

number of variables in a structure refinement. The following is based on Janner, Janssen & de Wolff (1983*a,b*). The diffraction pattern of tetragonal SAM, or SAW, can be divided unambiguously into sets of main reflections and of satellite reflections. Main reflections are those which become the cubic reflections above T_c . They correspond to a (pseudo-cubic) tetragonal I lattice. The main reflections are surrounded cuboctahedrally by satellite reflections ($h + \alpha, k, l + \theta$), ($h, k + \alpha, l + \theta$), ($h + \alpha, k + \alpha, l$). These can be described by linear combinations of basic modulation vectors $q_1 = (\alpha, 0, 0)$, $q_2 = (0, \alpha, 0)$ and $q_3 = (0, 0, \theta)$. For the sake of simplicity it is assumed that α and θ deviate slightly from the rational value $\frac{1}{2}$. The positions and intensities of all reflections with wavevectors $k = ha^* + kb^* + lc^* + m_1q_1 + m_2q_2 + m_3q_3$ are invariant under the point group of the pattern of main reflections. Hence the Bravais class is $I4/mmm$ ($\alpha, 0, 0; 0, 0, \theta$), i.e. No. 3-170 in Table 1 of Janner, Janssen & de Wolff (1983*a*). A preliminary attempt to apply the superspace approach was undertaken by Yamamoto (1988). He used the X-ray single-crystal data of SAM 11/82, which have been reported earlier as including a considerable number of questionable reflections (see *Experimental*). The refinement, employing the REMOS82 (Yamamoto, 1982) program, did not converge. Without a proof to the contrary it is assumed that this failure is attributable to the low crystal quality.

We are grateful to M. Ruedlinger for his contribution to the computational analysis of the data.

References

- DEPMEIER, W. (1984*a*). *Acta Cryst.* **C40**, 226–231.
 DEPMEIER, W. (1984*b*). *Acta Cryst.* **B40**, 185–191.
 DEPMEIER, W. (1988*a*). *Phys. Chem. Miner.* **15**, 419–426.
 DEPMEIER, W. (1988*b*). *Acta Cryst.* **B44**, 201–207.
 DEPMEIER, W., SCHMID, H., SETTER, N. & WERK, M. L. (1987). *Acta Cryst.* **C43**, 2251–2255.
 FISCHER, P. (1985). *IUCr Neutron Diffr. Newsl.* (April 1985), pp. 15–16.
 FLACK, H. D. (1987). *Acta Cryst.* **A43**, 564–568.
 HAZEN, R. M. & FINGER, L. W. (1982). *Comparative Crystal Chemistry*. New York: John Wiley.
 HENDERSON, C. M. B. & TAYLOR, D. (1978). *Phys. Chem. Miner.* **2**, 337–347.
 JANNER, A., JANSSEN, T. & WOLFF, P. M. DE. (1983*a*). *Acta Cryst.* **A39**, 658–666.
 JANNER, A., JANSSEN, T. & WOLFF, P. M. DE. (1983*b*). *Acta Cryst.* **A39**, 671–678.
 PRINCE, E. (1984). *Acta Cryst.* **A40** (Suppl.), C-433.
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
 SETTER, N. & DEPMEIER, W. (1984). *Ferroelectrics*, **56**, 45–48.
 SETTER, N., MENDOZA-ALVAREZ, M.-E., DEPMEIER, W. & SCHMID, H. (1984). *Ferroelectrics*, **56**, 49–52.
 STOKES, H. T. & HATCH, D. M. (1988). *Isotropy: Subgroups of the 230 Crystallographic Space Groups*. Singapore: World Scientific.
 WILES, D. B. & YOUNG, R. A. (1981). *J. Appl. Cryst.* **14**, 149–151.
 WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* **A37**, 625–636.
 YAMAMOTO, A. (1982). REMOS82. A computer program for the refinement of modulated structures. National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan.
 YAMAMOTO, A. (1988). Private communication.

Acta Cryst. (1991). **B47**, 206–209

Structure of Oxonium Hexafluoroantimonate(V)

By E. M. LARSON*

Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

AND KENT D. ABNEY,† ALLEN C. LARSON‡ AND P. GARY ELLER†

Los Alamos National Laboratory, Los Alamos, NM 87545, USA

(Received 30 April 1990; accepted 22 October 1990)

Abstract. $[\text{H}_3\text{O}][\text{SbF}_6]$, $M_r = 2038.09$, cubic, $I2_13$, $a = 10.120(7) \text{ \AA}$, $V = 1036.43 \text{ \AA}^3$, $Z = 8$, $D_x = 3.265 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha_1) = 0.70930 \text{ \AA}$, $\mu = 54.09 \text{ cm}^{-1}$, $F(000) = 928$, $T = 238 \text{ K}$, $R = 0.059$ and

$wR = 0.045$ for 288 reflections with $F_o \geq 3\sigma(F_o)$. Antimony lies at the center of a somewhat distorted octahedral array $[\text{F}—\text{Sb}—\text{F} = 84.4(3), 87.3(3), 92.2(4), 95.6(4)$ and $171.3(4)^\circ$, with $\text{Sb}—\text{F} = 1.891(7)$ and $1.854(9) \text{ \AA}$] of F atoms. Three fluorines are connected to the O atoms through hydrogen bonds as indicated by the $\text{F}—\text{O}$ distances of $2.622(12) \text{ \AA}$ and the other three F atoms have

* Address correspondence to this author.

† Isotope and Nuclear Chemistry Division.

‡ Manuel Lujan Jr Neutron Scattering Center, LANSCE.

F—O distances of 2.713 (10) Å. The six F atoms surrounding the oxygen form a squashed octahedron with F—O—F angles of 108.7 (5) and 109.2 (4)°.

Introduction

In the course of our studies of the reactions of uranium dioxide with the superacid, HF/SbF₅, crystals of oxonium hexafluoroantimonate were obtained as a reaction product. The crystals were identified from the lattice constants and space group published by Christe, Charpin, Soulie, Bougon, Fawcett & Russell (1984). However, an examination of the published structure revealed that a satisfactory refinement of the structure had not been achieved and the *R* value had not been reduced below 12%. In addition, Christe *et al.* (1984) noted some ambiguity in the space-group choice and raised the question of disorder. In contrast, we were able to solve the structure in a straightforward manner with our data set and obtained an ordered solution with a final *R* factor below 5%. As described below, our final analysis leads us to believe that the material of Christe *et al.* (1984) may not have been disordered, but that a subtle but incorrect choice of origin was made for their data set.

Experimental

A crystal in the form of a cube of about 0.2 mm on an edge was mounted in a glass capillary. Data were collected by θ - 2θ scans ($2\theta_{\max} = 70^\circ$) on an Enraf-Nonius CAD-4 diffractometer using Mo $K\alpha_1$ (0.70930 Å) radiation and a graphite monochromator. The sample temperature was held at 238 ± 5 K using a stream of cold nitrogen gas. The unit-cell dimension was determined initially from precession photographs and finally by a least-squares refinement of 25 centered reflections ($9 \leq \theta \leq 21^\circ$) and is $a = 10.120$ (7) Å. The initial choice of space group, $Ia\bar{3}$, was based on systematically absent reflections, the observed symmetry and subsequent refinement. A total of 1460 reflections in a quadrant with indices $0 \leq h \leq 16$, $0 \leq k \leq 16$ and $0 \leq l \leq 16$ were collected. Data were corrected for absorption using a combination of spherical absorption (sphere radius = 0.15 mm) and ψ -scan data (maximum and minimum transmission coefficients were 0.390 and 0.282 respectively), and corrections for Lorentz and polarization factors were performed. The 643 space-group-allowed reflections in this set were then averaged to yield 369 unique reflections of which 227 were considered observed with $F_o \geq 3\sigma(F_o)$. The weighted *R* value based on F_o for merging of equivalent reflections was 0.042.

The structure was solved by standard Patterson methods and refined by full-matrix least-squares

Table 1. *Atom positions as fractional coordinates and anisotropic thermal parameters* ($\text{\AA}^2 \times 10^3$) *from the* $Ia\bar{3}$ *refinement*

The temperature factor is defined as $\exp[-2\pi(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

	x	y	z						
Sb	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$						
O	0	0	0						
F	0.1458 (3)	0.3095 (4)	0.1096 (3)						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}			
Sb	1.72 (3)	U_{11}	U_{11}	0.41 (3)	U_{12}	U_{12}			
O	3.80 (30)	U_{11}	U_{11}	1.74 (38)	U_{12}	U_{12}			
F	3.00 (19)	4.20 (24)	2.62 (19)	1.04 (19)	-0.43 (17)	0.62 (19)			

using the *General Structure Analysis System* (GSAS) (Larson & Von Dreele, 1986). The function minimized was $w(F_o - F_c)^2$ with weights determined by $w = (2F_o/\sigma F_o^2)^2$ and $\sigma F_o^2 = C(I + B + 0.01I^2)$, where *C* contains all of the corrections mentioned above. The final residuals for this refinement were $R = 0.050$ and $wR = 0.046$ and reduced $\chi^2 = 17.7$. Fifteen variables were refined including a scale factor and type II extinction parameter [final value, 2.4 (4) $\times 10^{-5}$] (Larson, 1970; Zachariasen, 1967) as well as positional and thermal parameters. Scattering factors including those for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). There were no significant features in the final difference Fourier map, the largest peak being 1.8 e \AA^{-3} located near the Sb atom *versus* observed Fourier map values of 20.9 e \AA^{-3} for the O atom and 18.6 e \AA^{-3} for the F atom. Atom positions and thermal parameters from this refinement are given in Table 1.

Careful reading of the paper by Christe *et al.* (1984) led us to wonder if the hydrogens in this material might be ordered, making the true space group $I2_13$. A reexamination of our data revealed that we had measured a few odd indexed $hk0$ reflections with I greater than $3\sigma(I)$, but only one at more than $9\sigma(I)$, and that one, 110, occurs at a very low θ value where background corrections are suspect. Of the 726 reflections measured with $h + k + l = 2n + 1$, none was observed with $I > 3\sigma(I)$. Examination of the normal probability plot (Abrahams & Keve, 1971), Fig. 1, revealed a tailing off of the curve at large $w(F_o - F_c)$. Plots of the weighted residuals *versus* F_o indicated that nearly all of the large $w(F_o - F_c)$ values came from weak reflections. The class of reflections with two odd indices contains no contribution from antimony and oxygen if the space group is $Ia\bar{3}$ and would have only a small contribution from them in $I2_13$ unless these atoms are significantly off the special positions at 0,0,0 and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. The thermal-motion ellipsoid for the oxygen did show some elongation along the threefold axis, however, the antimony ellipsoid was very nearly spherical.

We felt that it was unlikely that we would be able to refine the data in $I2_13$, but tried to do so anyway, using only the data from the reflection set allowed for the space group $Ia\bar{3}$. To our surprise, the refinement proceeded without problems, moving the oxygen slightly off 0,0,0 and shifting the two F atoms slightly, creating two Sb—F distances which differed by more than 10σ . The R factors for this refinement were $R = 0.037$ and $wR = 0.030$. At this point we reran the data-merge step to include all of the reflections allowed by $I2_13$. 734 space-group-allowed reflections in this set yielded 419 unique reflections, 288 of which were observed with $F_o \geq 3\sigma(F_o)$. The weighted R value based on F_o for the merging of equivalent reflections was 0.047. The final refinement in $I2_13$ involved 26 variables and yielded R factors of $R = 0.057$ and $wR = 0.046$ and a reduced $\chi^2 = 16.6$. The normal probability plot, Fig. 2, from this refinement is much more nearly linear than the $Ia\bar{3}$ refinement. Plots of the weighted residuals against F_o and d^* showed normal, expected distributions. It might be noted that two solutions were found in $I2_13$ with the oxygen displaced slightly in opposite directions from 0,0,0. These solutions had very similar R factors. One of these solutions

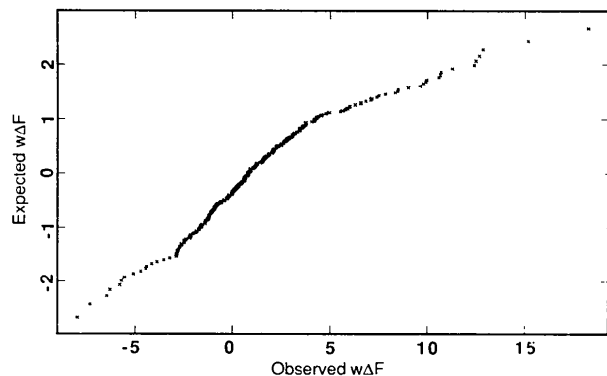


Fig. 1. Normal probability plot for the $Ia\bar{3}$ refinement.

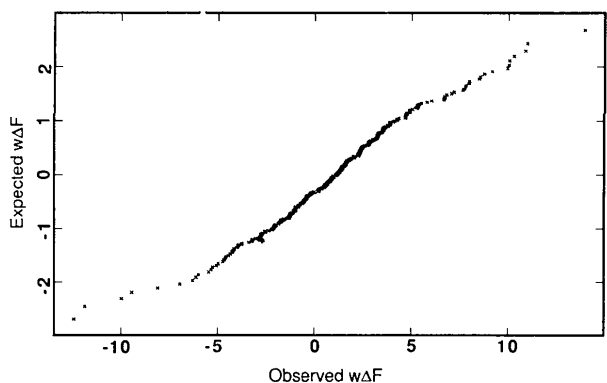


Fig. 2. Normal probability plot for the $I2_13$ refinement.

Table 2. Atom positions as fractional coordinates and anisotropic thermal parameters ($\text{\AA}^2 \times 10^2$) from the $I2_13$ refinement

Temperature factor as defined in Table 1.						
	x	y	z			
Sb	0.25016 (14)	x	x	U_{11}	U_{22}	U_{33}
O	0.0015 (12)	x	x	U_{11}	U_{11}	U_{12}
F(1)	0.1443 (7)	0.2980 (7)	0.1038 (7)	U_{11}	U_{12}	U_{12}
F(2)	0.3547 (8)	0.1779 (8)	0.3822 (9)	U_{11}	U_{12}	U_{12}
H	0.059	-0.072	-0.048	U_{11}	U_{12}	U_{23}
Sb	1.69 (3)	U_{11}	U_{11}	0.37 (3)	U_{13}	U_{12}
O	4.1 (3)	U_{11}	U_{11}	2.8 (5)	U_{12}	U_{12}
F(1)	2.7 (4)	2.0 (3)	0.9 (3)	0.9 (3)	0.4 (3)	0.3 (3)
F(2)	4.0 (5)	3.3 (4)	4.2 (5)	0.7 (4)	-1.8 (4)	-0.2 (4)

produced a non-positive-definite thermal ellipsoid on one F atom while the other, which we are reporting here, did not. These two solutions were obviously not very different.

The quality of our data does not warrant attempting to locate the H atoms, but Christie *et al.* (1984) include in their paper a neutron powder pattern collected at ILL, Grenoble. The GSAS crystal structure package is able to generate simulated powder patterns for a known structure, so it was used to calculate powder patterns in which the hydrogen was in turn placed along each of the O—F bonds at 1.05 Å from the oxygen with $U_{\text{iso}} = 0.05 \text{ \AA}^2$. The calculated powder pattern shows the extra lines noted by Christie *et al.* (1984) and the one with the hydrogen placed along the O—F(2) vector seemed to fit their pattern the best. Therefore, we ran a final least-squares refinement with the H atoms placed according to this model and report those results. The final R factors and χ^2 values are as given above, with no improvement on including H atoms, and the final value of the type II isotropic extinction parameter is $1.9(3) \times 10^{-5}$. The final atom positions and thermal parameters are given in Table 2.*

Discussion

Selected distances and angles from the $I2_13$ refinement, which we take as the best solution, appear in Table 3. Fig. 3 shows the environment of the SbF_6^- octahedra and Fig. 4 shows the environment of the H_3O^+ ion. The antimony coordination polyhedron is a somewhat distorted octahedron and similar to that reported in many SbF_6^- salts. While H atoms were not definitely located, their estimated positions based on the arguments presented above, are given. Overall our results are quite similar to those presented by Christie *et al.* (1984) from Rietveld

* The calculated and observed structure-factor data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53624 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected distances (Å) and angles (°) from the $I2_13$ refinement

Sb—F(1)	1.891 (7)	O—F(1)	2.713 (10)
Sb—F(2)	1.854 (9)	O—F(2)	2.622 (12)
F(1)—Sb—F(1)	84.4 (3)	F(1)—Sb—F(2)	87.3 (3)
F(2)—Sb—F(2)	95.6 (4)	F(1)—Sb—F(2)	92.2 (4)
F(1)—Sb—F(2)	171.3 (4)	F(1)—O—F(1)	109.2 (4)
F(2)—O—F(2)	108.7 (5)		

refinement of their neutron powder data as noted below. Except for an apparent misprint in the F(2) x value, their neutron structure is the same as our structure with positions transformed by $\frac{1}{4} + y$, $\frac{1}{4} + x$, $\frac{1}{4} + z$ to account for the change in origin.

Since it would appear that the primary difference between the solution reported herein and the previously published one is simply a shift of the origin (0,0,0 to $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), some discussion regarding this point is in order. Although both of these sites have $\bar{3}$ point symmetry, the two sites are not totally equivalent.

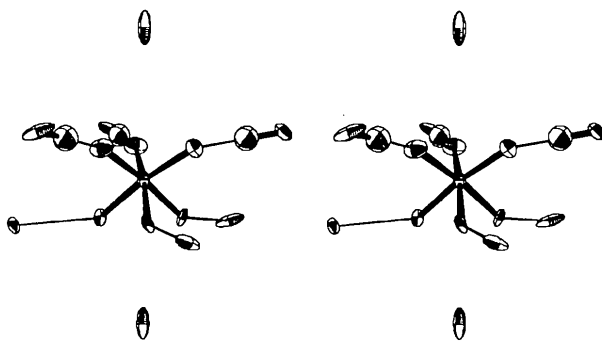


Fig. 3. Stereo plot of the antimony environment.

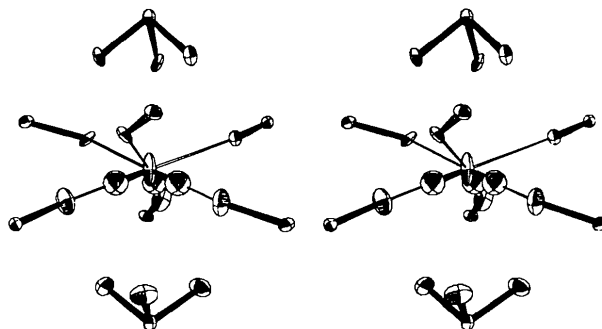


Fig. 4. Stereo plot of the oxygen environment.

The $\bar{3}$ site at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ is located at the intersection of glide mirrors bca while the $\bar{3}$ site at 0,0,0 is located at the intersection of glide mirrors cab . While the point symmetry of these two sites is identical, the environment about them is enantiomorphic. Which of these sites is needed to correctly describe the structure is determined by which of the two sets of enantiomorphic corners of the crystal is chosen to define the origin of the lattice. If Christe *et al.* (1984) had mounted their crystal such that an adjacent corner was chosen as the origin and thus the data collected was indexed as $kh'l$ relative to what was used for their structure, they probably would have had little difficulty in the refinement. As noted above, the final result can be easily transformed from one origin choice to the other by transposing x and y and adding the origin shift $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

However, another caveat should be added. On the basis of differential scanning calorimetry, Christe *et al.* (1984) reported three 'ordered' phases between 293 and 363 K and an additional disordered phase above 373 K, all attributed to rotation. Those observations could well indicate that the two crystals which were used for single-crystal data may have been different phases. It would seem more likely that the first of these phase transitions is similar to the ferroelectric transition in KDP, namely a disordering of the H atoms and a raising of the symmetry to $Ia\bar{3}$ on warming through the phase transition. The higher-temperature phase transitions could be a further disordering accompanied with a further increase in the symmetry, possibly to $Ia\bar{3}d$.

This work was carried out under the auspices of the US Departments of Energy, Office of Basic Energy Sciences Division of Material Sciences and Office of Nuclear Materials Production. We wish to acknowledge useful discussions of the symmetry problems presented here with Dr Robert Von Dreele and Professor John Rollett.

References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
 CHRISTE, K. O., CHARPIN, P., SOULIE, E., BOUGON, R., FAWCETT, J. & RUSSELL, D. R. (1984). *Inorg. Chem.* **23**, 3756–3766.
 LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291–294. Copenhagen: Munksgaard.
 LARSON, A. C. & VON DREELE, R. B. (1986). *GSAS. General Structure Analysis System*. Report LAUR-86-748. Los Alamos National Laboratory, NM, USA.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.