

The expansivities and the thermal degradation of some layer compounds

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The thermal expansion coefficients and the decomposition products at high temperatures under vacuum have been determined for a number of layer compounds; SnS_2 , SnSe_2 , SnSSe , ZrS_2 , HfS_2 and TiS_2 , all of which have crystal structures based on that of cadmium iodide, and ϵ -GaSe. In all compounds the expansion perpendicular to the layers ($\parallel c$) is much greater than that parallel to the layers ($\perp c$). This is ascribed to the effect of the weak van der Waal's bonding between layers. Thermal degradation at high temperatures (up to 900°C) under vacuum usually follows a route via the monochalcogenide or the sub-chalcogenide to the oxide.

1. Introduction

The sulphides and selenides of tin, titanium, zirconium and hafnium are members of a group of compounds which crystallize in space-group $R\bar{3}m$ with the characteristic cadmium iodide layer structure (Fig. 1). The crystal lattice comprises close-packed nets of chalcogenide atoms, X , (sulphur or selenium) with the metal cation, M , nestled in

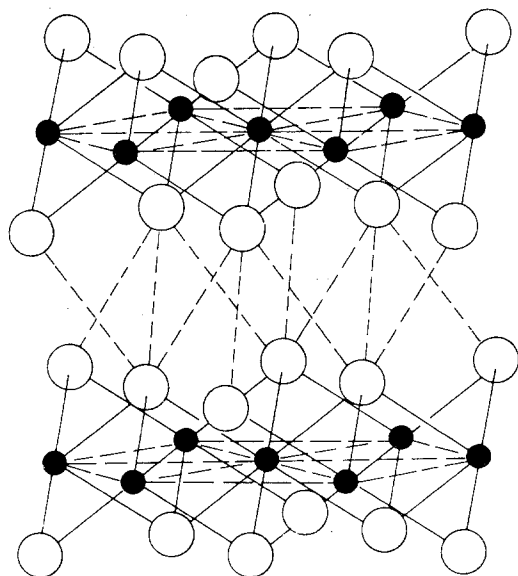


Figure 1 The cadmium iodide layer structure. The shaded atoms are metal ions and the open atoms are anions in octahedral co-ordination.

octahedral interstices. Half the octahedral interstices are filled to form minimal layers $X-M-X$ of metal ions sandwiched on either side by chalcogenide. The atomic stacking sequence is $AcB : AcB$. Bonding within the layers is strong, through the partially covalent $X-M$ bond, whereas bonding between the layers is weak, mainly via a van der Waal's $X-X$ bond. The intralayer forces are at least 100 times greater than the interlayer forces [1].

Gallium selenide is a compound which crystallizes in a similar hexagonal layer structure, but here the metal co-ordination is tetrahedral, and defines a minimal sandwich of the type $X-M-M-X$, with two layers of metal ions between the chalcogenide planes. A similar anisotropy of bonding is maintained within the lattice, with covalent bonding within the layers and van der Waal's bonding between the layers.

A broad study of layer compounds of this type is being undertaken at Brighton Polytechnic: electrical properties are measured in conjunction with examination of single crystals by X-ray diffraction and electron microscopy. As part of this study, the effect of heat on the structures of a number of layered materials has been ascertained by X-ray diffraction.

Single crystal specimens of tin disulphide (SnS_2), tin diselenide (SnSe_2), tin sulpho-selenide

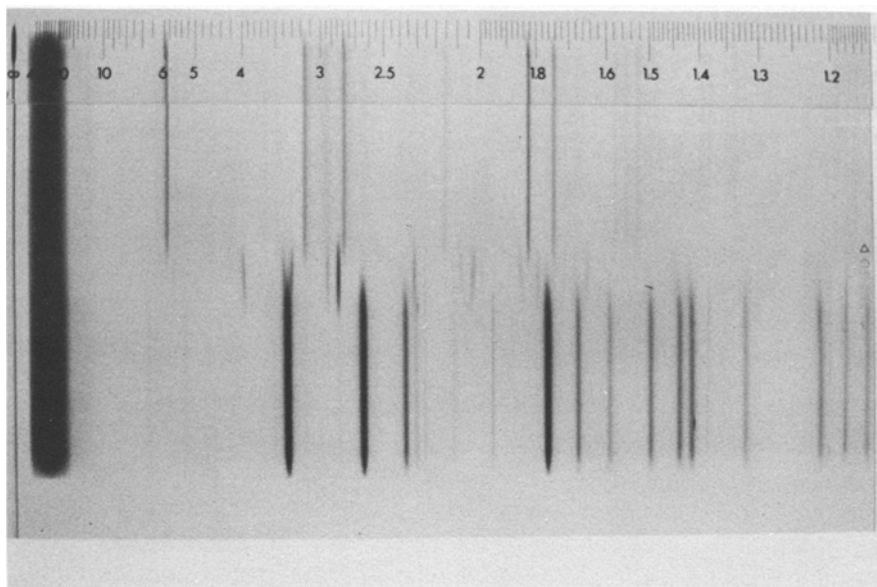


Figure 2 Photographic trace recorded from a sample of SnS_2 when heated between room temperature and 900°C .

(SnSSe), zirconium disulphide (ZrS_2), hafnium disulphide (HfS_2), titanium disulphide (TiS_2) and gallium selenide (GaSe , ϵ -phase), were prepared by the iodine vapour transport technique. The method used is described briefly by Rimmington and Balchin [2] and at greater length by Al-Alamy and Balchin [3]. X-ray powder diffraction patterns of the materials were recorded while subjecting the samples to heating and cooling cycles in an Enraf-Nonius Guinier-Lenné focussing X-ray camera.

2. Construction of the camera; camera calibration

The Enraf-Nonius Guinier-Lenné camera [4] records changes in the X-ray powder diffraction pattern caused by expansion or contraction of the crystal lattice, or by changes of phase, as a continuous photographic trace which may be correlated with specimen temperature. In design the camera is of the focussing type, employing a curved quartz crystal monochromator in the reflecting mode. Monochromatic X-rays are focussed through a flat powder specimen supported on a platinum mesh to give a focussed X-ray diffraction pattern on a curved cylindrical film mounted around the Rowland Circle. The powder sample is mounted at the centre of a furnace winding of platinum wire in a water-cooled, evacuated enclosure. The enclosure is fitted with beryllium windows to permit entry and

exit of the incident and diffracted X-ray beams. The specimen is heated or cooled by furnace current variation at the same time as a recording film is raked continuously through the camera. A photographic trace results on which the X-ray powder line position is recorded as a function of temperature. Examples of the traces recorded, e.g. from SnS_2 and HfS_2 heated between room temperature and 900°C are given in Figs. 2 and 3.

Since the monochromator is used in the reflection mode, and the diffracted beams are recorded after transmission through the sample, the camera only records X-ray reflections for which the Bragg angle is less than 45° . The low-angle lines are, however, relatively insensitive to small variations of interplanar spacing, and this is disadvantage when the camera is used for the measurement of lattice parameters or thermal expansion coefficients. Nevertheless, the camera traces show clearly the changes of phase induced by heating. Fig. 2, for example, illustrates the successive transitions from SnS_2 at room temperature, to SnS at 550°C and then to SnO_2 at 650°C . Similarly Fig. 3 shows the transition from HfS_2 to HfO_2 at 735°C .

Because only low-angle lines are recorded, careful camera calibration is required to achieve accurate values of lattice parameters. In the present instance the films were calibrated by comparison with a series of powder photographs of 99.9999% pure sodium chloride (Koch-Light Laboratories

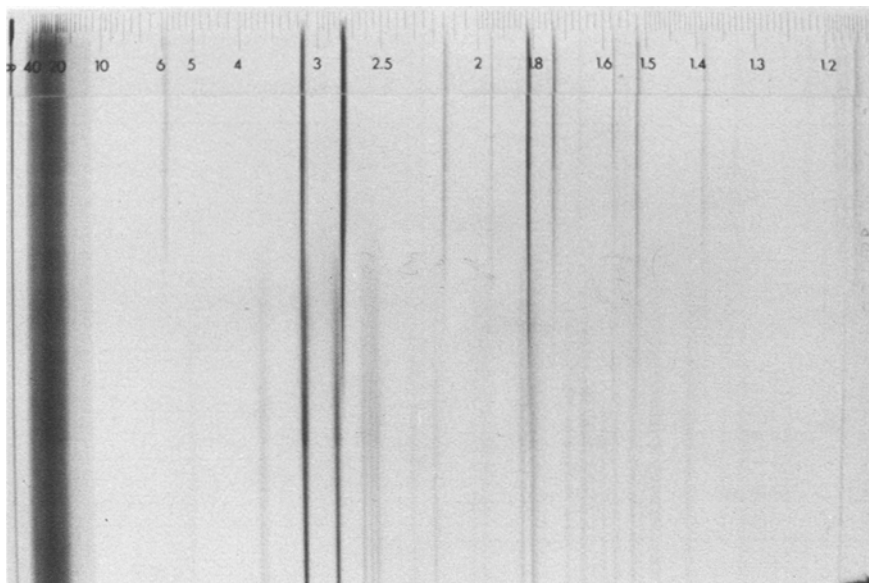


Figure 3 Photographic trace recorded from a sample of HfS_2 when heated between room temperature and 900°C .

Ltd.) at room temperature. The lattice parameter of this standard [5] was taken as 5.6402 \AA .

Measured interplanar spacings were also checked by reference to the powder diffraction lines recorded from the platinum sample holder. These were visible in all high temperature photographs, and could be used as an internal standard.

Shrinkage of the X-ray film caused by processing and drying causes a systematic shift in line positions which was estimated from subsidiary experiments. A film shrinkage correction of 0.69% was incorporated in all measurements of line position from processed films.

The furnace control unit supplied with the camera offers a range of film speeds and heating and cooling temperature cycles. Specimen temperatures are recorded by a Pt/Pt–Rh thermocouple mounted in the sample holder. Temperatures may be related to the recorded film trace by linear interpolation when the film speed and rate of temperature variation are known.

3. Results

3.1. Lattice parameters

The variation of lattice parameters with temperature, as measured from the X-ray diffraction photographs for SnS_2 , SnSe_2 , SnSSe , ZrS_2 , HfS_2 , TiS_2 and GaSe are given in Table I to VII respectively. Corresponding values of expansivities are listed in Table VIII.

The results obtained for TiS_2 and HfS_2 are of especial interest. TiS_2 is well known as a non-stoichiometric compound. It has the property of taking up titanium ions into the relatively empty van der Waal's region between layers of the titanium disulphide structure to form a range of non-stoichiometric materials. Their structures vary from that of nickel–arsenide–like TiS to that of cadmium–iodide–like TiS_2 . In TiS_2 , the width of the van der Waal's region between atomic layers also allows intercalation of the layers by alkali metal ions, such as lithium, or by organic molecules, such as collidine.

The values of lattice parameters, a and c , measured for the present compound suggest, by comparison with results of Bernard and Jeannin [12] that the S:Ti ratio is nearer to 1.90 than 2.00. Similar lattice parameters and compositions were found for other samples of TiS_2 given by the iodine vapour transport technique under differing conditions of growth, even when prepared from a stoichiometric 1:2 mix of the elements.

The presence of excess titanium atoms between the structural layers would modify the thermal expansion coefficient, α_c , measured parallel to the c -axis of TiS_2 . Smaller values of α_c would obtain from an increase in the strength of bonding caused by the replacement of the van der Waal's bonds by covalent bonds. The expansivities of $\text{TiS}_{1.9}$ given in Table VI may be compared with the only

TABLE I Variation of lattice parameters with temperature for tin disulphide, SnS₂.

Temperature (°C)	a (Å) ± 0.001	c (Å) ± 0.001
23	3.645	5.891
75	3.647	5.894
125	3.648	5.898
175	3.650	5.902
230	3.652	5.907
285	3.654	5.911
335	3.656	5.915
385	3.658	5.920
440	3.659	5.924
495	3.661	5.928
550	3.663	5.933

TABLE II Variation of lattice parameters with temperature for tin diselenide, SnSe₂.

Temperature (°C)	a (Å) ± 0.001	c (Å) ± 0.001
23	3.807	6.128
65	3.809	6.133
110	3.811	6.137
160	3.814	6.143
205	3.816	6.148
250	3.819	6.153
300	3.821	6.158
345	3.823	6.162
390	3.826	6.167

TABLE III Variation of lattice parameters with temperature for tin sulpho-selenide, SnSSe.

Temperature (°C)	a (Å) ± 0.001	c (Å) ± 0.001
23	3.728	6.037
65	3.731	6.043
110	3.734	6.049
150	3.737	6.055
195	3.740	6.059
235	3.743	6.064
290	3.746	6.069
330	3.749	6.075
380	3.752	6.080

TABLE IV Variation of lattice parameters with temperature for zirconium disulphide, ZrS₂.

Temperature (°C)	a (Å) ± 0.001	c (Å) ± 0.001
20	3.657	5.824
95	3.660	5.831
176	3.662	5.838
258	3.665	5.845
338	3.668	5.851
420	3.672	5.859
500	3.674	5.865

TABLE V Variation of lattice parameters with temperature for hafnium disulphide, HfS₂.

Temperature (°C)	a (Å) ± 0.001	c (Å) ± 0.001
23	3.622	5.848
120	3.623	5.854
225	3.624	5.860
325	3.625	5.865
425	3.626	5.871
530	3.628	5.877
630	3.629	5.883
735	3.631	5.887

TABLE VI Variation of lattice parameters with temperature for titanium disulphide, TiS₂*.

Temperature (°C)	a (Å) ± 0.001	c (Å) ± 0.001
20	3.402	5.716
100	3.406	5.724
185	3.411	5.733
265	3.414	5.740
350	3.418	5.746
430	3.422	5.759
515	3.427	5.768
590	3.431	5.778

*More probably composition TiS_{1.9} (see text).

TABLE VII Variation of lattice parameters with temperature for gallium selenide, ε-GaSe.

Temperature (°C)	a (Å) ± 0.001	c (Å) ± 0.001
20	3.754	15.945
90	3.756	15.951
160	3.756	15.960
230	3.757	15.966
300	3.758	15.973
370	3.759	15.982
440	3.761	15.986
510	3.762	15.993
580	3.763	16.002
650	3.764	16.009

TABLE VIII Thermal expansion coefficients for the investigated layer compounds.

Compound	Temperature range (°C)	α _a (10 ⁻⁵ (°C) ⁻¹)	α _c (10 ⁻⁵ (°C) ⁻¹)
SnS ₂	23-550	0.95 ± 0.02	1.35 ± 0.01
SnSe ₂	23-390	1.33 ± 0.02	1.74 ± 0.01
SnSSe	23-380	1.75 ± 0.02	1.94 ± 0.01
ZrS ₂	20-500	1.00 ± 0.02	1.45 ± 0.02
HfS ₂	23-735	0.34 ± 0.03	0.93 ± 0.02
TiS ₂ *	20-590	1.51 ± 0.02	1.90 ± 0.01
ε-GaSe	20-650	0.40 ± 0.04	0.64 ± 0.01

*More probable composition TiS_{1.9} (see text).

others available, measured by Whittingham and Thompson [13] at low temperatures between 5 and 300 K:

$$\alpha_a = 0.96 \times 10 \text{ K}^{-1}; \alpha_c = 1.94 \times 10 \text{ K}^{-1}$$

for TiS_2 .

Of all the cadmium–iodide–like compounds, that with the smallest expansivity, and therefore the strongest bonding, is hafnium disulphide, HfS_2 . Experience has shown that this compound is notoriously refractory, and is one of the most difficult to grow by the iodine vapour transport technique. Growth times, often in excess of 1000 h, are required to obtain single crystals of millimetre dimensions [6].

3.2. Thermal decomposition

3.2.1. Tin disulphide

Under a vacuum of 10^{-4} Torr, tin disulphide decomposes to tin monosulphide at 550°C . This is in accord with observations made in the electron microscope by Tatlock and White [7], who subjected SnS_2 to local beam heating under electron bombardment.

When the monosulphide, SnS , is heated to a higher temperature, a two-phase mixture of $\text{SnS} + \text{SnO}_2$ is formed between 650 and 675°C . At 675°C oxidation to SnO_2 is complete, and above 675°C only the oxide is recorded (Fig. 2).

The sub-sulphides, Sn_2S_3 and Sn_3S_4 , reported near 550°C by Karakhanava *et al.* [8] have not been observed in the present experiments. Otherwise the results are in agreement with those of Karakhanova *et al.*, and also with those obtained by Volyskii and Sevryakov [9].

3.2.2. Tin diselenide

In a similar way, when SnSe_2 is heated *in vacuo*, selenium is evolved. The mono-selenide, SnSe is formed at 370°C . This again confirms results by Tatlock and White, and by Albers and Verbekt [10]. The lower temperature of formation of SnSe indicates that Se is evolved from SnSe_2 more easily than S is evolved from SnS_2 , and suggests weaker bonding.

The present results are in contrast to those of Karakhanova *et al.* [11] who by heating SnSe_2 in closed, evacuated quartz ampoules, demonstrated the formation of Sn_2Se_3 at 625°C . This phase was not observed in the present experiments. At 490°C SnSe was oxidized completely to SnO_2 .

3.2.3. Tin sulpho-selenide

This compound is a random trigonal solid solution of SnS_2 and SnSe_2 in the ratio 1 : 1. Sulphur and selenium occupy at random the chalcogenide sites in the cadmium–iodide–like lattice. Accurate measurement of the interplanar spacings of the decomposition products shows that SnSSe decomposes on heating at a temperature of 390°C to form tin mono-selenide, SnSe . At 450°C this begins to oxidize to SnO_2 , a reaction which is complete at 530°C .

3.2.4. Zirconium disulphide

Decomposition of ZrS_2 at 500°C to form Zr_3S_4 is followed by the formation of ZrO_2 at 600°C . At this temperature tetragonal ZrO_2 and Zr_3S_4 co-exist as a two-phase mixture. At 650°C some of the tetragonal ZrO_2 is converted to the monoclinic form; the resulting 3-phase mixture of $\text{Zr}_3\text{S}_4 + \text{ZrO}_2$ (tetragonal) + ZrO_2 (monoclinic) remains stable to temperatures as high as 900°C .

3.2.5. Hafnium disulphide

HfS_2 decomposes at 735°C to form HfO_2 as the final product (Fig. 3.). This is in contrast to results of *in situ* electron microscope examination by Tatlock and White, who identified an intermediate phase, HfS , at high temperatures near 700°C [15].

3.2.6. Titanium disulphide

Chemical decomposition of TiS_2 at 595°C forms TiO_2 (anatase). At 600°C , TiO_2 (rutile) is also formed in co-existence with the anatase. Oxidation of TiS_2 is complete at 610°C leaving a two-phase mixture of the two oxide forms.

3.2.7. Gallium selenide

At 520°C , GaSe decomposes to form Ga_2Se_3 , a phase first identified by Suzuki and Mori [14] by differential thermal analysis of the Ga–Se system. The sub-selenide is oxidized at 700°C to form monoclinic $\beta\text{-Ga}_2\text{O}_3$ as a final product. Free gallium metal is presumably formed at the same time as Ga_2Se_3 , but at these temperatures it would be in the liquid state.

The decomposition route taken by GaSe is the same for samples grown by iodine vapour transport or by sublimation.

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