X-Ray and Transmission Electron Microscopy Investigations of the New Solids In₅S₅Cl, In₅Se₅Cl, In₅S₅Br, and In₅Se₅Br

Hans-Jörg Deiseroth^{a,*}, Christof Reiner^a, Kledi Xhaxhiu^a and Marc Schlosser^a, and Lorenz Kienle^b

^a Siegen, Anorganische Chemie der Universität

^b Stuttgart, MPI für Festkörperforschung

Received June 10th, 2004.

Professor Martin Jansen zum 60. Geburtstag gewidmet

Abstract. The compounds In_5Ch_5X (Ch = S, Se; X = Cl, Br) represent new mixed valence solids with indium occurring simultaneously in three different oxidation states: In^+ , In^{3+} and In^{2+} where the latter appears as covalently bonded dumbbells $(In_2)^{4+}$. Although the ionic formulation ($In_5Ch_5X = In^+ 2In^{3+} (In_2)^{4+} 5Ch^{2-} X^-$) is the same for all compounds, they crystallise in two structure types (In_5Ch_5Cl -type: monoclinic, $P2_1/m$, Z = 2; In_5Ch_5Br -type: orthorhombic, $Pmn2_1$, Z = 2). Ignoring the distribution of the halogen atoms, the anionic partial structure is very similar in both structure types. The main difference is an exchange of (In^+) by ($In_2)^{4+}$ and vice versa on selected positions. This is possible due to

the nearly identical coordination of both ions (tri-capped trigonal prisms). HRTEM investigations show remarkable differences in the real structures of In_5Ch_5Cl and In_5Ch_5Br . In contrast to the perfectly ordered crystals of the bromides, the chlorides exhibit a variety of nanoscaled crystal defects, i.e. twinning, polylamellar intergrowth of polymorphs and lamellar intergrowth of structurally related compounds as demonstrated in In_5S_5Cl/In_6S_7 . The occurrence of these defects is discussed using an appropriate structure model.

Keywords: Chalcogen; Indium; Crystal structure; HRTEM; Real structure

Röntgen- und transmissionselektronenmikroskopische Untersuchungen der neuen Feststoffe In₅S₅Cl, In₅Se₅Cl, In₅Se₅Br und In₅Se₅Br

Inhaltsübersicht. Die Verbindungen In_5Ch_5X (Ch = S, Se, X = Cl, Br) repräsentieren neue gemischtvalente Verbindungen in welchen Indium gleichzeitig in drei unterschiedlichen Oxidationsstufen auftritt: In⁺, In³⁺ und In²⁺ in Form von $(In_2)^{4+}$ Hanteln mit kovalenter In-In-Bindung. Obwohl die ionische Formulierung ($In_5Ch_5X =$ $In^+ 2In^{3+} (In_2)^{4+} 5Ch^{2-} X^-$) für alle Verbindungen übereinstimmt, kristallisieren sie in zwei unterschiedlichen Strukturtypen (In_5Ch_5Cl -Typ: monoklin, $P2_1/m$, Z = 2; In_5Ch_5Br -Typ: orthorhombisch, $Pmn2_1$, Z = 2). Unter Vernachlässigung der Halogenverteilung ist die Anionen-Teilstruktur für beide Strukturtypen vergleichbar. Der Hauptunterschied ist ein Austausch von (In⁺) durch $(In_2)^{4+}$ und vice versa auf einigen ausgewählten Positionen. Dies ist möglich, wegen nahezu identischer Koordination beider Ionen (dreifach überkappte trigonale Prismen). HRTEM Untersuchungen zeigen bemerkenswerte Unterschiede in den Realstrukturen von In₅Ch₅Cl und In₅Ch₅Br. Im Gegensatz zu den perfekt geordneten Kristallen der Bromide, zeigen die Chloride eine Vielzahl von nanoskaligen Kristalldefekten, wie Verzwillingung, polylamellare Verwachsung von Polymorphen und polylamellare Verwachsung von strukturell verwandten Verbindungen, wie z. B. für In₅S₅Cl/ In₆S₇ gezeigt. Das Auftreten dieser Defekte wird mit einem geeigneten Strukturmodell diskutiert.

Introduction

Starting from the binary mixed valence compounds $In_6Ch_7 = (In^+ 3In^{3+} (In_2)^{4+} 7Ch^{2-}; Ch = S, Se) [1-3]$ we characterized quite recently a series of ternary solids with a close structural relation [4]. The first solids of this series, $TlIn_5S_7$ [5], KIn_5S_7 and $NaIn_5S_7$ [6] were obtained by a simple isomorphic exchange of In^+ in the above mentioned binary compound. Further investigations led us to the MIn_5S_6 (M = Tl, K, [6, 7]) and MIn_7Ch_9 (M = Rb, Cs;

Ch = S, Se, [4]) structure types. As in the case of MIn_5Ch_7 , these structure types can be described by mixed valence formulas: $MIn_5S_6 = M^+ In^{3+} 2(In_2)^{4+} 6S^{2-}$ and $MIn_7S_9 =$ M^+ $3In^{3+} 2(In_2)^{4+} 9S^{2-}$. In all three structure types a similar two dimensional motif of the structure is observed, composed of *cis* and *trans* edge-sharing (InCh₆)-octahedra double chains which are connected by ethane-analogous In₂Ch₆ units, c.f. Figure 1. This common feature results in two nearly equivalent lattice constants, however, the third one is defined by specific additional interlayers which are characteristic for the considered structure type. The intermediate layers are Ch₃In-InCh₄ units (MIn₅S₆), cis and trans edge sharing InCh₆ octahedra (MIn₅Ch₇) and corner sharing InCh₄ chains (MIn₇Ch₉). The connection of the common and characteristic layers leads each structure type to have different sizes of cavities occupied by M⁺ atoms. In the present work our principle objective was to use these different buil-

^{*} Prof. Dr. H.-J. Deiseroth Inst. f. Anorg. Chemie I Universität Siegen D-57068 Siegen Fax: +49-(0)271-7402555 E-mail: deiseroth@chemie.uni-siegen.de

ding blocks as a construction kit for the synthesis of new solids with related structures.



Fig. 1 Projections of the MIn_5Ch_6 (above), MIn_5Ch_7 (middle) and MIn_7Ch_9 (below) stucture types, showing their relationship.

With the title compounds In_5Ch_5X (In⁺ $2In^{3+}$ (In₂)⁴⁺ 5 $Ch^{2-} X^-$; Ch = S, Se; X = Cl, Br) we obtained the second example of mixed valence indium chalcogeno halogenides (first example: $In_3Te_3I = In^{3+} (In_2)^{4+} 3Te^{2-} I^-$, [8]). Although the AXY formulas are equal, they crystallise in two structure types, namely the chloride and the bromide type. In particular, the chloride type can be easily rationalized as a product of the construction kit in which the above mentioned common layers occur. A closer inspection of the bromide type shows that this type can be classified according to this concept too.

Results and Discussion

X-ray investigations

The new compounds are obtained as fine needle-shaped crystals with lengths up to a few millimetres but with small diameters (max. 30μ m). By using an optical microscope, a

significant difference between the bromides and chlorides becomes obvious: crystals of In_5Ch_5Cl [9] splice and intergrow to a great extent whereas crystals of In_5Ch_5Br show more or less regular orthorhombic shapes.

Actually, this macroscopic observation is a result of fundamental differences in the real structures. A summary of all important data for the single crystal measurements and refinements is given in the tables 1-3. In₅S₅Br and In₅Se₅Br crystallize orthorhombically in the space group *Pmn*2₁. The single crystal measurements, solutions and refinements succeed without any anomalies and the refinements show good figures of merit.

The chlorides crystallize monoclinically (space group $P2_1/m$) showing different anomalies in single crystal investigations. All crystals of In_5S_5Cl and In_5S_5Cl are twinned by reticular pseudomerohedry. Even if the superimposed reflections are neglected, the refinements show bad figures of merit and significant residual electron densities. A description of the twinning and further anomalies of the In_5S_5Cl -structure type are discussed below. Taking into account the lattice parameters and the similar AXY formulas, one could assume a topologically uniform structure type with slightly different atomic positions. However, the structures show fundamental differences in the arrangement of atoms and atom groups.

Structures of In₅Ch₅X

Irrespective of the considered structure type, the In_5Ch_5X compounds can be described with the same mixed valence formula $(In^+ 2In^{3+} (In_2)^{4+} 5Ch^{2-} X^-)$.

The three different indium species exhibit characteristic coordinations. Hence, according to the nomenclature proposed by Robin [10], they belong to class I mixed valence compounds. In both structure types the local coordination of the different indium species is similar: octahedral for In^{3+} , ethane analogous In_2S_6 -dumbbells for In^{2+} (eclipsed conformation, covalent In-In-bonds) and tri-capped trigonal prismatic for In⁺. These basic units built up chains along the short axis (a or b, according to the structure type, Fig. 2). The difference between the two structure types is based on the arrangement of these chains (Fig. 2). Apparently, some of the In₂-dumbbells and In⁺ atoms exchange their positions in the chloride and bromide type, respectively, while the position of the cis and trans edge-sharing InCh₆/InCh₄X₂ octahedra double-chains remains unchanged. In the following, these double chains will be labelled double octahedra according to their appearance in the selected projections. A closer inspection of the $(In_2)^{4+}$ coordination sphere surprisingly shows, that the first and second sphere together are in good agreement with the first coordination sphere of In⁺ (Fig. 3). Thus, the observed exchange can be rationalised. Visualising only the trigonal prisms (due to the appearance in the selected projections labelled as triangles) around In^+ and $(In_2)^{4+}$, both structure types look similar: every double octahedra is surrounded by six triangles. In the bromide type three of the six triangles are

Sum formula Formula weight /g mol ⁻¹	In_5S_5Cl M = 769.85	In_5Se_5Cl M = 1004 35	In_5S_5Br M = 814 31	In_5Se_5Br $M = 1048\ 81$
Temperature /K	112 705100	T =	293(2)	101 1010101
Wavelength /pm		ΜοΚα, γ	y = 71.073	
Crystal System	mono	oclinic	orthe	orhombic
Space group	$P2_1/m$	(No. 11)	Pmn2	1 (No. 31)
Cell dimensions /pm /°	a = 892.7(1)	a = 923.058(8)	a = 392.01(3)	a = 409.32(3)
	b = 390.62(5)	b = 408.66(3)	b = 905.62(8)	b = 933.31(7)
	c = 1495.1(2)	c = 1529.4(2)	c = 1481.2(1)	c = 1525.1(2)
<i>(</i>)	$\beta = 93.48(2)$	$\beta = 92.47(1)^{\circ}$		
Volume /10 ⁶ pm ³	V = 520.4(1)	V = 576.36(9)	V = 525.83(8)	V = 582.60(8)
Formula units per unit cell	Z = 2	Z = 2	Z = 2	Z = 2
Density (calc.) /g cm ^{-3}	$\rho = 4.913$	$\rho = 5.787$	$\rho = 5.143$	$\rho = 5.979$
Absorption coefficient /mm ⁻¹	$\mu = 12.102$	$\mu = 25.809$	$\mu = 15.522$	$\mu = 28.733$
F(000)	684	864	720	900
Diffractometer		IPDS (Stoe), oriented g	graphite monochromator	
Scan type			φ	
Measured θ range	$3.45^{\circ} \le \theta \le 31.68^{\circ}$	$3.39^{\circ} \le \theta \le 30.35^{\circ}$	$3.55^{\circ} \le \theta \le 31.65^{\circ}$	$3.45^{\circ} \le \theta \le 30.30^{\circ}$
Index ranges	$-12 \le h \le 13$	$-12 \le h \le 11$	$-5 \le h \le 5$	$-5 \le h \le 5$
	$-5 \le k \le 5$	$-5 \le k \le 5$	$-12 \le k \le 13$	$-13 \le k \le 13$
	$-21 \le l \le 22$	$-21 \le l \le 21$	$-21 \le l \le 21$	$-21 \le l \le 21$
Measured reflections	2056	5209	5062	6605
Independent reflections	1044	1515	1954	1951
	$(R_{\rm int} = 0.0725)$	$(R_{\rm int} = 0.1383)$	$(R_{\rm int} = 0.0288)$	$(R_{\rm int} = 0.0468)$
Completeness to θ	52.5 %	77.1 %	99.4 %	99.2 %
Absorption correction		Numer	rical [15]	
Max, min. transmission	$T_{\rm max} = 0.9199$	$T_{\rm max} = 0.6070$	$T_{\rm max} = 0.8702$	$T_{\rm max} = 0.7153$
	$T_{\min} = 0.3912$	$T_{\min} = 0.3603$	$T_{\min} = 0.5296$	$T_{\min} = 0.1369$
Crystal dimension /mm	0.48 imes 0.03 imes 0.01	0.46 imes 0.03 imes 0.02	0.10 imes 0.02 imes 0.01	0.20 imes 0.03 imes 0.01
Structure solution		Direct me	ethods [16]	
Structure refinement		Full-matrix least	-squares on F^2 [17]	
Data/restraints/parameters	1044 / 0 / 68	1515 / 0 / 68	1954 / 1 / 69	1951 / 1 / 69
Goodness-of-Fit on F^2	1.225	1.101	1.012	1.207
Weighting Scheme ^{a)}	A = 0.0186	A = 0.1266	A = 0.0339	A = 0.0286
	B = 159.6971	B = 43.0696	$\mathbf{B} = 0$	B = 7.4116
R values $[I \ge 2\sigma (I)]$	$R_1 = 0.0840$	$R_1 = 0.0790$	$R_1 = 0.0248$	$R_1 = 0.0323$
	$wR_2 = 0.2288$	$wR_2 = 0.2289$	$wR_2 = 0.0534$	$wR_2 = 0.0790$
R values (all data)	$R_1 = 0.0982$	$R_1 = 0.0860,$	$R_1 = 0.0312,$	$R_1 = 0.0357$
	$wR_2 = 0.2348$	$wR_2 = 0.2346$	$wR_2 = 0.0553$	$wR_2 = 0.0800$
Absolute structure parameter			0.38(2)	0.49(2)
Difference Fourier residuals	$ \rho_{\rm max.} = 3.406 $	$ \rho_{\rm max.} = 3.980 $	$ \rho_{\rm max.} = 2.030 $	$ \rho_{\rm max.} = 2.010 $
$/e \ 10^{-6} \ pm^{-3}$	$ \rho_{\rm min.} = -4.401 $	$ \rho_{\rm min.} = -4.532 $	$ \rho_{\rm min.} = -1.459 $	$ \rho_{\rm min.} = -1.861 $

Table 1	l Summary	of	data	collection	and	refinement	details	for	In ₅ Ch ₅	Х	(Ch	= S,	Se;	X =	Cl,	, Br	:).
---------	-----------	----	------	------------	-----	------------	---------	-----	---------------------------------	---	-----	------	-----	-----	-----	------	-----

^{a)} $w = 1/[\sigma^2(F_0^2) + (AP)^2 + BP)], P = (F_0^2 + 2F_c^2)/3$

centred by In^+ and three by $(In_2)^{4+}$, i. e. 3,3-arrangement, whereas in the chloride type 4,2- and 2,4-arrangements of the triangles occur (4,2: $4 \times In^+$, $2 \times (In_2)^{4+}$; 2,4: $2 \times In^+$, $4 \times (In_2)^{4+}$, Fig. 3). Topologically, both structure types can be described by layers perpendicular to [001] for the orthorhombic and to [1 0 10] for the monoclinic phases. The monoclinic phases are built up of two different layers. Layer type 1 includes double octahedra with 4,2-arrangement, layer type 2 double octahedra with 2,4-arrangement. The orthorhombic phases contain one layer with 3,3-arrangement. This model is helpful for the description of the different kinds of real structures which occur in particular for In_5Ch_5Cl (see below).

The determination of the halogen position is based on the single crystal investigations of In_5Se_5Cl for the chloride type and In_5S_5Br for the bromide type. In both cases the arrangement of the halogen atoms is fully ordered. For In_5S_5Cl and In_5Se_5Br the non-metal atoms cannot be distinguished crystallographically, but we assume a similar ordering based on that of the chloride and the bromide type, respectively. Table 4 gives an overview of the most important interatomic distances in these new solids. An evaluation of the distances $d_{In(3+)-anion}$ demonstrates that the postulated halogen positions exhibit the longest distances in all compounds. Simultaneously, due to the lower local charge compensation and the resulting higher attraction force, the average distances In-S and In-Se for the halogen containing InCh₄X₂ octahedra are significantly shorter in comparison to the In-S and In-Se distances in InCh6-octahedra without halogen atoms (e.g. In_5S_5Br : \bar{d}_{In2-S} = 255.2 pm and $\bar{d}_{In1-S} = 263.2$ pm). The average distances In-Ch in the InCh₆ octahedra (In_5S_5Cl : 262.4 pm; In_5S_5Br : 263.2 pm; In₅Se₅Cl: 276.6 pm; In₅Se₅Br: 275.7 pm) are in good agreement with comparable distances in other solids with octahedrally coordinated In^{3+} e.g. $d_{In-S} = 264$ pm in NaInS₂ [11], $d_{\text{In-Se}} = 275.8 \text{ pm}$ in NaInSe₂ [11]. Significantly shorter are the average distances In-Ch in the ethane analogous In₂Ch₆ units (In₅S₅Cl: $d_{In3-Ch} = 255.4$ pm, d_{In4-Ch} = 252.4 pm; In_5S_5Br : \bar{d}_{In3-Ch} = 253.7 pm, \bar{d}_{In4-Ch} = 253.6 pm; In₅Se₅Cl: $\bar{d}_{In3-Ch} = 265.9$ pm, $\bar{d}_{In4-Ch} = 265.6$ pm; In₅Se₅Br: $\bar{d}_{In3-Ch} = 265.9 \text{ pm}, \ \bar{d}_{In4-Ch} = 266.3 \text{ pm}$). Again these values as well as the covalent In-In-bonds (272.3 -274.8 pm, see table 4) agree with corresponding distances in other solids containing such units, for example In_6S_7 ($d_{In-In} =$

Table 2 Atomic coordinates, Wyckoff notations and equivalent isotropic displacement parameters U_{eq} /10⁴ pm² for In₅S₅Cl and In₅Se₅Cl (second line). U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor; *s.o.f.* = 1.

Atom	Wyck.	x	у	z	U _{eq}		
Inl	2e	0.6575(3)	3/4	0.4455(2)	0.0094(6)		
		0.6599(2)		0.4451(1)	0.0139(4)		
In2	2e	0.1344(4)	3/4	0.0637(2)	0.0134(7)		
		0.1308(2)		0.0633(1)	0.0207(5)		
In3	2e	0.9577(3)	1/4	0.3565(2)	0.0159(7)		
		0.9528(2)		0.3484(1)	0.0171(5)		
In4	2e	0.2360(3)	1/4	0.2914(2)	0.0109(7)		
		0.2312(2)		0.2915(1)	0.0120(4)		
In5	2e	0.6171(5)	1/4	0.1575(3)	0.0330(1)		
		0.6053(3)		0.1456(2)	0.0405(7)		
Cl	2e	0.327(1)	1/4	0.0055(7)	0.014(2)		
		0.3267(7)		0.0027(4)	0.023(1)		
Ch1	2e	0.467(1)	1/4	0.3994(7)	0.008(2)		
		0.4671(2)		0.3967(2)	0.0104(5)		
Ch2	2e	0.834(1)	1/4	0.5024(7)	0.009(2)		
		0.8375(2)		0.5031(2)	0.0124(5)		
Ch3	2e	0.318(1)	3/4	0.2002(7)	0.008(2)		
		0.3201(2)		0.1964(2)	0.0109(5)		
Ch4	2e	0.968(1)	1/4	0.1024(7)	0.010(2)		
		0.9586(3)		0.1040(2)	0.0148(6)		
Ch5	2 <i>e</i>	0.792(1)	3/4	0.2984(7)	0.011(2)		
		0.7892(2)		0.2902(2)	0.0128(5)		

Table 3 Atomic coordinates, Wyckoff notations and equivalent isotropic displacement parameters $U_{\rm eq}$ /10⁴ pm² for In₅S₅Br and In₅Se₅Br (second line). $U_{\rm eq}$ is defined as one-third of the trace of the orthogonalised $U_{\rm ij}$ tensor; *s.o.f.* = 1.

Atom	Wyck.	x	у	z	$U_{ m eq}$
In1	2 <i>a</i>	0	0.88742(6)	0.40220(4)	0.0108(1
			0.8945(1)	0.40439(6)	0.0156(2
In2	2a	1/2	0.60636(6)	0.52635(4)	0.0112(1
			0.6060(1)	0.52381(6)	0.0169(2
In3	2a	1/2	0.18659(6)	0.30168(4)	0.0146(1
			0.1943(1)	0.30369(7)	0.0192(2
In4	2a	1/2	0.47837(6)	0.25592(3)	0.0102(1
			0.4765(1)	0.25430(6)	0.0150(2
In5	2a	1/2	0.8588(1)	0.11160(5)	0.0305(2
			0.8538(2)	0.11299(9)	0.0340(3)
Br	2a	0	0.40268(9)	0.45688(5)	0.0125(2
			0.4073(2)	0.4552(1)	0.0173(3
Ch1	2a	1/2	0.7016(2)	0.3608(1)	0.0078(3
			0.7059(1)	0.35846(8)	0.0111(3
Ch2	2a	1/2	0.4344(2)	0.6621(1)	0.0090(3)
			0.4284(1)	0.65933(8)	0.0114(3)
Ch3	2a	0	0.7715(2)	0.5651(1)	0.0086(3
			0.7750(2)	0.56868(8)	0.0123(3
Ch4	2a	1/2	0.0611(2)	0.4541(1)	0.0087(3)
			0.0711(2)	0.45940(9)	0.0135(3)
Ch5	2a	0	0.0296(2)	0.2501(1)	0.0102(3
			0.0342(2)	0.24865(9)	0.0137(3

274.2 pm, $\bar{d}_{\text{In-S}} = 255.4$ and 255.9 pm) and In_6Se_7 ($d_{\text{In-In}} = 275.9$ pm, $\bar{d}_{\text{In-S}} = 267.4$ and 268.5 pm) [1, 3]. As expected, the longest In-Ch- and In-X-distances with values ranging from approx. 313 up to 400 pm are observed for the In⁺ ions. According to these distances the coordination number of In⁺ would be better described by 8+1, because for all these compounds one of the chalcogen atoms is nearly 400 pm apart from the central atom.



Fig. 2 above: Connection of the InS_8Br , InS_6/InS_4Br_2 and In_2S_6 units in In_5Ch_5Br along *a*. Neglecting the distribution of the halogen atoms, the connection in In_5Ch_5Cl is similar.

below: Projections of the structures of In_5Ch_5Cl (left) and In_5Ch_5Br along b/a, respectively.



Fig. 3 above: Tri-capped trigonal prismatic coordinations of In^+ and $(In_2)^{4+}$ in In_5Ch_5Br . Neclecting the distribution of the halogen atoms, the coordinations are similar for In_5Ch_5Cl .

below: 4,2 and 2,4 arrangement in In_5Ch_5Cl (left) and 3,3 arrangement in In_5Ch_5Br (right) emphasizing the $InCh_4X_2/InCh_6$ octahedra and the trigonal prisms around $In^+/(In_2)^{4+}$, see text.

Taking into account the anomalies in the X-ray experiments (especially for In_5Ch_5Cl) on the one hand and the close relation of the structure types on the other hand, HRTEM investigations were carried out.

Basic HRTEM observations

Detailed HRTEM investigations were performed on representatives of the bromide and chloride structure types, namely In_5S_5Cl and In_5S_5Br . The homogeneity of the samples

Table 4 Selected interatomic distances d/pm for In_5Ch_5X .

		In ₅ S ₅ Cl	In ₅ Se ₅ Cl
In1	- S/Se5	257(1)	279.8(3)
	- S/Se2 (2×)	262.0(7)	274.3(2)
	- S/Se1	263(1)	273.4(3)
	- S/Se1 (2×)	265.3(7)	278.9(2)
In2	- S/Se3	254(1)	262.5(3)
	- S/Se4 (2×)	254.4(7)	267.8(2)
	- S/Se4 (2×)	259(1)	265.4(3)
	- Cl (2×)	277.6(7)	290.7(5)
In3	- S/Se2	250(1)	263.6(3)
	- S/Se5 (2×)	257.1(7)	267.1(2)
In3	- In4	272.3(4)	274.8(2)
In4	- S/Se3 (2×)	251.7(7)	265.8(2)
	- S/Se1	254(1)	265.1(3)
In5	- Cl (2×)	318.7(9)	313.6(6)
	- S/Se5 (2×)	320.6(9)	341.0(3)
	- S/Se4	328(1)	335.0(4)
	- Cl	334(1)	330.3(7)
	- S/Se3 (2×)	339.8(9)	344.7(3)
	- S/Se1	393(1)	409.8(4)
		In ₅ S ₅ Br	In ₅ Se ₅ Br
Inl	- S/Se5	259.5(2)	271.0(2)
	- S/Se4 $(2\times)$	262.8(1)	275.8(1)
	- S/Se3	263.1(2)	274.2(2)
	- S/Se1 $(2\times)$	265.5(1)	278.9(1)
In2	- S/Se3 (2×)	253.2(1)	267.3(1)
	- S/Se2	254.4(2)	264.9(2)
	- S/Se1	260.0(2)	268.9(2)
	- Br (2×)	288.15(7)	295.3(1)
In3	- S/Se4	252.7(2)	263.9(2)
	- S/Se5 (2×)	254.0(1)	267.0(1)
In3	- In4	272.79(8)	273.9(2)
In4	$-$ S/Se2 (2 \times)	253.0(1)	266.0(1)
	- S/Se1	254.9(2)	266.7(2)
In5	- S/Se4 (2×)	313.3(2)	318.9(2)
	- S/Se5 (2×)	323.1(2)	336.2(2)
	- Br	329.5(1)	342.5(2)
	- S/Se2 (2×)	338.4(2)	341.0(2)
	G/G 2	241 0(2)	252 0(2)
	- S/Se3	341.8(2)	332.9(Z)

was examined via a methodical combination of EDX and SAED. In the case of In_5S_5Br samples, only small amounts of byproducts were observed, in particular separated crystals of In_6S_7 . No significant fluctuations of the stoichiometry can be detected within the In_5S_5Br crystals. Samples with the nominal composition In_5S_5Cl are strongly inhomogeneous (byproduct: In_6S_7). Crystals – or at least domains of them – can be assigned by electron diffraction to the monoclinic structure described above. No significant discrepancies between simulated and experimental HRTEM micrographs in several zone axes were observed. In addition to this finding, SAED and EDX indicate a complex domain structure with pronounced discontinuities of the stoichiometry in extended regions of the microcrystals (see below).

In₅S₅Cl and In₅S₅Br show remarkable differences in their real structures. In the case of In₅S₅Br, we observed a perfectly ordered real structure as indicated by SAED patterns of systematic tilting series. All SAED patterns exhibit no diffuse scattering, but sharp Bragg reflections only. The patterns can be indexed assuming the metrics of In₅S₅Br derived from X-ray diffraction. Simulated patterns based on this structure agree convincingly with the experimental SAED patterns. These observations are additionally supported by the comparison of experimental with simulated HRTEM micrographs, where all crystals are built out of layers with 3,3-arrangement.

The real structure of In_5S_5Cl is characterized by a variety of crystal defects. All of them are interconnected with a two-dimensional order of the real structure. In most cases, the ordered units are the above mentioned layers with 3,3-, 4,2- and 2,4-arrangement. The non-periodic and nanoscaled nature of the real crystals suggest the use of the term lamellar nanostructure.

Three different kinds of lamellar real structures were observed by HRTEM:

1) Intergrowth of two different polymorphs of In₅S₅Cl

2) Polysynthetic twinning

3) Lamellar intergrowth of In_5S_5Cl and In_6S_7

SAED and EDX can be applied to provide evidence for these types of lamellar real structures, however, as the thikkness of the lamellas reaches the nanoscale, HRTEM is the preferable method for detection and characterization.

The most suitable zone axes for HRTEM observations are those with the layers aligned perpendicular to the projection plane, for instance [010]mon. The latter zone axis was selected to highlight characteristic HRTEM contrasts which enable us to distinguish the different arrangements. The simulated micrographs of Fig. 4a were calculated for Scherzer defocus. The 3,3-arrangement of In₅S₅Cl is characterized by bright oval contrasts (see outline in Fig. 4a, right). This simulation is based on the In₅S₅Br-type. However, an ordering of S and Cl atoms is not introduced in the simulated micrographs. This is practicable, as the ordering of S- and Cl-atoms is beyond the experimental significance of HRTEM micrographs recorded with Philips CM30ST. This was checked by the indistinguishability of simulated micrographs based on different S, Cl-orderings. In the monoclinic structure S-shaped bright contrasts (see outline in Fig. 4a, left) occur in the simulations corresponding to cavities in layers with 4,2-arrangement (see below). Again, ordering of S and Cl atoms was neglected in the simulated micrographs for the reasons discussed above.

The black and white contrasts of the simulated micrographs of Fig. 4a correlate with the projections of the structures. Taking into account the weak phase object approximation (WPOA), the intensity of an image is proportional to the transparency of the object. Hence, for Scherzer defocus, the direct interpretation of the images is possible, i. e. black dots correspond to columns of atoms and white dots to cavities. This becomes evident when comparing the simulated micrographs with projections of the structures, cf. Fig. 4a. On the other hand, unknown defect structures can be determined from experimental images recorded on thin crystals close to Scherzer defocus. The latter is important for the determination of the lamellar nano structures in In_5S_5CI .

Polymorphs of In₅S₅Cl

The order of the real structure in terms of alternating 4,2and 2,4-arrangement is observed within small domains of



Fig. 4 Structure types of In₅S₅Cl. a) Simulated micrographs for the alternating 4,2- and 2,4-arrangement (left) and the 3,3-arrangement ($\Delta f = -55$ nm, thickness: 2 nm). Characteristic contrasts are highlighted by the outline. b) Separated domains of both polymorphs with inserted simulations ($\Delta f = -50$ nm, thickness: 2 nm).

 In_5S_5Cl only. As a rule, this periodic arrangement is frequently disturbed by thin lamellas with a 3,3-arrangement. In rare cases, the crystals contain more extended domains of one polymorph, as depicted in the HRTEM micrographs of Fig. 4b (right: 3,3-arrangement, left: 4,2- and 2,4-arrangement). The inserted simulations are based on the monoclinic structure derived from X-ray analysis (4,2- and 2,4arrangement) or on the In₅S₅Br-type structure (3,3-arrangement). According to EDX analyses, the 3,3-arrangement does not originate from Br-impurities, i. e. from an intergrowth of In₅S₅Br (3,3-arrangement) and In₅S₅Cl with 4,2and 2,4-arrangement. The existence of 3,3-arrangements in In₅S₅Cl crystals can also be evidenced by SAED patterns recorded on separated or multiple domains. In the latter case, the [010]_{mon} diffraction patterns exhibit characteristic splitting of the reflections which can be reproduced in simulated patterns based on a superposition structure of orthorhombic and monoclinic domains (SPS, see below). The lattice parameters of the orthorhombic polymorph of In₅S₅Cl can be estimated from SAED patterns recorded on separated domains of differently orientated crystals ($a_{\rm ortho} \sim$ 391 pm, $b_{\rm ortho} \sim 893$ pm, $c_{\rm ortho} \sim 1492$ pm). Simulated SAED patterns for several zone axes based on a 3,3-arrangement of In₅S₅Cl and experimental patterns show good agreement.



Fig. 5 Structure at the two possible intergrowths of the polymorphs with simulated HRTEM micrographs. a) Boundary between lamellas with 3,3- and 2,4-arrangement. b) Boundary between lamellas with 3,3- and 4,2-arrangements.

The nanoscaled intergrowth of polymorphs as depicted in Fig. 5 and 6, is the rule for In₅S₅Cl. It can be modeled within suitable triclinic supercells (space group: P1) as the special metrics of the supercells enable to describe orthorhombic and monoclinic structures of In₅S₅Cl in one common unit cell. Following the general principle of separating a SPS into not superimposed structures at an experimentally observed boundary, the strategy for the construction of the lamellar intergrowth is a four step one:

1) The monoclinic structure is transformed to the rectangular metrics of the supercell (lattice parameters a' =390.7 pm, b' = 892.9 pm, c' = 14917.4 pm; $\alpha = \beta = \gamma =$ 90°) by applying the matrices P and Q (the conventions of transformations refer to [12]):

$$(\boldsymbol{a}', \boldsymbol{b}', \boldsymbol{b}') = (\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) \boldsymbol{P}; \text{ with } \boldsymbol{P} = \begin{pmatrix} 0 & \overline{1} & \overline{1} \\ \overline{1} & 0 & 0 \\ 0 & 0 & \overline{10} \end{pmatrix}, \text{ and: } \begin{pmatrix} u' \\ v' \\ w' \end{pmatrix} = \boldsymbol{Q} \begin{pmatrix} u \\ v \\ w \end{pmatrix},$$
with $\boldsymbol{Q} = \begin{pmatrix} 0 & \overline{1} & 0 \\ \overline{1} & 0 & \frac{1}{10} \\ 0 & 0 & \frac{1}{10} \end{pmatrix}$

2) The orthorhombic structure of In_5S_5Cl was transformed to the metrics of the supercell with c' = 10c.

3) Both structures were superimposed to form a hypothetical SPS.



Fig. 6 Polymorphic intergrowth of In_5S_5Cl . a) Bright-field image. b) SAED pattern with diffuse streaks (zone axis: [100]_{ortho}). c) Simulated (left) and experimental (right) HRTEM micrograph for [100]_{ortho}.

4) In the last step, both structures were separated at the domain boundaries. The position of the domain boundary had been derived from HRTEM micrographs.

There are exactly two different types of boundaries (see Fig. 5), i.e. boundaries between layers with 3,3 and 2,4- or boundaries between layers with 3,3- and 4,2-arrangements. The simulated micrographs (Fig. 5a and b, right) were calculated for both cases. The compatibility of the lamellas at the boundaries is perfect, no significant misfit occurs. The experimental evidence for the nanoscaled intergrowth is presented in Fig. 6. The bright field image of Fig. 6a exhibits pronounced stripes originating from the nanoscaled intergrowth. The observed crystal contains a majority of layers with 3,3-arrangement and non-periodic insertions of 2,4- and 4,2-arrangements. The diffraction pattern of this region is characterized by diffuse streaks (cf. Fig. 6b) along [001]^{*}_{ortho}. The HRTEM micrograph presented in Fig. 6c gives clear evidence for the nanoscaled nature of the intergrowth, as the characteristic contrasts of the different arrangements are plainly visible. The simulated micrograph (Fig. 6c, left) is composed of suitable sections of the simulated micrographs of Fig. 5. The convincing agreement of simulated and experimental micrograph emphasize that a mixing of different arrangements is possible without any significant strain.

Polysynthetic twinning

A second type of lamellar intergrowth is connected with a polysynthetic twinning of the monoclinic polymorph of In_5S_5Cl . This twinning is observed in the X-ray experiments too (see above); however, the atomic structure at the twin boundary is unknown. The lamellas are aligned perpendicular to [1 0 10]mon, and their thickness is in the range of 2-500 nm. The polysynthetic twinning was demonstrated by various techniques, cf. Fig. 7. In the zone axis [010]mon, the lamellas are separated as they are displayed edge on. SAED patterns recorded sequentially indicate the systematic orientations of neighboring lamellas, see Fig. 7a, left and right, for the separated domains and Fig. 7c, left for a selected area with contributions of both lamellas. This type of lamellar nanostructure can be visualized using the strong diffraction contrast (see Fig. 7b) in dark-field images. The lamellas with different orientations are displayed as bright or dark stripes in [010]mon orientations. The twinning can be described as twinning by reticular pseudomerohedry as reflections h0l with h = 5n coincide exactly. This feature of the twinning can be demonstrated in simulations. The simulated diffraction pattern in Fig. 7c, right, was calculated from the SPS of two twinned monoclinic lamellas. The SPS was constructed in the triclinic supercell mentioned above, but two mirrored monoclinic structures were chosen as components of the SPS.



Fig. 7 Polysynthetic twinning of monoclinic $In_5S_5Cl.$ a) SAED patterns of neighboring lamellas, zone axis $[010]_{mon}$. b) Dark-field image, zone axis $[010]_{mon}$. c) SAED pattern of two neighbored lamellas (left) with simulated pattern (right).

A thorough derivation of the twin law from diffraction experiments is not trivial. In order to work out all features of the twinning it is important to analyze high resolution micrographs (Fig. 8a, right, Scherzer defocus, [010]_{mon}). The characteristic S-shaped contrasts on both sides of the twin boundary are mirrored, indicating perpendicular orientation of the twin boundary and [1 0 10]mon. Additionally, the position of neighboring twinned lamellas is shifted by $t \sim 0.44a_{\text{mon}}$, as highlighted by the arrows in Fig. 8a, left. This shift was included in a model of the real structure by a corresponding shift of the monoclinic components of the SPS. The separation of this SPS leads to a surprising result. A perfect fit of shifted and mirrored domains requires the insertion of exactly one layer with a 3,3-arrangement between two twinned domains, see Fig. 8a, left. This remarkable feature of the twinned real structure is evidenced by the good agreement between simulated and experimental micrographs with different defocus values, cf. Fig. 8b. The simulated and experimental micrographs of Fig. 8a, center and right (Scherzer defocus), plainly display the characteristic oval contrasts of a 3,3-arrangement at the boundary of the twin domains. Hence, the high compatibility of the different arrangements is not only expressed by the polymorphic intergrowth, but in particular by the connection of incompatible mirrored and shifted monoclinic domains via layers with 3,3-arrangement.



Fig. 8 Real structure at the twin boundary. a) Projection of the real structure (left), simulated ($\Delta f = -60$ nm, thickness: 2 nm) and experimental micrograph. b) Series of images with variable defocus Δf with simulated micrographs.

Intergrowth of different compounds

A high compatibility of different lamellas is the subject of a third type of nanostructures which deals with a systematic intergrowth of different compounds, i. e. lamellas of In₅S₅Cl and In₆S₇. The common features of the In₆S₇ and In₅S₅Cl structures facilitate the formation of lamellar real structures. Both structures contain layers with 2.4-arrangement which could serve for the interconnection of monoclinic In₅S₅Cl and In₆S₇. However, an intergrowth of In₆S₇ with 3,3-arrangements of In₅S₅Cl is also possible. In this case, the 2,4-arrangements of In₆S₇ must be exchanged by the 3,3-arrangements of In₅S₅Cl. The latter was observed in In_5S_5Cl crystals with polymorphic intergrowth (see above). On the other hand, pure In₆S₇ shows features of the real structure which remind one of In_5S_5Cl , in particular a polysynthetic twinning like the one observed for monoclinic In₅S₅Cl.

The experimental evidence for a lamellar intergrowth of In_5S_5Cl and In_6S_7 is presented in Fig. 9. The SAED patterns of Fig. 9a were recorded sequentially on a crystal containing large separated domains of In₆S₇ and orthorhombic In₅S₅Cl (layers with 3,3-arrangement). The [100]_{ortho} pattern in Fig. 9a, left, was recorded in section A (see dark field image Fig. 9b, left). The pattern of section B is characteristic for twinned In₆S₇, as shown by simulated micrographs based on the SPS of twinned In₆S₇. In order to show discontinuous jumps of the composition within one crystal, EDX analysis were performed in the scanning mode of Philips CM30ST. The mapping of Cl-K (Fig. 9b, right) clearly shows the presence of two components, with only one of them containing Cl. The quantification of EDX point analyses in regions A and B verify the formation of In₆S₇ domains within In₅S₅Cl crystals.



Fig. 9 Lamellar intergrowth of In_5S_5Cl and In_6S_7 . a) SAED in regions A and B. Left: In_5S_5Cl [100]_{ortho}, right: In_6S_7 [010]_{mon} (twinned). b) Dark field image (left) and Cl-EDX-mapping (right) of the aligned crystal.

zaac.wiley-vch.de

Experimental Part

Synthesis: Single crystals of In₅Ch₅X were prepared by heating stoichiometric mixtures of the elements In, S or Se together with the required amount of the binary compound InX_3 (X = Cl, Br) in evacuated dry quartz glass ampoules (e.g. $In + Se + InCl_3$ in the ratio 14:15:1). The ampoule content was heated up to 773 K and annealed at this temperature for one week. The resulting fine, needle-shaped, not markedly air-sensitive crystals were reddish brown in the case of In₅S₅X and dark brown to black for In₅Se₅X. In all cases the products are inhomogeneous. The by-products are black needles of In_6Ch_7 (Ch = S, Se) and crystals of In_2S_3 for In_5S_5X samples. Using a special temperature program (heating with 2 K/h up to 773 K, annealing for two weeks, cooling with 5 K/h) bigger crystals were obtained, nevertheless the samples were inhomogeneous. Almost homogeneous products were achieved by annealing pellets of binary compounds InCh, In₂Ch₃ and InX in the ratio 2:1:1. The composition of all compounds was verified by quantitative Energy Dispersive X-ray (EDX) measurements. For In₅S₅Br and In₅Se₅Cl the results agree with the refined compositions of the X-ray experiments. For In₅S₅Cl and In₅Se₅Br, where the anions are indistinguishable in the single crystal X-ray diffraction experiment, the expected composition was confirmed too.

Electron microscopy: Microcrystalline samples with nominal compositions In₅S₅Cl and In₅S₅Br were crushed under n-butanol. Copper grids were covered with the suspension, leaving the crystallites in random orientations after drying. These sample carriers were fixed in a side-entry, double-tilt holder with a maximum tilt of \pm 25° in two directions. HRTEM and SAED were performed in a Philips CM30ST (300 kV, LaB₆ cathode). The SAED patterns were obtained using a diaphragm which limited the diffraction to a circular area of approximately 10⁵ pm in diameter. The EMS program package, see [13], served for the simulation of HRTEM micrographs (spread of defocus: 7000 pm, illumination semiangle: 1.2 mrad) and SAED patterns (kinematical approximation). All images were recorded with a Multiscan CCD Camera (Gatan, Software: Digital Micrograph 3.6.1, Gatan). A small amount of noise resulting from an amorphous surface layer on the crystals can be reduced by filtering Fourier transforms with a suitable band-pass mask. It was checked for all cases whether image processing leads to a loss of essential real structure information. EDX was performed in the scanning- and nanoprobe mode of Philips CM30ST with a Si/ Li-EDX detector (Noran, Vantage System).

Crystallography: X-ray powder diagrams show good agreements to calculated ones assuming the structure models of the single crystal investigations. Especially the patterns of In_5S_5Cl and In_5Se_5Cl give no evidence for additional orthorhombic phases.

Crystals of suitable size for X-ray structure determination were separated from the bulk product under a polarizing microscope. The crystals were fixed at the top of glass capillaries and mounted on a STOE IPDS I diffractometer using graphite-monochromated Mo-K_{α} radiation. Experimental details are summarized in Table 1. The STOE IPDS Program package [14] was used to analyze the measured data. A close examination of the reciprocal space using the program RECIPE [14] shows that all examined chlorine compounds (In₅Ch₅Cl (Ch = S, Se)) have overlapping and interpenetrating lattices. In the case of In₅S₅Cl the above mentioned results were obtained from a systematically twinned crystal with the approximate volume ratio of 1:1. The data for In₅Se₅Cl are based on a crystal which consist of two systematically twinned domains with an approximate volume ratio of 3:1. The programs INDEX [14] and CELL [14] were used to index the lattices and to obtain the orientation matrices for the twin components. Reciprocal planes calculated from imaging plate data (SPACE [14]) show, that the twinning can be described as a twinning by reticular pseudomerohedry, reflections h0l with h = 5n coincide exactly (see above).

Due to the existence of partly overlapping reflections beside completely overlapping and separated ones, a refinement using the SHELX HKLF 5 Format [17] is unfavorable. The Program TWIN [14] allows a simultaneous integration of reflections from all domains by rejecting all completely and partly overlapping ones. Using this strategy, the results of the refinement of both structures (In₅Ch₅Cl (Ch = S, Se)) are satisfactory although the datasets are incomplete.

The observed systematic extinctions are consistent with the space groups $P2_1$ and $P2_1/m$. The latter which is centrosymmetric was chosen. This choice was supported by means of the distribution of the normalized structure factors (E-statistic, N(Z)-test). The large maximum residual electron density and the relatively high *R*-values can be ascribed to the incomplete data sets and to a variety of crystal defects described above (HRTEM investigations).

In case of the bromine compounds $(In_5Ch_5Br (Ch = S, Se))$ a close examination of reciprocal space shows no anomalies in contrast to the chlorine compounds. Again the programs INDEX [14] and CELL [14] were used to index the lattices and to obtain the orientation matrix for In₅S₅Br and In₅Se₅Br, respectively. The following integration had to be applied by the program INTEGRATE [14]. The observed systematic extinctions are consistent with the space groups *Pmmn* and *Pmn2*₁. Whereas the structure solution and the refinement converged well in the latter acentric space group. Attempts to solve the structure in the centrosymmetric space group Pmmn did not lead to satisfactory result. The choice of the noncentrosymmetric space group was also confirmed by means of the distribution of the normalized structure factors (E-statistic, N(Z)test). Both structures of the bromine crystals were refined as an inversion twin with a fractional contribution of 0.38(2) (In₅S₅Br) and 0.49(2) (In₅Se₅Br), respectively.

The trial structures for In_5Ch_5X (Ch = S, Se; X = Cl, Br) were obtained by direct methods (SHELXS97 [16]) and refined using SHELXL97 [17]. A summary of crystal and structure refinement data for In_5Ch_5X (Ch = S, Se; X = Cl, Br) is reported in Tables 1–3.

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-414218 (In_5Se_5Br), -414219 (In_5S_5Br), -414220 (In_5Se_5Cl), -414221 (In_5S_5Cl), the name of the author(s), and citation of the paper.

Conclusion

The initial point of our investigation was the occurrence of similar (cis and trans edge-sharing (InCh₆)-octahedra connected by ethane analogues In_2Ch_6 unites) and different two dimensional building units in the mixed valence compounds MIn_5Ch_6 , MIn_5Ch_7 and MIn_7Ch_9 .

We expected new structure types based on different combinations of these building units in the sense of a construction kit. In fact, the presented compounds fulfill this concept in several ways. On the one hand both new structuretypes can be classified in the framework of this concept. On the other hand, nanoscale defects of the real structure of In_5Ch_5Cl can easily be explained by combinations of elements of the construction kit. Our HRTEM investigations demonstrate the necessity of high resolution methods for a complete determination of such lamellar nanostructures. Standard X-ray diffraction methods are applicative for the characterization of the components of a lamellar structure provided that the single lamellas are sufficiently large and diffuse scattering in diffraction patterns is not significant. However, in the case of crystals originating from the samples In₅S₅Cl the thickness of the lamellas reaches the nano regime and diffuse scattering is a prominent feature of the diffraction patterns. Additionally, the diffraction methods give no information about the exact structures at boundaries between the lamellas, e. g. about the shift at the twin boundaries which is observed in pure In₅S₅Cl. Such discontinuous changes of the local structure can be analyzed by HRTEM and SAED. Hence, essential properties of the real structures like fluctuations of the composition (intergrowth In_5S_5Cl/In_6S_7), as well as the detailed atomic arrangement at boundaries (layers with 3,3 arrangement at twin boundaries in In₅S₅Cl) can unambiguously be determined by transmission electron microscopy.

Acknowledgement. The authors would like to thank Viola Duppel for practical electron microscopy work, *Prof. Dr. Dr. hc. mult. Arndt Simon* for providing the microscope and the "Deutsche Forschungsgesellschaft" for their continuous financial support.

References

- [1] J. H. C. Hogg, W. J. Duffin, Acta Crystallogr. 1973, A23, 111.
- [2] H. J. Deiseroth, H. Pfeifer, A. Stupperich, Z. Kristallogr. 1993, 207, 45.
- [3] J. H. C. Hogg, Acta Crystallogr. 1971, B27, 1630.
- [4] C. Reiner, H. J. Deiseroth, M. Schlosser, L. Kienle, Z. Anorg. Allg. Chem. 2002, 628, 249.
- [5] R. Walther, H. J. Deiseroth, Z. Kristallogr. 1996, 211, 51.
- [6] H. J. Deiseroth, C. Reiner, Z. Anorg. Allg. Chem. 1998, 624, 1839.
- [7] H. J. Deiseroth, R. Walther, Z. Kristallogr. 1995, 210, 88.
- [8] S. Paashaus, R. Kniep, Z. Naturforsch. 1990, 45b, 667.
- [9] L. Kienle, O. Oeckler, Hj. Mattausch, V. Duppel, A. Simon, C. Reiner, M. Schlosser, K. Xhaxhiu, H. J. Deiseroth, *Mater. Sci. Semicond. Process.* 2003, 6, 393.
- [10] M. B. Robin, P. Day, Adv. Inorg. Chem. Radiochem. 1967, 10, 247.
- [11] R. Hoppe, W. Lidecke, F.-C. Frorath, Z. Anorg. Allg. Chem. 1961, 309, 49.
- [12] T. Hahn (ed.), *International Tables for Crystallography*, Volume A, Kluwer Academic Publishers, Dordrecht/Boston/London, 2002, p. 69.
- [13] P. A. Stadelmann, Ultramicroscopy 1987, 21, 131.
- [14] STOE & CIE, IPDS-Software, Version 2.93, Darmstadt, 1999.
- [15] STOE & CIE, X-SHAPE 1.06, Crystal Optimisation for Numerical Absorption Correction, Darmstadt, 1999.
- [16] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, 1997.
- [17] G. M. Sheldrick, SHELXL-97, Program for Structures Refinement, Universität Göttingen, Germany, 1997.