cohésion entre les chaînes est assurée par les tétraèdres PO_4 et MoO_4; l'ensemble forme ainsi un réseau tridimensionnel délimitant des tunnels dans la direction [010] où vient s'insérer le sodium.

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Structure of the 1:1 Silver(II) Fluoride–Arsenic(V) Fluoride Adduct, $AgF_2.AsF_5$

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Abstract. $M_r = 315\cdot8$, orthorhombic, $Pnma$, $a = 7\cdot585\,(1)$, $b = 6\cdot997\,(6)$, $c = 9\cdot852\,(1)$ Å, $V = 522\cdot9$ Å^3, $Z = 4$, $D_x = 4\cdot01$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 97\cdot3$ cm^{-1}, $F(000) = 572$, $T = 293$ K, final $R = 0\cdot032$, $wR = 0\cdot033$ for 520 unique observed reflections [$I > 3\sigma(I)$]. The structure consists of an extended F-bridged $[AgF]_n^{n+}$ chain with Ag—F distances 1·995 (5), 2·004 (5) Å, linked to $[AsF_6]^-$ anions by longer Ag—F distances in the range 2·394–2·439 (6) Å.

Introduction. A number of hexafluoroarsenates of the type $MF_2.AsF_5$ have been prepared (Birchall, Dean & Gillespie, 1971; Dean, 1975; Golič & Leban, 1977; Frlec, Gantar & Holloway, 1982) and a structural investigation of the tin compound has been carried out (Golič & Leban, 1977). X-ray powder photography for the series of adducts has shown that none of them is isostructural. However, the single-crystal work on $SnF_2.AsF_5$ showed that the adduct contains cyclic $[(Sn-F)_3]^{3+}$ cations of D_{3h} symmetry and $[AsF_6]^-$ anions. The only previous structural information for $AgF_2.AsF_5$ has come from Raman spectroscopy which indicated that the solid contains $[AsF_6]^-$ octahedra of C_{4v} symmetry or less.

The synthesis of the blue solid has been described elsewhere (Frlec, Gantar & Holloway, 1982).

Experimental. Single crystals of the solid were grown from anhydrous HF solution in FEP–Teflon (perfluoropropene–tetrafluoroethylene copolymer) tubes. An irregular crystal (approximated to an eight-faceted block showing $\{011\}$, $\{01\bar{1}\}$, $\{100\}$, $\{110\}$, $\{\bar{2}\bar{1}0\}$, $\{2\bar{1}0\}$ and with approximate dimensions 0·24 × 0·16 × 0·14 mm) was transferred under vacuum into a Pyrex capillary and sealed. The crystal was aligned about the b axis on a Stoe Stadi-2 Weissenberg diffractometer. Cell parameters were obtained by least-squares refinement of 28 $h0l$ reflection 2θ values, $48 < 2\theta < 56°$, which in turn were obtained by profile fitting well-resolved α_1, α_2 step-scan data in the θ–2θ mode (a,c); b was obtained from $0k0$ reflection measurements. A total of 604 reflections with $7 < 2\theta < 54°$ from layers $k = 0$–8 were measured by a variable ω scan with $\Delta\omega = (1\cdot4 + 0\cdot3 \sin\mu\cot Y)°$ and a 42 s scan with two 10 s background measurements. No significant deterioration of the crystal was observed. Corrections for Lorentz, polarization and absorption (max. and min. transmission 37·6, 17·1%) were applied. The structure was solved by Patterson and difference Fourier syntheses. Final cycles of full-matrix least-squares refinement included anisotropic thermal parameters for all atoms.* The final difference Fourier map was featureless apart from ripples < 1·2 e Å^{-3} near the Ag and As atoms. Final $R = 0\cdot032$, $wR = 0\cdot033$,

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43583 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$w = 0{\cdot}576/[\sigma^2(F_o) + 0{\cdot}001(F_o)^2]$, quantity minimized was $\sum w(F_o - F_c)^2$ which showed an even distribution over $\sin\theta/\lambda$ and F_o ranges, $\Delta/\sigma_{\max} = 0{\cdot}006$. Computer program used: *SHELX*76 (Sheldrick, 1976); atomic scattering factors from same source.

Discussion. The final atomic coordinates are listed in Table 1 and relevant distances and angles are given in Table 2. Fig. 1 shows a view of the environment of the Ag and As atoms, and Fig. 2 a stereoview of the crystal packing. Atoms Ag, As, F(1), F(2) and F(3) lie on a crystallographic mirror plane.

The crystal structure is built up from an infinite, F-bridged $(\mathrm{Ag{-}F})_n^{n+}$ chain lying along the *a* axis [average Ag–F(1) = 2·000 (5) Å, F–Ag–F = 175·5 (2)° and Ag–F–Ag = 143·3 (3)°], and $[\mathrm{AsF_6}]^-$ octahedra cross-linked to these chains *via* further F bridges. The Ag environment approximates to a pentagonal bipyramid with F(1) atoms at the apices. Of the F atoms in the pentagonal plane (Fig. 1), two F(4) atoms bridge to the same As atom [Ag–F(4) = 2·438 (4) Å], while one F(2) and two F(5) atoms bridge to different As atoms [Ag–F(2) = 2·439 (6), Ag–F(5) = 2·394 (4) Å]. The $\mathrm{AsF_6}$ ions are close to octahedral; the single non-bridging F(3) atom is closer [1·677 (7) Å] than the remainder, which span the range 1·714 (4)–1·729 (6) Å.

The structure of $\mathrm{AgF_2.AsF_5}$ is very different from that of $\mathrm{AgF_2}$ itself (Fischer, Schwarzenbach & Rietveld, 1971) and from that of $\mathrm{AgF_2.2SbF_5}$ (Gantar, Leban, Holloway & Frlec, 1987), in both of which the coordination around the Ag atom is probably best regarded as square planar. The average bond length of the Ag–F bonds in the square plane about Ag in $\mathrm{AgF_2.2SbF_5}$ [2·114 (5) Å] is a little longer than the equivalent in $\mathrm{AgF_2}$ [2·071 (6) Å]. The average Ag–F distance in $[\mathrm{Ag{-}F}]_n^{n+}$ is somewhat shorter than both and probably reflects the cationic nature of the chain. The Ag–F distances in the pentagonal plane about Ag in $\mathrm{AgF_2.AsF_5}$ are of the same order as the elongated bonds in the $\mathrm{AgF_2.2SbF_5}$ structure [*i.e.* Ag–F(2$^{\mathrm{ii}}$), Ag–F(2$^{\mathrm{iii}}$) at 2·431 (3) Å], but are shorter than those of the next nearest neighbours in $\mathrm{AgF_2}$ [2·584 (6) Å]. This is a consequence of the small covalent interaction through F bridging anions and cations in the two adducts.

The observation of linear $(\mathrm{Ag{-}F})_n^{n+}$ and cyclic $(\mathrm{Sn{-}F})_3^{3+}$ chains in the structures of $\mathrm{AgF_2.AsF_5}$ and $\mathrm{SnF_2.AsF_5}$ coupled with the knowledge that none of the related metal difluoride adducts is isostructural, suggests that other novel cationic species may occur in this class of compounds.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2)

$U_{\mathrm{eq}} = \frac{1}{3}\sum U_{ii}$.

	x	y	z	U_{eq}
As	0·29822 (13)	0·25000	0·56139 (9)	0·0216 (5)
Ag	0·13105 (8)	0·25000	0·24264 (6)	0·0186 (4)
F(1)	0·3849 (7)	0·25000	0·1861 (6)	0·032 (3)
F(2)	0·5031 (9)	0·25000	0·4844 (6)	0·040 (3)
F(3)	0·0992 (9)	0·25000	0·6357 (8)	0·059 (4)
F(4)	0·2294 (7)	0·0808 (7)	0·4453 (4)	0·041 (2)
F(5)	0·3729 (6)	0·0764 (6)	0·6699 (4)	0·040 (2)

Table 2. *Bond lengths* (Å) *and angles* (°)

F(1$^{\mathrm{i}}$)–Ag	1·995 (5)	F(2)–As	1·729 (4)
F(1)–Ag	2·004 (5)	F(3)–As	1·677 (7)
F(2$^{\mathrm{i}}$)–Ag	2·439 (7)	F(4)–As	1·727 (4)
F(4)–Ag	2·438 (4)	F(5)–As	1·714 (4)
F(5$^{\mathrm{ii}}$)–Ag	2·394 (4)		
F(1)–Ag–F(1$^{\mathrm{i}}$)	175·5 (2)	F(2$^{\mathrm{i}}$)–Ag–F(5$^{\mathrm{ii}}$)	73·8 (1)
F(2$^{\mathrm{i}}$)–Ag–F(1$^{\mathrm{i}}$)	87·1 (2)	F(2$^{\mathrm{i}}$)–Ag–F(4)	150·8 (1)
F(2$^{\mathrm{i}}$)–Ag–F(1)	97·3 (2)	F(2)–As–F(3)	179·9 (1)
F(4$^{\mathrm{iv}}$)–Ag–F(1$^{\mathrm{i}}$)	89·9 (2)	F(2)–As–F(4)	88·9 (2)
F(4)–Ag–F(1)	86·2 (2)	F(2)–As–F(5)	88·6 (2)
F(5$^{\mathrm{ii}}$)–Ag–F(1$^{\mathrm{i}}$)	95·4 (1)	F(4)–As–F(3)	91·0 (3)
F(5$^{\mathrm{ii}}$)–Ag–F(1)	85·9 (1)	F(5)–As–F(3)	91·5 (2)
F(4$^{\mathrm{iv}}$)–Ag–F(4)	58·1 (2)	F(4$^{\mathrm{iv}}$)–As–F(4)	86·6 (2)
F(5$^{\mathrm{iii}}$)–Ag–F(5$^{\mathrm{ii}}$)	145·1 (1)	F(4$^{\mathrm{iv}}$)–As–F(5$^{\mathrm{iv}}$)	91·6 (2)
F(4$^{\mathrm{iv}}$)–Ag–F(5$^{\mathrm{ii}}$)	77·6 (1)	F(4$^{\mathrm{iv}}$)–As–F(5)	177·0 (2)
F(4)–Ag–F(5$^{\mathrm{iii}}$)	135·4 (2)	F(5$^{\mathrm{iv}}$)–As–F(5)	90·2 (2)
Ag$^{\mathrm{v}}$–F(1)–Ag	143·3 (3)	Ag–F(4)–As	107·6 (2)
Ag$^{\mathrm{v}}$–F(2)–As	139·5 (3)		

Superscripts refer to the following transformations: (i) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (iv) $x, \frac{1}{2}-y, z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$.

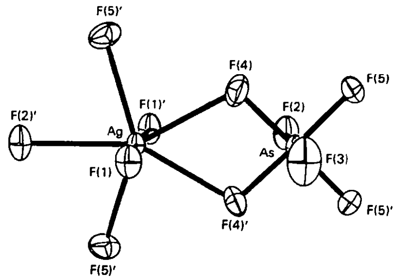

Fig. 1. A view of the structure showing the Ag and As atoms.

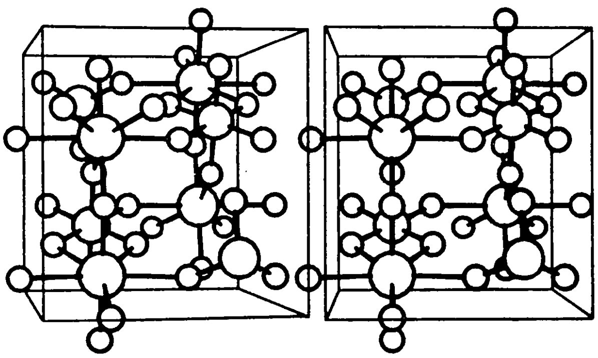

Fig. 2. A stereoview showing the crystal packing.

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Triclinic $ReAl_{\sim 4}$, a Periodic Domain Structure Variant of the Monoclinic WAl_4 Type

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Dedicated to Professor Kurt Komarek, University of Vienna, on the occasion of his 60*th birthday*

Abstract. $Re_{14}Al_{57-x}$ with $x = 2\cdot25$, $M_r = 4145\cdot08$ (for 14/57), triclinic, *aP*71 (for 14/57), $P\bar{1}$, $a = 5\cdot159$ (1), $b = 9\cdot106$ (1), $c = 23\cdot755$ (2) Å, $\alpha = 100\cdot94$ (1), $\beta = 90\cdot30$ (1), $\gamma = 93\cdot00$ (1)°, $V = 1094\cdot0$ (3) Å^3, $Z = 1$ (for 14/57), $D_x = 6\cdot291$ Mg m^{-3} (for 14/57), λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 43$ mm^{-1}, $F(000) = 1791$ (for 14/57), $T = 293$ K, $R = 0\cdot086$ for 2141 contributing independent reflections. $Re_{14}Al_{57-x}$ can be described as a stacking of two slabs, both about 11·6 Å thick, one cut parallel to (110) and the second cut parallel to ($\bar{1}10$) from the monoclinic WAl_4 structure. In one unit cell of $Re_{14}Al_{57-x}$ two WAl_4-type slabs, one of each kind, are stacked parallel to (001). Two kinds of antidomain boundary are found, one with perfect match and a second with less perfect match which provides space for an extra Al site. However, since all Al atom sites at or close to the second antidomain boundary are only partially occupied, the overall composition, despite the extra Al site, has fewer Al atoms than expected for 1:4 stoichiometry.

Introduction. The binary system Re–Al, recently investigated by Schuster (1984), is characterized by the formation of six binary compounds which all decompose before melting. The structures of two compounds tentatively labelled $ReAl_3$ and $ReAl_4$ are unknown. We report here on the structure of the latter for which d'Alte da Veiga (1963) assumed a triclinic unit cell with $a = 9\cdot13$, $b = 13\cdot8$, $c = 5\cdot16$ Å, $\alpha = 99\cdot5$, $\beta = 94$ and $\gamma = 103\cdot5°$. The cited author expected a close structural relationship between the triclinic $ReAl_4$ structure and the monoclinic WAl_4 type (Bland & Clark, 1958) [found also with $MoAl_4$ (Leake, 1964)] based simply on the presence of axes about 5·2 Å along in both structure types, and he made a proposal how the $ReAl_4$ cell could be fitted to the WAl_4 cell. We shall see from our complete structure determination that there is really a close geometrical relationship between both structure types; however, the unit-cell relationship between $ReAl_4$ and WAl_4 proposed by d'Alte da Veiga (1963) does not hold. Only two unit-cell vectors of his proposed cell for $ReAl_4$ are correct.

Experimental. A cold pressed powder mixture $Re_{0.1}$-$Al_{0.9}$ (Re 99·99%, Al 99·999%) was arc melted under argon atmosphere. The particular composition was chosen to allow the growth of $ReAl_4$ crystals at 1273 K. From the phase diagram $ReAl_4$ is in equilibrium with liquid aluminium at this temperature. The heat treatment of the sample was made in an alumina crucible which was placed inside an evacuated quartz tube. After 48 h the sample was water quenched and the unreacted Al dissolved in HCl. The residue consisted of needle-shaped metallic crystals containing 20·5–20·7 at.% Re (by atomic absorption analysis). The only major impurity found by spectrographic analysis was silicon. The rather complex powder diffraction pattern indicated this phase to be related to, but not isotypic with, the WAl_4 type. A needle with mean diameter of 0·015 mm and of 0·1 mm length (volume equal to that of a sphere of 0·0175 mm radius) was chosen.

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