

## Unusual Lone Pairs in Tellurium and Their Relevance for Superconductivity\*\*

Shuiquan Deng, Jürgen Köhler, and Arndt Simon\*

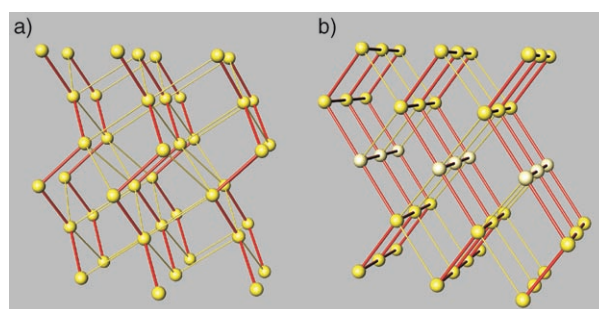
“Lone-pair” configurations of nonbonding electron pairs have always been used by chemists and physicists as a basis for rationalizing the structures of elements, molecules, and solid-state compounds.<sup>[1,2]</sup> Prominent examples are molecular structures described with the valence-shell electron-pair repulsion (VSEPR) model,<sup>[3]</sup> hypervalent compounds,<sup>[4]</sup> as well as the structural properties of “lone-pair ions” with the  $ns^2$  configuration, for example,  $\text{In}^+$ ,  $\text{Sn}^{2+}$ , and  $\text{Sb}^{3+}$ . The stereochemical activity of a lone pair depends on the types of ligands coordinated to the atom, on the temperature and pressure,<sup>[2,5]</sup> and, in particular, on the atomic number. Relativistic effects cause a larger decrease in energy for s than for p states with the same principal quantum number, resulting in an inert pair effect.<sup>[1c,d,6]</sup> This effect is also relevant for  $s^2p^n$  configurations, for example, the  $s^2p^4$  configuration of the chalcogen elements.<sup>[7]</sup> These elements exhibit a rich structural chemistry,<sup>[8]</sup> with phases ranging from insulating to superconducting.<sup>[9]</sup>

Chemical bonding in the chalcogens has been analyzed with the vector charge density wave (VCDW) model,<sup>[7b,c]</sup> by treating the  $ns^2$  pair as a core state because of the large s–p separation.<sup>[10]</sup> Interestingly, the resulting  $np^4$  valence electron configuration is threefold degenerate ( $(p_xp_y p_z)$ ,  $(p_xp_y p_z)$ , and  $(p_xp_y p_z)$ ), which means that the lone pair can have three different orientations. In spite of their crucial importance within the VCDW model, the existence and ordering of  $p^2$ -type lone pairs in the structures of the chalcogens have not been demonstrated quantitatively to date.

Herein, we present results from ab initio calculations, which allow a quantitative description of these types of lone pairs in a localized state, of their breakdown and delocalization under pressure, and of their relevance for superconductivity. We chose the element tellurium, because the first members, Te-I and Te-II, in a series of high-pressure phases up to Te-V, are structurally well characterized and exhibit semiconducting, metallic, and superconducting properties.

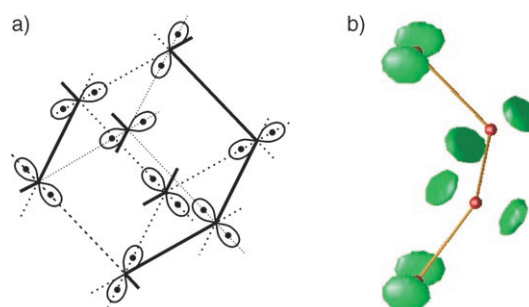
The ambient-pressure phase Te-I is composed of helical chains with 283.5 pm intra- and 349.1 pm interchain distances.<sup>[11]</sup> In the structure of Te-II, which is formed above approximately 4 GPa, these discrete chains are condensed into puckered layers with intralayer Te–Te distances ranging from 284.8 to 309.8 pm and shortest interlayer Te–Te dis-

tances of 333.3 pm.<sup>[12]</sup> Both structures are compared in Figure 1.



**Figure 1.** Perspective drawings of the crystal structures of a) Te-I and b) Te-II (Te1: light yellow spheres, Te2: yellow spheres). The red sticks correspond to the short Te–Te distances (283.5 pm in Te-I, and 284.8–309.8 pm in Te-II), and the thinner yellow sticks to longer Te–Te distances (349.1 pm in Te-I, and 333.3–340 pm in Te-II).

The electron localization function (ELF)<sup>[13]</sup> is a measure of the localization of an electron, which is based on the Pauli exclusion principle.<sup>[13a]</sup> It is defined to take maximum values in the “bosonic” regime of the electronic states.<sup>[13c]</sup> Since a lone pair is composed of a pair of electrons with opposite spin, it can be viewed as a localized boson. Thus, the ELF is often used as a tool to visualize a lone pair.<sup>[13]</sup> In Figure 2 a, the lone



**Figure 2.** a) VCDW model of a cubic primitive lattice of tellurium. For clarity, only lone pairs and covalent bonds (thick lines) are shown; the two one-electron components of the vector field on each lattice site have been omitted. b) ELF visualization of the TB-LMTO model. The calculated isosurface corresponding to a value 0.8 is shown for a single helical chain of Te-I.

pairs as described by the VCDW model for Te-I are shown. For comparison, the result of an ab initio tight-binding linear muffin tin orbital (TB-LMTO) calculation,<sup>[14,15]</sup> visualized through the ELF is shown in Figure 2b. With respect to a primitive cubic arrangement of the atoms, the lone pairs lengthen four of the nearest-neighbor distances around each site, while the two single-electron components are involved in bonds, which are indicated by thick lines in Figure 2a. In the VCDW model, the degeneracy of the lone pairs is removed by lowering the symmetry from cubic to trigonal.

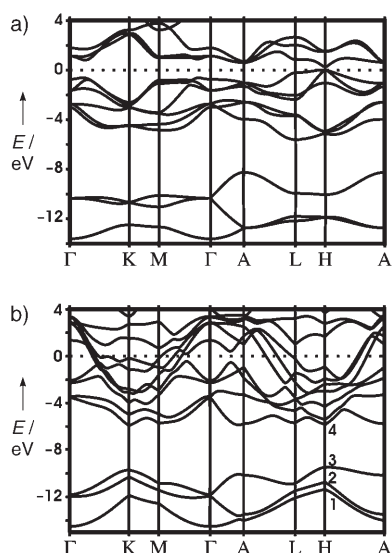
The chemical and structural significance of electron–electron repulsion is incorporated within the VSEPR model; however, this is only done qualitatively in terms of repulsion

[\*] Dr. S. Deng, Priv.-Doz. Dr. J. Köhler, Prof. Dr. A. Simon  
 Max-Planck-Institut für Festkörperforschung  
 Heisenbergstrasse 1, 70569 Stuttgart (Germany)  
 Fax: (+49) 711-689-1642  
 E-mail: a.simon@fkf.mpg.de

[\*\*] The authors thank Dr. O. Gunnarsson for helpful discussions.

between lone pairs, as well as between lone and bonding pairs. As first suggested by Fukutome,<sup>[7b,c]</sup> the unusual lone pair in the  $np^4$  configuration results from the Coulomb interaction ( $U$ ) among the p electrons, as the four valence electrons should otherwise be evenly distributed over the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals with an occupancy of  $4/3$ . Herein, we calculate  $U_p$  for the tellurium atom,<sup>[16]</sup> and for Te-I,<sup>[17]</sup> using the ab initio constrained occupation number approach.<sup>[18]</sup> For the tellurium atom,  $U_p^0 = 8.31$  eV is calculated, which agrees well with the value of 8.59 eV determined semiempirically from the experimental atomic spectra.<sup>[19]</sup> The repulsion is significantly reduced by Coulomb screening, which leads to calculated values of  $U_p = 1.16$  eV for the atom and  $U_p^{\text{solid}} = 1.09$  eV for Te-I.<sup>[20]</sup> The small difference between both values clearly indicates that the screening is mainly due to interaction of the electrons on a single atom, and that the low value of  $U_p$  is the origin of the lone pair. The value of  $U_p^{\text{solid}}$  provides a rough estimate for the stability of the lone pairs in Te-I. Hence, energy changes on the order of 1 eV that, for example, occur through a closer mutual approach of the tellurium atoms under high pressure, can break the lone pair.

Band-structure calculations for Te-I<sup>[21]</sup> and Te-II<sup>[22]</sup> reveal the differences in the chemical bonding of the two modifications. In the energy window between  $-14$  and  $4$  eV, the band structure of Te-I is composed of four groups of bands (Figure 3a). Each group comprises three bands which arise from the helical modulation of a straight chain of tellurium atoms. The group centered at  $-12$  eV is of mainly s character, while those at  $-3$ ,  $-1$ , and  $1$  eV correspond to p-type bonding states, or to p-type lone-pair states with antibonding character.<sup>[23]</sup> The band gap determined from our TB-LMTO calculations is  $0.336$  eV,<sup>[24]</sup> in very good agreement with the experimental value of  $0.334$  eV.<sup>[25]</sup> Note that both our TB-LMTO and our full-potential (FP) LMTO calculations clearly show that the frontier orbitals have a significant s component.



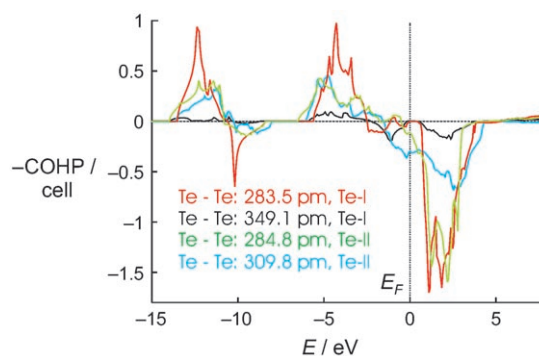
**Figure 3.** Band structures along selected symmetry directions from FP-LMTO calculations for a) Te-I and b) Te-II. In (b), the band states at point H are numbered consecutively from bottom to top (for clarity, only 1 to 4 are indicated).

Without sp hybridization, the band structure is dramatically changed, and Te-I develops metallic character. This result is consistent with the structure shown in Figure 2b, in which the Te-Te-Te angle is, however,  $103.14^\circ$  instead of  $90^\circ$ , and the relative orientation of the lone pairs shown in the ELF plot deviates from the  $90^\circ$  angle predicted by the VCDW model. However, qualitatively, the VCDW model agrees quite well with the ELF description.

Clearly, the treatment of the  $5s^2$  level as a corelike state in the VCDW model is over-simplified. The sp hybridization stabilizes the lone pair and changes the relative orientation of the lone pairs, as compared to the VCDW model. The importance of sp mixing in understanding many puzzling structural phenomena in hypervalent compounds has also been emphasized by other authors.<sup>[4]</sup>

The localized lone pairs are lost under pressure in Te-II, which is metallic. This change is clearly seen in the band structure calculated for Te-II, which is presented in Figure 3b. For better comparison, the first Brillouin zone was chosen to be identical to that for Te-I,<sup>[26]</sup> because both crystal structures are very similar. The results of earlier band-structure calculations have to be revised,<sup>[27]</sup> as they were based on monoclinic, instead of the recently discovered triclinic, symmetry of Te-II.<sup>[12]</sup>

The separation of s and p bands remains for Te-II, and the low-lying s bands do not change much, apart from the removal of degeneracy at the zone boundaries as a result of the triclinic distortion. In particular, the band dispersions along  $\Gamma$ -A are almost identical in Te-I and Te-II, reflecting similar interactions in the chain directions for both modifications. However, pronounced changes occur to the p-type bands, because of the formation of interchain bonds in Te-II. Figure 4 shows a comparison of the chemical bonding in Te-I



**Figure 4.** Selected COHP curves for intra- and interchain Te-Te bonds in Te-I and Te-II.

and Te-II, as measured with the crystal orbital Hamilton population (COHP).<sup>[28]</sup> In Te-I, the intrachain interaction is much stronger than the interchain one. The top of the lone-pair bands has antibonding character, in agreement with an earlier analysis.<sup>[29]</sup> It is clear from Figure 4 that for Te-II the intra- and interchain interactions are comparable below the Fermi level. However, both display a more pronounced antibonding character near the Fermi level. This observation is easily rationalized in terms of an increased Coulomb

repulsion between the lone pairs owing to reduced interchain distances. The rather small absolute values of COHP around the Fermi level in Te-I, as well as the band gap in this modification, along with the changes in these features with the transition from Te-I to Te-II give further evidence for the existence of lone pairs in Te-I and their breakdown in Te-II. The calculated orbital compositions of these bands confirms their p character.<sup>[23]</sup>

The strong antibonding interaction near the Fermi level in Te-II transforms lone-pair bands into highly dispersive (“steep”) bands along several directions, for example, H–A or A–L (Figure 3b). In addition, parts of the p-type antibonding conduction band are pushed down in energy, for example, at the H, K, L, and M points. This process results in a band with little dispersion along the  $\Gamma$ –K direction, and in a tiny flat feature near the Fermi level in the M– $\Gamma$  direction. Such characteristic sections of bands satisfy the conditions of a “flat” band in the flat/steep-band scenario for superconductivity.<sup>[30]</sup> The localized lone pairs of Te-I are broken into itinerant electrons in Te-II. Indeed, the ELF isosurface of Te-II, calculated at the value of 0.8 used for Te-I in Figure 1b, reveals only insignificant lone-pair characteristics for both kinds of tellurium atoms.

Whereas Te-I is semiconducting, Te-II is a superconductor,<sup>[31]</sup> and its band structure satisfies the condition for superconductivity in our flat/steep-band scenario. We have shown earlier that this condition is necessary, but not sufficient.<sup>[32]</sup> The required conditions are closely related to the presence of a lone pair in Te-I and its “virtual” presence through electron–phonon coupling in Te-II. The flat/steep-band scenario for Te-II originates from the lone pair, that is, a pair of electrons with opposite spin, which can be viewed as a hard-core boson or Anderson bipolaron.<sup>[33]</sup> Under ambient conditions in Te-I, the electron pair forms a boson lattice with negligible hopping probability. In Te-II, these bosons exist virtually in a “gaseous” state, which “condenses” to a “liquid” in the superconducting state.

In summary, we have quantitatively characterized an unusual type of lone pair formed by Coulomb interactions. Its transition from a localized to an itinerant state has been studied with first-principle methods. Our work documents the origin of the flat/steep-band features in the electronic structure of the high-pressure Te-II modification, which are prerequisites for superconductivity. These arguments can also be applied to other elements, for example, bismuth and its transition from semimetal, to metal, to superconductor under pressure<sup>[34]</sup> and in the amorphous state.<sup>[35]</sup> A quite general perspective emerges, in that holes can be introduced into lone-pair bands (for example, through chemical doping) to make compounds with lone pairs metallic and even superconducting.

Received: July 29, 2005

Revised: September 8, 2005

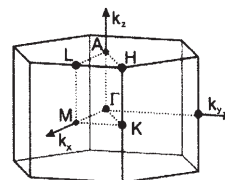
Published online: December 19, 2005

**Keywords:** ab initio calculations · ELF (Electron Localization Function) · high-pressure chemistry · superconductivity · tellurium

- [1] a) H. G. Grimm, A. Sommerfeld, *Z. Phys.* **1926**, *36*, 36; b) N. V. Sidgwick, H. M. Powell, *Proc. R. Soc. London Ser. A* **1940**, *176*, 153; c) M. L. Cohen, V. Heine, *Solid State Phys.* **1970**, *24*, 37; d) V. Heine, D. Weaire, *Solid State Phys.* **1970**, *24*, 250.
- [2] a) U. Häussermann, P. Berastegui, S. Carlson, J. Haines, J.-M. Léger, *Angew. Chem.* **2001**, *113*, 4760; *Angew. Chem. Int. Ed.* **2001**, *40*, 4624; b) I. Lefebvre, M. A. Szymanski, J. Olivier-Fourcade, J. C. Jumas, *Phys. Rev. B* **1998**, *58*, 1896.
- [3] R. J. Gillespie, R. S. Nyholm, *Q. Rev. Chem. Soc.* **1957**, *11*, 339.
- [4] a) G. A. Papoian, R. Hoffmann, *Angew. Chem.* **2000**, *112*, 2500; *Angew. Chem. Int. Ed.* **2000**, *39*, 2408; b) A. Ienco, R. Hoffmann, G. Papoian, *J. Am. Chem. Soc.* **2001**, *123*, 2317.
- [5] U. Schwarz, H. Hillebrecht, M. Kaupp, K. Syassen, H. G. von Schnering, G. Thiele, *J. Solid State Chem.* **1995**, *118*, 20.
- [6] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.
- [7] a) J. D. Joannopoulos, M. Schlüter, M. L. Cohen, *Phys. Rev. B* **1975**, *11*, 2186; b) H. Fukutome, *Prog. Theor. Phys.* **1984**, *71*, 1; c) T. Oka, H. Fukutome, *Prog. Theor. Phys.* **1988**, *79*, 608.
- [8] a) Y. Akahama, M. Kobayashi, H. Kawamura, *Phys. Rev. B* **1993**, *47*, 20; b) Y. Akahama, M. Kobayashi, H. Kawamura, *Phys. Rev. B* **1993**, *48*, 6862; c) H. Fujihisa, Y. Akahama, H. Kawamura, H. Yamawaki, M. Sakashita, T. Yamada, K. Honda, T. Le Bihan, *Phys. Rev. B* **2004**, *70*, 134106.
- [9] E. Gregoryanz, V. Struzhkin, R. J. Hemley, M. I. Erements, H.-K. Mao, Y. A. Timofeev, *Phys. Rev. B* **2002**, *65*, 064504.
- [10] The energy gaps between the  $ns^{1/2}$  and  $np^{1/2}$  levels for the respective atoms were obtained from full relativistic calculations based on the local-density approximation (LDA).<sup>[10a,b]</sup> The values are 10.00, 10.46, and 8.57 eV for sulfur ( $n=3$ ), selenium ( $n=4$ ), and tellurium ( $n=5$ ), respectively. a) J. F. Janak, V. L. Moruzzi, A. R. Williams, *Phys. Rev. B* **1975**, *12*, 1257; b) D. A. Liberman, D. T. Cromer, J. T. Waber, *Comput. Phys. Commun.* **1971**, *2*, 107.
- [11] C. Adenis, V. Langer, O. Lindqvist, *Acta Crystallogr. Sect. C* **1989**, *45*, 941.
- [12] C. Hejny, M. I. McMahon, *Phys. Rev. B* **2004**, *70*, 184109.
- [13] a) A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397; b) A. Savin, O. Jepsen, O. K. Andersen, H. Preuss, H. G. von Schnering, *Angew. Chem.* **1992**, *104*, 186; *Angew. Chem.* **1992**, *31*, 187; c) B. Silvi, A. Savin, *Nature* **1994**, *371*, 683; d) J. K. Burdett, T. A. McCormick, *J. Phys. Chem. A* **1998**, *102*, 6366.
- [14] R. Tank, O. Jepsen, A. Burkhardt, O. K. Andersen, *TB-LMTO-ASA (version 4.7)*, MPI für Festkörperforschung, Stuttgart, Germany, **1998**.
- [15] The experimental crystallographic data for Te-I reported in reference [11] were used throughout this work. The “combined correction”<sup>[15a]</sup> to the atomic-sphere approximation (ASA) was used to obtain more accurate Hamiltonian operators and overlap matrices. The exchange-correlation potential of the density functional theory was calculated according to von Barth and Hedin.<sup>[15b]</sup> Unless otherwise stated, the relativistic effect was always treated at the level of Darwin and with a mass-velocity correction. All  $k$ -space integrations were performed with the tetrahedron method, using 3050 irreducible  $k$  points.<sup>[15c]</sup> The tellurium 5s, 5p, 5d, and 5f orbitals were included in the calculations with the 5d and 5f orbitals down-folded, so that they were not included in the basis set. These two orbitals can carry charges without any contribution to the Hamiltonian operators and overlap matrices. To avoid overly large atomic sphere overlap, the interstitial region was filled with empty spheres, for which only the s orbital was included in the basis set. a) O. K. Andersen, *Phys. Rev. B* **1975**, *12*, 3060; b) U. von Barth, L. Hedin, *J. Phys. C* **1971**, *4*, 2064; c) P. Blöchl, O. Jepsen, O. K. Andersen, *Phys. Rev. B* **1986**, *34*, 2439.
- [16] The definitions of the respective parameters are the same as those for O in reference [18c].  $U_p^0: E(p^4s^0) + E(p^2s^0) - 2E(p^3s^0)$ ,

$U_p: E(p^4s^0) + E(p^2s^2) - 2E(p^3s^1)$ , where the superscript 0 of  $U$  denotes the pure parameter.

- [17] In an ideal situation, an “impurity” atom imbedded in an infinite crystal needs to be considered. In practice, a supercell of suitable size can often satisfy this requirement. For Te, a supercell which doubles the original unit cell along the  $c$  axis was chosen, because the nearest-neighbor distances along the  $a$  and  $b$  axes are already quite large. This supercell includes the second- and third-nearest neighbors with respect to the impurity tellurium atom, while in many cases it has been found that a supercell which includes only the nearest neighbors is sufficient.<sup>[18b,c]</sup>  $U$  can be calculated as the difference between the total energies of two crystals with different occupancies for the orbital of interest, or calculated by the change in the eigenvalue of the respective orbital [Eq. (1)], where  $i$  denotes the orbital of interest of the impurity atom, and  $\varepsilon_F$  is the Fermi energy introduced to correct the finite supercell effect.<sup>[18b]</sup> The numbers in parentheses denote the occupancies for the up and down spin states. In our calculations, all tellurium atoms have the same initial electronic configuration ( $5s^25p^4$ ) except for the impurity tellurium atom, for which the occupancy of the 5p orbital is assigned according to Equation (1). The total number of electrons was kept unchanged. The FP-LMTO method (NMTASA code)<sup>[17a]</sup> with an LDA formula from reference [17b] was used for the calculations. The 5p orbital of the impurity tellurium atom is isolated with respect to the system to avoid double counting and the change of its occupancy. a) S. Y. Savrasov, *Phys. Rev. B* **1996**, *54*, 16470; b) J. F. Janak, V. L. Moruzzi, A. R. Williams, *Phys. Rev. B* **1975**, *12*, 1257.
- $$U = \varepsilon_i(n/2 + 1/2, n/2) - \varepsilon_i(n/2 + 1/2, n/2 - 1) - \varepsilon_F(n/2 + 1/2, n/2) + \varepsilon_F(n/2 + 1/2, n/2 - 1) \quad (1)$$
- [18] a) O. Gunnarsson, O. K. Andersen, O. Jepsen, J. Zaanen, *Phys. Rev. B* **1989**, *39*, 1708; b) V. I. Anisimov, O. Gunnarsson, *Phys. Rev. B* **1991**, *43*, 7570; c) A. K. McMahan, R. M. Martin, S. Satpathy, *Phys. Rev. B* **1988**, *38*, 6650.
- [19] S. Fraga, J. Karwowski, K. M. S. Saxena, *Atomic energy levels*, Vol. 4, Elsevier, New York, **1979**.
- [20] For solid Te-I, the 6s and 5d orbitals are treated as bands. Thus, the change in the number of conduction electrons owing to the variation of the occupancy of the “impurity” Te-5p orbital can be accommodated by the whole crystal. The occupancies of all orbitals in the atom are fixed. Therefore, the dynamic effects of the screening are fully neglected in the calculations.
- [21] For the TB-LMTO-ASA calculations on Te-I, we used the same parameters as in reference [15]. However, the code was changed to let the crystallographic  $c$  axis coincide with the  $z$  axis of the Cartesian system and to let the  $a$  axis be in the  $xz$  plane. This change was made to allow a better comparison with the electronic structure of tellurium under pressure. For the FP-LMTO (NMTPLW code) calculations on Te-I,<sup>[17a]</sup> a  $2\kappa$ -5s, 5p, 5d basis set was used for the valence states of Te, while the 4d state was treated as a semicore state. In the interstitial region, the pseudo-LMTOs were expanded in plane waves up to 10.2, 15.4, and 22.0 Ryd (388, 708, and 1204 plane waves) for the 5s, 5p, and 5d orbitals, respectively. An  $18 \times 18 \times 18$   $k$  mesh was used in the self-consistent calculations for the energy states. The general-gradient approximation (GGA)<sup>[21a]</sup> was used to correct the LDA of reference [17b]. a) J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.
- [22] The crystallographic data for Te-II were taken from reference [12]. However, since the original unit cell setting was nonstandard, we transformed it into a standard one. The final unit cell parameters are  $a = 776.07$ ,  $b = 780.29$ ,  $c = 735.77$  pm,  $\alpha = 156.66$ ,  $\beta = 148.42$ ,  $\gamma = 45.75^\circ$ . The atomic coordinates were also transformed accordingly. In this setting, the helical chain of tellurium atoms runs along the  $c$  axis, as it does in Te-I. For the TB-LMTO calculations on Te-II, an  $18 \times 18 \times 18$   $k$  mesh was chosen. The other parameters were chosen as for Te-I (see reference [15]). For the FP-LMTO calculations on Te-II, the pseudo-LMTOs were expanded in plane waves up to 8.54, 12.4, and 18.1 Ryd. (240, 412, and 722 plane waves) for the 5s, 5p, and 5d orbitals of Te1, respectively, while for Te2, the pseudo-LMTOs were expanded in plane waves up to 10.0, 14.6, and 21.4 Ryd. (286, 536, and 946 plane waves) for the 5s, 5p, and 5d orbitals, respectively.
- [23] The calculated compositions for some band states are  $\psi(H1) = 95.5\% \text{ Te}(5s) + 4.14\% \text{ Te}(5p) + 0.36\% \text{ Te}(5d)$ ;  $\psi(H5) = 1.12\% \text{ Te}(5s) + 96.88\% \text{ Te}(5p) + 1.99\% \text{ Te}(5d)$ ;  $\psi(H9) = 4.31\% \text{ Te}(5s) + 93.16\% \text{ Te}(5p) + 2.53\% \text{ Te}(5d)$ ;  $\psi(H10) = 3.42\% \text{ Te}(5s) + 88.17\% \text{ Te}(5p) + 8.41\% \text{ Te}(5d)$ .
- [24] The very good agreement between the TB-LMTO band gap and the experimental value seems accidental, because LDA often underestimates the band gap. Moreover, our FP-LMTO method gives a band gap of only 0.247 eV.
- [25] C. B. à la Guillaume, J. M. Debever, *Solid State Commun.* **1965**, *3*, 19.
- [26] Brillouin zone for Te-I and Te-II:



- [27] a) G. Doerre, J. D. Joannopoulos, *Phys. Rev. Lett.* **1979**, *43*, 1040; b) Y. Shimoi, H. Fukutome, *Prog. Theor. Phys.* **1992**, *87*, 307.
- [28] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617.
- [29] A. Decker, G. A. Landrum, R. Dronskowski, *Z. Anorg. Allg. Chem.* **2002**, *628*, 295.
- [30] a) A. Simon, *Angew. Chem.* **1997**, *109*, 1872; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1788; b) S. Deng, A. Simon, J. Köhler, *Angew. Chem.* **1998**, *110*, 664; *Angew. Chem. Int. Ed.* **1998**, *37*, 640; c) S. Deng, A. Simon, J. Köhler, *Struct. Bonding (Berlin)* **2005**, *114*, 103.
- [31] a) F. P. Bundy, K. J. Dunn, *Phys. Rev. Lett.* **1980**, *44*, 1623; b) Y. Akahama, M. Kobayashi, H. Kawamura, *Solid State Commun.* **1992**, *84*, 803.
- [32] S. Deng, A. Simon, J. Köhler, *Solid State Sci.* **2000**, *2*, 31.
- [33] R. Micnas, J. Ranninger, S. Robaszkiewicz, *Rev. Mod. Phys.* **1990**, *62*, 113.
- [34] M. A. Il'ina, E. S. Itskevich, E. M. Dizhur, *Sov. Phys.-JETP* **1972**, *34*, 1263.
- [35] a) J. S. Moodera, R. Meservey, *Phys. Rev. B* **1990**, *42*, 179; b) T. T. Chen, J. T. Chen, J. D. Leslie, H. J. T. Smith, *Phys. Rev. Lett.* **1969**, *22*, 526.