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The germanium chalcogenolates (PhSe)<sub>4</sub>Ge and (PhTe)<sub>4</sub>Ge were synthesized from activated hydrogenated germanium (Ge\*) and diphenyldiselenide or diphenylditelluride, respectively. (PhTe)<sub>4</sub>Ge is the first homoleptic organotellurolate of germanium. It was characterized spectroscopically and by X-ray crystal structure analysis. (PhTe)<sub>4</sub>Ge crystallizes in the

monoclinic space group  $P2_1/c$  with  $a = 12.8018(14)$ ,  $b = 9.1842(9)$ ,  $c = 23.690(3)$  Å and  $\beta = 105.458(8)^\circ$ . The molecules show a tetrahedral  $\text{GeTe}_4$  core. Weak Te-Te interactions connect neighbouring tetrahedra to infinite helices along [010]. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

## Introduction

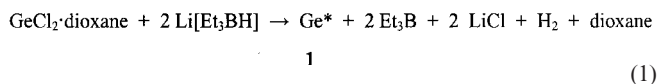
In the last two decades, organochalcogenolates of group 14 elements have gained increasing importance as molecular precursors for IV/VI semiconductors.<sup>[1–3]</sup> In the case of the homoleptic series (RCh)<sub>4</sub>E with Ch = Se, S and E = Ge, Sn only rather elaborate and low-to-medium yield synthetic routes are known in the literature.<sup>[4–6]</sup> Analogous tellurolates (RTe)<sub>4</sub>E with E = Ge or Sn have not been described so far.

Hence, a direct synthesis of this class of compounds from  $R_2CH_2$  ( $R$  = alkyl, aryl;  $Ch$  = Se, Te) and the group 14 element is highly desirable, especially in the case of the tellurium compounds.

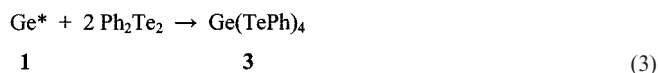
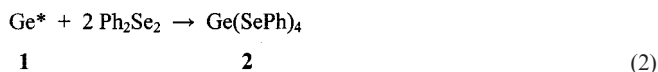
## Results and Discussion

Commercially available elemental germanium or tin powder does not react with diorganodichalcogenides at temperatures below the decomposition temperature of these organoelement compounds. Thus, a chemical activation of germanium is necessary in order to make such a direct reaction feasible.

We used solvochemically produced hydrogenated germanium, which is highly reactive and a good reductand and can be obtained from  $\text{GeCl}_2 \cdot \text{dioxane}$  and  $\text{Li}[\text{Et}_3\text{BH}]$  in THF according to Equation (1).<sup>[7]</sup>



The activated germanium thus obtained indeed inserted into the Se–Se bond and Te–Te bond of Ph<sub>2</sub>Se<sub>2</sub> and Ph<sub>2</sub>Te<sub>2</sub> at surprisingly low temperatures to give homoleptic (PhSe)<sub>4</sub>Ge (**2**) at 65 °C and (PhTe)<sub>4</sub>Ge (**3**) at room temperature [Equation (2) and (3)].



The same type of direct reaction with  $\text{Ph}_2\text{Se}_2$  has also been observed for activated nanocrystalline tin and also yielded the homoleptic product  $(\text{PhSe})_4\text{Sn}$ .<sup>[8]</sup>

In the reaction of Ge\* (**1**) with diphenyldiselenide at 65 °C in THF solvent, the selenolate **2** is obtained in 92% yield. This yield is significantly higher than the 60–65% yield that could be obtained in reactions of LiSePh with GeCl<sub>4</sub>.<sup>[4,5]</sup> In addition, our direct synthesis from activated germanium and Ph<sub>2</sub>Se<sub>2</sub> does not produce any by-products in significant amounts and therefore no separation procedure is required.<sup>[5]</sup>

The reaction of **1** with  $\text{Ph}_2\text{Te}_2$  is less straightforward, but tellurolate **3** was obtained in 26% yield as a deep red solid. Although all suspended  $\text{Ge}^*$  was consumed after two hours of stirring at room temperature and a clear red solution had formed, we were not able to isolate pure **3** from that solution. Instead, a mixture of  $\text{Ph}_2\text{Te}_2$ , amorphous brownish

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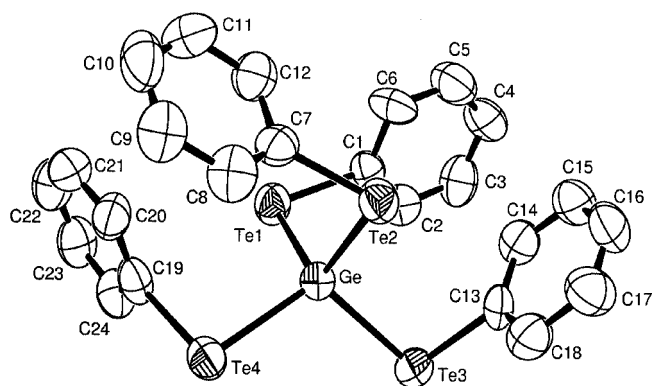


Figure 1. Molecular structure of (PhTe)<sub>4</sub>Ge (**3**) (ORTEP representation<sup>[19]</sup>); thermal ellipsoids are represented at a 50% probability level

germanium and product **3** was obtained after removal of the tetrahydrofuran. This mixture was re-dissolved in diethyl ether and the amorphous germanium was separated by filtration. The filtrate was evaporated to dryness and Ph<sub>2</sub>Te<sub>2</sub> and **3** were separated by an extraction with ice-cold

Table 1. Experimental parameters for the X-ray diffraction measurement and details concerning the structure determination for GeTe<sub>4</sub>C<sub>24</sub>H<sub>20</sub> (**3**)

|                                                       |                                        |
|-------------------------------------------------------|----------------------------------------|
| Crystal system                                        | monoclinic                             |
| Space group                                           | <i>P</i> 2 <sub>1</sub> / <i>c</i>     |
| <i>a</i> [Å]                                          | 12.8018(14)                            |
| <i>b</i> [Å]                                          | 9.1842(9)                              |
| <i>c</i> [Å]                                          | 23.690(3)                              |
| β [°]                                                 | 105.458(8)                             |
| <i>V</i> [Å <sup>3</sup> ]                            | 2684.6(5)                              |
| Calculated density [g/cm <sup>3</sup> ]               | 2.22                                   |
| Crystal shape                                         | Prismatic                              |
| Crystal colour                                        | Dark red                               |
| Crystal size [mm]                                     | 0.02 × 0.04 × 0.03                     |
| Diffractometer                                        | Stoe IPDS II                           |
| 1st run; 2nd run                                      | φ = 0; ω = 0–180;<br>φ = 90; ω = 0–180 |
| Δω [°]                                                | 1                                      |
| Exposure time [min]                                   | 10                                     |
| Detector distance [mm]                                | 100                                    |
| Wavelength [Å]                                        | 0.71073                                |
| 2θ-range for data collection [°]                      | 2.3–59.5                               |
| <i>hkl</i> <sub>min</sub> , <i>hkl</i> <sub>max</sub> | –17, –17, –19;<br>–17, 17, 19          |
| Absorption coefficient [mm <sup>–1</sup> ]            | 5.41                                   |
| Absorption correction                                 | Gaussian                               |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>     | 0.2766, 0.8018                         |
| Total number of reflections                           | 22297                                  |
| Unique reflections                                    | 5949 (3149 > 3σ)                       |
| Structure solution                                    | Sir97 <sup>[17]</sup>                  |
| Structure refinement                                  | Jana2000 <sup>[18]</sup>               |
| Parameters refined                                    | 325                                    |
| <i>R</i> (obs) (> 3σ)                                 | 0.0418                                 |
| <i>R</i> <sub>w</sub> (obs) (> 3σ)                    | 0.0273                                 |
| <i>R</i> (all)                                        | 0.0764                                 |
| <i>R</i> <sub>w</sub> (all)                           | 0.0276                                 |
| Twin matrix                                           | (–1 0 0   0 1 0  <br>–2/7 0 1)         |
| Volume fraction individual I                          | 0.867(1)                               |
| Volume fraction individual II                         | 0.133(1)                               |
| Extinction coefficient                                | 0.408(9)                               |

Table 2. Atomic coordinates and isotropic displacement parameters of **3**

| Atom | <i>x</i>    | <i>y</i>    | <i>z</i>   | <i>U</i> <sub>iso</sub> |
|------|-------------|-------------|------------|-------------------------|
| Ge   | 0.14730(8)  | 0.01670(9)  | 0.82455(4) | 0.0504(4)               |
| Te1  | 0.25306(6)  | 0.23134(6)  | 0.88289(3) | 0.0634(3)               |
| Te2  | 0.27185(5)  | –0.18240(6) | 0.80162(3) | 0.0620(3)               |
| Te3  | 0.02920(5)  | 0.09922(7)  | 0.72343(3) | 0.0615(2)               |
| Te4  | 0.02559(5)  | –0.07486(7) | 0.88825(3) | 0.0637(3)               |
| C1   | 0.3212(7)   | 0.2951(8)   | 0.8146(4)  | 0.052(3)                |
| C2   | 0.2708(9)   | 0.3988(9)   | 0.7752(4)  | 0.067(4)                |
| C3   | 0.3187(11)  | 0.4432(10)  | 0.7315(5)  | 0.082(5)                |
| C4   | 0.4195(10)  | 0.3873(12)  | 0.7285(5)  | 0.077(5)                |
| C5   | 0.4664(9)   | 0.2864(13)  | 0.7683(6)  | 0.087(5)                |
| C6   | 0.4212(8)   | 0.2351(10)  | 0.8123(5)  | 0.074(5)                |
| C7   | 0.3340(7)   | –0.2477(10) | 0.8899(4)  | 0.059(4)                |
| C8   | 0.2895(9)   | –0.3591(9)  | 0.9127(5)  | 0.072(5)                |
| C9   | 0.3345(12)  | –0.4047(12) | 0.9700(5)  | 0.081(6)                |
| C10  | 0.4256(13)  | –0.3392(15) | 0.0040(6)  | 0.094(6)                |
| C11  | 0.4716(10)  | –0.2248(17) | 0.9815(6)  | 0.109(7)                |
| C12  | 0.4270(9)   | –0.1779(11) | 0.9254(5)  | 0.074(5)                |
| C13  | 0.1342(8)   | 0.0011(10)  | 0.6777(3)  | 0.059(4)                |
| C14  | 0.2310(8)   | 0.0652(10)  | 0.6766(4)  | 0.064(4)                |
| C15  | 0.2967(9)   | –0.0048(11) | 0.6480(4)  | 0.071(5)                |
| C16  | –0.2656(11) | 0.3603(14)  | 0.8777(5)  | 0.087(6)                |
| C17  | –0.1748(10) | 0.2952(11)  | 0.8765(5)  | 0.082(5)                |
| C18  | –0.1022(9)  | 0.3620(11)  | 0.8472(5)  | 0.081(5)                |
| C19  | 0.1225(8)   | 0.0246(9)   | 0.9661(4)  | 0.063(4)                |
| C20  | 0.2144(9)   | –0.0489(11) | 0.9993(4)  | 0.070(4)                |
| C21  | 0.2761(9)   | 0.0221(13)  | 0.0480(5)  | 0.078(5)                |
| C22  | 0.2526(11)  | 0.1571(12)  | 0.0647(5)  | 0.081(5)                |
| C23  | 0.1664(11)  | 0.2256(11)  | 0.0317(5)  | 0.076(5)                |
| C24  | 0.0954(9)   | 0.1649(10)  | 0.9826(4)  | 0.070(5)                |

diethyl ether in which only Ph<sub>2</sub>Te<sub>2</sub> is soluble. The deep-red product that remained was pure **3** and was recrystallized at room temperature by slow evaporation of a concentrated solution in diethyl ether.

The X-ray crystal structure of germanium telluroate **3** is depicted in Figure 1. Details of the crystal structure determination are given in Table 1, and atomic coordinates can be found in Table 2.

The structure of the molecule is similar to that of (PhSe)<sub>4</sub>Ge and (PhSe)<sub>4</sub>Sn, of which an orthorhombic and a monoclinic polymorph are known.<sup>[5]</sup> The germanium centre is surrounded by an almost regular tetrahedron of tellurium atoms. The Ge–Te bond lengths span from 257.5 pm to 258.2 pm (Table 3) and are similar to the distances

Table 3. Selected bond lengths [pm] and bond angles [°] of **3**

|            |            |            |           |
|------------|------------|------------|-----------|
| Ge–Te1     | 257.51(10) | Te1–C1     | 211.6(10) |
| Ge–Te2     | 257.75(11) | Te2–C7     | 211.7(8)  |
| Ge–Te3     | 258.24(10) | Te3–C13    | 213.8(10) |
| Ge–Te4     | 258.17(13) | Te4–C19    | 213.4 (9) |
| Te3–Te4'   | 393.23(8)  |            |           |
| Te1–Ge–Te2 | 112.95(4)  | Ge–Te1–C1  | 93.8(2)   |
| Te1–Ge–Te3 | 111.54(3)  | Ge–Te2–C7  | 94.8(3)   |
| Te1–Ge–Te4 | 104.39(4)  | Ge–Te3–C13 | 93.1(2)   |
| Te2–Ge–Te3 | 104.76(4)  | Ge–Te4–C19 | 93.7(3)   |
| Te2–Ge–Te4 | 113.32(4)  |            |           |
| Te3–Ge–Te4 | 110.03(4)  |            |           |

found in the literature for other GeTe<sub>4</sub> tetrahedra (e.g. K<sub>2</sub>GeTe<sub>4</sub>: 250.8–264.0 pm;<sup>[9]</sup> Ag<sub>8</sub>GeTe<sub>6</sub>: 254.4 pm;<sup>[10]</sup> Cs<sub>4</sub>GeTe: 253.7–262.3 pm<sup>[11]</sup>).

The angles around the four symmetrically independent tellurium atoms range from 93.1° to 94.8° and are generally more oblique than in the related selenium compounds [(PhSe)<sub>4</sub>Ge (**2**): 96.2–96.7°; orthorhombic (PhSe)<sub>4</sub>Sn: 95.9–96.4°]. Only in monoclinic (PhSe)<sub>4</sub>Sn are similar angles (93.5–95.6°) observed.

The main difference between (PhTe)<sub>4</sub>Ge (**3**) and the other related compounds becomes evident when looking at the spatial arrangement of the molecules. In the orthorhombic compounds the molecules are arranged in such a way that the tetrahedral cores are relatively isolated from each other and, consequently, the intertetrahedral Se–Se distances are significantly longer than the intratetrahedral distances [(PhSe)<sub>4</sub>Ge: intratetrahedral distances: 374.7–397.4; shortest intertetrahedral distance: 468.5 pm; orthorhombic (PhSe)<sub>4</sub>Sn: intratetrahedral distances: 403.2–424.6 pm; shortest intertetrahedral distance: 434.9 pm]. In the monoclinic polymorph of (PhSe)<sub>4</sub>Sn some of the intertetrahedral distances (the shortest is 382.3 pm) are shorter than the intratetrahedral distances (404.1–414.4 pm), yet still too long to assume Se–Se interactions. In (PhTe)<sub>4</sub>Ge (**3**) the shortest intertetrahedral Te–Te distance is 393.2 pm, which is significantly shorter than all intratetrahedral distances (407.44–431.0 pm). Furthermore, this distance is well below the sum of the van der Waals radii (440 pm)<sup>[12]</sup> and in this case it is indeed reasonable to assume weak, attractive Te–Te interactions. These interactions connect Te atoms of neighbouring tetrahedra and lead to the formation of helical chains consisting of germanium and tellurium atoms along the crystallographic *b* direction (see Figure 2 and 3). The type of helix that is formed by the tellurium and germanium atoms in the backbone of the chain resembles the anionic chain of tetrahedra in K<sub>2</sub>GeTe<sub>4</sub><sup>[9]</sup> and the chain of tellurium atoms found in the tellurium subchloride Te<sub>3</sub>Cl<sub>2</sub>,<sup>[13]</sup> except for the differences in the bond angles. The observed Te–Te distance in **3** is similar to that observed in other compounds, for example in Te[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (377 pm),<sup>[14]</sup> with van der Waals interactions between the tellurium atoms. These distances are longer than the interchain distance in elemental tellurium (350 pm),<sup>[15]</sup> but they are again similar to the Te–Te distances at the van der Waals gap of extended layered tellurides such as Ta<sub>2</sub>Te<sub>3</sub>,<sup>[16]</sup> where a value of 373 pm was found.

## Conclusion

Activated hydrogenated germanium **1** allows the direct one-step synthesis of (PhSe)<sub>4</sub>Ge (**2**) and (PhTe)<sub>4</sub>Ge (**3**) from Ph<sub>2</sub>Se<sub>2</sub> or Ph<sub>2</sub>Te<sub>2</sub> and **1** in an oxidative addition leading directly to the tetravalent germanium species. The homoleptic tellurolate **3** shows short intertetrahedral Te–Te contacts that lead to the formation of helical chains consisting of germanium and tellurium atoms in this compound. The easy accessibility of (PhSe)<sub>4</sub>Ge (**2**) and (PhTe)<sub>4</sub>Ge (**3**) makes

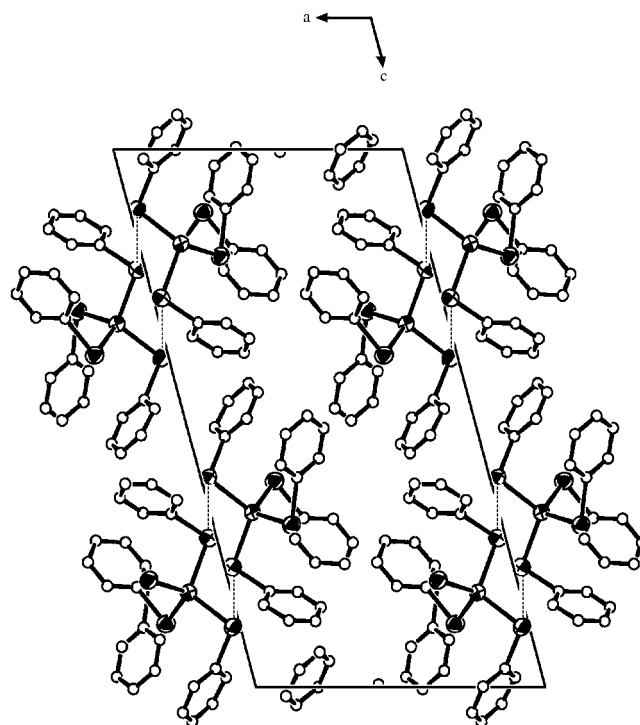


Figure 2. Projection of the crystal structure of **3** along [010]; Te–Te interactions are indicated as dashed lines (ORTEP representation<sup>[19]</sup>); thermal ellipsoids are represented at a 50% probability level

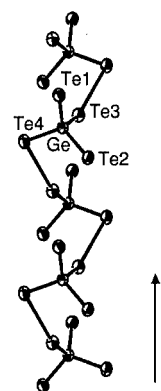


Figure 3. Helical chain of interconnected tetrahedra of GeTe<sub>4</sub> units (ORTEP representation<sup>[19]</sup>); thermal ellipsoids are represented at a 50% probability level

these compounds ideal candidates for molecular precursors leading to IV/VI semiconductors. Investigations on the low-temperature synthesis of germanium(II) chalcogenides from (PhSe)<sub>4</sub>Ge and (PhTe)<sub>4</sub>Ge are currently under way.

## Experimental Section

All manipulations were carried out under dry, oxygen-free argon, except where stated otherwise. Li[Et<sub>3</sub>BH] (1 M in THF), diphenylditelluride, diphenyldiselenide and tetrahydrofuran were purchased from Aldrich. GeCl<sub>2</sub>·dioxane was purchased from ABCR. THF

was dried over  $\text{CaH}_2$  under argon atmosphere and freshly distilled prior to use. The reactions were carried out in standard Schlenk glassware. Activated hydrogenated germanium (**1**) was prepared as described in the literature.<sup>[7]</sup>

**(PhSe)<sub>4</sub>Ge (2):**  $\text{GeCl}_2$ -dioxane (232 mg, 1.0 mmol) was reduced to  $\text{Ge}^*$  (**1**) by 2.0 mL of a 1.0 M solution of  $\text{Li}[\text{Et}_3\text{BH}]$  in THF as described previously.<sup>[7]</sup> The resulting **1** was suspended in 60 mL of THF and  $\text{Ph}_2\text{Se}_2$  (624 mg, 2.0 mmol) was added. The reaction mixture was heated to gentle reflux for 4 h and a clear yellow solution was obtained. This was allowed to cool to room temperature and then the THF was removed under vacuum. The yellow solid obtained was washed with 10 mL of hexane and dried again. The product was identified as  $(\text{PhSe})_4\text{Ge}$  (**2**)<sup>[5]</sup> by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectroscopy, elemental analysis and powder diffraction data. Yield: 641 mg (92%).

**(PhTe)<sub>4</sub>Ge (3):**  $\text{GeCl}_2$ -dioxane (232 mg, 1.0 mmol) was reduced with 2.0 mL of a 1 M solution of  $\text{Li}[\text{Et}_3\text{BH}]$  in THF as described above. The resulting **1** was suspended in 60 mL of THF and  $\text{Ph}_2\text{Te}_2$  (818 mg, 2.0 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and a clear red solution formed. The THF was quickly evaporated under vacuum and an orange-red powder remained. Diethyl ether (40 mL) was added and the solution was filtered. The filtrate was evaporated to dryness under vacuum and the remaining mixture of  $\text{Ph}_2\text{Te}_2$  and **3** was extracted with  $3 \times 5$  mL of ice-cold diethyl ether. A dark red solid remained. Yield: 232 mg (26%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  = 7.19 (t, 8 H), 7.38 (t, 4 H), 7.61 (t, 8 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  = 129.1, 130.0, 141.5 ppm. IR (nujol mull):  $\tilde{\nu}$  1573  $\text{cm}^{-1}$  (w), 1153 (w), 1014 (w), 996 (w), 688 (m), 450 (m,  $\nu\text{Te-C}$ ), 252 (m,  $\nu\text{Ge-Te}$ ), 238 (m,  $\nu\text{Ge-Te}$ ), 178 (w). MS (EI, 70 eV):  $m/z$  (%) = 766 (2)  $[(\text{PhTe})_2\text{Ge}(\text{Te})(\text{TeC}_2\text{H}_3)]^+$ , 561 (10)  $[(\text{PhTe})\text{Ge}(\text{Te})(\text{TeC}_2\text{H}_3)]^+$ , 410 (20)  $[\text{Ph}_2\text{Te}_2]^+$ , 305 (50)  $[(\text{PhTe})\text{Ge}(\text{C}_2\text{H}_3)]^+$ , 206 (30)  $[\text{PhTeH}]^+$ , 154 (42)  $[\text{TeC}_2\text{H}_3]^+$ , 77 (100)  $[\text{Ph}]^+$ .  $\text{C}_{24}\text{H}_{20}\text{GeTe}_4$  (891.01): calcd. C 32.32, H 2.24; found C 32.03, H 2.51.

**X-ray Crystallographic Study:** The overall distribution of intensities in the diffraction pattern of  $\text{Ge}(\text{TePh})_4$  (**3**) can be explained assuming a monoclinic lattice with  $a = 12.8018(14)$ ,  $b = 9.1842(9)$ ,  $c = 23.690(3)$  Å and  $\beta = 105.458(8)$  and an additional twinning operation (Figure 4). Two twin individuals of different volume fractions have to be taken into account. The twinning can be classified as

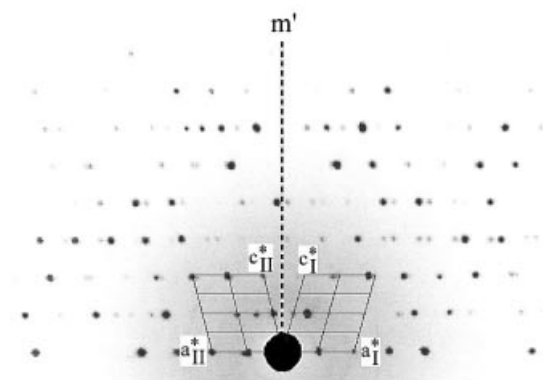


Figure 4.  $h0l$  plane of the reciprocal space of  $(\text{PhTe})_4\text{Ge}$ ; unit cells of the two different twin individuals and the twinning operation are indicated

twinning by reticular merohedry. The two individual lattices have the  $hk0$  plane in common and generally all reflections  $l = 7n$  overlap completely, while reflections  $l \neq 7n$  correspond to reflections of a single individual. This implies that it is inevitable to consider the twinning operation in the refinement process. If the two twin individuals were of equal volume, orthorhombic Laue symmetry  $2/m2/m2/m$  would be simulated for the overall diffraction pattern. The reduction of the symmetry of one individual to Laue class  $2/m$  leaves the remaining four symmetry operations  $2'/m' - 2'/m'$  as possible choices for the twinning operation. We chose the mirror plane perpendicular to  $a^*$  as twin law corresponding to the matrix  $(-1\ 0\ 0\ | 0\ 1\ 0\ | -2/7\ 0\ 1)$ .

Although in the structure solution process (with the program SIR97<sup>[17]</sup>) all reflections were taken into account (i.e. also the overlapping ones) no problems were encountered and the positions of all heavy atoms were easily identified. Structure refinement employing the above -described twin law was carried out with the program Jana2000.<sup>[18]</sup> Hydrogen atoms were taken from the difference Fourier synthesis map.

CCDC-190899 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.ac.uk/conts/retrieving.html](http://www.ccdc.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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