of the molecule leads to r.m.s. distances for the corresponding atoms of 0·120 and 0·094 Å for molecule (I) and (II), respectively. The molecular packing of the compound, Fig. 2, displays no intermolecular approaches with distances less than the sum of the van der Waals radii.

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References

BERRY, R. S. (1960). *J. Chem. Phys.* **32**, 933–938.

CROMER, D. & MANN, J. (1968). *Acta Cryst.* A**24**, 321–324.

GILLESPIE, P., HOFFMANN, P., KLUSACEK, H., MARQUARDING, D., PFOHL, S., RAMIREZ, F., TSOLIS, E. A. & UGI, I. (1971). *Angew. Chem.* **83**, 691–721.

HIRSHFELD, F. L. & RABINOVICH, D. (1973). *Acta Cryst.* A**29**, 510–513.

HOFFMANN, R., HOWELL, J. M. & MUETTERTIES, E. L. (1972). *J. Amer. Chem. Soc.* **94**, 3047–3058.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KEPERT, D. L. (1973). *Inorg. Chem.* **12**, 1942–1944.

SPRATLEY, R. D., HAMILTON, W. C. & LADELL, J. (1967). *J. Amer. Chem. Soc.* **89**, 2272–2278.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WIEBER, M. & HOOS, W. R. (1968). *Tetrahedron Lett.* **51**, 5333–5334.

WUNDERLICH, H. & MOOTZ, D. (1973). First European Crystallographic Meeting. Bordeaux.

WUNDERLICH, H. & MOOTZ, D. (1974). *Acta Cryst.* B**30**, 935–939.

WUNDERLICH, H., MOOTZ, D., SCHMUTZLER, R. & WIEBER, M. (1974). *Z. Naturforsch.* In the press.

X-RAY (1972). Technical Report TR-192 of the Computer Science Center, Univ. of Maryland, June 1972.

ZEMANN, J. (1963). *Z. anorg. allgem. Chem.* **324**, 241–249.

Acta Cryst. (1974). B**30**, 945

The Two-Dimensional Tunnel Structures of $K_3Sb_5O_{14}$ and $K_2Sb_4O_{11}$*

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The structures of $K_3Sb_5O_{14}$ and $K_2Sb_4O_{11}$ have been solved by the single-crystal X-ray direct method and the heavy-atom method, respectively. The structure of $K_3Sb_5O_{14}$ is orthorhombic, with space group *Pbam* and cell parameters $a=24{\cdot}247$ (4), $b=7{\cdot}157$ (2), $c=7{\cdot}334$ (2) Å, $Z=4$. The structure of $K_2Sb_4O_{11}$ is monoclinic, with space group $C2/m$ and cell parameters $a=19{\cdot}473$ (4), $b=7{\cdot}542$ (1), $c=7{\cdot}198$ (1) Å, $\beta=94{\cdot}82$ (2)°, $Z=4$. A full-matrix least-squares refinement gave $R=0{\cdot}072$ and $R=0{\cdot}067$, respectively. In both structures, oxygen atoms form an octahedron around each Sb atom and an irregular polyhedron around each K atom. By sharing corners and edges, the octahedra form a skeleton network having intersecting *b*-axis and *c*-axis tunnels. The K^+ ions, which have more than ten oxygen near neighbors, are located in these tunnels. Evidence for K^+-ion transport within and between tunnels comes from ion exchange of the alkali ions in molten salts and anisotropic temperature factors that are anomalously large in the directions of the tunnels.

Introduction

Unlike Nb^{5+} and Ta^{5+}, the Sb^{5+} ion does not form structures having 180° Sb–O–Sb linkages (Goodenough & Kafalas, 1973). Thus $KSbO_3$ does not form the cubic perovskite structure. At atmospheric pressure it generally has the rhombohedral ilmenite structure. However, Spiegelberg (1940) reported synthesizing two cubic phases of $KSbO_3$ by annealing the ilmenite $KSbO_3$ for 3 weeks at 1000°C in a porcelain crucible. The structure of one of these, *Pn*3, was determined by him. The structure of the other, *Im*3, was elucidated by the present author (Hong, Kafalas & Goodenough, 1973). Both cubic structures contain Sb_2O_{10} edge-shared octahedra. These octahedral-site pairs share corners to form a three-dimensional skeleton structure containing empty tunnels of face-shared octahedra that run parallel to the cubic diagonals. In the *Pn*3 structure, the K^+ ions are ordered on the

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octahedral sites of these tunnels, while in *Im*3 the K^+ ions are distributed randomly on these octahedral sites. The *Im*3-$KSbO_3$ structure can be ion-exchanged (Hong *et al.*, 1973) to $MSbO_3$ (M = Li, Na, Rb, Ag, Tl) in molten salt.

The Sb^{5+} ion, preferring to form pairs of edge-shared oxygen octahedra, should produce other examples of three-dimensional networks containing large-mouth tunnels or voids. Such skeleton structures are of potential interest for fast-ion transport (Hong *et al.*, 1973). We have therefore synthesized two compounds, $K_3Sb_5O_{14}$ and $K_2Sb_4O_{11}$, to demonstrate other skeleton structures built by these Sb_2O_{10} pairs of edge-shared octahedra. The structure of $K_3Sb_5O_{14}$ was solved by the direct method in space group *Pbam*, which is different from that previously reported (Aurivillius, 1966) as *Pba*2. The $K_2Sb_4O_{11}$ compound was synthesized and its structure determined for the first time.

Experimental procedure

Single crystals of $K_3Sb_5O_{14}$ were obtained by first heating overnight at 800°C in platinum crucibles K_2CO_3 and Sb_2O_3 in the molar ratio 3:5. The product was then ground and fired at 1100°C for two days. A number of square-plate, single crystals were formed in this preparation. The thickness of a plate, which is the direction of the longest axis, was about one-third of its square edge.

The compound $K_2Sb_4O_{11}$ was discovered by a wet preparation. A saturated K_2CO_3 water solution was neutralized by $SbCl_5$. The white precipitate was evaporated slowly to dryness, then fired up to 600°C overnight, ground and refired at 1100°C for two days. The single crystals formed in this procedure have a crystal habit similar to that of $K_3Sb_5O_{14}$. The square edge was about 0·1 mm to 0·5 mm in both compounds.

For X-ray diffraction studies, a small crystal of each compound was mounted on a goniometer head. The $K_3Sb_5O_{14}$ crystal measured 0·05 × 0·15 × 0·15 mm and was mounted about the *c* axis (0·15 mm), while the $K_2Sb_4O_{11}$ crystal measured 0·03 × 0·10 × 0·10 mm and was mounted about the *b* axis (0·1 mm). Oscillation and Weissenberg photographs showed diffraction symmetry *mmm* for $K_3Sb_5O_{14}$, and the systematic absences were $0kl$, $k=2n+1$, and $h0l$, $h=2n+1$, which is consistent with space groups *Pba*2 and *Pbam*. For $K_2Sb_4O_{11}$, the diffraction symmetry is $2/m$ and the systematic absences were hkl, $h+k=2n+1$, which is consistent with space groups *Cm*, *C*2 and *C*2/*m*.

Three-dimensional intensity data to $2\theta \leq 50°$ were collected – a total of 952 independent reflections for $K_3Sb_5O_{14}$ and 1003 independent reflections for $K_2Sb_4O_{11}$ – by the stationary-crystal, stationary-counter method using Zr-filtered Mo $K\alpha$ radiation and a 5° take-off angle. Each peak was counted for 10 s and the background (at 2° below the 2θ value of the peak) was also counted for 10 s. Lorentz, polarization and φ-angle absorption corrections were applied. The intensity variation on the φ angle was within 15% for $K_3Sb_5O_{14}$ and 20% for $K_2Sb_4O_{11}$. The equation

$$\sigma(F)=\tfrac{1}{2}\left[K\frac{1+I_B/I_P}{1-I_B/I_P}\right]^{1/2}$$

was used to estimate the variance for the structure factors, where I_B is the background count, I_P is the peak count, and K is the product of the Lorentz, polarization and absorption corrections.

Structure determinations

$K_3Sb_5O_{14}$

The direct method for determination of phases was used in the solution of this structure. First, a Wilson plot was constructed. This plot provided an approximate scale factor and also indicated a centric distribution of intensities so that the space group *Pbam* was chosen. The sequence of computer programs *FAME-MAGIC-LINK-SYMPL* (R. Dewar & A. Stone, Univ. of Chicago) was used to generate 250 phases from seven symbol-assigned reflections. Two *E* maps were generated using different sign combinations for the symbolic assignments, and the correct map was ascertained by checking interactions between the largest peaks against the Patterson map. The correct *E* map displayed a uniform distribution of peak heights, and the heights were in the appropriate ratio of the atomic numbers of the atoms. Two independent K and three independent Sb positions were clearly visible; the oxygen atoms could not be unambiguously assigned as there were a number of spurious peaks with heights equivalent to those of the oxygen atoms. A structure-factor calculation based on the K and Sb positions gave a value of 0·18 for the discrepancy index $R=$

Table 1. *Final atomic parameters and isotropic temperature factors in* $K_3Sb_5O_{14}$

Space group: *Pbam*, $Z=4$.
Unit-cell dimensions:
$a=24{\cdot}247$ (4), $b=7{\cdot}157$ (2), $c=7{\cdot}334$ (2) Å.
Standard deviations are given in parentheses.

	x	y	z	β (Å^2)
K(1)	0·0152 (6)	0·219 (2)	½	4·7 (3)
K(2)	0·2934 (6)	0·111 (2)	0	5·6 (3)
K(3)	0·3839 (6)	0·102 (2)	½	4·5 (3)
Sb(1)	0·0570 (1)	0·4169 (5)	0	0·51 (5)
Sb(2)	0·4379 (1)	0·4045 (5)	0	0·60 (5)
Sb(3)	0·2564 (1)	0·3249 (4)	½	0·51 (5)
Sb(4)	0·14506 (9)	0·1086 (3)	0·2646 (3)	0·51 (4)
O(1)	0	½	0·159 (4)	2·7 (7)
O(2)	0·017 (1)	0·156 (4)	0	1·6 (6)
O(3)	0·117 (1)	0·175 (5)	½	2·5 (7)
O(4)	0·136 (1)	0·024 (5)	0	2·8 (7)
O(5)	0·279 (1)	0·066 (4)	½	1·5 (6)
O(6)	0·410 (1)	0·154 (5)	0	2·9 (7)
O(7)	0·1046 (9)	0·336 (3)	0·188 (3)	2·0 (4)
O(8)	0·2096 (8)	0·254 (3)	0·284 (2)	1·4 (3)
O(9)	0·3150 (8)	0·379 (3)	0·316 (2)	1·6 (4)
O(10)	0·4249 (8)	0·460 (3)	0·251 (3)	2·2 (4)

$\sum|F_o-F_c|/\sum|F_o|$. A Fourier map immediately revealed the positions of eight independent oxygen atoms. The atom parameters, scale and isotropic temperature factors were then refined with a full-matrix, least-squares program to a final R value of 0·072 for all reflections and a weighted $R_w=0{\cdot}067$, where

$$R_w=[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}, \quad w=1/\sigma^2\,.$$

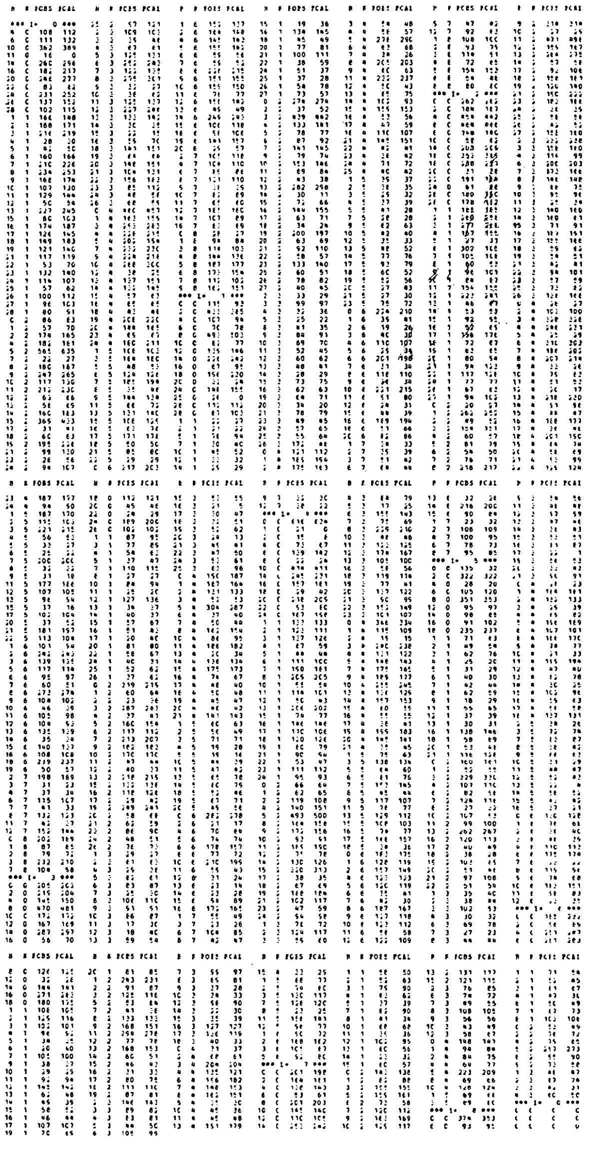
After this structure was solved, the author learned that Aurivillius (1966) had reported $K_3Sb_5O_{14}$ as having space group *Pba*2. Based on this space group, a least-squares refinement on our data gave $R=0{\cdot}075$ and $R_w=0{\cdot}069$ with negative temperature factors for those atomic positions having z coordination other than 0 or $\frac{1}{2}$. This indicates that the c axis contains mirror planes at $z=0$ and $z=\frac{1}{2}$. Thus three pieces of evidence indicate that *Pbam* is the right space group: (1) a Wilson plot showed a center of symmetry, (2) with

Table 2. *Distances* (Å) *and angles* (°) *in* $K_3Sb_5O_{14}$

Octahedron around Sb(1)			
Sb(1)-O(1)	2 × 1·90 (2)	O(1)-O(1)	2·33 (6)
Sb(1)-O(7)	2 × 1·89 (2)	O(1) O(2)	2·76 (3)
Sb(1)-O(2)	2·10 (3)	O(1)-O(6)	2·71 (3)
Sb(1)-O(6)	1·88 (3)	O(1)-O(7)	2·80 (2)
Sb(1)-Sb(2)	3·009 (5)	O(2)-O(6)	3·89 (4)
Sb(1)-Sb(2)	3·492 (5)	O(2)-O(7)	2·84 (3)
Sb(1) Sb(4)	3·632 (3)	O(6)-O(7)	2·68 (4)
Octahedron around Sb(2)			
Sb(2)-O(10)	2 × 1·91 (2)	O(2)-O(2)	2·38 (6)
Sb(2)-O(2)	1·97 (2)	O(2)-O(4)	3·93 (4)
Sb(2)-O(2)	2·11 (3)	O(2)-O(6)	2·93 (4)
Sb(2)-O(4)	1·99 (3)	O(2)-O(10)	2·71 (3)
Sb(2)-O(6)	1·92 (3)	O(4)-O(6)	2·87 (5)
Sb(2)-Sb(4)	3·154 (3)	O(4)-O(10)	2·40 (3)
Sb(2)-Sb(2)	3·307 (5)	O(6)-O(10)	2·83 (3)
Octahedron around Sb(3)			
Sb(3)-O(8)	2 × 2·01 (2)	O(5)-O(5)	3·84 (2)
Sb(3)-O(9)	2 × 2·00 (2)	O(5)-O(8)	2·68 (3)
Sb(3)-O(5)	1·93 (3)	O(5)-O(8)	2·75 (3)
Sb(3)-O(5)	1·93 (3)	O(5)-O(9)	2·97 (3)
Sb(3)-Sb(3)	3·592 (1)	O(5)-O(9)	2·76 (3)
Sb(3)-Sb(4)	3·558 (3)	O(8)-O(9)	2·72 (3)
Sb(3)-Sb(4)	3·579 (3)	O(8)-O(9)	2·76 (3)
Octahedron around Sb(4)			
Sb(4)-O(3)	1·92 (1)	O(3)-O(7)	2·58 (3)
Sb(4)-O(4)	2·04 (1)	O(3)-O(8)	2·80 (3)
Sb(4)-O(7)	1·98 (2)	O(3)-O(9)	3·00 (3)
Sb(4)-O(8)	1·88 (2)	O(3)-O(10)	2·60 (3)
Sb(4)-O(9)	1·94 (2)	O(4)-O(7)	2·73 (4)
Sb(4)-O(10)	2·00 (2)	O(4)-O(8)	3·19 (3)
Sb(4)-Sb(2)	3·154 (3)	O(4)-O(9)	2·80 (2)
Sb(4)-Sb(1)	3·632 (3)	O(4)-O(10)	2·40 (3)
Sb(4)-Sb(3)	3·558 (3)	O(7)-O(10)	2·82 (3)
Sb(4)-Sb(3)	3·579 (3)	O(9)-O(10)	2·77 (3)
Sb-O-Sb angles			
Sb(1)-O(2)-Sb(2)	121 (1)	Sb(1)-O(1)—Sb(1)	104 (1)
Sb(2)-O(2)-Sb(2)	108 (1)	Sb(4)-O(3)—Sb(4)	129 (2)
Sb(2)-O(2)-Sb(1)	129 (1)	Sb(3)-O(5)—Sb(3)	137 (1)
Sb(2)-O(4)-Sb(4)	103·0 (7)	Sb(1)-O(6)—Sb(2)	134 (1)
Sb(4)-O(4)-Sb(6)	143 (2)	Sb(1)-O(7)—Sb(4)	139 (1)
Sb(6)-O(4)-Sb(2)	103·0 (7)	Sb(3)-O(8)—Sb(4)	131·7 (9)
		Sb(3)-O(9)—Sb(4)	130 (1)
		Sb(2)-O(10)-Sb(4)	107 (1)
Polyhedron around K(1)		Polyhedron around K(2)	
K(1)-O(1)	2 × 3·23 (2)	K(2)-O(4)	1 × 3·42 (4)
K(1)-O(2)	2 × 3·695 (4)	K(2)-O(5)	2 × 3·698 (4)
K(1)-O(3)	1 × 2·49 (3)	K(2)-O(6)	1 × 2·84 (3)
K(1)-O(7)	2 × 3·26 (2)	K(2)-O(7)	2 × 3·44 (2)
K(1)-O(10)	2 × 2·98 (2)	K(2)-O(8)	2 × 3·08 (2)
K(1)-O(10)	2 × 3·13 (2)	K(2)-O(8)	2 × 3·29 (2)
		K(2)-O(9)	2 × 3·06 (2)

Polyhedron around K(3)	
K(3)-O(1)	2 × 3·83 (2)
K(3)-O(3)	1 × 3·06 (4)
K(3)-O(5)	1 × 2·56 (3)
K(3)-O(6)	2 × 3·740 (6)
K(3)-O(7)	2 × 2·99 (2)
K(3)-O(8)	2 × 3·72 (2)
K(3)-O(9)	2 × 2·93 (2)
K(3)-O(10)	2 × 3·30 (2)

Table 3. *Observed and calculated structure factors for* $K_3Sb_5O_{14}$



more variable parameters *Pba*2 gave the higher *R* index, (3) negative temperature factors appeared on those atomic positions that should have a mirror-symmetry operation.

The final atomic parameters and isotropic temperature factors are listed in Table 1. The bond distances and angles are listed in Table 2. Table 3 contains the structure factors.

$K_2Sb_4O_{11}$

The composition of the $K_2Sb_4O_{11}$ crystals was initially unknown. Nevertheless, because Sb is considerably heavier than either K or O, it was possible to solve the structure by using the heavy-atom method of structure analysis. A three-dimensional Patterson map was generated to distinguish between the three possible space groups *C*2, *Cm* and *C*2/*m*. If *Cm* is correct,

Table 4. *Final atomic parameters and anisotropic temperature factors in* $K_2Sb_4O_{11}$

Space group: *C*2/*m*, $Z=4$.
Unit-cell dimensions: $a=19{\cdot}473$ (4), $b=7{\cdot}542$ (1), $c=7{\cdot}198$ (1) Å, $\beta=94{\cdot}82$ (2)°.
The temperature factor is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	0·2383 (9)	0	0·005 (2)	0·0022 (3)	0·017 (2)	0·013 (2)	0	0·0010 (7)	0
K(2)	0·0103 (6)	0	0·261 (1)	0·0022 (3)	0·019 (3)	0·018 (2)	0	0·0009 (7)	0
Sb(1)	0·4246 (1)	0	0·3824 (3)	0·00014 (6)	0·0001 (4)	0·0000 (4)	0	0·0000 (1)	0
Sb(2)	0·4281 (1)	0	0·9029 (3)	0·00016 (6)	0·0001 (4)	0·0001 (4)	0	0·0000 (1)	0
Sb(3)	0·17445 (8)	0·2418 (2)	0·4349 (2)	0·00004 (4)	0·0006 (3)	0·0003 (2)	0·0000 (1)	0·00008 (7)	0·0000 (2)
O(1)	0	0·335 (3)	0	0·0006 (6)	0·002 (4)	0·011 (5)	0	0·000 (1)	0
O(2)	0·160 (1)	0	0·348 (3)	0·0009 (9)	0·011 (6)	0·009 (5)	0	0·000 (1)	0
O(3)	0·382 (1)	0	0·131 (4)	0·0013 (9)	0·030 (9)	0·007 (5)	0	0·000 (1)	0
O(4)	0·335 (1)	0	0·483 (3)	0·0007 (8)	0·011 (6)	0·007 (5)	0	0·000 (1)	0
O(5)	0·522 (1)	0	0·353 (3)	0·003 (1)	0·012 (6)	0·003 (5)	0	0·001 (1)	0
O(6)	0·412 (1)	0·257 (3)	0·433 (2)	0·0028 (7)	0·005 (3)	0·011 (4)	0·000 (1)	0·000 (1)	0·002 (3)
O(7)	0·2654 (9)	0·296 (2)	0·342 (2)	0·0017 (6)	0·009 (4)	0·006 (3)	0·000 (1)	0·000 (1)	0·001 (3)
O(8)	0·1296 (9)	0·309 (2)	0·189 (2)	0·0013 (5)	0·005 (3)	0·011 (3)	0·000 (1)	0·001 (1)	0·003 (3)

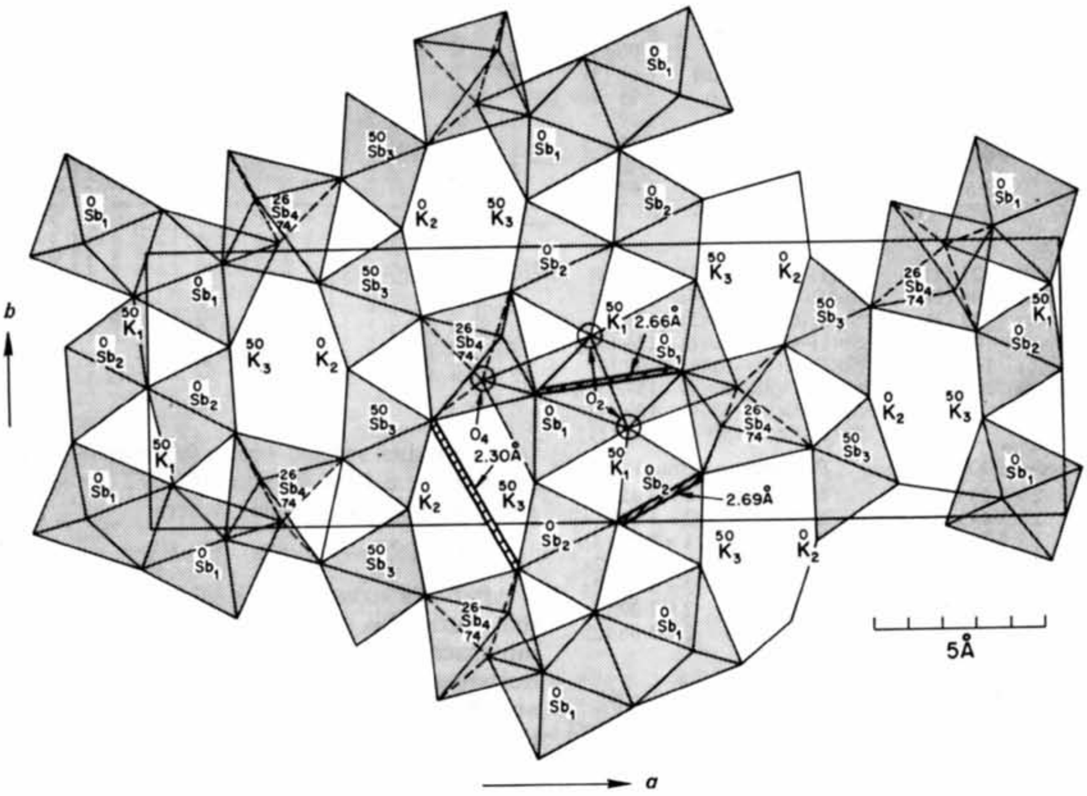


Fig. 1. An *ab* projection of the arrangement of SbO_6 octahedra in $K_3Sb_5O_{14}$, showing the tunnels that run parallel to the *b* axis and the *c* axis. The shaded bars represent the narrowest point along or between tunnels.

then a large number of interactions should be observed on the section $[0,y,0]$; and this was not the case: $(0,\frac{1}{2},0)$ is the only major peak. If $C2$ is the right space group, there is no mirror symmetry to produce the $(0,\frac{1}{2},0)$ peak, so $C2/m$ was chosen.

On the Patterson map, all major peaks appeared at y equal to 0, $\frac{1}{4}$ and $\frac{1}{2}$, which indicated that the heavy atom Sb would be located at special positions. Based on the prior knowledge that Sb readily forms pairs of edge-shared octahedra, it was possible to build a model for testing. Three independent Sb positions were located to give $R=0{\cdot}24$. A Fourier map based on this model revealed two independent K positions and eight O atoms. The atomic positions, scale and anisotropic temperature factors were then refined with a full-matrix, least-squares program to a final $R=0{\cdot}067$ and $R_w=0{\cdot}080$ for all reflections. A three-dimensional electron-density difference map calculated with the parameters in Table 4 showed no physically significant peaks. It was then evident that the compound had the chemical formula $K_2Sb_4O_{11}$ with four molecules per unit cell. The compound $K_2Sb_4O_{11}$ can also be synthesized by heating a mixture of K_2CO_3 and $2Sb_2O_3$ at 1100°C for two days. The bond distances and angles are listed in Table 5. Table 6 contains the observed and calculated structure factors.

Table 5. *Distances* (Å) *and angles* (°) *in the structure of* $K_2Sb_4O_{11}$

Octahedron around Sb(1)

Sb(1)–O(3)	1·93 (3)	O(3)–O(4)	2·76 (3)
Sb(1)–O(4)	1·94 (2)	O(3)–O(5)	3·04 (3)
Sb(1)–O(5)	1·93 (2)	O(3)–O(6)	2·93 (3)
Sb(1)–O(5)	2·09 (2)	O(4)–O(5)	2·93 (3)
Sb(1)–O(6)	2 × 1·99 (2)	O(4)–O(6)	2·49 (2)
Sb(1)–Sb(3)	2 × 3·109 (2)	O(5)–O(6)	2·98 (2)
Sb(1)–Sb(1)	3·264 (4)	Sb(1)–Sb(2)	3·741 (3)
Sb(1)–Sb(2)	3·458 (2)	Sb(1)–Sb(2)	3·666 (3)

Octahedron around Sb(2)

Sb(2)–O(1)	2 × 1·958 (2)	O(1)–O(1)	2·489 (4)
Sb(2)–O(8)	2 × 1·91 (2)	O(1)–O(3)	2·84 (2)
Sb(2)–O(3)	1·94 (3)	O(1)–O(5)	2·83 (2)
Sb(2)–O(5)	2·15 (2)	O(1)–O(8)	2·77 (2)
Sb(2)–Sb(2)	3·022 (4)	O(3)–O(5)	3·04 (3)
Sb(2)–Sb(3)	2 × 3·588 (2)	O(3)–O(8)	2·71 (3)
		O(5)–O(8)	2·87 (2)

Octahedron around Sb(3)

Sb(3)–O(2)	1·941 (7)	O(2)–O(6)	2·86 (3)
Sb(3)–O(4)	2·048 (7)	O(2)–O(7)	2·98 (2)
Sb(3)–O(6)	2·00 (2)	O(2)–O(8)	2·64 (2)
Sb(3)–O(7)	1·93 (2)	O(4)–O(6)	2·49 (2)
Sb(3)–O(7)	1·99 (2)	O(4)–O(7)	2·76 (2)
Sb(3)–O(8)	1·97 (2)	O(4)–O(8)	2·80 (2)
Sb(3)–Sb(3)	3·014 (3)	O(6)–O(7)	2·89 (2)
		O(7)–O(7)	2·50 (3)
		O(7)–O(8)	2·78 (2)

Sb–O–Sb angles

Sb(1)–O(4)–Sb(3)	102·3 (6)	Sb(2)–O(1)–Sb(2)	101·0 (1)
Sb(3)–O(4)–Sb(3)	144 (1)	Sb(3)–O(2)–Sb(3)	140 (1)
Sb(3)–O(4)–Sb(1)	102·3 (6)	Sb(1)–O(3)–Sb(2)	127 (1)
Sb(1)–O(5)–Sb(1)	108 (1)	Sb(1)–O(6)–Sb(3)	102 (1)
Sb(1)–O(5)–Sb(2)	123 (1)	Sb(3)–O(7)–Sb(3)	100·7 (7)
Sb(2)–O(5)–Sb(1)	128 (1)	Sb(2)–O(8)–Sb(3)	135·0 (8)

Polyhedron around K(1)		Polyhedron around K(2)	
K(1)–O(2)	1 × 3·01 (3)	K(2)–O(1)	2 × 3·145 (5)
K(1)–O(3)	1 × 2·86 (3)	K(2)–O(2)	1 × 2·93 (2)
K(1)–O(4)	1 × 3·78 (3)	K(2)–O(5)	2 × 3·832 (4)
K(1)–O(7)	2 × 3·31 (2)	K(2)–O(6)	2 × 2·99 (2)
K(1)–O(7)	2 × 2·93 (2)	K(2)–O(6)	2 × 3·15 (2)
K(1)–O(8)	2 × 3·35 (2)	K(2)–O(8)	2 × 3·36 (2)
K(1)–O(8)	2 × 3·48 (2)		

Table 6. *Observed and calculated structure factors for* $K_2Sb_4O_{11}$

H	K	FOBS	FCAL
*** L= 0 ***			
2	0	10	6
4	0	146	129
6	0	31	7
8	0	311	364
10	0	85	37
12	0	473	472
14	0	18	17
16	0	211	158
18	0	75	37
20	0	415	364
22	0	26	20
1	1	278	296
3	1	47	44
5	1	272	267
7	1	283	260
9	1	172	166
11	1	99	51
13	1	190	167
15	1	219	198
17	1	48	34
19	1	169	129
21	1	217	185
0	2	71	67
2	2	343	373
4	2	101	88
6	2	419	449
8	2	20	17
10	2	35	33
12	2	15	9
14	2	415	401
16	2	46	34
18	2	211	198
20	2	38	8
22	2	285	231
1	3	233	233
3	3	29	31
5	3	211	200
7	3	372	321
9	3	221	226
11	3	120	110
13	3	197	172
15	3	116	99
17	3	19	4
19	3	181	155
21	3	222	191
0	4	711	725
2	4	14	3
4	4	134	127
6	4	13	11
8	4	362	337
10	4	38	35
12	4	397	383
14	4	18	2
16	4	135	117
18	4	33	26
20	4	369	327
1	5	209	193
3	5	83	88
5	5	248	244
7	5	206	196
9	5	85	86
11	5	46	22
13	5	150	140
15	5	235	206
17	5	70	65
19	5	127	108
0	6	90	102
2	6	254	248
4	6	45	45
6	6	324	342
8	6	61	40
10	6	30	26
12	6	27	11
14	6	301	329
16	6	55	48
1	7	204	236
3	7	42	39
5	7	92	93
7	7	207	188
9	7	160	159
11	7	126	125
13	7	160	186
0	8	361	370
2	8	21	21
4	8	105	88
6	8	11	7
8	8	279	288
10	8	39	15
*** L= 1 ***			
0	0	304	304
2	0	57	34
4	0	204	287
6	0	352	255
8	0	111	74
-2	0	302	284
-4	0	32	24
-6	0	265	254
-8	0	470	447
10	0	38	37
12	0	298	292
14	0	219	257
16	0	96	95
18	0	175	159
20	0	133	120
22	0	81	69
-10	0	91	78
-12	0	155	148
-14	0	232	215
-16	0	23	22
-18	0	27	12
-20	0	260	220
-22	0	182	170
1	1	75	59
3	1	43	36
5	1	44	52
7	1	28	30
9	1	40	43
-1	1	13	9
-3	1	77	31
-5	1	12	1
-7	1	33	12
-9	1	11	6
11	1	13	8
13	1	33	25
15	1	92	86
17	1	49	40
19	1	44	29
21	1	85	33
-11	1	24	16
-13	1	68	59
-15	1	24	19
-17	1	29	22
-19	1	28	22
-21	1	19	18
0	2	357	386
2	2	112	103
4	2	173	157
6	2	54	50
8	2	157	150
-2	2	335	325
-4	2	77	67
-6	2	145	149
-8	2	210	223
10	2	155	151
12	2	231	214
14	2	222	208
16	2	17	13
18	2	167	159
20	2	196	185
22	2	45	37
-10	2	93	90
-12	2	150	163
-14	2	178	177
-16	2	166	150
-18	2	70	70
-20	2	149	138
-22	2	192	162
1	3	20	19
3	3	79	78
5	3	82	79
7	3	80	73
9	3	13	10
-1	3	126	125
-3	3	23	19
-5	3	76	68
-7	3	83	88
-9	3	56	56
11	3	79	25
13	3	29	29
15	3	98	101
17	3	18	7
19	3	86	32
21	3	82	32
-11	3	67	80
-13	3	42	39
-15	3	77	29
-17	3	52	51
-19	3	59	46
-21	3	20	9
0	4	283	257
2	4	39	31
4	4	219	212
6	4	201	307
8	4	61	60
-2	4	196	167
-4	4	11	3
-6	4	217	206
-8	4	318	301
10	4	33	27
12	4	249	243
14	4	153	182
16	4	88	73
18	4	355	188
20	4	107	101
-10	4	109	96
-12	4	184	136
-14	4	199	191
-16	4	57	59
-18	4	19	21
-20	4	224	187
1	5	60	58
3	5	36	11
5	5	13	8
7	5	44	49
9	5	92	88
-1	5	50	48
-3	5	73	69
-5	5	50	45
-7	5	58	27
-9	5	15	16
11	5	23	24
13	5	61	62
15	5	30	27
17	5	61	61
-11	5	85	88
-13	5	57	59
-15	5	18	10
-17	5	40	62
-19	5	21	16
0	6	245	237
2	6	52	49
4	6	121	116
6	6	130	144
8	6	116	111
-2	6	179	159
-4	6	31	35
-6	6	7	11
-8	6	150	136
10	6	108	106
12	6	177	169
14	6	119	101
16	6	20	13
-10	6	93	81
-12	6	107	103
-14	6	156	150
-16	6	158	141
1	7	14	20
3	7	84	95
5	7	36	29
7	7	58	49
9	7	48	45
-1	7	48	38
-3	7	62	66
-5	7	69	69
-7	7	48	40
-9	7	25	18
11	7	40	39
13	7	25	11
-11	7	53	58
-13	7	20	1
0	8	168	165
2	8	37	34
4	8	180	138
6	8	205	205
8	8	51	51
-2	8	108	105
-4	8	17	4
-6	8	122	120
-8	8	192	167
-10	8	79	66
*** L= 2 ***			
0	0	298	293
2	0	229	219
4	0	470	550
6	0	49	38
8	0	97	96
-2	0	78	48
-4	0	388	418
-6	0	102	97
-8	0	581	573
10	0	30	29
12	0	439	494
14	0	109	108
16	0	268	263
18	0	17	2
20	0	113	131
-10	0	92	83
-12	0	67	61
-14	0	122	120
-16	0	353	369
-18	0	131	138
-20	0	177	166
-22	0	31	28
1	1	36	27
3	1	231	217
5	1	162	148
7	1	10	2
9	1	208	193
-1	1	275	252
-3	1	356	346
-5	1	179	157
-7	1	10	11
-9	1	275	269
11	1	310	311
13	1	122	117
15	1	74	65
17	1	175	182
19	1	100	97
21	1	20	8
-11	1	192	183
-13	1	28	12
-15	1	201	198
-17	1	187	177
-19	1	109	111
-21	1	100	97
0	2	139	126
2	2	308	288
4	2	27	15
6	2	424	450
8	2	115	110
-2	2	118	135
-4	2	99	95
-6	2	117	120
-8	2	105	97
10	2	149	168
12	2	61	60
14	2	81	79
16	2	35	37
18	2	331	330
20	2	27	28
-10	2	530	540
-12	2	178	167
-14	2	220	224
-16	2	81	28
-18	2	159	148
-20	2	112	111
-22	2	307	299
1	3	16	6
3	3	259	289
5	3	251	250
7	3	86	54
9	3	138	123
-1	3	223	212
-3	3	205	188
-5	3	210	197
-7	3	87	82
-9	3	287	286
11	3	288	289
13	3	92	88
15	3	103	109
17	3	151	156
19	3	43	45
-11	3	178	170
-13	3	33	30
-15	3	146	143
-17	3	175	172
-19	3	52	58
-21	3	101	92
0	4	287	236
2	4	180	178
4	4	869	890
6	4	17	7
8	4	72	69
-2	4	93	85
-4	4	323	318
-6	4	25	80
-8	4	481	486
10	4	30	27
12	4	369	378
14	4	104	98
16	4	240	238
18	4	19	2
-10	4	116	118
-12	4	92	66
-14	4	112	108
-16	4	322	326
-18	4	98	100
-20	4	162	149
1	5	91	83
3	5	196	190
5	5	109	108
7	5	67	62
9	5	189	191
-1	5	188	176
-3	5	316	305
-5	5	75	68
-7	5	13	10
-9	5	204	190
11	5	217	216
13	5	41	80
15	5	82	25
17	5	183	177
-11	5	169	187
-13	5	62	38
-15	5	187	151
-17	5	181	133
0	6	106	98
2	6	190	193
4	6	19	5
6	6	272	288
8	6	71	88
-2	6	347	339
-4	6	99	95
-6	6	72	73
-8	6	57	41
10	6	278	281
12	6	17	3
14	6	76	65
-10	6	328	332
-12	6	120	118
-14	6	167	145
-16	6	27	25
1	7	39	37
3	7	193	202
5	7	164	160
7	7	65	65
9	7	69	66
-1	7	147	138
-3	7	135	145
-5	7	181	184
-7	7	60	67
-9	7	200	147
11	7	211	218
-11	7	90	75
-13	7	48	43
0	8	166	161
2	8	91	101
4	8	319	326
6	8	17	10
8	8	55	46
-2	8	52	41
-4	8	216	217
-6	8	72	68
-8	8	292	273
*** L= 3 ***			
0	0	38	21
2	0	142	122
4	0	437	425
6	0	266	265
8	0	41	83
-2	0	230	213
-4	0	90	74
-6	0	55	44
-8	0	265	256
10	0	283	289
12	0	33	42
14	0	59	65
16	0	177	170
18	0	202	205
20	0	19	3
-10	0	280	272
-12	0	108	96
-14	0	116	122
-16	0	224	219
-18	0	83	66
-20	0	92	86
-22	0	148	156
1	1	52	44
3	1	64	57
5	1	100	97
7	1	73	69
9	1	32	22
-1	1	9	2
-3	1	119	112
-5	1	35	35
-7	1	22	19
-9	1	18	18
11	1	56	63
13	1	38	32
15	1	25	26
17	1	80	70
19	1	60	59
-11	1	60	62
-13	1	14	16
-15	1	68	61
-17	1	23	8
-19	1	17	16
-21	1	26	16
0	2	193	183
2	2	154	105
4	2	315	317
6	2	164	90
8	2	91	53
-2	2	192	196
-4	2	248	238
-6	2	35	23
-8	2	205	205
10	2	181	190
12	2	247	251
14	2	52	46
16	2	147	150
18	2	95	58
20	2	81	87
-10	2	177	169
-12	2	68	62
-14	2	130	126
-16	2	195	193
-18	2	145	129
-20	2	54	52
1	3	29	14
3	3	27	3
5	3	82	72
7	3	115	119
9	3	28	5
-1	3	43	47
-3	3	65	47
-5	3	64	63
-7	3	12	14
-9	3	22	4
11	3	20	4
13	3	15	2
15	3	49	50
17	3	75	69
19	3	117	111
-11	3	77	37
-13	3	15	17
-15	3	34	23
-17	3	38	11
-19	3	18	17
0	4	11	8
2	4	135	123
4	4	306	287
6	4	213	211
8	4	86	90
-2	4	208	206
-4	4	145	139
-6	4	47	48
-8	4	208	192
10	4	187	189
12	4	55	67
14	4	46	50
16	4	151	146
18	4	208	203
-10	4	200	231
-12	4	53	45
-14	4	166	151
-16	4	220	188
-18	4	11	46
1	5	76	72
3	5	27	12
5	5	91	97
7	5	14	7
9	5	88	58
-1	5	36	27
-3	5	73	46
-5	5	67	63
-7	5	56	60
-9	5	30	28
11	5	59	60
13	5	60	60
15	5	18	10
-11	5	80	84
-13	5	48	49
-15	5	62	59
-17	5	18	7
0	6	130	130
2	6	119	113
4	6	189	178
6	6	69	52
8	6	59	58
-2	6	145	152
-4	6	213	205
-6	6	25	12
-8	6	175	169
10	6	117	127
12	6	208	213
14	6	36	44
-10	6	182	174
-12	6	29	16
-14	6	80	95
1	7	76	37
3	7	33	33
5	7	22	16
7	7	102	110
9	7	41	30
-1	7	70	71
-3	7	87	87
-5	7	57	61
-7	7	39	47
-9	7	16	2
11	7	25	33
-11	7	47	39
0	8	16	10
2	8	78	77
4	8	180	133
-2	8	160	163
-4	8	124	117
-6	8	17	25
*** L= 4 ***			
0	0	219	209
2	0	16	2
4	0	216	217
6	0	225	228
8	0	377	391
-2	0	218	226
-4	0	473	512
-6	0	210	207
-8	0	41	29
10	0	67	68
12	0	36	44
14	0	306	311
16	0	283	293
18	0	158	157
-10	0	117	115
-12	0	248	245
-14	0	170	175
-16	0	224	218
-18	0	29	6
-20	0	193	188
1	1	298	297
3	1	192	178
5	1	57	47
7	1	197	191
9	1	129	135
-1	1	196	188
-3	1	17	13
-5	1	230	219
-7	1	222	229
-9	1	51	47
11	1	26	25
13	1	189	156
15	1	163	156
17	1	67	71
19	1	81	80
-11	1	153	157
-13	1	198	190
-15	1	96	95
-17	1	65	62
-19	1	196	201
-21	1	58	101
0	2	161	158
2	2	441	477
4	2	276	276
6	2	63	79
8	2	72	62
-2	2	130	131
-4	2	42	48
-6	2	306	295
-8	2	303	312
10	2	242	259
12	2	116	122
14	2	239	209
16	2	68	67
18	2	150	130
-10	2	248	277
-12	2	85	56
-14	2	107	96
-16	2	175	173
-18	2	303	305
-20	2	171	168
1	3	253	245
3	3	225	217
5	3	31	22
7	3	216	219
9	3	82	86
-1	3	230	225
-3	3	57	54
-5	3	183	171
-7	3	150	145
-9	3	40	38
11	3	23	16
13	3	101	111
15	3	173	173
17	3	105	103
-11	3	117	119
-13	3	256	260
-15	3	78	66
-17	3	70	65
-19	3	158	156
0	4	199	189
2	4	43	40
4	4	212	206
6	4	181	185
8	4	320	327
-2	4	201	198
-4	4	198	197
-6	4	141	138
-8	4	18	12
10	4	87	92
12	4	27	36
14	4	107	105
16	4	268	273
-10	4	103	105
-12	4	252	263
-14	4	169	179
-16	4	180	179
-18	4	25	3
1	5	261	258
3	5	118	113
5	5	61	65
7	5	122	118
9	5	124	140
-1	5	100	96
-3	5	18	8
-5	5	179	162
-7	5	217	216
-9	5	60	60
11	5	47	61
13	5	159	170
-11	5	153	160
-13	5	130	116
-15	5	106	111
0	6	124	125
2	6	298	303
4	6	182	176
6	6	72	75
8	6	50	40
-2	6	45	47
-4	6	30	22
-6	6	260	258
-8	6	226	229
10	6	224	245
12	6	105	118
-10	6	273	273
-12	6	24	27
-14	6	74	69
1	7	124	125
3	7	181	133
5	7	25	1
7	7	197	210
-1	7	170	176
-3	7	67	61
-5	7	172	180
-7	7	94	89
-9	7	17	11
*** L= 5 ***			
0	0	185	128
2	0	240	274
4	0	97	104
6	0	13	19
8	0	93	63
-2	0	128	120
-4	0	181	176
-6	0	180	180
-8	0	43	41
10	0	225	225
12	0	28	22
14	0	158	168
16	0	117	110
-10	0	197	202
-12	0	185	182
-14	0	15	11
-16	0	111	104
-18	0	185	197
1	1	41	25
3	1	47	58
5	1	26	27
7	1	49	70
9	1	108	102
-1	1	17	9
-3	1	107	100
-5	1	23	30
-7	1	13	5
-9	1	85	83
11	1	85	85
13	1	28	22
15	1	16	32
17	1	59	77
-11	1	43	34
-13	1	49	52
-15	1	38	38
-17	1	16	7
-19	1	18	7
0	2	187	180
2	2	95	100
4	2	200	208
6	2	70	67
8	2	257	256
-2	2	97	93
-4	2	357	360
-6	2	197	176
-8	2	67	72
10	2	125	113
12	2	46	44
14	2	86	86
16	2	246	257
-10	2	104	123
-12	2	167	173
-14	2	15	9
-16	2	164	171
-18	2	168	134
1	3	117	103
3	3	54	52
5	3	13	1
7	3	14	13
9	3	53	58
-1	3	58	88
-3	3	63	52
-5	3	13	16
-7	3	14	4
-9	3	77	78
11	3	134	140
13	3	16	14
15	3	30	36
-11	3	24	33
-13	3	31	27
-15	3	16	25
-17	3	17	7
0	4	90	78
2	4	283	262
4	4	72	85
6	4	14	17
8	4	105	101
-2	4	94	96
-4	4	152	132
-6	4	129	128
-8	4	15	19
10	4	109	196
12	4	27	15
14	4	186	153
-10	4	183	191
-12	4	124	128
-14	4	81	33
-16	4	104	106
1	5	18	18
3	5	50	58
5	5	71	63
7	5	72	81
9	5	108	97
-1	5	35	40
-3	5	101	100
-5	5	77	38
-7	5	28	22
-9	5	16	8
11	5	23	31
-11	5	41	39
-13	5	60	68
0	6	87	79
2	6	96	103
4	6	163	168
6	6	39	47
8	6	218	221
-2	6	58	55
-4	6	287	283
-6	6	155	95
-8	6	38	40
-10	6	95	108
1	7	89	77
3	7	80	50
-1	7	76	80
-3	7	23	18
-5	7	17	14
*** L= 6 ***			
0	0	213	231
2	0	152	163
4	0	129	113
6	0	62	57
8	0	245	236
-2	0	232	233
-4	0	48	83
-6	0	182	184
-8	0	258	261
10	0	249	271
12	0	194	194
14	0	73	83
-10	0	239	205
-12	0	177	171
-14	0	69	61
-16	0	85	68
1	1	24	21
3	1	134	131
5	1	212	208
7	1	134	116
9	1	63	65
-1	1	136	128
-3	1	144	139
-5	1	21	22
-7	1	185	184
-9	1	192	194
11	1	137	128
13	1	129	136
-11	1	168	134
-13	1	78	70
-15	1	108	150
-17	1	115	119
0	2	54	65
2	2	170	170
4	2	224	233
6	2	234	228
8	2	193	190
-2	2	208	198
-4	2	309	311
-6	2	223	224
-8	2	119	121
10	2	28	26
12	2	77	85
14	2	229	238
-10	2	15	8
-12	2	201	197
-14	2	213	229
-16	2	253	265
1	3	20	23
3	3	150	167
5	3	154	153
7	3	107	95
9	3	18	41
-1	3	192	196
-3	3	119	108
-5	3	14	11
-7	3	121	119
-9	3	203	201
11	3	165	166
13	3	107	110
-11	3	107	96
-13	3	75	79
-15	3	138	132
0	4	227	236
2	4	167	159
4	4	107	92
6	4	48	18
8	4	193	188
-2	4	231	215
-4	4	66	57
-6	4	135	127
-8	4	212	203
10	4	227	238
-10	4	208	216
-12	4	156	157
-14	4	61	59
1	5	22	30
5	5	197	206
7	5	151	87
-1	5	77	76
-3	5	155	159
-5	5	11	27
-7	5	177	182
-9	5	131	131
-11	5	133	126
0	6	43	53
2	6	129	137
4	6	185	198
-2	6	145	152
-4	6	231	231
-6	6	172	175
*** L= 7 ***			
0	0	138	118
2	0	191	196
4	0	29	35
6	0	220	235
8	0	73	76
-2	0	92	87
-4	0	67	78
-6	0	191	209
-8	0	32	33
10	0	59	62
-10	0	16	27
-12	0	139	134
-14	0	192	195
1	1	97	82
3	1	29	20
5	1	30	32
7	1	87	94
9	1	32	38
-1	1	82	89
-3	1	14	3
-5	1	31	37
-7	1	71	62
-9	1	85	83
11	1	54	56
-11	1	25	3
-13	1	60	58
0	2	267	267
2	2	71	74
4	2	59	55
6	2	99	87
-2	2	15	17
-4	2	186	187
-6	2	114	129
-8	2	179	167
10	2	80	82
-10	2	18	46
-12	2	218	215
1	3	59	58
3	3	67	61
5	3	35	48
7	3	60	72
9	3	16	15
-1	3	77	81
-3	3	50	53
-5	3	33	30
-7	3	45	47
-9	3	16	21
-11	3	17	14
0	4	98	95
2	4	170	180
4	4	16	28
6	4	175	192
-2	4	100	102
-4	4	68	78
-6	4	175	192
-8	4	39	37
1	5	41	47
-1	5	74	46
*** L= 8 ***			
0	0	69	59
2	0	221	233
4	0	193	198
6	0	174	195
-2	0	68	77
-4	0	89	77
-6	0	230	263
-8	0	139	136
1	1	135	138
3	1	113	110
5	1	30	35
-1	1	25	30
-3	1	119	114
-5	1	173	172
-7	1	77	75
-9	1	17	25
0	2	244	297
2	2	42	43
4	2	18	10
-2	2	164	158
-4	2	180	188
-6	2	18	11
-8	2	128	131
-1	3	28	28
-3	3	110	99
*** L=**** ***			
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Description of the structures

$K_3Sb_5O_{14}$

The $K_3Sb_5O_{14}$ structure is as described by Aurivillius (1966) except for a mirror symmetry perpendicular to the *c* axis. It contains four $K_3Sb_5O_{14}$ molecules with Sb(1) and Sb(2) atoms at $z=0$. As shown in Fig. 1, Sb(1)–Sb(1) pairs of octahedra have a common edge in the *ab* plane centered at a body corner or the center of an *ab* face. Along the *b* axis, the Sb(1)–Sb(1) pairs are joined by corner-sharing with Sb(2)–Sb(2) pairs having their common edge parallel to the *c* axis. Chains of corner-shared Sb(3) octahedra centered at $z=\frac{1}{2}$ also run parallel to the *b* axis. The Sb(1)–Sb(2) ribbons and Sb(3) chains are connected only by Sb(4) octahedra centered at $z=26$, 74 and sharing a common edge with an Sb(1) octahedron, common corners with an Sb(2) and two Sb(3) octahedra.

The oxygen atoms O(2) and O(4) are each common to three octahedra (see circles in Fig. 1). The O(4) atom is common to two corner-shared Sb(4) octahedra, one above the other along **z**, as well as to an Sb(1) octahedron. All other oxygen atoms are common to only two octahedra. This sharing of the oxygen atoms is compatible with an O/Sb ratio of 2·8.

The $(Sb_5O_{14})^{3-}$ skeleton has tunnels parallel to the *c* axis that contain, zigzag fashion, the K^+-ion positions K(2) and K(3). These *c*-axis tunnels are intersected by *b*-axis tunnels containing positions K(1). The position K(3) can be considered common to a *c*-axis and a *b*-axis tunnel.

$K_2Sb_4O_{11}$

The $(Sb_4O_{11})^{2-}$ skeleton of the $K_2Sb_4O_{11}$ structure is entirely built from pairs of edge-shared octahedra. The Sb(1)–Sb(1) and Sb(3)–Sb(3) pairs have their common edge in the *ac* plane whereas the Sb(2)–Sb(2) pairs have their common edge parallel to the *b* axis, as can be seen from Figs. 2 and 3. The Sb(1)–Sb(1) and Sb(2)–Sb(2) pairs share common corners to form ribbons at $y=0, \frac{1}{2}$ running parallel to the *c* axis at $x=\frac{1}{2}$ and 0, respectively. These ribbons are bridged by Sb(3)–Sb(3) pairs, which form corner-shared columns parallel to the *b* axis. The Sb(3)–Sb(3) pairs share common octahedral-site edges with Sb(1)–Sb(1) pairs, common corners with Sb(2)–Sb(2) pairs. This skeleton structure produces tunnels parallel to both the *b* and *c* axes, and the K^+ ions are located in these tunnels. The irregular polyhedra around the K(1) and K(2) positions contain more than ten oxygen atoms, and the K–O distances are all longer than 2·76 Å, the sum of the ionic radii. From Table 5, the shortest K–O distance is K(1)–O(3) = 2·86 Å.

From Table 4, the temperature factors are anoma-

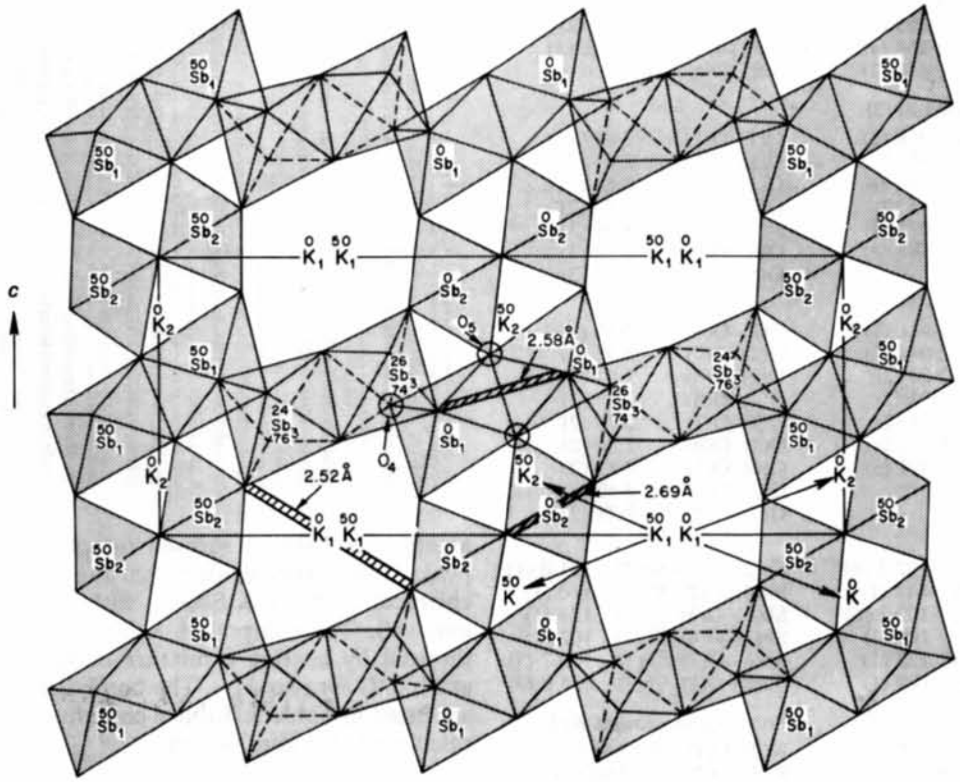

Fig. 2. An *ac* projection of the arrangement of SbO_6 octahedra in $K_2Sb_4O_{11}$, showing the tunnels formed along the *b* axis. The shaded bars are the narrowest points along or between tunnels.

lously larger for K(1) and K(2) than for the Sb atoms. Moreover, the thermal motions of K(1) and K(2) along the *b* axis, which are about the same as those along the *c* axis, are eight times bigger than those along the *a* axis. This anomalous thermal motion along the *b* and *c* axes indicates that a K$^+$ ion can move within and between tunnels.

The O(4) and O(5) anions (see circles in Fig. 2) are common to three octahedra: two Sb(3) and an Sb(1); two Sb(1) and one Sb(2), respectively. All the other oxygen atoms are common to only two octahedra. This type of sharing is consistent with an O/Sb ratio of $\frac{11}{4}$.

Discussion

The $K_3Sb_5O_{14}$ and $K_2Sb_4O_{11}$ structures have two-dimensional tunnels. In both structures, the K$^+$ ions are located in intersecting *b*-axis and *c*-axis tunnels. Although the K positions are fully occupied, there are a number of interstitial voids existing in the skeleton, so that K$^+$ ions may be transported in and between tunnels. These interstitial positions, large K–O distances, and anomalous temperature factors are consistent with the fact that both compounds can be ion-exchanged by Na$^+$, Ag$^+$, Rb$^+$ and Tl$^+$ in molten salts. The skeletons are all intact after ion-exchange, except that $K_3Sb_5O_{14}$ transforms to $Na_2Sb_4O_{11}$ in molten $NaNO_3$. This transformation is apparently due to the fact that the Na$^+$ ion is too small to support the $K_3Sb_5O_{14}$ skeleton, especially as the $K_2Sb_4O_{11}$ skeleton is intrinsically more stable because all its octahedra are paired by edge-sharing.

The narrowest point along the tunnels, designated herein as 'bottle-necks', can be used as a criterion for fast-ion transport. In $K_3Sb_5O_{14}$, the bottle-neck along the *b* tunnels, the *c* tunnels and from a *b* tunnel to a *c* tunnel are rectangular planes having shortest K–O distances of 2·66, 2·30, and 2·69 Å, respectively. (In Fig. 1, the bottle-necks are indicated by the heavy lines.) From these distances we can expect the K$^+$ ions to move within the *b* tunnel or from a *b* tunnel to a *c* tunnel, but they will transport along the *c* tunnels with a higher activation energy. In $K_2Sb_4O_{11}$, the bottle-neck along the *b* tunnels and the *c* tunnels and from a

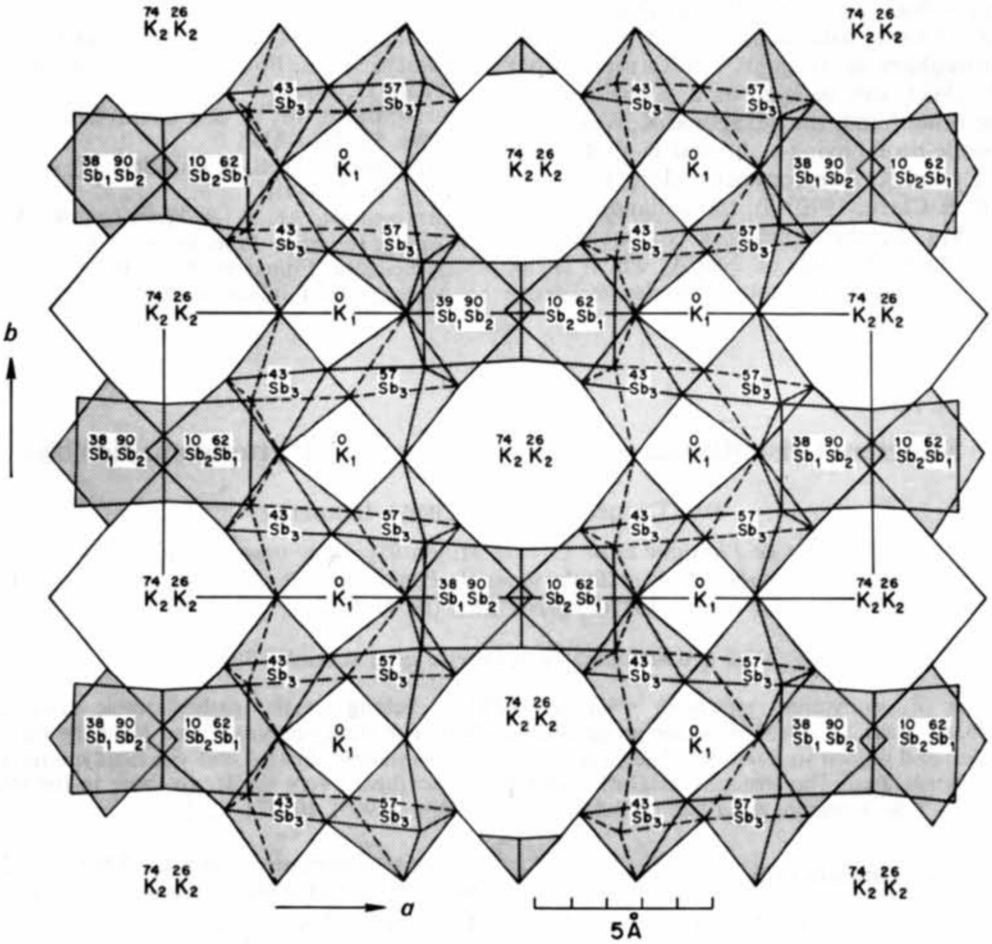

Fig. 3. An *ab* projection of the arrangement of SbO_6 octahedra in $K_2Sb_4O_{11}$, showing the tunnels that run parallel to the *c* axis.

b tunnel to a *c* tunnel are rectangular planes having shortest K–O distances of 2·58, 2·52, and 2·69 Å, respectively, as shown in Fig. 2. Here we would expect the K^+ ions to transport readily along both the *b* and *c* axes.

The same criterion can be applied to all tunnel structures. For instance, in the cubic perovskite structure, the bottle-neck is a square along the tunnels parallel to the principal axes. The alkali–oxygen distance in this square is half of the axis, or about 1·9 Å, which is just big enough for H–O bonding or Li–O bonding. This may explain why Vannice, Boudart & Fripiat (1970) reported that the protons in high-surface-area H_xWO_3 were mobile at liquid-nitrogen temperature and why Whittingham & Huggins (1972) found that Li_xWO_3 can be used as a lithium-ion reversible electrode, whereas Smith & Danielson (1954) found an extremely low diffusion coefficient for cubic Na_xWO_3 even at elevated temperatures. Tetragonal K_xWO_3 (Magnéli, 1949) has two kinds of tunnels running along the *c* axis; one has a square bottle-neck similar in size to the cubic perovskite; another is a pentagon bottle-neck with a K–O distance of 2·17 Å. It is obvious that K^+ ions cannot move easily along these tunnels. Even a Na^+ ion is too big to pass through the bottle-neck without some activation energy. Nevertheless, Whittingham & Huggins (1971) report that tetragonal Na_xWO_3 can be used as a reversible electrode. On the other hand, the hexagonal K_xWO_3, with a six-sided bottle-neck having a shortest K–O distance of 2·87 Å, is a good K^+-ion conductor along the *c* axis (Whittingham & Clark, 1970). In the hollandite structure, $Ba_xTi_{8-x}Mg_xO_{16}$, the bottle-neck is a square having a shortest Ba–O distance of 2·60 Å, which is big enough for a Ba^{2+} ion to transport (Dryden & Wadsley, 1953). The *Im*3-$NaSbO_3$ structure has a three-sided bottle-neck along the diagonal tunnel with a shortest Na–O distance of 2·40 Å, and the Na^+ ion is mobile (Hong *et al.*, 1973).

Whereas one-dimensional tunnels are probably not practical for polycrystalline membranes, because of interruption at grain boundaries, structures having two-dimensional and three-dimensional tunnel networks could be suitable.

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References

AURIVILLIUS, B. (1966). *Ark. Kem.* **25**, 505–514.
DRYDEN, J. S. & WADSLEY, A. D. (1953). *Trans. Faraday Soc.* **54**, 1574–1580.
GOODENOUGH, J. B. & KAFALAS, J. A. (1973). *J. Solid State Chem.* **6**, 493–501.
HONG, H. Y.-P., KAFALAS, J. A. & GOODENOUGH, J. B. (1973). *J. Solid State Chem.* In the press.
MAGNÉLI, A. (1949). *Ark. Kem.* **1**, 213–221.
SMITH, J. F. & DANIELSON, G. E. (1954). *J. Chem. Phys.* **22**, 266.
SPIEGELBERG, P. (1940). *Ark. Kem.* **14**A, 1–12.
VANNICE, M. A., BOUDART, M. & FRIPIAT, J. J. (1970). *J. Catal.* **17**, 359.
WHITTINGHAM, M. S. & CLARK, L. D. (1970). *J. Chem. Phys.* **53**, 4114–4115.
WHITTINGHAM, M. S. & HUGGINS, R. A. (1971). *J. Chem. Phys.* **54**, 414–416.
WHITTINGHAM, M. S. & HUGGINS, R. A. (1972). *Solid State Chemistry, Proceedings of 5th Materials Research Symposium.* Edited by R. S. ROTH & S. J. SCHNEIDER. NBS Special Publication 364, pp. 139–154.

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Structure Cristalline du Sulfure de Néodyme et d'Ytterbium, $NdYbS_3$

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Crystals of neodymium ytterbium sulphide, $NdYbS_3$, belong to the orthorhombic system, $a=12·545$, $b=9·438$, $c=3·853$ Å, space group $B22_12$, $Z=4$. The structure was solved from the Patterson function and refined to $R=0·047$. The ytterbium atoms are six-coordinated and the neodymium atoms eight-coordinated. The structure exhibits coordination polyhedra very similar to those in the yttrium sulphide, Y_5S_7, structure described by Adolphe [*Ann. Chim.* (1965). **10**, 271–275].

Introduction

L'étude systématique des sulfures doubles de terres rares a conduit Khodadad & Vo Van Tien (1969) à isoler une phase nouvelle à partir d'un mélange en quantité équimoléculaire de Yb_2S_3 et de Nd_2S_3. Ce mélange est chauffé en tube scellé à 1000°C pendant deux jours. Des cristaux suffisamment gros s'obtiennent en laissant pendant un mois, à 850°C, de la poudre cristalline dans du bromure de potassium fondu.