Table 2. *Final positional and thermal parameters with e.s.d.'s (all $\times 10^4$)*

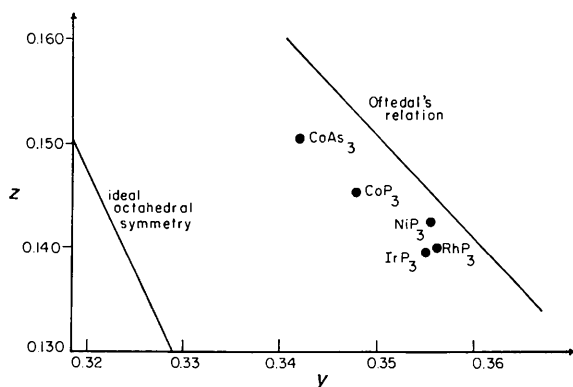|	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	$(\frac{1}{4})$	$(\frac{1}{4})$	$(\frac{1}{4})$	45 (2)	$(=\beta_{11})$	$(=\beta_{11})$	4 (4)	$(=\beta_{12})$	$(=\beta_{12})$
As	(0)	3431 (1)	1503 (1)	27 (1)	35 (1)	32 (1)	(0)	(0)	2 (3)

Fig. 2. Oftedal's relation *versus* ideal octahedral symmetry, with phosphide structures from Rundqvist & Ersson (1968).

Three quantities are of particular interest in discussing the structure: the Co–As distance, the distortion of the As_4 groups from a square, and the degree of distortion of the $CoAs_6$ octahedron. For the two As–As distances equal, $2(y+z)=1$. This trival equation has been called the Oftedal relation. For regular octahedral coordination about the Co atom, the parameters y and z for the As atoms must satisfy the relation $y(2z-1)=z-\frac{3}{8}$. Deviation from this relationship leads to a trigonal antiprismatic distortion from octahedral symmetry. The distances for the Oftedal structure are Co–As = 2·35 Å, and As–As = 2·45 Å. Ventriglia's distances are Co–As = 2·23 Å, As–As = 2·55 and 4·09 Å. Ventriglia stated that these distances agreed better with experimental data, but gave no observed or calculated structure factors. The distances found in the present study are Co–As = 2·334 ± 0·001 Å, As–As = 2·572 ± 0·002 and 2·464 ± 0·002 Å. The two As–Co–As angles in the octahedron are 95·4 and 84·6°. Fig. 2 shows the relation between y and z for regular octahedral coordination and for equal As–As distances. Note, as was also pointed out by Rundqvist & Ersson (1968), that both 'ideal' conditions cannot be realized simultaneously without a change in the structure type, as mentioned below.

Following the discussion of Rundqvist & Ersson (1968), an increasing trigonal distortion of the ideal octahedral symmetry of the ligands about the Co atoms presumably leads to a less favorable energetic situation as regards the Co–As bonds. On the other hand, a departure from the Oftedal relation, which means an elongation of two of the As–As bonds, probably leads to a less favorable bonding in the As_4 rings. As seen in Fig. 2, Oftedal's relation and the condition for ideal octahedral symmetry cannot be simultaneously fulfilled, except for a drastic structural change to the ReO_3-type structure. This condition occurs at the intersection of the extension of the two lines in Fig. 2, at $y= z=\frac{1}{4}$. Since the presence of As–As bonding is apparently essential for the stability of the compounds, a compromise is reached between the two opposing factors.

Note that in the skutterudite-type phosphides, the shorter P–P bond distance is virtually constant at $2·23 \pm 0·01$ Å which corresponds well with the P–P distances of 2·21 Å in P_4 and 2·25 Å in P_4S_3 (Sutton, 1958). In skutterudite itself the shorter As–As distance of 2·46 Å is in good agreement with distances of 2·45 Å in $(AsCF_3)_4$ (Mandel & Donohue, 1971), 2·43 Å in $(AsCH_3)_5$ (Burns & Waser, 1957), 2·46 Å in $(AsC_6H_5)_6$ (Hedberg, Hughes & Waser, 1961), and of 2·44 Å in gaseous As_4 (Maxwell, Hendricks & Moseley, 1935).

References

Burns, J. H. & Waser, J. (1957). *J. Amer. Chem. Soc.* **79**, 859.
Hedberg, K., Hughes, E. W. & Waser, J. (1961). *Acta Cryst.* **14**, 369.
International Tables for X-ray Crystallography (1967). Vol. II, p. 300. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1968). Vol. III, p. 201. Birmingham: Kynoch Press.
Mandel, N. & Donohue, J. (1971). *Acta Cryst.* B**27**, 476.
Maxwell, L. R., Hendricks, S. B. & Moseley, V. M. (1935). *J. Chem. Phys.* **3**, 699.
Oftedal, I. (1928). *Z. Kristallogr.* A**66**, 517.
Rundqvist, S. & Ersson, N. O. (1968). *Ark. Kemi*, **30**, 103.
Sutton, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* London: The Chemical Society.
Ventriglia, U. (1957). *Period. Miner.* **26**, 345.

A simple 'direct' solution of the crystallographic phase problem.

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The 'difference' Patterson function, based on neutron-diffraction data, between a hydrogen compound and its deuteriate led to a direct, and absolute, structure determination.

We have recently completed precise structure analyses of potassium hydrogen di-trifluoroacetate, $KH(CF_3CO_2)_2$, and its deuteriate, $KD(CF_3CO_2)_2$, based on full neutron-diffraction data (Macdonald & Speakman, 1971). We then com-

puted the 'difference' Patterson function, with coefficients $(F_D^2-F_H^2)$, where $|F_D|$ and $|F_H|$ are the respective neutron structure amplitudes, each on an absolute scale. The outcome is represented on the left-hand side of Fig. 1.

As these acid salts are almost identically isomorphous, as the single hydrogen atom lies at a centre of symmetry ($I2/a$, $Z=4$), and as the neutron-scattering lengths of D and H are $+6\cdot5$ and $-3\cdot8$ fermi, the map shows a complete image of the structure. The nine peaks shown are the nine highest, and only significant, independent peaks of the Patterson function. (The peak representing the hydrogen atom has a poor profile in the y direction, but this (origin) peak is sensitive to slight errors in the data.)

This exercise is a logical, and obvious, extension of a method of absolute structure determination developed in the 1930's (Beevers & Lipson, 1934; Robertson, 1936; Robertson & Woodward, 1940). Whether we refer to the heavy-atom method or to that of isomorphous replacement may be debated. We prefer to regard the 'difference atom', (D–H), as 'heavy', with a scattering power of $+10\cdot3$ fermi.

A crystal belonging to the space group $I2/a$ yields a vector pattern in $I2/m$; hence any image of the true structure is doubled by a mirror-plane. Fortunately all the atoms are free from overlap except for the one oxygen atom which, consequently, has a peak of nearly double height. So we easily recognize an acceptable molecule in a correct position in the cell. The mirror ambiguity would equally have compromised the absolute structure determination of platinum phthalocyanine ($P2_1/a \rightarrow P2/m$) had it been possible, at the time, to apply the method three-dimensionally.
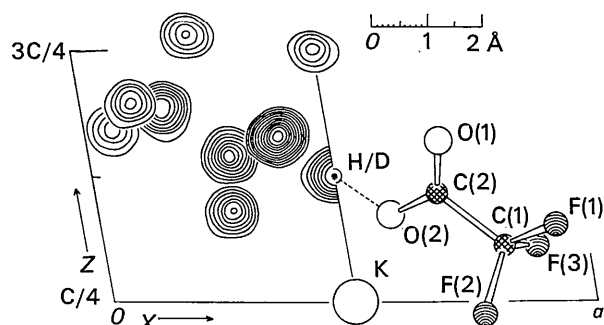

Fig. 1. On the left-hand side are sections from the three-dimensional 'difference' Patterson function, with positive contours at 4,6,8 ... in arbitrary units. On the right is the crystal structure established and refined by normal X-ray and neutron diffraction analysis. (The asterisk symbolizes a centre of inversion at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$.)

References

Beevers, C. A. & Lipson, H. (1934). *Proc. Roy. Soc.* A **146**, 570.

Macdonald, A. L. & Speakman, J. C. (1971). *J. Chem. Soc.* To be published. (See also Golić, L. & Speakman, J. C. (1965). *J. Chem. Soc.* p. 2530.)

Robertson, J. M. (1936). *J. Chem. Soc.* p. 1195.

Robertson, J. M. & Woodward, I. (1940). *J. Chem. Soc.* p. 36.

The crystal structure of K₇Th₆F₃₁.* By George Brunton, *Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.*

The complex fluoride $K_7Th_6F_{31}$ is isostructural with $Na_7Zr_6F_{31}$. It is trigonal, $R\bar{3}$, with hexagonal axes $a_0=15\cdot293$ (2) and $c_0=10\cdot449$ (2) Å, $Z=3$ and $\varrho_{cal}=5\cdot307$ g.cm⁻³. The eight Th–F distances range from $2\cdot24$ (1) to $2\cdot41$ (1) Å. The K–F distances range from $2\cdot63$ (2) to $3\cdot36$ (2) Å.

The structure of $K_7Th_6F_{31}$ is identical to that of $Na_7Zr_6F_{31}$ (Burns, Ellison & Levy, 1968) and was determined to confirm the supposition that all $7AF.6MF_4$ complexes are probably isostructural, ($A=Na$, K, Rb and NH₄, and $M=$most of the tetravalent lanthanides and actinides) (Thoma, 1962).

The reflection data were collected from an ellipsoidal

Table 1. *Lattice and atomic parameters for* K₇Th₆F₃₁

Space group $R\bar{3}$, $a_0=15\cdot293$ (2), $c_0=10\cdot449$ (2) Å, $Z=3$, $\varrho_{cal}=5\cdot307$ g.cm⁻³.

Standard errors in parentheses, corresponding to the last significant digit, are given by the variance–covariance matrix.

	x	y	z	$*\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12}=10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
K(1)	0·0824 (4)	0·3088 (4)	0·4948 (5)	30 (3)	37 (3)	53 (4)	20 (2)	−4 (3)	1 (3)
K(2)	0	0	$\frac{1}{2}$	26 (4)	β_{11}	37 (8)	$(\frac{1}{2}\beta_{11})$	0	0
Th	0·18917 (4)	0·05122 (4)	0·17732 (6)	16 (1)	14 (1)	24 (1)	7 (1)	1 (1)	1 (1)
F(1)	0·3548 (7)	0·1126 (7)	0·0938 (9)	1·4 (2)†					
F(2)	0·1834 (8)	0·0551 (8)	0·392 (1)	1·8 (2)					
F(3)	0·2747 (8)	0·3717 (8)	0·425 (1)	1·7 (2)					
F(4)	0·2103 (9)	0·1602 (9)	0·004 (2)	2·8 (3)					
F(5)	0·2442 (9)	0·544 (1)	0·446 (2)	2·9 (3)					
F(6)	0	0	0·03 (2)	10 (6)					

* Coefficients in the temperature factor: $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$.

† Isotropic B.