Acta Cryst. (1990). **B46**, 449–455

Refinement of SnS_2 Polytypes 2*H*, 4*H* and 18*R*

By B. Pałosz

High Pressure Research Center of the Polish Academy of Sciences 'Unipress', ul. Sokolowska 29/37,
01142 *Warszawa, Poland*

and W. Steurer and H. Schulz

Institut für Kristallographie und Mineralogie der Universität, Theresienstr. 41, *D*-8000 *München* 2,
Federal Republic of Germany

(*Received* 22 *February* 1989; *accepted* 9 *November* 1989)

Abstract

The 2*H*, 4*H* and 18*R* polytype structures of SnS_2 have been refined using X-ray single-crystal data. Chemical analysis, density measurements and the refined structure models show that the 4*H* and 18*R* polytypes have stoichiometric compositions, whereas the composition of the 2*H* polytype is SnS_{2-x} ($0{\cdot}15 \le x \le 0{\cdot}18$). The occupancies of the hexagonal S and Sn layers vary within the range 0·8–1·0 and are modulated in the stacking direction. Space group $P\bar{3}m1$ (No. 164) was assigned to the 2*H*, $P3m1$ (No. 156) to the 4*H* and $R\bar{3}m$ (No. 166) to the 18*R* polytype. The structures have been refined to $R = 0{\cdot}013$, $wR = 0{\cdot}019$ for the 2*H*, $R = 0{\cdot}026$, $wR = 0{\cdot}030$ for the 4*H* and $R = 0{\cdot}056$, $wR = 0{\cdot}056$ for the 18*R* polytype using 99, 552 and 422 unique reflections, respectively. Crystal data at room temperature: $M_r = 182{\cdot}90$, $a_{2H} = a_{4H} = a_{18R} = 3{\cdot}6470\ (8)$, $c_{2H} = 5{\cdot}8990\ (5)$, $c_{4H} = 11{\cdot}811\ (2)$, $c_{18R} = 53{\cdot}118\ (7)$ Å; $Z_{2H} = 1$, $Z_{4H} = 2$, $Z_{18R} = 9$, $V_{2H} = 67{\cdot}98\ (4)$, $V_{4H} = 136{\cdot}11\ (8)$, $V_{18R} = 612{\cdot}1\ (3)$ Å^3, $D_{m2H} = 3{\cdot}4\ (2)$, $D_{m4H} = 4{\cdot}1\ (1)$, $D_{m18R} = 3{\cdot}9\ (1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71061$ Å, $\mu = 10{\cdot}51$ mm^{-1}, $F(000)_{2H} = 82$, $F(000)_{4H} = 164$, $F(000)_{18R} = 738$.

Introduction

Polytypism is regarded as arising through different ways of stacking compatible units which are, in the case of simple polytype materials, hexagonal layers or molecular packages composed of hexagonal layers. Compatibility of the layers leads to different stacking variants occurring as different structural modifications of the material (polytypes).

As long as only a few polytypic materials were known polytypism was regarded as an exceptional phenomenon. In recent years there has been increasing evidence of polytypic materials. The number of the polytypic substances and the variety of structural types in which polytypes have been observed has expanded and seems to be unlimited. At the same time it should be observed that only some isostructural materials exhibit polytypism and occur in a number of structural modifications (periodic and/or disordered) while other isostructural materials behave like 'ordinary' crystals and adopt the structure of one or several polymorphic forms. It is clear that the geometry of the crystal structure and the compatibilty of the structural units are necessary conditions for forming various stacking variants, and that there are defined forces behind the polytypic behaviour of the crystals.

Various models have been suggested to explain the nature and origin of polytypism. Most of them assume full compatibility of the structural units: the layers preserve their structure in all stacking sequences and, as a consequence of this assumption, the translation period along the stacking direction is a simple multiple of a certain unit, the interlayer distance. In this model it is accepted that the atoms within a single unit layer have identical surroundings and also that second- or higher-order coordinations of the atoms do not depend on the structure whatever the layer stacking is. In such an idealized model of polytype structures the lattice-energy variation for polytypes should be extremely small, if any. Of course within such a model no simple explanation can be given for polytype formation and for structure stability based on lattice-energy variation.

Several models of polytypism have been proposed to justify the purely geometrical model of polytypes. First, Jagodzinsky (1954) showed using equilibrium thermodynamics that there are some specific stacking variants: the fully ordered and randomly disordered variants are expected to be stabilized by entropy. This gives a reasonable thermodynamical basis for polytypism (in fact it is obvious that there cannot be a disagreement between what we observe and thermodynamics) but this entropy model cannot predict whether a given material will form one or a number of polytypic structures. The model also does not

0108-7681/90/040449-07$03.00

describe the relative stability of the observed structures. Another explanation suggested for polytypism, which has been discussed and modified over the past 30 years, is based on a purely geometrical model of the screw-dislocation mechanism of crystal growth (Verma & Krishna, 1966). In fact this model can explain how the stacking sequences are formed, but does not explain the nature of the phenomenon and why it only occurs in some isotypical crystals. In recent years an Ising spin model, which was originally considered for magnetic materials (Elliot, 1961), has been developed for polytypic materials in the *ANNNI* model, see Yeomans & Price (1986). This model, which considers long-range ordering starting from short-range interactions, also does not answer the basic questions of polytypism: namely, the stability of basic polytype structures and the conditions of occurrence of polytypes.

There is extensive experimental evidence on differences in the physical properties of simple polytype structures which cannot be understood using purely geometrical models of polytype crystal structures built from identical compatible units. What we found surprising was that while many complicated polytypic structures of prominent polytypic materials like ZnS, SiC, CdI$_2$, SnS$_2$ and PbI$_2$ have been reported, the structures of their most common simplest polytypes have never been refined: one exception is the 6*H* structure of SiC refined by Gomes de Mesquita (1967) who showed that the interlayer spacings in cubic *c* and in hexagonal *h* arrangements are significantly different within a single 6*H* cell.

In this paper we present the results of the refinements of the basic structures of the 2*H*, 4*H* and 18*R* polytypes of SnS$_2$. It will be shown that these three structures are very similar because of their construction principles, but that they differ substantially in the chemical composition of their S–Sn–S units.

Experimental

The structure refinements were performed with the use of *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

The crystals of SnS$_2$ were grown by the chemical transport method (Pałosz, Pałosz & Gierlotka, 1986): 2*H* predominantly below 873 K, 4*H* above 1073 K and 18*R* in the intermediate temperature range. Single crystals were obtained as yellow platelets, up to 0·2 mm thick and 3–4 mm in diameter. As-grown crystals were used for X-ray measurements: the crystals are extremely soft and, to prevent deformation and induction of strains or crystal structure defects in the samples, we did not try to correct their shape. Preliminary examinations of the crystals by X-ray photographic methods (Laue, oscillation and precession photographs) were used to eliminate samples with a nonuniform or a disordered structure.

Table 1. *Chemical composition of* SnS$_2$ *polytypes found by electron microprobe analysis*

Standard for S	Sample	Concentration (weight %) S	Sn	Atomic ratio S:Sn
	—	35·07	64·93	2:1
4*H*	2*H*	33·8 (5)	66·2 (5)	1·89:1
	18*R*	35·5 (5)	64·5 (5)	2·04:1
18*R*	2*H*	33·3 (5)	66·7 (5)	1·85:1
	4*H*	34·6 (5)	65·4 (5)	1·96:1

Table 2. *Calculated and measured densities* (Mg m^{-3}) *for* SnS$_2$ *polytypes*

	D_c	D_x	D_m
2*H*	4·469	4·32	3·4 (2)
4*H*	4·474	4·18	4·1 (1)
18*R*	4·472	3·91	3·9 (1)

Notes: D_c is the crystallographic density calculated for fully occupied crystal structures, with *a* and *c* measured on powders (Pałosz & Salje, 1989): $a_{2H} = a_{4H} = a_{18R} = 3·647$ Å; $c_{2H} = 5·899$, $c_{4H} = 5·906$, $c_{18R} = 5·902$ Å. D_x is the density calculated for the refined structures with the most dense layer normalized to full occupancy 1·0. D_m is the measured density.

Chemical analysis

The 2*H*, 4*H* and 18*R* samples were too small to determine the absolute S and Sn contents. Therefore, we decided to perform a comparative chemical analysis of the samples of the three polytypes by microprobe analysis. The measurements were performed on a Jeol JXA 50A electron microprobe analyser. It is always difficult to measure the S content precisely by microprobe analysis so it was based instead on accurate measurements of the Sn content of the samples. The analysis was performed in two steps: the 2*H*, 4*H* and 18*R* samples and pure Sn were placed on the target and at first the 4*H* sample was taken as the stoichiometric material SnS$_2$ and used as a standard to calculate the S contents in the 2*H* and 18*R* samples. Then, the same procedure was repeated with 18*R* taken as the standard for S. A pure Sn sample was employed as the standard for this element in the 4*H* and 18*R* measurements.

Table 1 gives the results of the measurements after a numerical correction for X-ray absorption and anomalous dispersion. The deviation of the S and Sn concentrations from a stoichiometric composition in samples 4*H* and 18*R* is within the experimental error (estimated to *ca* 1% weight) of the method used. The 2*H* sample exhibits a substantial deviation from the stoichiometric composition.

Table 3. *R values obtained for the refined* 2*H*, 4*H and* 18*R polytypes of* SnS_2

Structure	No. of measured reflections	Space group	No. of unique reflections	No. of variables	Model	*wR*
2*H*	852	$P\bar{3}m1$	99	8	Full occupancy	0·024
					Modulated occupancy	0·019
4*H*	2448	$P6_3mc$	197	12	Full occupancy	0·038
			552*		Full occupancy	0·055
		$P3m1$	552	20	Full occupancy	0·035
					Modulated occupancy	0·030
18*R*	3588	$R\bar{3}m$	422	20	Full occupancy	0·061
					Modulated occupancy	0·056

*Merged in Laue class $3m$ to obtain the same number of reflections for the refinements in $P6_3mc$ and $P3ml$, which is important for the Hamilton test.

Density measurements

The densities of the 2*H*, 4*H* and 18*R* polytypes were measured by hydrostatic methods (Henning, 1964) using water and isooctane at 295 K. The surface tension of water was too high for the 2*H* samples which were very badly wetted; for the 2*H* samples only isooctane was used, therefore. The 4*H* and 18*R* samples were measured in water and isooctane. The measurements were performed twice for each structure using different samples. The accuracy of the measurements depends strongly on the amount of sample: *ca* 0·010 g of 2*H*, 0·015 g of 18*R* and *ca* 0·030 g of 4*H*. The D_m values obtained are given in Table 2.

Data collection

Data collection was performed with an Enraf–Nonius CAD-4 four-circle diffractometer, $\omega/2\theta$ scans, one intensity control reflection measured every hour remained constant within counting statistics; three orientation-control reflections; $\theta_{\max} = 30°$; for 2*H* 852 ($-5 \le h,k \le 5$, $-8 \le l \le 8$), 4*H* 2448 ($-5 \le h,k \le 5$, $-16 \le l \le 16$) and 18*R* 3588 ($-5 \le h,k \le 5$, $0 \le l \le 84$) reflections collected; 99, 552 and 422 unique reflections, respectively, after averaging ($R_{\text{int}} = 0{\cdot}024$, 0·037 and 0·070, respectively). Lattice parameters were determined from a least-squares fit of 25 reflections. Weights were proportional to $1/\sigma^2(F)$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974); Lp correction, numerical absorption correction, secondary-extinction correction. The ratios of the maximum least-squares shift to e.s.d. in the final refinement cycles were: 2*H* 0·05, 4*H* 0·17 and 18*R* 0·57.

Results

Space groups $P\bar{3}m1$, $P6_3mc$ and $R\bar{3}m$ have traditionally been assigned to the 2*H*, 4*H* and 18*R* polytypes of SnS_2. The above space groups are deduced from the packing geometry of fully occupied hexagonal layers, which are combined in S–Sn–S molecular sandwiches. For the three polytypes under examination the above three space groups and also space group $P3m1$ were considered based on the observed Laue symmetry $\bar{3}m$. Additionally, the Hamilton (1965) test confirmed the assignement of $P3m1$ to the 4*H* polytype. The numbers of measured reflections, unique reflections and *wR* values are given in Table 3.

Before refinement of the structures of the polytypes a simple test was performed on some of the reflection intensities to check the compatibility of layer packing in the stacking sequences of 2*H*, 4*H* and 18*R*. From a simple analysis of close packing of hexagonal layers it can be shown (Verma & Krishma, 1966) that some reflections are insensitive to the stacking of the layers and their relative intensities should be the same whatever the layer stacking is, *e.g.* the reflections for which $(h-k) = 0$ and $l = 0$, $1N$, $2N$ ... (N is the number of the layers in the polytype cell). A comparison of the intensities calculated for the perfect 2*H* structure (with fully occupied sites) with those measured for 2*H*, 4*H* and 18*R* samples is given in Table 4. From this comparison it can be clearly seen that in the crystal structures studied there are deviations from the model involving perfectly packed identical S–Sn–S sandwiches.

Although no streaks or reflection broadening were observed on the X-ray photographs, models including random disorder were examined. A disorder within single layers was introduced by including occupancies of two additional sites, *e.g.* if the layer is of type *A* the sides *B* and *C* were added and their occupancies refined. This kind of disorder is expected if partial dislocations are present in the crystals. The models with disorder did not converge and were rejected.

The final refinement of the SnS_2 polytypes was performed with released and unconstrained occupancies of Sn and S layers. The largest occupancy of a single layer was fixed to 1·0 and relative occupancies were calculated for the rest of the layers in the polytype cell.

Table 4. *Relative intensities of equivalent reflections of the* 2*H*, 4*H* *and* 18*R* *polytypes of* SnS_2

	Calculated	Experimental		
Reflection	2*H*	2*H*	4*H*	18*R*
110	100	100·00 (8)	100·00 (9)	100·00 (8)
112 (2*H*) 114 (4*H*) 1118 (18*R*)	36·4	35·95 (5)	43·82 (6)	39·41 (3)
114 (2*H*) 118 (4*H*) 1136 (18*R*)	79·6	78·68 (11)	84·83 (19)	75·53 (10)
116 (2*H*) 1112 (4*H*) 1154 (18*R*)	15·1	14·92 (8)	19·69 (6)	16·3 (2)

In the following, the occupancies of the S and Sn layers obtained for the refined models were normalized to the densities of the polytypes measured experimentally (D_m). As seen in Table 2, the densities of the 4*H* and 18*R* polytypes, calculated as the crystallographic densities D_x of the structures with modulated occupancies and largest occupancy 1·0, fit perfectly to the measured densities D_m. The density D_m of the polytype 2*H* is much smaller than that calculated for the structure with fully occupied Sn layers D_x, and the occupancies obtained for the refined model were multiplied by the factor D_m/D_x = 3·4/4·3. The stacking sequences and occupancies of the hexagonal layers of S and Sn are presented in Fig. 1.

The results of the refinements fully agree with the chemical analyses of the samples: the 4*H* and 18*R* polytypes have similar chemical compositions corresponding, within experimental error, to the stoichiometric compound SnS_2. The 2*H* polytype is nonstoichiometric with an excess of Sn relative to the composition Sn:S = 1:2 (Table 1).

The average chemical compositions (with an error of *ca* 0·02) of the three basic structures of SnS_2 are: 2*H*, $Sn_{0\cdot79}S_{1\cdot43}$; 4*H*, $Sn_{0\cdot93}S_{1\cdot83}$; 18*R*, $Sn_{0\cdot89}S_{1\cdot76}$.

Note that in the crystal structure of the 2*H* polytype only 79% of the sites in the hexagonal Sn layers are occupied and only 72% of the sites in the S layers. Comparatively fewer vacancies can be found in the 4*H* and 18*R* polytypes.

The temperature factors for all three polytypes under examination have similar values; the values of u_{11} and u_{33} do not differ significantly from typical values of other inorganic crystals. The root-mean-square displacements of the atoms in the layer plane are similar for S and Sn and in the range 0·07–0·1 Å; in the *c* direction the range is 0·1–0·14 Å.* The thermal vibration ellipsoids of the Sn atoms are elongated slightly more in the *c* direction than those

---

* Lists of structure factors, atomic coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52796 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

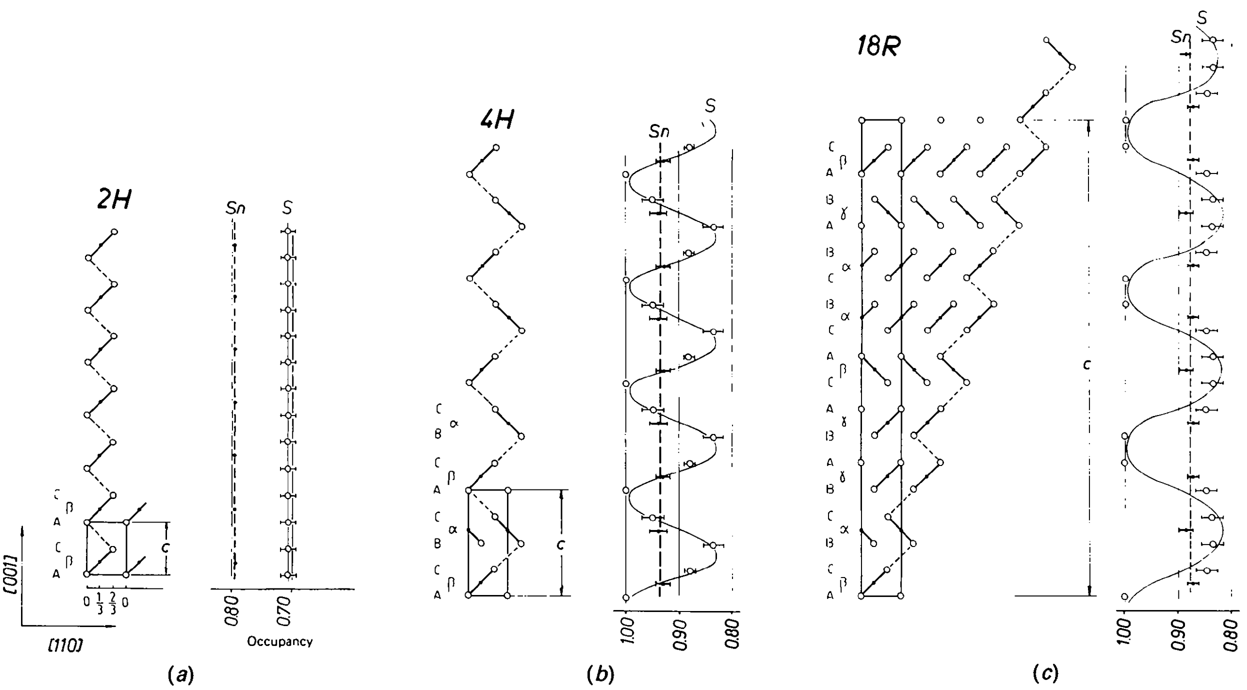

Fig. 1. Layer-stacking sequence of SnS_2 polytypes (*a*) 2*H*, (*b*) 4*H* and (*c*) 18*R*. The occupancy modulation waves, corresponding to the variation of the site occupancies along the stacking direction, are shown schematically. Open circles, S atoms; closed circles, Sn atoms.

of the S atoms: the axial ratio $(u_{11}/u_{33})^{1/2}$ = 1·7 for Sn and 1·3 for S atoms.

The interlayer distances are given in Table 5: the distance between two subsequent hexagonal S layers belonging to one S–Sn–S sandwich is 2 × 0·247 = 0·494, while between the S layers belonging to two sequent sandwiches it is 0·506 (the distances are given in fractions of c_{2H}). It should be stressed that the interlayer distances are the same for 2*H*, 4*H* and 18*R* structures. This means that the geometry of the packing is the same within a wide range of layer occupancies (80–100% of the total number of atomic sites).

Difference Fourier maps obtained after the final refinement exhibit residual electron densities with maxima reaching 0·37 e Å^{-3} for 2*H*, 0·48 e Å^{-3} for 4*H* and 0·75 e Å^{-3} for 18*R*.

Discussion

The large number of unoccupied sites in the polytypes demonstrates that the idealized model of polytype structures, where rigid and perfect hexagonal layers form closely packed stacking sequences, is a poor approximation of the real crystal structure of SnS_2. In the perfect crystal structure with fully occupied atomic sites the coordination of the atoms does not depend on the layer stacking and consequently the lattice-energy differences between polytypes would be negligibly small. The coordination numbers in the structure with modulated occupancies vary along the stacking direction and the occupancies are different for different stacking variants. The layers are geometrically compatible units but the S–Sn–S sandwiches have different chemical compositions, so they are in fact different layers. Lattice-constant measurements (Pałosz & Salje, 1989) show that the geometry of hexagonal layers does not change with occupancy: the differences of the lattice constant *a* within the layer plane are smaller than 0·0001 Å. There are, however, measurable differences in the *c* lattice parameters of the polytypes: the interlayer distance is a function of the layer stacking. If we consider different layer stackings occuring sequentially in one crystal at room temperature, the only nonvanishing component of the spontaneous strain tensor $e_3 = \Delta c/c = 0{\cdot}5 \times 10^{-3}$ for the crystal structure constructed of 2*H* and 18*R* domains, $0{\cdot}6 \times 10^{-3}$ for 4*H*–18*R* and $1{\cdot}2 \times 10^{-3}$ at the interdomain boundary between the 2*H* and 4*H* stackings (Pałosz & Salje, 1989).

Table 5. *Interlayer spacings (fractions of c_{2H}) in 2H, 4H and 18R polytypes*

Layer	z_{2H}	$z_{4H}/2$	$z_{18R}/9$	Spacing
Sn	0·0	0·0	0·0	
				0·247
S	0·2471 (3)	0·2467 (7)	0·2471 (5)	
				0·506
S	0·7529 (3)	0·7537 (6)	0·7535 (5)	
				0·247
Sn	1·0	1·0003 (4)	1·001 (1)	
				0·247
S	1·2471 (3)	1·2478 (7)	1·2484 (5)	
				0·506
S	1·7529 (3)	1·7529 (4)	1·7529 (5)	

To discuss the stability of polytypes we have to consider thermodynamical and chemical factors, and decide which of them dominates the actual structure of the crystal. Usually, it has been assumed that the chemical composition of polytypes is stoichiometric (in most cases nothing was said about stoichiometry) and in discussions of the growth of polytypes or of the conditions for polytype transitions only the role of temperature and/or of pressure was considered.

The crystals of SnS_2 which we analysed were grown by chemical transport methods in which the crystallization environment plays an important role in crystal structure formation. In this case the temperature and pressure as well as the transporting agent determine the chemical composition of the crystals. When we previously analysed the effect of growth conditions on the polytypic structure of SnS_2 we assumed that the crystals had a stoichiometric SnS_2 composition and we tried to find a correlation between crystallization temperature and the polytypic structure of the crystals (Pałosz, Pałosz & Gierlotka, 1986). We observed that the 2*H* polytype is the dominant structure below 873 K and 4*H* above 1073 K. We suggested that these two structures represent the low-and high-temperature modifications of SnS_2. At the same time we found some inconsistencies in the experimental results, particularly between crystals grown using different transporting agents. Also, our conclusions did not agree with results of other authors, *e.g.* Mitchell, Fujiki & Ishizawa (1974) and Whitehouse & Balchin (1979), who used different crystallization techniques. The nonstoichiometry makes it clear that we cannot expect unique correlation between temperature and structure when the chemistry of the material changes.

The variation of the layer occupancies which we found in SnS_2 polytypes is very large and could easily be confirmed by density measurements. The nature of this behaviour of the crystals in the Sn–S system can be understood as a natural tendency of the material to form various chemical compositions. Earlier two orthorhombic structures were reported: SnS (Wiedemeyer & von Schnering, 1978) and Sn_2S_3 (Mootz & Puhl, 1967). The polytypes of SnS_2 have structures built up of hexagonal layers of S and Sn atoms and exhibit trigonal symmetry. The characteristic of SnS_2 which permits polytypes to be formed is that the crystal structure does not loose its stability within a certain range of chemical composition: the present work shows that the occupancy of the layers can be as low as 80% with the basic trigonal structure preserved. The 2*H*, 4*H* and 18*R* polytypes dominate the structures representing the most stable structural modifications in this compound. The driving forces for the polytypism of SnS_2 seem to originate from variations of the chemical composition. There are a variety of large-period polytypes observed in the SnS_2 crystals which accompany the basic structures 2*H*, 4*H* and 18*R*, and most probably they have chemical compositions intermediate between that of 2*H* and stoichiometric SnS_2.

The large-period polytypes which we have identified in SnS_2 have stacking sequences which are combinations of the stackings of the three basic structures. They are not simple layer-stacking variants which are permitted by geometry but are definitely structures intermediate between the basic ones. However, we observed that while there is a variety of the structures involving combinations of 2*H* and 18*R* stackings and also of 4*H* and 18*R* stackings, there are no structures intermediate between 2*H* and 4*H* (Pałosz, Pałosz & Gierlotka, 1986). Even in the crystals in which these two structures occurred in coalescence they are always concentrated in large domains. In the absence of geometrical restrictions for combining 2*H* and 4*H* stackings (they occur in great numbers in CdI_2 polytype crystals) the only reason for the lack of this kind of polytypes must be the instability of such stackings or that they are less stable than the stackings involving 2*H*–18*R* or 4*H*–18*R* combinations. In fact when we compare the spontaneous strain component e_3 for the combined sequences of 2*H*, 4*H* and 18*R* structures (Pałosz & Salje, 1989) we see that the strongest strain field will be at the 2*H*–4*H* interdomain boundaries. Thus, there would be a natural tendency to replace 2*H*–4*H* stackings, if created, by those giving a smaller strain: 2*H*–18*R* and/or 4*H*–18*R*, or they would be rejected by the crystal structure. It is clear that in the same way as the basic structures have layer occupancies modulated in a defined way (Fig. 1), the large-period structures should have their occupancies modulated with a period corresponding to their lattice constant *c*. One could expect that the modulation waves are combinations of the modulation waves of the basic stackings. Unfortunately, the large-period polytypes occur in all small regions of the crystals and we did not succeed in finding a large-period polytype of suitable size for intensity data collection and structure refinement. Lattice-energy calculations performed for differently modulated structures and combinations of different layer stackings should help to understand the stability of polytype crystal structures of the basic and large-period structures formed in the Sn–S system. There is considerable evidence in the literature for the effect of chemical composition on polytypism of the crystals. Close connections between chemical composition and crystal structure have been reported for different materials, *e.g.* for the Ti–S system (Legendre, Moret, Tronc & Huber, 1983) or for Si–Al–O–N (Hendry & Jack, 1977). Polytypes can be strongly influenced by dopands; the classical example is the effect of Al on the structure of SiC (Verma & Krishna, 1966). They can also be modified by the composition of solid solutions, *e.g.* ZnS–CdS or ZnS–ZnSe (Kozielski, 1976).

For most of the polytypic materials there is no information available on their chemical composition, homogeneity of the atomic distribution in the crystal structure, presence of vacancies, impurities *etc.* It cannot be excluded that like SnS_2, which was always considered as a stoichiometric material, other polytypic materials may exhibit some characteristic deviations from perfectly packed hexagonal structures. This must be taken into account when we try to understand the nature and behaviour of the polytypes.

It is difficult to estimate how large the deviations from a perfect lattice should be to activate polytypism. However, until the structures of polytypic materials have been refined and the materials defined and characterized, the discussion on the nature and origin of polytypism can only be more or less speculative.

The authors are grateful to Dr A. Belzner for help in performing the calculations with *PROMETHEUS* and to Dr O. Generowicz for the chemical analysis of the samples. BP gratefully acknowledges the receipt of a fellowship from the Alexander von Humboldt Foundation.

References

ELLIOTT, R. J. (1961). *Phys. Rev.* **124**, 346–353.

GOMES DE MESQUITA, A. H. (1967). *Acta Cryst.* **23**, 610–617.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

HENDRY, A. & JACK, K. H. (1977). *Inst. Phys. Conf. Ser.* **36**, 157–161.

HENNING, I. (1964). *J. Res. Natl Bur. Stand. Sect. A*, **68**, 529–533.

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

JAGODZINSKI, H. (1954). *Neues Jahrb. Mineral. Abh.* **3**, 49–65.

KOZIELSKI, M. J. (1976). *Rep. Inst. Phys. Warsaw Tech. Univ.* **16**.

LEGENDRE, J. J., MORET, R., TRONC, E. & HUBER, H. (1983). In *Progress in Crystal Growth and Characterization.* Oxford: Pergamon Press.

MITCHELL, R. S., FUJIKI, Y. & ISHIZAWA, Y. (1974). *Nature (London)*, **247**, 537–538.

MOOTZ, D. & PUHL, H. (1967). *Acta Cryst.* **23**, 471–476.

PAŁOSZ, B., PAŁOSZ, W. & GIERLOTKA, S. (1986). *Bull. Mineral.* **109**, 143–150.

PAŁOSZ, B. & SALJE, E. (1989). *J. Appl. Cryst.* **22**, 622–623.

VERMA, A. R. & KRISHNA, P. (1966). *Polymorphism and Polytypism in Crystals.* New York: Wiley.

WHITEHOUSE, C. R. & BALCHIN, A. A. (1979). *J. Cryst. Growth*, **47**, 203–212.
WIEDEMEYER, H. & VON SCHNERING, H. G. (1978). *Z. Kristallogr.* **148**, 295–303.
YEOMANS, J. M. & PRICE, G. D. (1986). *Bull. Mineral.* **109**, 3–13.
ZUCKER, U. H., PERENTHALER, E., KUHS, W. F., BACHMANN, R. & SCHULZ, H. (1983). *J. Appl. Cryst.* **16**, 11–16.

Acta Cryst. (1990). **B46**, 455–458

Comparative Investigation of Microarea Quasilattice Parameters of Al–Si–Mn and Al–Cu–Fe Icosahedral Phases using HOLZ Line Patterns*

BY MINGXING DAI AND RENHUI WANG

Department of Physics, Wuhan University, 430072 *Wuhan, People's Republic of China,*
and Beijing Laboratory of Electron Microscopy, Academia Sinica, PO Box 2724, 100080 *Beijing,*
People's Republic of China

(*Received* 30 *October* 1989; *accepted* 1 *February* 1990)

Abstract

Some differences between the higher-order Laue zone (HOLZ) line patterns of $Al_{76}Si_4Mn_{20}$ and $Al_{65}Cu_{20}Fe_{15}$ icosahedral phases (*I* phases) have been observed. These differences originate from the fact that $Al_{76}Si_4Mn_{20}$ belongs to a simple icosahedral quasilattice whereas $Al_{65}Cu_{20}Fe_{15}$ belongs to an ordered face-centred icosahedral quasilattice, and from the minor difference in their quasilattice parameters. By computer simulation of these HOLZ line patterns using a 'standard' quasilattice parameter of 0·460 nm for the *I* phase of $Al_{76}Si_4Mn_{20}$, the quasilattice parameter of the *I* phase of $Al_{65}Cu_{20}Fe_{15}$ has been determined to be 0·8966 nm.

1. Introduction

Owing to the sensitivity of higher-order Laue zone (HOLZ) line patterns in convergent-beam electron diffraction (CBED) patterns to changes in lattice parameters (and thus to changes in the wavelength), HOLZ line patterns have been used to accurately measure the microarea lattice parameters in crystals [see, for example, Jones, Rackham & Steeds (1977), Ecob, Shaw, Porter & Ralph (1981) and Wang, Zou & Jiao (1986)]. We have recently obtained experimental HOLZ line patterns of an $Al_{76}Si_4Mn_{20}$ quasicrystalline icosahedral phase (*I* phase) with a large angular range by connecting a series of conventional CBED patterns and performing a theoretical simulation (Dai & Wang, 1990). The agreement between the experimental and theoretical HOLZ line patterns of the *I* phase has encouraged us to use HOLZ line patterns to measure the quasilattice parameter of the *I* phase accurately.

Tsai, Inoue & Masumoto (1987) reported a stable *I* phase, the $Al_{65}Cu_{20}Fe_{15}$ phase. Its composition, as determined by energy-dispersive X-ray spectrometric quantitative analysis, is $Al_{63}Cu_{24}Fe_{13}$ (Shindo, Hiraga, Williams, Hirabayashi, Inoue & Masumoto, 1989). Ebalard & Spaepen (1989) have recently studied the structure of the *I* phase of $Al_{65}Cu_{20}Fe_{15}$ by selected-area electron diffraction. They found that there are extra diffraction spots along the fivefold directions and explained this by ascribing a face-centred icosahedral (f.c.i.) structure to the *I* phase of $Al_{65}Cu_{20}Fe_{15}$, in contrast to the simple icosahedral (s.i.) structures of the *I* phases of Al_4Mn and $Al_{76}Si_4Mn_{20}$. They described the f.c.i. *I* phase of $Al_{65}Cu_{20}Fe_{15}$ as a superlattice of the s.i. lattice by placing two kinds of atomic clusters at even and odd vertices (ordering). Moreover, we expect there would be a minor difference between the quasilattice parameters of the *I* phases of $Al_{76}Si_4Mn_{20}$ and $Al_{65}Cu_{20}Fe_{15}$ owing to differences in both the chemical composition and the ordering.

The purpose of the present work is to observe whether there are extra HOLZ lines in the *I* phase of $Al_{65}Cu_{20}Fe_{15}$ caused by superreflections, and to determine the quasilattice parameter of this phase for comparison with that of the *I* phase of $Al_{76}Si_4Mn_{20}$.

2. Experimental and simulation

The rapidly solidified ternary $Al_{76}Si_4Mn_{20}$ and $Al_{65}Cu_{20}Fe_{15}$ ribbons were obtained from prealloyed ingots by the melt-spinning method. Specimens for transmission electron microscopy were then prepared by ion milling and observed with a Philips EM420 electron microscope operated at an accelerating voltage of 100 kV. The CBED patterns were photographed at liquid-nitrogen temperature using a low-temperature double-tilting stage.

---

* Project supported by the National Natural Science Foundation of China.

0108-7681/90/040455-04$03.00