Discussion. Recently 21 polytypes of SnS_2 were reported and a multiphase model for characterization of their structures was suggested (Pałosz *et al.*, 1985). The structural series of polytypes with intermediate structures $2H$–$18R$, $4H$–$18R$ and $2H$–$4H$–$18R$ were derived theoretically with the use of a multiphase model of polytype structures (Pałosz, 1983) and only polytypes of these three kinds were found in SnS_2 crystals. Most of the polytypes presented here also belong to these three main structural groups: $2H$–$18R$: $42H_1$, $44H_1$, $36R_1$, $54R_1$, $84R_2$, $96R_1$, $96R_2$, $114R_1$, $132R_2$ and $144R_1$; $4H$–$18R$: $22H_1$, $40H_2$, $30R_2$, $48R_2$, $138R_1$; $2H$–$4H$–$18R$: $12H_1$. Besides these simple polytypes some polytypes were found to have a more complicated composition: they contain the stackings of layers not belonging to basic structures $2H$ (stackings o), $4H$ (t) or $18R$ ($f1f5f1$), namely $f1f2$ ($8H_1$, $10H_2$, $12H_2$, $14H_2$) or $f2f2$ ($24H_1$, $24R_2$, $42R_2$, $72R_1$). The stackings of layers (zig-zag sequences of S–Sn–S molecules) corresponding to simple mixed structures $2H$–$18R$ and $4H$–$18R$ are presented in Fig. 25. As has already been seen, structures of this kind may be considered to be composed of domains of pure basic structures. Here each molecular layer belongs to one of the simple phases: $o,t,f1f5f1$. Note that in this case no faulted arrangements of layers occur in the interphase interfaces. Fig. 26 presents the stackings $f1f2$ and $f2f2$ found in polytypes of SnS_2. These two 'faulted sequences' may be considered as a kind of interdomain boundary occurring between neighbouring domains of the same structure: faults $f1f2$ occur in the $2H$–$2H$ interface (between the domains $2H$ having different orientations of molecules); faults $f2f2$ occur in the multidomain structure $18R$. Note that the structures presented in Fig. 26 are similar to the multidomain structure $4H$ called structure D and occurring frequently in CdI_2 and PbI_2 crystals (Pałosz, 1983). The layers $f1$ and $f2$ occur frequently in polytypes of CdI_2 and PbI_2 and, as discussed elsewhere (Pałosz, 1983), these layers were found to be interdomain boundaries between domains $2H$ and $4H$. The same layers occurring in SnS_2 polytypes, however, can in no case be regarded as $2H$–$4H$ boundaries. The $2H$ and $4H$ polytypes occur in SnS_2 as in CdI_2 and PbI_2, but no polytypes were found to be constructed of domains $2H$ (o layers) and $4H$ (t) with layers $f1$ and $f2$ occurring between the domains.

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References

Pałosz, B. (1982). *Acta Cryst.* B**38**, 3001–3009.
Pałosz, B. (1983). *Phys. Status Solidi A*, **80**, 11–41.
Pałosz, B., Pałosz, W. & Gierlotka, S. (1985). *Acta Cryst.* C**41**, 807–811.
Pałosz, W., Pałosz, B. & Gierlotka, S. (1984). Abstracts: Int. Conf. on Crystal Growth and Characterization of Polytype Structures, Marseille.

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Polytypism of $SnSe_2$ Crystals Grown by Chemical Transport: Structures of Six Large-Period Polytypes of $SnSe_2$

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Abstract. The polytype structure of $SnSe_2$ single crystals grown by chemical transport is examined by X-rays. Frequencies of occurrence of different polytype structures are given and structures of six large-period polytypes are identified: $12H_1$: $f2(o)_2f1f2f1/2(11)_3211$ (t–o–f/Zhdanov notations); $48H_1$: $(f1f5f1)_4[f1f5f1(o)_3]_2/(2121)_4[2121(11)_3]_2$; $24R_1$: $f1f5f1o/212111$; $24R_2$: $f2f2f1f1/211121$; $30R_1$: $f2of2f1f1/2(11)_2121$; $54R_1$: $f2(o)_5f2f1f1/2(11)_6121$.

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Introduction. Polytypism of $SnSe_2$ crystals has been reported several times in the literature, *e.g.* Minagawa (1980), Acharya & Srivastava (1981). It was established that the common structures of $SnSe_2$ were the polytypes 2*H* and 18*R* with Zhdanov sequences 11 and $(1212)_3$, respectively. Minagawa (1980) reported that crystals grown from a melt always have the structure 18*R* and those grown by chemical transport have two alternative basic structures 2*H* and 18*R*. Also, some complex structures, large-period polytypes and disordered structures, were found in the crystals; their structures, however, have not been identified completely.

Below we present the results of a structural analysis of $SnSe_2$ crystals grown by chemical transport. The occurrence of 2*H* and 18*R* polytypes as basic structures is confirmed and the structures of six polytypes are given.

Experimental. Single crystalline samples were prepared by chemical transport reactions in closed silica glass crucibles and with several kinds of transport agents (I_2, ICl_3, Br_2). The compounds are prepared from the elements in growth ampoules that are usually 20–30 cm in length and about 2 cm in diameter. Before the growth reaction, the source material (reacted compound) was transported several times from one side of the ampoule to the other, with large temperature gradients. The growth temperatures for the crystals were around 873 K and the temperature gradients of the order of 50 K. Single crystals in the shape of flakes up to a few cm^2 could be grown. Small crystals were also easily obtained without a transport agent in somewhat larger temperature gradients.

Single crystals of $SnSe_2$ were examined by X-rays (Co *K* radiation) with a 43 mm radius camera and 0·7 mm collimator. Crystals were oscillated around a^*, where the angle between the *c* axis and incident beam varied between 18 and 33°. With the above conditions reflexions $10.l$ and $1\bar{1}.l$ are registered in the patterns for which *l* values satisfy the condition $1{\cdot}5 \le l/N \le 2{\cdot}5$; *N* is the number of Se layers in the unit cell.

The method of layer-stacking identification in the polytype cell used here is the same as that used earlier for CdI_2 and SnS_2 polytypes (Pałosz & Gierlotka, 1984; Pałosz, Pałosz & Gierlotka, 1985). In this method the reflexion intensities measured on the patterns by photometry are compared with the intensities calculated theoretically for structural models; *cf.* standard expression for MX_2 crystals (Gyaneshwar, Chadha & Trigunayat, 1973). The lattice constants used for the calculations were $a = 3{\cdot}81$, $c_0 = 3{\cdot}067$ Å (after Minagawa, 1980); the f_{Sn} and f_{Se} factors were approximated by the analytical function given by Lee & Pakes (1969); the reflexion intensities were multiplied by the Lorentz–polarization factor Lp^{-1}. The experimental and theoretical values of reflexion intensities were compared on intensity diagrams of $10.l/1\bar{1}.l$ reflexions (Figs. 1–6).*

The measurements of the reflexion intensities on the patterns for the $SnSe_2$ polytypes under investigation were very troublesome for several reasons: As discussed by Whitehouse & Balchin (1979), precise determination of intensity values requires the use of absorption coefficients. This factor strongly depends on the shape and dimensions of the sample and in the case of irregularly shaped crystals it cannot be calculated accurately. The crystals examined usually had irregular shapes and the polytypes were always observed in coexistence with basic structures and frequently with a certain disorder. Absorption has a very strong effect on small-angle reflexions (small values of l/N) and a comparatively small effect on the intensities of large-angle reflexions. So, we decided to ignore the absorption coefficient in the calculations of the theoretical values of the intensities and to use only reflexions for which $2{\cdot}0 \le l/N \le 2{\cdot}5$. [Note: In our previous studies on MX_2 polytype identification we used the reflexions for which $1{\cdot}5 \le l/N \le 2{\cdot}5$ or $2{\cdot}5 \le l/N \le 3{\cdot}5$ (Pałosz & Przedmojski, 1980).] The intensity diagrams prepared for these reflexions enable one to observe the special symmetry of the diagrams, *cf.* calculated intensities in Figs. 1–6. Using this symmetry and having intensities for $2{\cdot}0 \le l/N \le 2{\cdot}5$, one can easily calculate reflexion intensities for the second part of the diagram, for $1{\cdot}5 \le l/N \le 2{\cdot}0$. So, in fact, the measurements of reflexion intensities for $2{\cdot}0 \le l/N \le 2{\cdot}5$ are enough for a unique determination of the structure of a polytype and this property of the $10.l/1\bar{1}.l$ reflexion diagrams is used here for $SnSe_2$ polytypes.

Discussion. The structures of more than 40 single crystals of $SnSe_2$ were examined and two basal faces of each sample were analysed independently. The frequencies of occurrence of different polytype structures found in the crystals are given in Table 1. In this table the present results are compared with those reported by Minagawa (1980) for the crystals grown at about 840 K. As already known, polytypism is a function of growth conditions: For CdI_2 and PbI_2 (Pałosz, 1983) and for SnS_2 (Pałosz, Pałosz & Gierlotka, 1984) it has been found that the relative frequencies of occurrence of basic structures and the structures of polytypes strongly depend on temperature of crystallization. Similar relations probably occur for $SnSe_2$ but no experimental data concerning this problem have been published yet.

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* Figs. 1–6 and tables listing calculated and observed intensities for $SnSe_2$ polytypes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42252 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Structures of six new polytypes of $SnSe_2$ are listed in Table 2 where they are described in the *t–o–f* notation and in the Zhdanov notation. The intensity diagrams for the identified polytypes are given in Figs. 1–6 where reflexion intensities calculated for $1{\cdot}5 \leq l/N \leq 2{\cdot}5$ and measured for $2{\cdot}0 \leq l/N \leq 2{\cdot}5$ are shown.

As we showed earlier for all known MX_2 polytype materials the polytypes may always be regarded as structures intermediate between basic polytypes (Pałosz, 1983; Pałosz *et al.*, 1985). Depending on the basic structures of a material, specific arrangements of molecular layers occur in the crystals forming complex structures: these are multilayer polytypes. The basic structures of $SnSe_2$ are $2H$ and $18R$ polytypes and we expected that the large-period polytypes of $SnSe_2$ would be similar to the polytypes of SnS_2 identified recently and grown in coexistence with $2H$ and $18R$ (Pałosz *et al.*, 1984). The latter consisted of two kinds of stacking of layers: $f1–f5–f1$ and $f2–f2–f1–f1$ and of basic layers o. So, in constructing models of $SnSe_2$ polytypes (stackings of layers in a cell) we considered only structures composed of two kinds of structures. For the identified polytypes the following models were considered:

$12H_1$ $(f2of1)_2$ and $f2(o)_2f1f2f1$;
$48H_1$ $(f1f5f1)_6(o)_6$, $(f1f5f1)_5(o)_3f1f5f1(o)_3$, $(f1f5f1)_5(o)_2f1f5f1(o)_4$, $(f1f5f1)_5of1f5f1(o)_5$, $(f1f5f1)_5f2(o)_5f2f1f1$, $(f1f5f1)_4[f2(o)_2f2f1f1]_2$;
$24R_1$ and $24R_2$ $f1f5f1o$ and $f2f2f1f1$;
$30R_1$ $f1f5f1(o)_2$, $f2of2f1f1$, $f2f2f1of1$;
$54R_1$ $f1f5f1(o)_6$, $f2(o)_5f2f1f1$, $f2f2f1(o)_5f1$, $f2(o)_4f2f1of1$, $f2of2f1(o)_4f1$, $f2(o)_3f2f1(o)_2f1$ and $f2(o)_2f2f1(o)_3f1$.

As seen from the above the assumption of multiphase character of polytype structures allowed a very simple determination of the structure of the polytypes.

The small number of known polytypes of $SnSe_2$ does not make it possible to derive rules governing the formation of the polytype structure of the crystals. The similarity between SnS_2 and $SnSe_2$ polytypes is evident. However, it should be noted that while the structures intermediate between $2H$ and $18R$ without faults $[(f1f5f1)_n(o)_m]$ are typical for SnS_2, among the six known polytypes of $SnSe_2$ only two are of this kind; four polytypes contain 'faulted layers' $f2$.

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Table 1. *Frequencies of occurrence of polytypes in* $SnSe_2$ *crystals grown by a chemical transport reaction at about* 873 K

Polytype	Number of samples	% of structure Present study	% of structure Minagawa (1980)
$2H$	69	70	67
$18R$ (pure)	15	20	13
$18R$ (reverse + obverse)	5		
Polytypes:			
Structure determined	6 (Table 2)	10	20
Structure undetermined	3 ($54R$, $60R$, $108R$)		

Note: In two crystals only the polytype $18R$ was found to occur on both crystal faces. In most cases $18R$ and large-period polytypes occurred in coalescence with $2H$.

Table 2. *Structures of known polytypes of* $SnSe_2$

Ramsdell symbol	*t–o–f* sequence	Zhdanov sequence
Basic structures		
$2H$	o	11
$18R$	$f1f5f1$	$(2121)_3$
Hexagonal polytypes		
$12H_1$	$f2(o)_2f1f2f1$	$2(11)_3211$
$48H_1$	$(f1f5f1)_4[f1f5f1(o)_3]_2$	$(2121)_4[212(11)_31]_2$
Rhombohedral polytypes		
$24R_1$	$f1f5f1o$	$(212111)_3$
$24R_2$	$f2f2f1f1$	$(211121)_3$
$30R_1$	$f2of2f1f1$	$[2(11)_2121]_3$
$54R_1$	$f2(o)_5f2f1f1$	$[2(11)_6121]_3$

References

Acharya, S. & Srivastava, O. N. (1981). *J. Cryst. Growth*, **55**, 395–397.

Gyaneshwar, Chadha, G. K. & Trigunayat, G. C. (1973). *Acta Cryst.* B**29**, 1791–1795.

Lee, J. D. & Pakes, H. W. (1969). *Acta Cryst.* A**25**, 712–713.

Minagawa, T. (1980). *J. Phys. Soc. Jpn*, **49**, 2317–2318.

Palosz, B. (1983). *Phys. Status Solidi A*, **80**, 11–41.

Palosz, B. & Gierlotka, S. (1984). *Z. Kristallogr.* **166**, 53–62.

Palosz, B., Palosz, W. & Gierlotka, S. (1985). *Acta Cryst.* C**41**, 807–811, 1402–1404.

Palosz, B. & Przedmojski, J. (1980). *Z. Kristallogr.* **151**, 31–48.

Palosz, W., Palosz, B. & Gierlotka, S. (1984). Abstracts: Int. Conf. on Crystal Growth and Characterization of Polytype Structures, Marseille.

Whitehouse, C. R. & Balchin, A. A. (1979). *Z. Kristallogr.* **149**, 241–247.