

Phase Relations in the $TlX-Tl_2Se$ Systems ($X = Cl, Br, I$) and the Crystal Structure of Tl_5Se_2I

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Received May 11, 1983; in revised form October 24, 1983

Each of the quasibinary systems $TlCl-Tl_2Se$, $TlBr-Tl_2Se$, and $TlI-Tl_2Se$ contains a region of solid solution up to 18 mole% Tl_2Se , which decomposes peritectically. The mixed crystals can be explained by a statistical substitution of Se by two I atoms on the fourfold sites of the Tl_2Se lattice. Compounds of the type Tl_5Se_2X were derived by complete substitution. Crystals of Tl_5Se_2I , suitable for a crystal structure determination, were grown by the Bridgman technique. Tl_5Se_2I is tetragonal, $I4/mcm$; $a = 866.3$ pm, $c = 1346.3$ pm, $Z = 4$. The structure is an ordered variation of the In_3Bi_3 structure and isopuntal to the Cr_3B_3 type. The structure is formed basically by layers of Tl_2Se , in which strings of TlI are introduced. The compounds Tl_5Se_2Br ($a = 861.1$ pm, $c = 1292.2$ pm) and Tl_5Se_2Cl ($a = 856.5$ pm, $c = 1273.3$ pm) have probably very similar structures. A tendency for immiscibility in the $TlX-Tl_2Se$ systems is shown by the existence of a miscibility gap in the system $TlCl-Tl_2Se$ and by the endothermic enthalpies of mixing in the system $TlBr-Tl_2Se$. In the $TlI-Tl_2Se$ system the compound Tl_6Se_4I system was encountered.

Introduction

In recent publications (1, 2) on the phase diagrams of thallos halide–thallos sulfide systems several compounds of the composition Tl_6X_4Y ($X = Cl, Br, I, Y = S$) were described. Their structure is based on the $TlCl$ structure (CsCl type) in which 1/5 of the Tl and X atoms are replaced by Tl_2S units in a regular manner. The coordination of the anions (X, S) is very similar to the coordination of Cl in $TlCl$ and S in Tl_2S , respectively.

Stasova and Vainshtein (3) have shown that the structure of Tl_2Se is formed by a sequence of Tl and Se layers with channels along the fourfold axis which are partly filled by Tl_2Se groups. In thallos halide–thallos sulfide mixtures the structure of

the intermediate compound Tl_6X_4Y exhibited a tendency to retain the coordination of the pure components. In this work the phase diagrams of thallos halide–thallos selenide were determined because it was expected that the Tl_2Se groups in the channels of the Tl_2Se structure might be exchanged by TlX .

Experimental

Thallos selenide was prepared from the proper amounts of high purity elemental solids (Tl 99.99% Preussag; Se 99.999%, Retorte) by encapsulating them under vacuum in quartz ampoules, melting in a flame, and annealing at 600 K for 1 month. The melting point of the product 654 ± 4 K is identical with that reported in the literature

(4). The phase, crystallizing in a tetragonal lattice, has lattice constants of $a = 856.2(2)$ and $c = 1249.0(5)$ pm; the c -axis considerably lower than the value reported by Stasova and Vainshtein (3) ($a = 854$ and $c = 1270(4)$ pm). The thallos halides $TlCl$, $TlBr$ and TlI (Merck, Optipur) were used after drying at 400 K and 10^{-2} Torr. The purity was checked by difference thermal and by X-ray analysis, Tl_2Se was additionally examined by metallographic methods.

The powders were mixed in the desired proportions in steps of 2 to 5 mole% and the mixtures sealed under vacuum in quartz ampoules. The mixtures were molten, well mixed by shaking, and then annealed for periods of between 1 week and 3 months. The annealing temperatures were chosen from preliminary experiments and were usually about 20–30 K below the solidus temperatures.

The apparatus and the method (5, 6) of the difference thermal analysis have already been described. The accuracy of the liquidus temperatures is ± 5 K, that of the three-phase equilibria lines ± 2 K. X-ray data of powders were measured with a Guinier-4 (radiation $CuK\alpha_1$) or a Huber-Guinier camera (radiation $CrK\alpha_1$) using SiO_2 as internal standard. Single crystal data were collected by a precession camera. Temperature-dependent X-ray data were obtained by means of a Guinier-Simon camera (Enraf Nonius, radiation $CuK\alpha_1$). In the latter experiments a heating rate of 5–10 K/hr was used. Metallographic and quantitative analyses were carried out with a microprobe (Superprobe 733, Jeol). Some enthalpies of mixing were measured in a high-temperature calorimeter (Calvet-type, Sctaram) at 800 K. All samples in the systems were subjected to thermal analysis and X-ray and metallographic studies.

Results

The system $TlCl-Tl_2Se$ is presented in

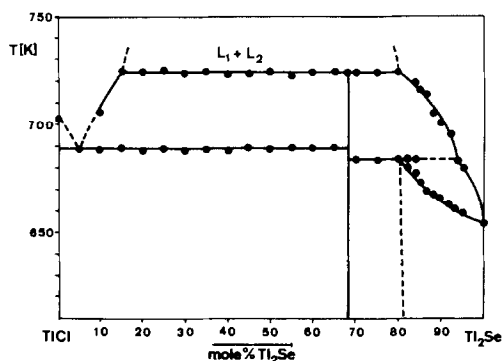


FIG. 1. The phase diagram $TlCl-Tl_2Se$.

Fig. 1. A eutectic temperature of 689 ± 2 K and a eutectic composition of 95 ± 2 mole% $TlCl$ were observed. At the Tl_2Se corner of the system the solid solubility of the $TlCl$ in

TABLE I
X-RAY DATA OF Tl_5Se_2X (ESTIMATED INTENSITIES)^a

Tl_5Se_2Cl		Tl_5Se_2Br		Tl_5Se_2I	
d_{obs}	I_{est}	d_{obs}	I_{est}	d_{obs}	I_{est}
6.37	1	4.43	2	4.53	2
6.06	2	3.69	4	3.72	3
4.39	3	3.59	1	3.06	3
3.67	4	3.23	1	2.95	3
3.55	2	3.05	3	2.93	5
3.28*	2	2.87	5	2.74	5
3.18	2	2.86	1	2.66	3
3.03	3	2.72	5	2.37	2
2.98*	2	2.58	2	2.27	2
2.84	5	2.35	2	2.24	2
2.82	2	2.22	1	2.21	2
2.73	2	2.15	4	2.17	2
2.71	5	2.09	3	2.12	2
2.65*	2	2.03	2	2.04	2
2.56	3	1.88	3	1.94	3
2.43*	2	1.79	3	1.90	2
2.33	2	1.72	2	1.82	3
2.14	3	1.69	2	1.51	3
2.07	3	1.67	3		
2.02	3	1.61	1		
1.87	2	1.59	1		
		1.52	1		
		1.50	3		

^a Reflections indicated with an asterisk were not observed in Tl_2Se .

Tl₂Se occurs up to 18 mole% TlCl. The solid solution decomposes in a peritectic reaction at 684 K. On cooling, the two liquids in the miscibility gap between 20 and 85 mole% TlCl react to produce the compound Tl₅Se₂Cl. This phase crystallizes in a tetragonal lattice with the lattice constants $a = 856.5(1)$ and $c = 1273.3(2)$ pm. The X-ray pattern (Table I) is very similar to that of pure Tl₂Se.

The phase relations of mixtures of TlBr with Tl₂Se are shown in Fig. 2. The eutectic is located at 705 ± 2 K and 90 ± 2 mole% TlBr. The Tl₂Se solid solutions from 0 to 18 mole% decompose in a peritectic reaction at 72 ± 2 K. The phase Tl₅Se₂Br has a melting point of 745 ± 5 K. The structure is tetragonal and isotypic with Tl₅Se₃, with lattice constants of $a = 861.1(1)$ and $c = 1292.2(2)$ pm. The very flat liquidus curve is associated with the tendency for immiscibility in the liquid state which was also detected by calorimetric experiments. Liquid-liquid mixing experiments in a high-temperature calorimeter at 800 K showed that the enthalpies of mixing were endothermic, with a maximum value of approximately 2 kJ mole^{-1} . These results indicate the tendency of liquid immiscibility. However, a miscibility gap could not be verified by metallographic examination. Except for the missing miscibility gap, the

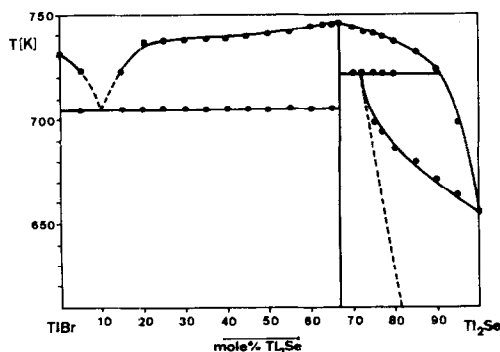


FIG. 2. The phase diagram TlBr-Tl₂Se.

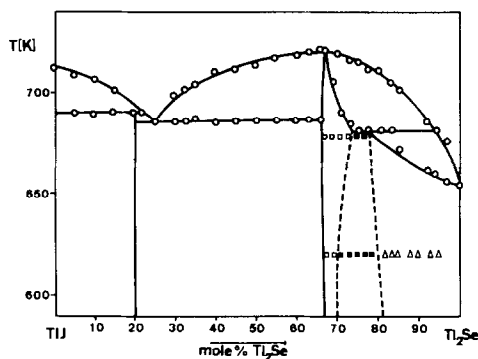


FIG. 3. The phase diagram TlI-Tl₂Se. Δ , Mixed crystals; \blacksquare , two phases; \square , Tl₅Se₂I.

system TlBr-Tl₂Se closely resembles that of TlCl-Tl₂Se.

The system TlI-Tl₂Se, described previously (2), is shown in Fig. 3. This system is again very similar to the two systems already described. In addition, the compound Tl₆SeI₄ appears in this system ($P4/mnc$, $Z = 2$, $a = 917.8(3)$ and $c = 967.5(1)$ pm).

Figure 4 shows the variation of the lattice parameter c for the three Tl₂Se solid solutions. The a -axis is not influenced by the formation of the mixed crystal (substitution of one selenium ion by two halide ions),

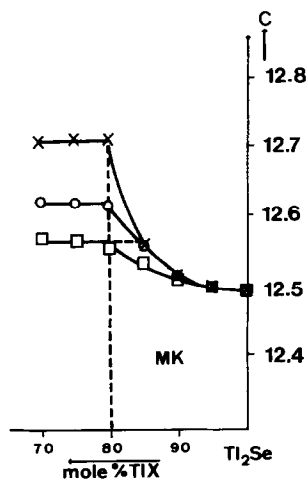


FIG. 4. Concentration dependence of the lattice parameter c in the Tl₂Se-based solutions. x, Tl₂Se + TlI; O, Tl₂Se + TlBr; \square , Tl₂Se + TlCl.

TABLE II
 ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE COEFFICIENTS U_{ij} FOR $\text{Tl}_5\text{Se}_2\text{I}$

Atom		X	Y	Z	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Tl(1)	4c	0	0	0	0.017(2)	0.017(2)	0.020(1)	0	0	0
Tl(2)	16l	0.1437(0)	0.6437(0)	0.3593(1)	0.0232(9)	0.0232(9)	0.0228(7)	0.0007(8)	0.006(1)	0
I	4a	0	0	0.25	0.021(3)	0.021(3)	0.015(2)	0	0	0
Se	8h	0.162(1)	0.662(1)	0	0.012(3)	0.012(3)	0.032(3)	0	0	0

whereas the c -axis increases with increasing halide concentration and increasing size of the halide ion.

Determination of the Structure of $\text{Tl}_5\text{Se}_2\text{I}$

Single crystals of the compound could be obtained in the region of primary crystallization by the Bridgman technique. The crystals with metallic luster crystallize in a tetragonal, body-centered lattice with the space group $I4/mcm$. The cell constants, obtained by least-square calculations from measurements on a Huber-Guinier camera, are $a = 866.3(1)$ pm, $c = 1346.3(1)$ pm, with $Z = 4$.

Intensity measurements for the structure determination were made at a CAD-4 (Enraf-Nonius) automatic diffractometer, using $\text{MoK}\alpha_1$ radiation. Independent reflections (670) were measured to an upper limit of $2\theta = 35^\circ$, 399 reflections with $I \geq 2\sigma_I$ were used for the calculations.

The structure was solved by application

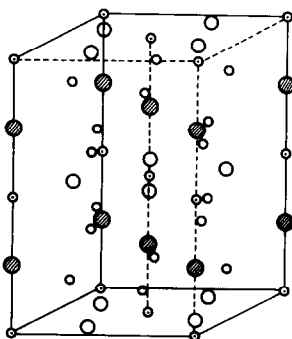


Fig. 5. The unit cell of $\text{Tl}_5\text{Se}_2\text{I}$. ●, I; ○, Tl(1); ○, Tl(2); ○, Se.

of the SDP program-packet (Enraf). The refinement using anisotropic temperature coefficients and an empirical absorption correction converges to $R = 0.087$. Table II contains the atomic parameters together with their standard deviations.

Description of the Structure

The unit cell of $\text{Tl}_5\text{Se}_2\text{I}$ is shown in Fig. 5. The structure can be regarded as formed by the successive stacking of 3^2434 nets of atoms (Fig. 6) and networks containing squares. Most of the Tl atoms—Tl(2)—are arranged in this type of nets. To achieve a better packing, successive layers are translated by half of the base diagonal of the unit cell. In $\text{Tl}_5\text{Se}_2\text{I}$ the sequence of Tl(2) layers is AA' A'A at $z = 0.1407, 0.3593, 0.6407,$ and 0.8593 . The A and A' nets generate a double layer of metal atoms consisting of tetrahedra linked by edges or corners. The structure also contains 3^2434 nets of Se atoms in A' orientation at $z = 0$ and at $z = 0.5$ in A orientation which are slightly displaced relatively to the Tl(2) nets. The squares of these nets are centered by a quadratic net of Tl(1) atoms located over the middle and the corners of the unit cell, while the I atoms form a net of squares at $z = 0.25$ and $z = 0.75$. The stacking sequence is thus $\underline{\underline{A}}_1\underline{\underline{A}}_1\underline{\underline{A}}_1\underline{\underline{A}}_1$ (9),¹ which places the Tl(1) atoms in an octahedral surrounding, with four equatorial Se atoms at 323.3

¹ Nomenclature as used by Pearson: underline, I atoms; double underline, Se atoms; ₁ centering of squares in layer, ₁ centering of antiprismatic holes between layers.

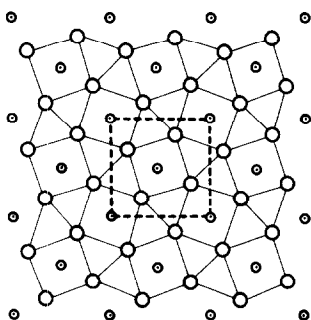


FIG. 6. The $3^2 4/34$ net of Se atoms in Tl_5Se_2I (A' orientation). The A' orientation is achieved by translating the A' net by a half of the base diagonal of the unit cell. The quadratic holes in this net are centered by the atoms of the $4^1 Tl(1)$ net. \circ , Se; \odot , $Tl(1)$.

pm and two axial I atoms at 336.3 pm. The I atoms are filling the cubic antiprismatic holes between successive $Tl(2)$ layers, and have a $2 + 8$ coordination of two $Tl(1)$ at 336.3 pm and 8 $Tl(2)$ atoms at 362.6 pm in this form of antiprism, a coordination which to date has not been reported in chalcogenide halides.

An eightfold coordination is found around the Se atoms. Six $Tl(2)$ neighbors are situated at the corners of a distorted trigonal prism and two outside the square faces of this prism. A Se atom lying above the third square face at a distance of 395 pm, is out of range of bonding interactions. The coordination of the $Tl(2)$ atoms is irregular, with three Se, two I, and one $Tl(2)$ atom as nearest neighbors. The latter atom, with a bond distance of 350 pm, points to a tendency for the formation of Tl pairs in this structure. The irregular shape of the coordination polyhedron—an extremely distorted octahedron—may be due to the nonbonding electron pair of the Tl^+ ion.

The interatomic distances are listed in Table III. The table shows that the $Tl-I$ and $Tl-Se$ distances agree quite well with those observed in the pure components. A consideration of the bond lengths suggests that the $Tl-Se$ and $Tl-I$ bonds are shorter than expected for pure ionic bonds ($Tl-Se$

(ionic) 348 pm, $Tl-I$ (ionic) 370 pm), indicating strong covalent contributions to bonding in this compound. The $Tl-I$ distance of 336 pm and the $Tl-Se$ distance of 303 pm are consistent with largely covalent bonding. The latter short distances are arranged in such a way that Tl_2Se “molecules” can be recognized in the lattice. The shortest $Tl-Tl$ distance found in this structure is comparable to the $Tl-Tl$ distances found in Tl_2S (10) 362 pm, $TlSe$ (11) 350 pm, and $\alpha-Tl$ (12) 345 pm.

Discussion

From the very similar diffraction patterns of Tl_5Se_2I and Tl_2Se we had already concluded (2) that the structure of Tl_5Se_2I is a ternary variant of the Tl_2Se lattice. The space group of the latter phase is, according to Stasova and Vainshtein (3), $P4/ncc$ or $P4/n$, according to Man *et al.* (13), $P4/n$ with $Z = 10$. The cell dimensions reported by both authors differ considerably in the c -axis, namely, $c = 1270$ pm (3) and 1238 pm (13) respectively. The homogeneity range of Tl_2Se is rather broad, so that this deviation may be explained by different composi-

TABLE III
INTERATOMIC DISTANCES IN PICOMETERS
(ESTIMATED ACCURACY BETWEEN 0.1 AND 0.3 pm)

	In Tl_5Se_2I	In Tl_2Se (3)	In $\alpha-Tl$ (7,8)
$Tl(1)-4Se$	323.3	322	
-2I	336.3		336
-8 $Tl(2)$	381.7		
$Tl(2)-1 + 2Se$	325.0,303.3	329	
-2I	362.6		349,383
-2 $Tl(1)$	381.7		
-1 $Tl(2)$	350.7	348	
$I-2Tl(1)$	336.3	280 ^a	336
-8 $Tl(2)$	362.6	328	349,383
$Se-2 + 4Tl(2)$	303.3,325.1	319,334,339	
- $Tl(1)$	323.3		322
-1Se	395.4	385	

^a The corresponding distances of $Tl-Se$ in Tl_2Se .

tions of the samples, especially as Stasova worked with thin-film samples.

In Tl_2Se two Se atoms at $z = 0$ and $z = 1/2$ occupy randomly four-fold sites (3). The remaining vacant sites can be filled by additional Se atoms up to the limit of Tl_5Se_3 , which explains the homogeneity range of this compound.

Tl_5Se_2I is of the same structural type, which can be derived from the Tl_2Se structure by substituting all randomly distributed Se ions by I ions. In order to preserve electroneutrality each Se ion must be replaced by two I ions. The composition is thus altered from $Tl_{20}Se_8Se_2$ (Tl_2Se with $Z = 10$) to $Tl_{20}Se_8I_4$ (Tl_5Se_2I with $Z = 4$). The filling of the positions between the $Tl(2)$ layers increases the symmetry; the space group changes from $P4/n$ (Tl_2Se) to $I4/mcm$. The new unit cell in which the lattice is represented as a body-centered tetragonal lattice, is generated from the unit cell of Tl_2Se by translation of the origin by $y = 1/2$ and $z = 1/4$ (Fig. 7).

The structure of the phases Tl_5Se_2Cl and Tl_5Se_2Br is similarly based on the Tl_2Se lattice. Due to the near-equality in size of the Cl^- and Br^- as compared to Se^{2-} ions, the Tl_2Se structure is retained; these halide

ions fit also into the cubic antiprismatic holes between the layers of the selenide structure. The compound Tl_5Se_2Cl was detected by the additional reflections in the diffraction pattern of Tl_2Se (Table I), which could not be indexed with the extinction conditions for the space group $P4/ncc$ (Tl_2Se). We assume that Tl_5Se_2Cl crystallizes in space group $P4/n$ similar to that of Tl_5Se_3 . The reflections could not be observed for the compound Tl_5Se_2Br , due to the nearly identical atomic scattering factors of Se and Br. The existence of this phase was deduced from the occurrence of a peritectic line in the phase diagram.

The Tl_5X_2Y structure is isopuntal with the Cr_5B_3 type. This structure type was frequently observed in the transition metal chemistry (14) among borides and silicides with radius ratios in the range 1.0–1.5, permitting good packing of the atoms.

In contrast to the transition metal compounds of the Cr_5B_3 type (A_5B_3) (14), in which the B atoms have a smaller size than the A atoms, the B atoms in the chalcogenides and chalcogide halides are larger. A plot (Fig. 8) of the axes ratios c/a vs the size ratios shows that for the Cr_5B_3 branch, r_A/r_B varies between 1.0 and 1.5, while for the Tl_5Se_3 branch, the range lies between 0.68 and 0.86. At the same time the c/a ratio decreases by approximately 25% for the latter compounds.

The close-packed layers at $z = 0$ and $z = 1/2$ contain small B and large Cr atoms as part of the Cr_5B_3 structure. These layers are strongly dilated if the B atoms (80 pm) are replaced by Se^{2-} ions (220 pm) and Cr (119 pm) by Tl^+ (140 pm). For geometric reasons the dilation in a is relatively larger than that of the c -axis. For the latter axis, this geometrical effect is partially compensated by the strong bonding between the unlike atoms on the fourfold sites (e.g., the $Tl-I$ in Tl_5Se_2I or the $Tl-Se$ bonds in Tl_5Se_3). This is indicated by the very short bonding distances in this direction. These

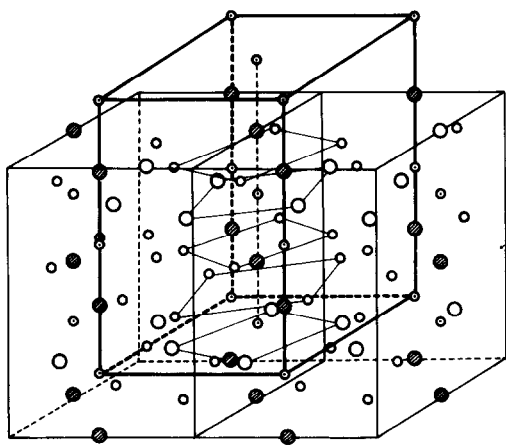


FIG. 7. Relation between unit cells of Tl_2Se and Tl_5Se_2I . —, Tl_2Se cells. —, Tl_5Se_2I cell.

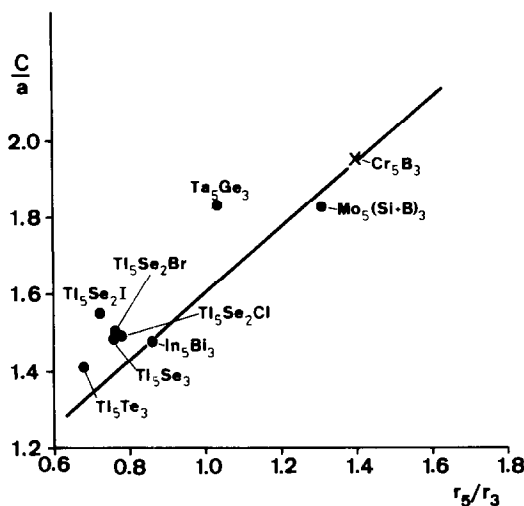


FIG. 8. Axial ratio c/a vs atomic-size ratio r_A/r_B for phases with the Tl_5Se_3 -type structure and some Cr_5B_3 -type structures.

are responsible for a relative contraction of c and therefore, for a reduced axial ratio c/a of these compounds. On comparison with the Cr_5B_3 type, this leads to a change of coordination of the atoms. In particular the fourfold position (occupied by Se_1 in Tl_5Se_3 respectively, by halide ions, in the Tl_5Se_2X compounds) changes from a $8 + 2$ to a $2 + 8$ coordination. This means that the compounds of the main group elements Tl_5Se_3 , Tl_5Te_3 (15), and In_5Bi_3 (16) rather than being isotypic with the Cr_5B_3 type (as has been claimed), and the new Tl_5X_2Y series are actually isopuntal and form an individual branch of the 3^2434 structure type.

The strong relation between this family and the Cr_5B_3 type is in addition, shown by the existence of the Tl_5Se_2X type. The latter is the ordered ternary form of the Tl_5Se_3 type, comparable to Mo_5SiB_2 (17), which is a representative of the ordered form of the Cr_5B_3 type.

The topology of the phase diagrams in the Tl_2Se corner of the systems can be ascribed to the structure of Tl_2Se . The substitution of Se at the fourfold sites in Tl_2Se by two halide ions occurs up to the composi-

tion $Tl_{20}Se_9X_2$ (18 mole% TLX, the observed phase border of the solution in all systems) with a statistical distribution of the additional X^- ions. The formation of this solid solution is entropically controlled. Additional introduction of X^- ions leads to regions with ordered distribution of the X^- ions and thus to the segregation of the phase Tl_5Se_2X , it exhibits no appreciable homogeneity range.

The liquid immiscibility, as observed in the Tl_2Se - $TlCl$ system and as indicated by the endothermic enthalpies of mixing in Tl_2Se - $TlBr$, can also be recognized as occurring in the lattices of the chalcogenide halides. In Tl_6X_4Y ($X = Cl, Br, I; Y = S, Se$) strings of Tl_2Y are introduced in the TLX lattice; in Tl_5Y_2X thallos halide strings are introduced in the Tl_2Y lattice. The short distances between unlike atoms in the compound Tl_5Se_2I indicate the existence of mainly covalent TII strings parallel to the fourfold axis, which are surrounded by Tl_2Se "molecules."

Acknowledgments

We express our gratitude to the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and to the Fonds der Chemie for supporting this work.

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