. 1 shows the sections *x*₁−*x*₄, *x*₂−*x*₄ and *x*₃−*x*₄ by this peak. The amplitudes of modulation movement of the arsenic can be directly determined from the pictures as one quarter of the difference between the smallest and the largest width of the maximum. To obtain good

Table 4. $KAsF_4(OH)_2$: final values for temperature parameters

The modulations of temperature parameters are expressed as $\mathbf{U}^v(x_4) = \mathbf{U}_0^v + \sum_n [\mathbf{u}_{s,n}^v \sin(2\pi n x_4) + \mathbf{u}_{c,n}^v \cos(2\pi n x_4)]$, where v represents the independent atoms, $\mathbf{u}_{s,n}^v = (A_{U^{11},s,n}^v, A_{U^{22},s,n}^v, A_{U^{33},s,n}^v, A_{U^{12},s,n}^v, A_{U^{13},s,n}^v, A_{U^{23},s,n}^v)$, $\mathbf{u}_{c,n}^v = (A_{U^{11},c,n}^v, A_{U^{22},c,n}^v, A_{U^{33},c,n}^v, A_{U^{12},c,n}^v, A_{U^{13},c,n}^v, A_{U^{23},c,n}^v)$.

Atom	Amplitude	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As		0.0163 (2)	0.0192 (2)	0.0189 (2)	0	0.0033 (1)	0
	s,1	0	0	0	-0.0015 (2)	0	0.0016 (2)
	c,1	0.0017 (2)	0.0001 (2)	0.0004 (2)	0	-0.0001 (2)	0
	s,2	0	0	0	0.0003 (2)	0	0.0020 (2)
	c,2	0.0004 (3)	-0.0009 (3)	-0.0002 (3)	0	0.0008 (2)	0
K		0.0333 (5)	0.0346 (5)	0.0272 (4)	0	0.0064 (4)	0
	s,1	0	0	0	-0.0037 (6)	0	0.0018 (5)
	c,1	-0.0002 (6)	-0.0067 (6)	0.0046 (6)	0	0.0003 (4)	0
	s,2	0	0	0	-0.0007 (7)	0	0.0009 (6)
	c,2	0.001 (1)	-0.0067 (9)	0.0028 (7)	0	0.0016 (6)	0
F1		0.038 (1)	0.048 (1)	0.0238 (9)	-0.0022 (8)	0.0126 (8)	0.0033 (8)
	s,1	0.006 (1)	-0.005 (2)	0.001 (1)	-0.008 (1)	0.003 (1)	-0.006 (1)
	c,1	0.002 (1)	-0.004 (2)	0.002 (1)	0.000 (1)	0.001 (1)	-0.001 (1)
	s,2	0.000 (2)	-0.007 (2)	0.000 (1)	0.004 (2)	0.002 (1)	0.000 (1)
	c,2	-0.006 (2)	0.004 (2)	-0.002 (1)	0.007 (2)	-0.004 (1)	0.000 (1)
F2		0.038 (1)	0.039 (1)	0.045 (1)	0.0158 (9)	0.0026 (9)	0.0071 (9)
	s,1	0.005 (2)	0.001 (2)	-0.007 (1)	0.001 (1)	-0.003 (1)	-0.001 (1)
	c,1	0.005 (2)	-0.010 (2)	-0.004 (1)	-0.001 (1)	0.004 (1)	-0.006 (1)
	s,2	0.000 (2)	0.008 (2)	0.001 (2)	0.004 (2)	-0.001 (2)	0.002 (1)
	c,2	-0.001 (2)	-0.001 (2)	-0.002 (2)	-0.006 (2)	-0.001 (2)	0.001 (1)
O3		0.034 (1)	0.046 (2)	0.051 (2)	-0.019 (1)	0.019 (1)	-0.023 (1)
	s,1	0.002 (2)	0.004 (2)	0.005 (3)	-0.001 (2)	0.001 (2)	-0.002 (2)
	c,1	-0.008 (2)	0.004 (2)	0.005 (2)	0.005 (1)	-0.003 (1)	-0.007 (1)
	s,2	-0.002 (2)	0.016 (3)	0.003 (3)	-0.006 (2)	-0.001 (2)	-0.012 (2)
	c,2	-0.004 (2)	-0.014 (3)	-0.018 (3)	0.014 (2)	-0.014 (2)	0.019 (2)

results it was necessary to calculate the sharpened Patterson. Another requirement is that the contour step in the pictures should be fine enough in order to determine exactly the place where the positive maximum merges into the zero-level plane of the map.

The resulting amplitudes were 0.007, 0.014 and 0.026 for the x_1-x_4 , x_2-x_4 and x_3-x_4 sections, respectively. As the arsenic is in a special position $(0, y_{\frac{1}{4}})$, its positional modulations resulting from the first harmonic wave can be expressed by the following equations

$$x = x_0 + A_{xs,1} \sin(2\pi x_4)$$

$$y = y_0 + A_{yc,1} \cos(2\pi x_4)$$

$$z = z_0 + A_{zs,1} \sin(2\pi x_4)$$

where $A_{xs,1}$, $A_{yc,1}$ and $A_{zs,1}$ are the parameters refined. Thus, $|A_{xs,1}| = 0.007$, $|A_{yc,1}| = 0.014$ and $|A_{zs,1}| = 0.026$. The first amplitude (with respect to the cell parameter a) is small and its sign is not important. The signs of the remaining two amplitudes can be $-,-$ (which is equivalent to $+,+$) or $-,+$ (equivalent to $+,-$). This uncertainty was resolved by the analysis of the section x_2-x_3 at $x_4 = 0.25$, where both displacements are combined. Fig. 2 shows that the checking Patterson corresponds to that calculated from observed intensities only if $A_{yc,1}$ and $A_{zs,1}$ have opposite signs.

Once the first harmonic wave of the arsenic was known, it was possible to calculate a Fourier synthesis and derive the modulation parameters of the light atoms. The accuracy of the estimated modulation para-

eters is demonstrated in Fig. 3, where the modulation function of F1 calculated from these coefficients is plotted against a background of the Fourier map based on the final model of the structure. The R factors of the structure model with positional and modulation parameters estimated from the Patterson/Fourier map and only with scale and isotropic temperature parameters refined are listed in Table 6. Then the second positional wave and two temperature waves were added for each atom and refined from small starting values with final R values of 0.054 for all reflections and 0.044 for main reflections.

Tables 3 and 4 list the final parameters of the structure. This model, however, is not the only one possible. The octahedron AsF_4O_2 is almost rigid and the structure can also be described using rigid-body modulation waves for positional modulations and the modulations of TLS tensors for rigid-body temperature parameters. The R factor of this model is worse, but it can be considerably improved if the temperature modulation parameters are refined individually. The R factors of various structure models are compared in Table 6.

In the molecular model [see model (IV) in Table 6] the modulations of the positional and temperature parameters of each atom of the octahedron AsF_4O_2 are fully determined by the molecular parameters of the actual molecular position. JANA96 (Petříček & Dušek, 1996) also allows the refinement of the complementary individual modulation of some atom of the octahedron to prove the rigidity of the molecule during modulation.

Table 5. Selected bond distances (Å) and angles (°)

KAsF ₆		
As—F	1.712 (1)	F—As—F 90.95 (7)
KAsF ₅ (OH)		
As1a—F1a	1.735 (3)	(F1a—As1a—F3a)—(O2a—As1a—F4a)
As1a—O2a	1.737 (3)	86.4 (2)—94.4 (2)
As1a—F3a	1.725 (3)	
As1a—F4a	1.719 (4)	As1a—O2a—Ha
As1a—F5a	1.732 (3)	105.4 (3)
As1a—F6a	1.711 (4)	
O2a—Ha	0.902 (3)	O2a—Ha—F1a ⁱ
Ha—F1a ⁱ	2.032 (4)	162.7 (3)
As2b—F1b		
As2b—F1b	1.730 (3)	(F1b—As2b—F5b)—(O2b—As2b—F5b)
As2b—O2b	1.733 (3)	86.5 (2)—94.0 (2)
As2b—F3b	1.710 (4)	
As2b—F4b	1.698 (5)	As2b—O2b—Hb
As2b—F5b	1.714 (4)	103.9 (3)
As2b—F6b	1.730 (4)	
O2b—Hb	1.024 (4)	O2b—Hb—F6b ⁱⁱ
Hb—F1b ⁱⁱ	2.112 (4)	168.1 (2)
As1c—F1c		
As1c—F1c	1.742 (3)	(F1c—As1c—F3c)—(O2c—As1c—F4c)
As1c—O2c	1.735 (3)	86.1 (2)—94.2 (2)
As1c—F3c	1.720 (4)	
As1c—F4c	1.700 (5)	As1c—O2c—Hc
As1c—F5c	1.705 (5)	108.3 (3)
As1c—F6c	1.708 (5)	
O2c—Hc	0.779 (3)	O2c—Hc—F1c ⁱ
Hc—F1c ⁱ	2.209 (4)	157.6 (3)
KAsF ₄ (OH) ₂		
As—F1	1.73 (2) av. 1.73 (2) min. 1.74 (2) max.	F1—As—F2 87.7 (1) av., 87.6 (1) min., 88.1 (1) max.
As—F2	1.75 (2) av. 1.74 (2) min. 1.76 (2) max.	F1—As—O3 91.4 (1) av., 90.7 (1) min., 92.0 (1) max.
As—O3	1.75 (3) av. 1.73 (3) min. 1.76 (3) max.	
O ₃ —O ₃	2.67 (4) av. 2.63 (4) min. 2.73 (4) max.	

Symmetry codes: (i) $\frac{1}{2} + x, -y, z$; (ii) $x - \frac{1}{2}, -y, z$.

The modulated parameters of such atoms are then expressed as a sum of its individual parameters and those derived from the molecular parameters. This method can be applied for more than one atom at once if the number of atoms having pure molecular modulation remains sufficient to introduce a molecular modulation. In our case the rigidity was tested by application of the method to each ligand separately.

Table 7 lists the complementary modulation of the positional parameters of all atoms of the octahedron in terms of multiples of 3 e.s.d.'s. The values close to 1 indicate that the corresponding individual parameters refined for this atom can be neglected because they are

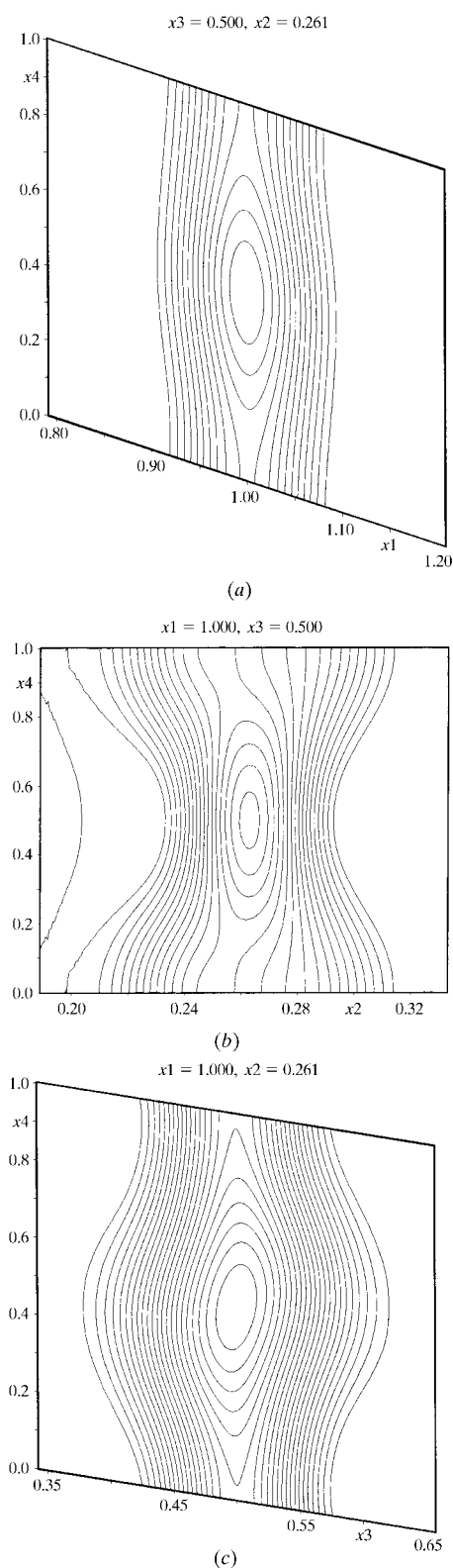


Fig. 1. KAsF₄(OH)₂. Sections of Patterson map calculated in the vicinity of the Patterson maximum (0.2y, $\frac{1}{2}$): (a) x₁–x₄ section; (b) x₂–x₄ section; (c) x₃–x₄ section.

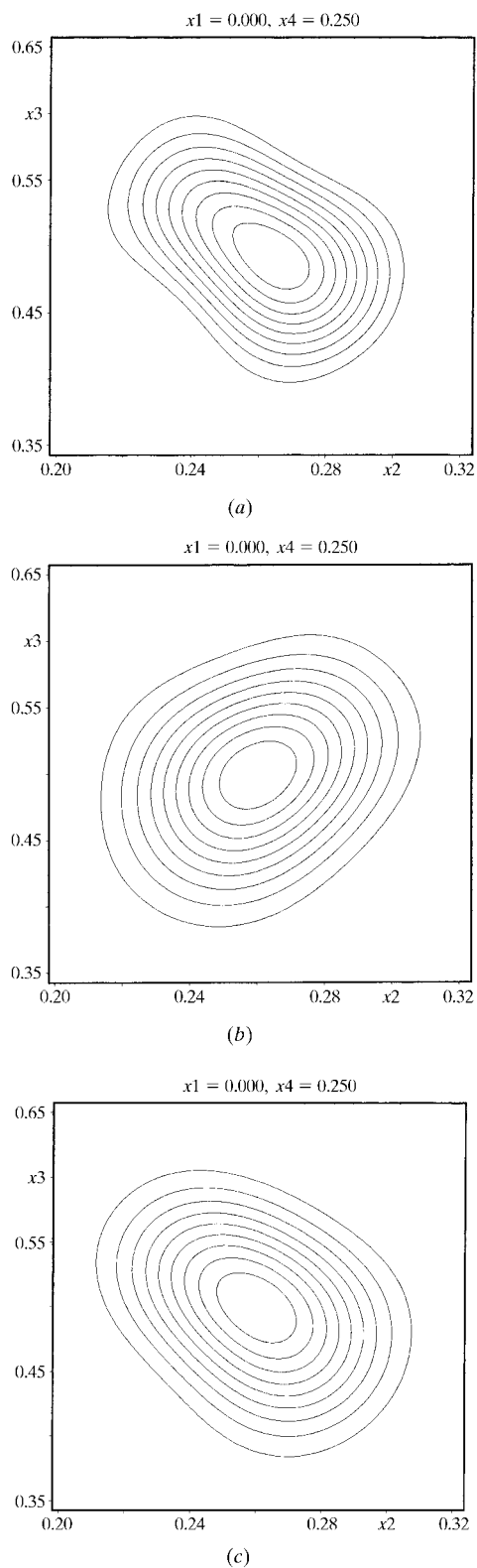


Fig. 2. $\text{KAsF}_4(\text{OH})_2$. The x_2 - x_3 section through the Patterson peak $(0, 2y, \frac{1}{2})$ at $x_4 = 0.25$: the Patterson synthesis based on (a) $F_o^2(\mathbf{h})$; (b) $F_c^2(\mathbf{h})$, the wrong solution; (c) $F_c^2(\mathbf{h})$, the correct solution.

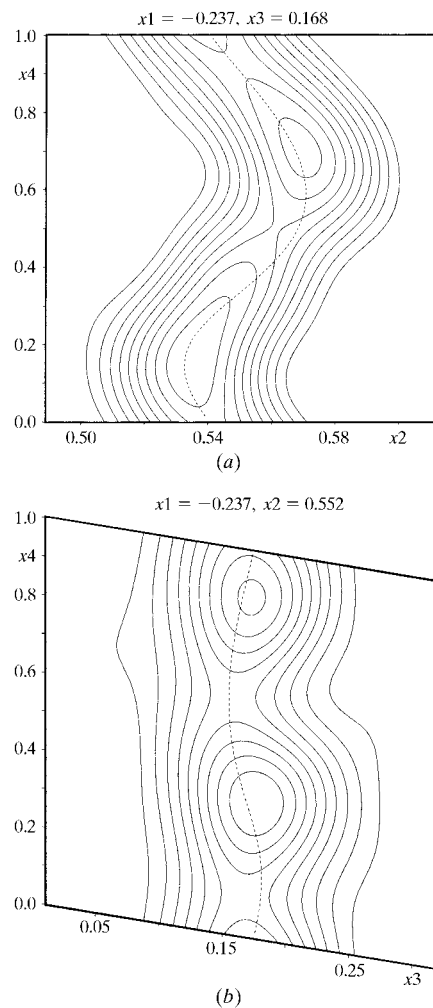


Fig. 3. $\text{KAsF}_4(\text{OH})_2$. The first estimation of the modulation function of the F1 atom plotted together with the Fourier map based on the final model of the structure. (a) The x_2 - x_4 and (b) the x_3 - x_4 section of the Fourier map in the vicinity of the F1 atom.

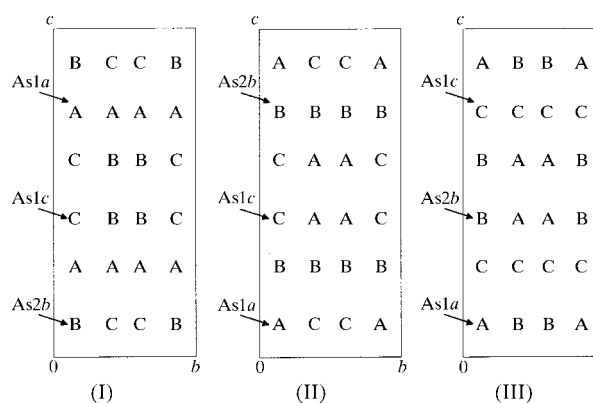


Fig. 4. Three possible transformations of average structure of $\text{KAsF}_5(\text{OH})$ to a superstructure. The letters represent three positions of three independent As atoms.

Table 6. *R* factors for several structure models of $KAsF_4(OH)_2$

(I) Model estimated from Patterson and Fourier; (II) atomic model without modulation of temperature parameters; (III) atomic model with modulation of temperature parameters (final model); (IV) molecular model with AsF_4O_2 molecules (the temperature parameters are refined as TLS tensors); (V) molecular model with AsF_4 molecules (the temperature parameters are refined individually).

Structure model	All reflections (2727)	Main reflections (729)	First-order satellites (1375)	Second-order satellites (623)
(I)	20.11	12.99	24.48	32.78
(II)	6.74	5.14	6.71	14.27
(III)	5.40	4.40	5.13	11.32
(IV)	5.71	4.56	5.53	11.86
(V)	5.54	4.44	5.27	11.89

Table 7. $KAsF_4(OH)_2$: individual positional parameters expressed as multiples of 3 e.s.d.'s

The values greater than 1 indicate deviations from molecular behaviour.

		<i>x</i>	<i>y</i>	<i>z</i>
As	$A_{s,1}$	0.3	0	0.7
	$A_{c,1}$	0	0.3	0
	$A_{s,2}$	0.1	0	0.2
F1	$A_{c,2}$	0	0	0
	$A_{s,1}$	0.6	1.1	0.3
	$A_{c,1}$	0.2	0.3	0.1
F2	$A_{s,2}$	0.1	0.7	0.4
	$A_{c,2}$	1.3	0	1.9
	$A_{s,1}$	1.2	1.1	0.6
O	$A_{c,1}$	0.7	0.5	0.7
	$A_{s,2}$	0	0.1	0.8
	$A_{c,2}$	0.3	1.3	0.9
O	$A_{s,1}$	0.3	1.6	2.1
	$A_{c,1}$	0.6	0.4	1.2
	$A_{s,2}$	0	0.3	0.5
	$A_{c,2}$	0	1.6	0.5

within the limit of 3 e.s.d.'s. Such an atom can be considered to be part of the molecule.

The most significant deviations of the molecular behaviour appear in the modulation parameters of

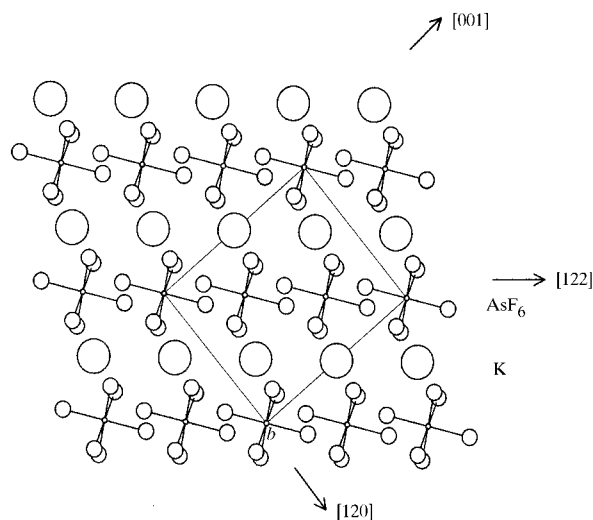


Fig. 5. $KAsF_6$. Projection of the structure along $[100]$ showing K and AsF_6 layers. The plane of the projection is $(\bar{1}20)$. The As and K planes are parallel to $(01\bar{1})$.

oxygen. The *R* factors of the molecular model with the molecule AsF_4 are very close to those of the completely atomic model (see Table 6).

3.2. $KAsF_5(OH)$

The diffraction data of $KAsF_5(OH)$ contain a set of weak reflections with indices $h, k = 2n + 1, l = 3n \pm 1$,

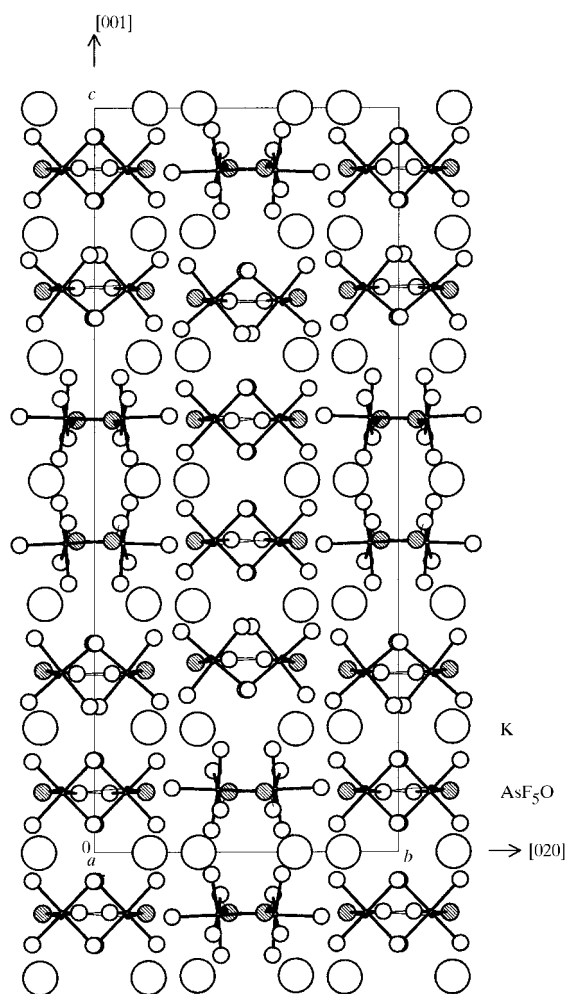


Fig. 6. $KAsF_5(OH)$. Projection of the structure along the *a* axis shows K and AsF_5O layers. The different orientations of the AsF_5O octahedra are responsible for the superstructure features of the compound.

which are responsible for the superstructure features of the compound. In the first stage of the solution these reflections were neglected and an average structure was solved by the heavy-atom method in a small unit cell, a , $b/2$, $c/3$, space group $Pcam$. The resulting R factor with all temperature parameters anisotropic was 0.073. The average structure consists of three partially overlapped AsF_5O octahedra with F and O atoms not distinguished.

The space group of the superstructure was determined as $Pnab$. The non-standard setting of the space group was chosen in order to retain the consistency between the average structure and the superstructure. The octahedra AsF_5O could be distributed in the supercell in three ways, which are shown in Fig. 4. All these possibilities were refined, but only one [(III) in Fig. 4] led to satisfactory R values.

The superspace theory of modulated structures also makes it possible to describe the structure as commensurably modulated with the superspace group $Pcam(0 \frac{1}{2} \gamma)$, $\gamma = \frac{1}{3}$ (de Wolff *et al.*, 1981). This superspace group induces for $t = x_4 - \mathbf{q} \cdot \mathbf{r} = 0$ the space group $Pnab$, as used in the supercell refinement mentioned above. However, this approach allowed neither a reduction of the number of refined parameters nor more straightforward solution and refinement. This is due to the fact that the octahedral positions are unique and strongly different.

3.3. $KAsF_6$

The structure was solved by the heavy-atom method. There were no problems in the solution of this compound.

3.4. Refinement of hydrogen

The existence of a heavy As atom indicated that the determination of H atoms was almost below the resolution of the experiment. The hydrogen positions of $KAsF_5(OH)$ could be determined from difference Fourier synthesis, but could not be refined because of

relatively large difference maxima around the arsenic. Their coordinates were fixed and only the overall isotropic temperature parameter was refined.

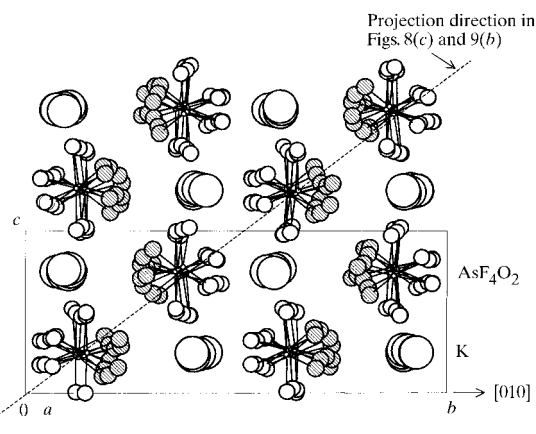


Fig. 7. $KAsF_4(OH)_2$. Projection of the structure along $[100]$ shows K and AsF_4O_2 layers. The width of the plot is $5a$. The angle between the slab and $[001]$ is 9.36° . The O atoms are shaded.

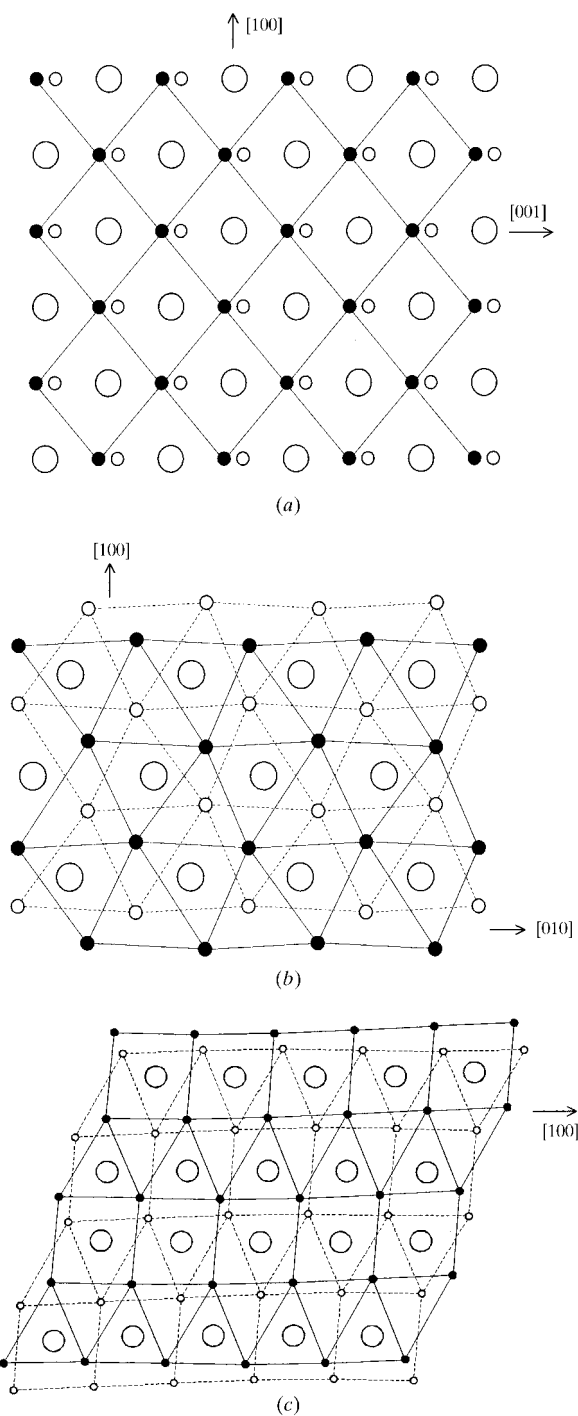


Fig. 8. The packing of three subsequent layers of the K and As cations. The K atoms (large circles) are in the central layer; the bottom layer is black. (a) $KAsF_6$, projection plane $(01\bar{1})$; (b) $KAsF_5(OH)$, projection along $[001]$; (c) $KAsF_4(OH)_2$, projection direction as indicated in Fig. 7.

In the case of $\text{KAsF}_4(\text{OH})_2$, the hydrogen maximum could be identified from difference Fourier maps only for several three-dimensional sections. Other sections showed only noise in the hydrogen positions and an attempt to refine hydrogen modulation functions was not successful. Thus, the H atoms were not included in the refinement.

4. Discussion

Figs. 5, 6 and 7 show the basic views of the structures of KAsF_6 , $\text{KAsF}_5(\text{OH})$ and $\text{KAsF}_4(\text{OH})_2$, respectively. All can be oriented in such a way that alternating planes of K atoms and $\text{AsF}_{6-n}\text{O}_n$ octahedra can be distinguished. Even though none is a layer structure, the packing and

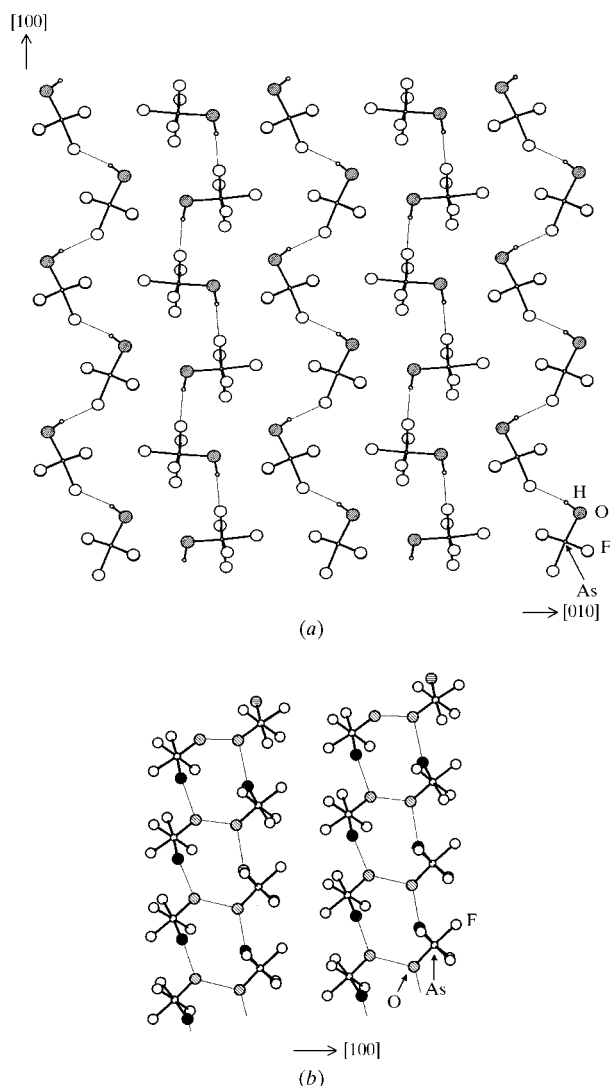


Fig. 9. Hydrogen bonding in one layer of $\text{AsF}_{6-n}(\text{OH})_n$ octahedra: (a) $\text{KAsF}_5(\text{OH})$; (b) $\text{KAsF}_4(\text{OH})_2$.

distance of the planes can be used as a base for their comparison.

The potassium in KAsF_6 (Fig. 8a) is surrounded by eight As atoms at the vertices of a deformed cube. The packing of the layers in $\text{KAsF}_5(\text{OH})$ (Fig. 8b) is closer and the environment of potassium can be described by a strongly deformed octahedron. The packing of $\text{KAsF}_4(\text{OH})_2$ (Fig. 8c) is an intermediate case with seven As atoms around the potassium.

The different packing of the As and K layers is obviously caused by hydrogen bonding. In the case of $\text{KAsF}_5(\text{OH})$, the hydrogen bonds $\text{F}\cdots\text{H}-\text{O}$ hold the AsF_5O octahedra inside the layer (see Fig. 9a), but there are no bonds between two parallel layers. The octahedra are drawn to lower levels than they have in hydrogen-free KAsF_6 , while the geometry inside the layer is fixed, but two parallel layers can still be easily shifted to fill the space effectively. This is the reason why the packing in $\text{KAsF}_5(\text{OH})$ is closer than that in KAsF_6 . Fig. 10 shows in detail two layers of the AsF_5O octahedra and one K atom in the centre. As the positions of the arsenic atoms are given, it is clear that the octahedra have to assume different orientations in order to avoid the coincidence of light atoms. This is the origin of superstructure features of $\text{KAsF}_5(\text{OH})$ (see Fig. 6).

In the case of $\text{KAsF}_4(\text{OH})_2$, the positions of the H atoms have not been fully determined. For this discussion, however, only the information on whether the hydrogen bonds exist between the O and F or between two O atoms is needed. With the help of Fig. 7, the zones where the hydrogen bonds could occur can easily be detected. The analysis of difference Fourier maps calculated in these volumes proved that there is no

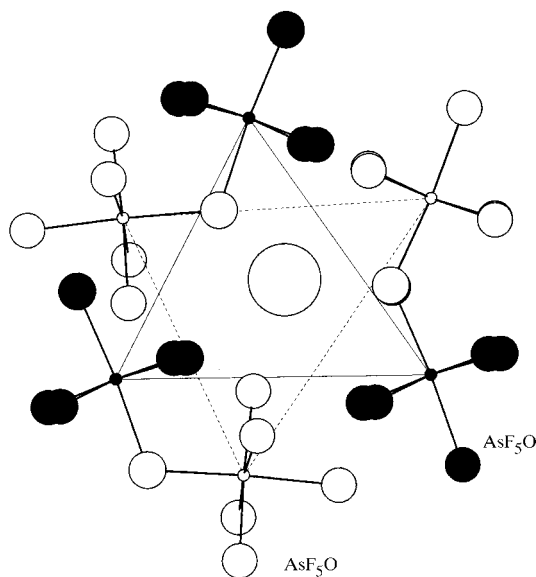


Fig. 10. The arrangement of $\text{AsF}_5(\text{OH})$ octahedra of two neighboring layers. The bottom layer is black.

chance for hydrogen bonds of the type $F \cdots H-O$ as the maps in the corresponding sections do not contain any appropriate maxima. The difference maxima found in the sections through the volume between two O atoms indicate that the hydrogen bonds of the $O \cdots H-O$ type are present with high probability.

The (hypothetical) hydrogen bonding in one layer of AsF_4O_2 is shown in Fig. 9(b) and is completely defined by one $O \cdots H-O$ bond, because there is only one independent oxygen in $KAsF_4(OH)_2$. Each oxygen participates in two hydrogen bonds. Three bonds of each octahedron form the network of hydrogen bonds inside the layer of octahedra, while the final bond joins the octahedra of two neighbouring layers. The O atoms participating in interlayer hydrogen bonds are denoted by black circles; the neighbouring layers are not included in the picture. Although the number of hydrogen bonds in $KAsF_4(OH)_2$ is greater than in $KAsF_5(OH)$ (Fig. 8b), the packing of the layers (Fig. 8c) is not so close. This can be explained by the fact that an optimum packing of two parallel layers of the octahedra is more difficult because the interlayer hydrogen bonds fix the geometry. The O atom has to balance between two hydrogen bonds, but it has only one independent position. This is probably the origin of the modulation behaviour of the structure because in a standard struc-

ture, the inter- and intralayer distances would be the same and the packing of the layers would be even more difficult.

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