Joswig, W., Fuess, H. & Ferraris, G. (1982). Acta Cryst. B38, 2798–2801.

Kvick, A., Koetzle, T. F., Thomas, R. & Takusagawa, F. (1974). J. Chem. Phys. 60, 3866–3874.

Olovsson, G., Olovsson, I. & Lehmann, M. S. (1984). Acta Cryst. C40, 1521–1526.

Robertson, B. E., Guttormson, R. J., Rutherford, J. S. & Russell, D. B. (1988). Can. J. Chem. In the press.

Rutherford, J. S. & Robertson, B. E. (1975). Inorg. Chem. 14, 2537–2540.

Speakman, J. C. (1973). Molecular Structure by Diffraction Methods, Vol. I, Pt II. London: The Chemical Society.

Vanhouteghem, F., Lenstra, A. T. H. & Schweiss, P. (1987). Acta Cryst. B43, 523–528.

Vega, J. R. de la (1982). Acc. Chem. Res. 15, 185–191.

Zachariasen, W. H. (1963). Acta Cryst. 16, 1139–1144.

Evidence for a New Structural Modification in KSn₂F₅

By S. Vilminot* and H. Schulz

Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, Stuttgart 80, Federal Republic of Germany

Abstract

Potassium pentafluorodistannate(II), $M_r = 371 \cdot 5$, trigonal, $P\bar{3}$, $a = 7 \cdot 330\,(1)$, $c = 9 \cdot 900\,(2)$ Å, $V = 460 \cdot 7$ Å^3, $Z = 3$, $D_m = 4 \cdot 01$, $D_x = 4 \cdot 017\,\mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo}\,K\alpha) = 0 \cdot 7107$ Å, $\mu = 91 \cdot 1\,\mathrm{cm^{-1}}$, $F(000) = 492$, $T = 408$ K, $R = 0 \cdot 026$, $wR = 0 \cdot 023$ for 907 unique reflections. A phase transition between room temperature and 408 K was revealed by structure refinement and was confirmed by specific heat measurements, which showed an anomaly at 378 K. The structure consists of a succession of layers in the c-axis direction. Evolution of the fluorine distribution between room temperature and 408 K is discussed. The conduction mechanism was determined from calculations of probability density functions.

Introduction

Structural determinations on superionic conductors have led to the conclusion that the mobile ion is displaced from its ideal position. Another approach is to consider that the mobile ion vibrates anharmonically around its rest position. Using relations determined from statistical thermodynamics (Willis, 1969), Zucker & Schulz (1982a) have shown that of the different formalisms proposed, the best results are obtained using the Gram–Charlier expansion to analyse the anharmonic thermal motions. Study of Li₃N (Zucker & Schulz, 1982b), whose deviations from harmonicity could not be interpreted by interstitial sites or split positions, illustrated the use of anharmonic temperature factors up to the sixth order and allowed the diffusion process to be explained. This interpretation used calculations of the probability density function

(PDF), Fourier transform of the temperature factor, and of the effective atomic potential. All calculations were performed with the program system PROMETHEUS (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

Conduction paths of the mobile ions have been studied in the case of cationic conductors: Ag⁺ in AgI, Ag₃SI and Ag₂S (Schulz & Zucker, 1981); Na⁺ in Nasicon (Kohler, Schulz & Melnikov, 1983); Cu⁺ in CuTeBr (Bachmann, Kreuer, Rabenau & Schulz, 1982); and anionic conductors: F⁻ in PbF₂ (Bachmann & Schulz, 1983). KSn₂F₅ belongs to the MSn₂F₅ family (M = Na, K, Rb, Cs, Tl and NH₄) which exhibits fluorine ionic conductivity (Al Uraibi, 1981). Above 428 K, it presents a superionic modification as revealed by conductivity measurements. A structure determination at room temperature (Vilminot, Bachmann & Schulz, 1983) revealed that KSn₂F₅ has an original structure, not deduced from fluorite for example. According to these results, the structure is strongly anisotropic and KSn₂F₅ can be considered as a two-dimensional ionic conductor. In order to obtain more information concerning the conduction process, we have undertaken structural determinations at higher temperatures. In this first part, we present the structure obtained at 408 K, that is below the superionic transition, and compare the results with those at room temperature.

Experimental

KSn₂F₅ prepared according to Vilminot et al. (1983). Crystal: irregular hexagonal plate $0 \cdot 30 \times 0 \cdot 22 \times 0 \cdot 06$ mm in glass capillary. D_m by pycnometry. Temperature achieved by blowing heated air. Philips PW 1100 diffractometer. Intensity measurements by $\omega/2\theta$ scans. Unit-cell dimensions from least-squares refinement on 25 reflections ($\theta > 15°$). Corrections for

* Alexander von Humbolt Fellow. Present address: Département Science des Matériaux EHICS, 1 rue B. Pascal, 67008 Strasbourg CEDEX, France.

Table 1. *Final atomic positions for* KSn₂F₅

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$

	x	y	z	Occu-pancy	$B_{eq}(\text{Å})^2$
Sn(12)	0·3270 (3)	−0·0046 (3)	0·32526 (8)	1·0	2·95
K(1)	0	0	0	1·0	2·83
K(23)	⅓	⅔	−0·0206 (7)	1·0	3·16
F(67)	0·319 (2)	−0·028 (2)	0·1233 (7)	1·0	4·11
F(45)	0·671 (2)	0·104 (2)	0·2841 (8)	0·83 (2)	4·38
F(28)	⅓	⅔	0·284 (3)	0·71 (5)	5·93
F(39)	0	0	0·288 (2)	1·0	5·41

absorption ($A_{max} = 5·73 - A_{min} = 2·28$). Sin$\theta/\lambda$ up to 0·7 Å⁻¹ ($\pm h = 0$–8, $\pm k = 0$–8, $l = 0$–13). Three standards for counting and orientation measured every 100 reflections: no significant trends. 2383 measured reflections, 907 symmetry unrelated with 372 observed [$I > 3\sigma(I)$] and 535 unobserved ($R_{int} = 0·036$). Isotropic extinction correction, according to Becker & Coppens (1974), type I with $G = 0·032$ (4). Refinement using F magnitudes from data at room temperature. Atomic positions and anisotropic thermal parameters refined. $R = 0·026$, $wR = 0·023$ ($w = 1/\sigma$). Max. least-squares shift to e.s.d. 0·01. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). PROMETHEUS (Zucker *et al.*, 1983) program system. Significant displacements of all atomic positions during refinement from room-temperature parameters (Vilminot *et al.*, 1983). The disappearance of position F(1) was compensated for by a new F(9) position, and the change of the F-atom distribution was described by introducing a centre of symmetry into the structure. The refinement revealed that a phase transition takes place between room temperature and 408 K, in which the space group
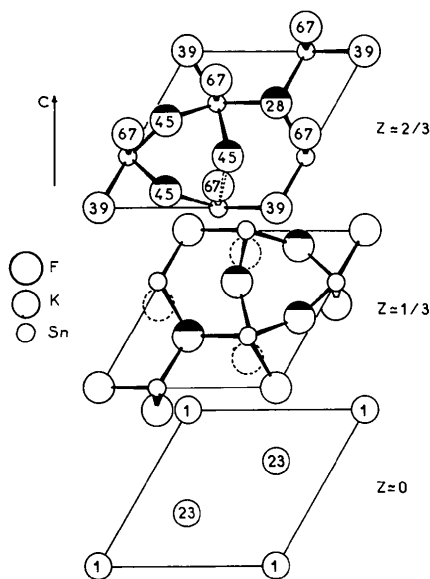
Table 2. *Bond lengths* (Å) *and angles* (°) (*at* 408 K) *for* KSn₂F₅

Tin environment

Sn(12)–F(67)	2·005 (7)		Sn(12)–F(39)	2·442 (3)	
Sn(12)–F(45)	2·201 (11)		Sn(12)–F(28)	2·468 (5)	
Sn(12)–F(45')	2·272 (11)				
F(67)–Sn–F(45)	80·2 (5)		F(45)–Sn–F(39)	76·1 (1)	
F(67)–Sn–F(45')	79·4 (4)		F(45)–Sn–F(28)	152·3 (5)	
F(67)–Sn–F(39)	82·3 (7)		F(45')–Sn–F(39)	153·4 (4)	
F(67)–Sn–F(28)	76·3 (8)		F(45')–Sn–F(28)	75·6 (3)	
F(45)–Sn–F(45')	82·3 (3)		F(39)–Sn–F(28)	119·1 (2)	

Potassium environment

K(1)–F(67)	2·739 (18) (×6)		K(1)–F(39)	2·852 (17) (×2)
K(23)–F(67)	2·696 (9) (×3)		K(23)–F(28)	3·014 (28)
K(23)–F(67)	2·791 (15) (×3)		K(23)–F(45)	3·113 (10) (×3)

changes from P3 (RT) to P$\bar{3}$ (408 K). For description in P$\bar{3}$, K(1) was shifted to the origin and all other atoms were shifted correspondingly. The phase transition was confirmed by specific heat measurements, which showed a reversible anomaly around 378 K. Table 1 gives the final atomic positions, and bond lengths and angles at 408 K are presented in Table 2.*

Discussion

The structure is very closely related to the structure model found at room temperature with a succession of three layers in the c-axis direction (Fig. 1). Therefore, both layers around the Sn atoms, at $z \simeq \frac{1}{3}$ and $z \simeq \frac{2}{3}$, are now equivalent as related by a centre of symmetry.

The Sn atoms all have the same SnF₅E environment (E = lone pair of electrons) defining a very distorted octahedron, with short [Sn–F(67) = 2·005 Å], intermediate [Sn–F(45) = 2·201 (11) and Sn–F(45) =

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44724 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
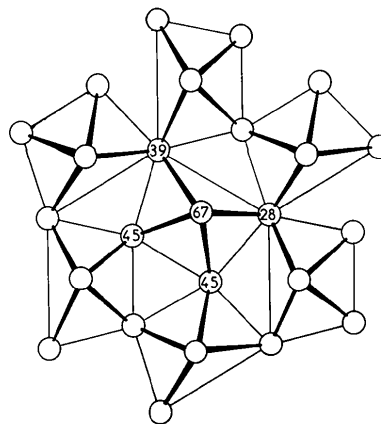

Fig. 1. Succession of the atomic layers in the c-axis direction. Shading of the F atoms is proportional to their underoccupancy.

Fig. 2. Environment of an SnF₅E octahedron.

2·272 (11) Å] and long [Sn—F(39) = 2·442 (3) and Sn—F(28) = 2·468 (3) Å] Sn—F bonds. This kind of environment is rarely observed for tin(II) fluorine compounds, the Sn atom usually exhibiting SnF_3E or SnF_4E environments. An octahedral environment has been previously observed for Sn atoms in SnF_2 (Denes, Pannetier, Lucas & Le Marouille, 1980), the formation of Sn_4F_8 tetramers explaining this result. Such a polymerization is observed in the layers at $z \simeq \frac{1}{3}$ and $z \simeq \frac{2}{3}$. Each octahedron shares four corners with six neighbouring octahedra; the last two corners, occupied by E and F(67) outside of the layers at $z \simeq \frac{1}{3}$ and $z \simeq \frac{2}{3}$, are not shared (Fig. 2). The layers can be described by the juxtaposition of Sn_6F_9 units, taking into account the threefold symmetry (Fig. 3).

The K atoms have two kinds of fluorine environments: eight-coordinate for the K(1) atoms, ten-coordinate for the K(23) atoms. The shortest K···F bonds always involve the F(67) atoms. Three kinds of fluorine coordination are observed in KSn_2F_5: F(67) is bonded to one Sn atom [Sn—F = 2·005 (7) Å], F(45) bridges two Sn atoms (Sn—F = 2·23 Å), and F(28) and F(39) are three-coordinated (Sn—F = 2·45 Å).

It appears that the structure is very anisotropic, anisotropy which must be reflected in the conductivity properties. The conduction mechanism is probably restricted to both layers at $z \simeq \frac{1}{3}$ and $z \simeq \frac{2}{3}$, without any communication between them. The F(67) atoms are strongly bonded to Sn and K and cannot be involved in the conduction. Using these results, a possible con-

Fig. 3. Sn_6F_9 units in the layer at $z \simeq \frac{2}{3}$.

Fig. 4. Joint PDF map at 408 K in the layer at $z = 0.285$.

duction mechanism will be proposed below, based on a comparison with the room-temperature determination.

In order to study the conduction path within a layer, we have calculated the joint probability density function of all F⁻ ions within such a layer (Bachmann, 1983). This involves Fourier transformation of the temperature factors of each F⁻ atomic position to generate the probability around the atomic positions (Zucker & Schulz, 1982a). Calculations of maps of the probability density function (PDF) and combining the PDF's to a joint PDF have been carried out for the F(28), F(39) and F(45) atoms in the plane at $z = 0.285$. The calculations were computed with the *PROMETHEUS* program using the expression derived by Bachmann (1983):

$$PDF = \sum_i w_i pdf_i(u),$$

where pdf_i is the probability of finding an atom i in the volume element d^3u when it is displaced by u from its mean position (Fourier transform of the temperature factor) and w_i is the occupancy of atom i. The calculated PDF map (Fig. 4) suggests a possible conduction path connecting the F atoms involved in this layer.

A calculation of the single-particle potential according to Bachmann (1983):

$$V(r) = -kT\ln[PDF(r)] + V_0,$$

where r is the position vector within the unit cell and V_0 is a constant obtained by setting the zero point of V at the maximum of PDF(r), gives an extrapolated potential barrier of 0·53 eV between the F-atom positions. This value is in good agreement with the value deduced from d.c. conductivity measurements (0·55 eV).

One question arises from the structural determination: why is there no change in the value of the conductivity at the first transition (378 K)? According to our previous conclusions (Vilminot *et al.*, 1983), the conduction takes place in only one layer at room temperature and in two layers at 408 K. One would expect therefore a conductivity twice as high at 408 K since the number of charge carriers is multiplied by two. An answer could be proposed by considering the F-atom distributions in both cases. At room temperature, in the conducting plane, all F-atom positions are underoccupied. At 408 K, two positions F(28) and F(39), are underoccupied, but the F(45) position is fully occupied. With F—F distances of the same order of magnitude, F—F = 2·890 and 2·907 Å at 293 and 408 K respectively, the distribution at 408 K appears to be less favourable than at 293 K for ionic conductivity.
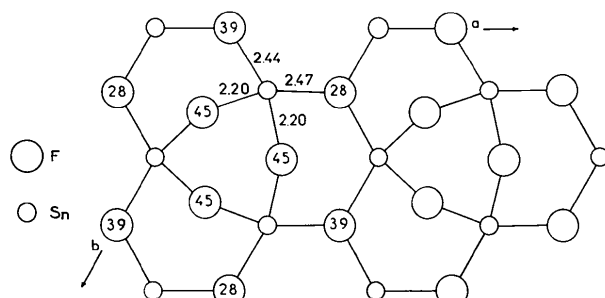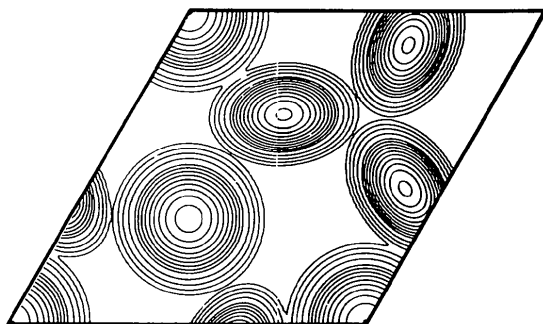
References

AL URAIBI, Z. (1981). PhD Thesis, Univ. of Montpellier, France.
BACHMANN, R. (1983). PhD Thesis, Univ. of Karlsruhe, Federal Republic of Germany.

BACHMANN, R., KREUER, K. D., RABENAU, A. & SCHULZ, H. (1982). *Acta Cryst.* B38, 2361–2364.

BACHMANN, R. & SCHULZ, H. (1983). *Solid State Ionics*, 9–10, 521–524.

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A30, 129–147.

DENES, G., PANNETIER, J., LUCAS, J. & LE MAROUILLE, J. Y. (1979). *J. Solid State Chem.* 30, 335–343.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KOHLER, H., SCHULZ, H. & MELNIKOV, O. (1983). *Mater. Res. Bull.* 18, 1143–1152.

SCHULZ, H. & ZUCKER, U. H. (1981). *Solid State Ionics*, 5, 41–46.

VILMINOT, S., BACHMANN, R. & SCHULZ, H. (1983). *Solid State Ionics*, 9–10, 559–562.

WILLIS, B. T. M. (1969). *Acta Cryst.* A25, 277–300.

ZUCKER, U. H., PERENTHALER, E., KUHS, W. F., BACHMANN, R. & SCHULZ, H. (1983). *J. Appl. Cryst.* 16, 358.

ZUCKER, U. H. & SCHULZ, H. (1982a). *Acta Cryst.* A38, 563–568.

ZUCKER, U. H. & SCHULZ, H. (1982b). *Acta Cryst.* A38, 568–576.

Oriented Intergrowth of an Antigorite and an Arsenate Mineral from Långban, Sweden. A Natural Composite Material

BY STAFFAN HANSEN* AND MICHAEL O'KEEFFE

Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA

Abstract

'Asbestos–hedyphane' is a well oriented intergrowth of antigorite and a Pb,Ca arsenate of apatite type from Långban, Sweden. The outer appearance is strikingly similar to that of a yellowish chrysotile–asbestos. Examination by scanning electron microscopy and energy dispersive analysis of emitted X-ray radiation reveals flexible antigorite laths of nearly ideal serpentine composition, $Mg_3Si_2O_5(OH)_4$, intergrown with a chloride-poor hedyphane-like mineral (hedyphane is $Pb_3Ca_2As_3O_{12}Cl$). Hexagonal unit cell of the arsenate, as determined by powder X-ray diffraction: $a = 10·0547(8)$, $c = 7·310(2)$ Å. Four fibers were examined by Weissenberg and oscillation techniques. The antigorite exhibits a monoclinic lattice with $a = m \times 2·5$, $b = 9·2$, $c = 7·3$ Å, $\beta = 91·5°$ (m integer). Electron diffraction patterns from nine antigorite laths showed that m is variable, with $14 \le m \le 20$. Texture of the intergrowth as determined from X-ray diffractographs: c(arsenate) ‖ b(antigorite) ‖ fiber axis; extensive rotational disorder around the fiber axis, though a preferred orientation is observed after every 60° of rotation. This is probably due to a lattice fit: (001)antigorite ‖ (10$\bar{1}$0)arsenate, $4a$(antigorite) $\simeq$ a(arsenate) and $4b$(antigorite)$\simeq 5c$(arsenate) if $m = 1$. A second preferred orientation, observed in the middle of the 60° intervals, may be due to a lattice fit: (001)antigorite ‖ (11$\bar{2}$0)arsenate, $7a$(antigorite) $\simeq$ $3^{1/2}a$(arsenate), $4b$(antigorite)$\simeq 5c$(arsenate).

* Present address: National Center for HREM, Inorganic Chemistry 2, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden.

Introduction

The mineral aggregate 'asbestos–hedyphane' from Långban, Sweden, was characterized by Sjögren (1891, 1892) as follows: 'The designation of a peculiar compound of two minerals, found at Långban for some years in different parts of the mine. It formed fibrous aggregates up to an inch in length of a grey to brownish colour and silky lustre. A microscopical examination has shown that it is composed of two different minerals of which one, in the form of thin needles with a starlike intersection permeates the other, and gives the whole compound a fibrous asbestos-like appearance. The needle-like mineral is a hydrous silicate of magnesia with a composition similar to that of serpentine; the other mineral is chiefly an arseniate of lead with some lead chloride, but it does not seem to be identical with the common hedyphane.' The chemical data were later published by Magnusson (1930, pp. 53–54). Dunn, Rouse & Nelen (1985) have described a fibrous hydroxyl-bearing hedyphane from Långban, but no silicate phase was characterized.

The present study was undertaken to elucidate further the nature of 'asbestos–hedyphane'. Since the cell parameters of serpentine minerals and hedyphane both exhibit a 7·3 Å repeat, the possibility of an epitaxial relationship between the two phases was indicated. An epitaxial relation was indeed found, but the 7·3 Å axes are perpendicular.

After the completion of this work, a study of a similar material (Kautz, 1967) has come to our attention. Kautz describes a crystallographically well ordered intergrowth of hedyphane and antigorite. The main conclusions of Kautz are confirmed in the present