Tin Sulfide, (Te$_2$)$_2$I$_2$, and Related Compounds: Symmetry-Controlled Deformations in Solid-State Materials

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The layered compound SnS normally adopts the GeS structure but is also observed to undergo a second-order phase transition to the more symmetric TII structure close to the melting point. GeS and TII, however, prefer the distorted low-temperature or the undistorted high-temperature structure, respectively, at ambient pressure. The band structures for both SnS modifications are constructed, and in a 2-dimensional picture the distortion can be traced to a mixing of the conduction band into the valence band, similar to a second-order Jahn-Teller distortion. The band gap (or the relative electronegativities) determines whether the distortion occurs. The derived picture can be used to examine the electronic structure of related compounds, such as (Te$_2$)$_2$I$_2$, InS, or HgCl.

The solid-state structures of 10-electron (per two atoms) compounds can be related to the rock salt structure by a successive bond-breaking process. Burdett and McLarnan$^2$ have given an enumeration of the resulting structures. While the As$^3$ or GeTe$^4$ structure types arise from a rhombohedral distortion, a quasi-bond-breaking process. Burdett and McLarnan$^3$ have given an enumeration of the resulting structures. While the As$^3$ or GeTe$^4$ structure types arise from a rhombohedral distortion, a quasi-tetragonal distortion leads to the structure of black P$^5$ or GeS$^6$ (1). This deformation transforms six "bonds" in the NaCl structure into three bonds in the GeS structure. Both Ge and S atoms have three neighbors at somewhat shorter (2.7 Å) and longer (3.3 Å) distances, so that GeS could be viewed as a distorted rock salt structure. Actually phosphorus is known to transform under high pressure to a rock salt modification.$^7$

In and Tl halides are isoelectronic with group IV (group 14$^{40}$) chalcogenides, although their structure looks different.$^8$ It can be built up, however, by stacking double layers from the NaCl structure, where consecutive layers are shifted due to the stereochemically active electron lone pairs. This is depicted schematically in 2. Every atom has 1 + 4 neighbors making up a distorted octahedron with one unoccupied position. There is a little buckling of alternate pairs of atoms in one direction, so that the cations project out of the layer. Interestingly enough SnS and SnSe were found to undergo a structural transformation from the GeS to the TII type, as shown in 3. The phase transition takes place just below the melting point, and it is a second-order transition.$^9$

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Supplementary Material Available: Anisotropic thermal parameters (Table S1), calculated hydrogen atom coordinates (Table S2), calculated mean planes and dihedral angles (Table S3), and $^1$H NMR spectra of 1 at 221 K (Figure 4c) and 200 K (Figure 4d) (6 pages); calculated and observed structure factors (Table S4) (8 pages). Ordering information is given on any current masthead page.

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We would like to understand the origin for the observed structural distortion in SnS. Some general statements can be made structurally and electronically about this transformation. The packing of the layers relative to each other is hardly different, but within each double double layer there is a change from a 3+2 to a 1+4 coordination. A bond order of \( n = 0.5 \) can be assigned to the four longer bonds by using Pauling's relation.\(^9\) This value is easy to rationalize if we assume hypervalent bonding for the pyramidal SnS\(_3^-\)fragments. For the axial bond, there is one bonding electron pair; for the basal bonds two bonding electron pairs are shared between four bonds. The situation is shown schematically for SnH\(_5^-\) in interaction diagram 4. On the left are given the orbitals of Sn\(^{2+}\), which transform as 2\(a_1\) + e under \(C_{6v}\) symmetry. On the right are the orbitals of 5H\(^-\), which transform as 2\(a_1\) + \(b_1\) + e. An important feature is that the \(b_1\) combination on the right finds no Sn orbital to interact with and remains completely ligand located and, therefore, Sn–H non-bonding. The \(b_1\) orbital is derived from the e set of an octahedral SnH\(_6^2-\)unit (as is the 3\(a_1\) orbital in the SnH\(_5^-\)composite). So, the SnH\(_5^-\)fragment has four equatorial bonding orbitals, but only two bonding electron pairs. For the axial bond, there is one bonding electron pair, which corresponds to a full Sn–H bond. The 3\(a_1\) orbital in 4 has a large contribution not only from central atom s and ligand orbitals but also from central atom p and axial ligand contributions. As a result of the p\(_x\) mixing, a lone pair (3\(a_1\)) is created, pointing to the vacant coordination site. Next, two cis equatorial H\(^-\)ligands are pulled off one by one. The evolution of the fragment orbitals is shown in 5. We are left finally in a situation which is familiar from simple AH\(_3\) molecules. For SnH\(_5^-\) on the right-hand side, there are bonding electron pairs for three bonds and one lone pair located on the tin atom. This matches the picture we see in SnS (GeS modification).

There are two simple ways to construct the individual layers in the TiI structure, and we are going to use these ways of geometrical construction to analyze the band structure as well. Following the hierarchy of interactions, we may start with a diatomic SnS monomer, which is surrounded by four other SnS units (generated by the glide planes perpendicular to b) pointing in the opposite direction, as shown in 6. This picture describes the layers as aggregated SnS units. In an alternative way, the SnS layers may be constructed from an AB stacking of slightly
We have built up substantial experience in the analysis of structures based on square nets, e.g. the ThCr₂Si₂\(^{11}\), BaAl₂\(^{12}\) and CaBe₂Ge₆\(^{13}\) phases as well as PbO\(^{14}\) and we have analyzed geometrically similar distortions in ZrSiS, ZrSi₂, and ATB₂ materials (A = alkaline-earth metal, La; T = Mn, Co, Cu, Zn; B = Sb, Bi).\(^{15}\) Structural maps for 10-electron compounds have been presented by various authors.\(^{16}\) We will use some of that experience in our analysis of the SnS phase transformation. It should be mentioned that previous calculations and XPS studies on the GeS modification of SnS exist in the literature.\(^{17}\) Our computations are of the extended Hückel type with details provided in the Appendix.

Building Up the SnS (TII) Electronic Structure

The simplest starting point to build up the SnS band structure in the TII form is a diatomic SnS monomer. An interaction diagram is shown in Figure 1. The lowest orbital is essentially sulfur 3s with a small amount of Sn 5p mixed in. Next, there is the \(s\) or \(s^\ast\) combination of 5s (Sn), with the two lone pairs between them. The bonding essentially results from a partial electron transfer from Sn to S. Next we move to an idealized two-dimensional layer, which was shown in two different views in 6. The actual structure is orthorhombic (space group Cmcm), but the lattice constants \(a\) and \(c\) are very similar. So we will assume for the moment a tetragonal structure to simplify the analysis. In the solid, each SnS unit in an upright position is surrounded by four nearest-neighbor units pointing down. In the primitive unit cell, the first SnS unit in Figure 2 is related to the second unit by an \(n\) glide plane. A schematic representation of the primitive unit cell and the corresponding Brillouin zone is given in 8 and 9. What we do here to derive the band structure is to use the maximum symmetry available, in particular, the glide plane symmetry. This reduces the number of bands to eight. The complete band structure may be generated later by a back-folding procedure, which projects areas or lines of the larger Brillouin zone for one SnS per asymmetric unit (that we use here) into the smaller Brillouin zone for the conventional SnS cell (which is half as large, since we have

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\(\text{Figure 1. Interaction diagram of Sn and S to form a SnS monomer.}\)

\(\text{Figure 2. Schematic 2D band structure for SnS (TII modification) along } \Gamma-M', \text{ using a glide plane as translation unit. Dashed lines indicate the shape bands would have without mixing.}\)
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Figure 3. Calculated 2D band structure for SnS (TII modification) along \( \Gamma - M' \). Dashed and dotted lines indicate the shape bands would have without mixing.

Figure 4. 2D band structure of SnS (TII modification).

In this "klasseungleich" transition, we lose a number of symmetry elements and shift the origin by \( \frac{1}{2}, \frac{1}{4}, 0 \). The pivotal symmetry element lost is a mirror plane. Our discussion did not yet include the lost translations. In going from the space group \( \bar{Ccmcm} \) to \( \bar{Pbnm} \), \( T = m \bar{d} + n \bar{b} + \pi \bar{c} \) remain, but \( T = (m + \frac{1}{2}) \bar{a} + (n + \frac{1}{2}) \bar{b} + \pi \bar{c} \) are lost. This implies that the transition corresponds to \( k = \bar{a}^* \), and this makes the connection to a Peierls distortion. \( k = \bar{a}^* \) identifies the wave vector of a soft phonon mode. The
From Figures 4 and 5, it is apparent that the band pairs 11, 12 and 13, 14 above the Fermi level are most affected, and from perturbation theory we know that these bands mix into the lower bands in a bonding fashion. The in-plane contributions of band pairs 9, 10 and 11, 12 are shown in Figure 7 in a top view on the SnS layer. In parts a and b of Figure 7, we draw the orbitals of the top layer; in parts d and e of Figure 7, those of the bottom layer are drawn. The pairs 9, 10 and 11, 12 have different symmetries in the undistorted structure. In the distorted structure, the symmetry is the same and the bands are allowed to mix. This process is shown for the bonding combination of top and bottom layers in parts c and f of Figure 7. Band pairs 9, 10 and 11, 12 are not the only candidates for mixing; the combinations 5, 6 and 13, 14 given in a side view in 10 and 11 certainly meet the symmetry requirements as well. In fact, all of these combinations mix. We are not going through all the details of this process; mixing of band pairs 13, 14 and 5, 6, and 11, 12 and 7, 8, respectively, as shown in a side view in 10 and 11, equilibrates the coefficients on Sn and S approximately. 10 and 11 can be combined to the wave function for band pair 5, 6 of the distorted structure, shown in a side view in 12 and in a top view on the top and bottom layer in 13 and 14.

We mentioned already that the phase transition can be described equally well as a Peierls type transition, and we identified the corresponding \( k \) vector. In the 3D structures 3 the “doubling” of the unit cell is connected to the loss of a twofold axis \( C_2 \) (\( x, 0, 0 \)) in the phase transition. In the 2D structures, we do not have
Figure 7. Crystal orbitals of a 2D layer at Z, relevant to the TII-GeS distortion, shown in a top view (only the in-plane component is shown): left, top layer; right, bottom layer. The crystal orbitals are symmetric and antisymmetric with respect to a mirror plane as indicated in parts a and d. The symmetric combinations a and d are not allowed to mix with the antisymmetric combinations b and e in the high-symmetry TII structure type. In the absence of the mirror plane in the low-symmetry GeS structure, however, both crystal orbitals mix, resulting in a stabilized (parts c, f) and destabilized (not shown) combination.

A symmetry restriction that prevents bands from mixing in the TII modification but not in the GeS polymorph. However, a glimpse at the band structures in Figures 4 and 5 shows that the band gap widens considerably at X. The reason can easily be rationalized from an orbital picture. At X, each band is represented by a degenerate pair of crystal orbitals. In 15 and 16, we show the orbitals for pairs 9, 10 and 13, 14 (TII modification). In 15 and 16, we show the orbitals for pairs 9, 10 and 13, 14 (TII modification). In 15 and 16, we show the orbitals for pairs 9, 10 and 13, 14 (TII modification).

At X. For reasons of clarity, only the in-plane component is given. In the undistorted structure we observe only a negligible amount of mixing of these two combinations. In the distorted structure, however, the mixing is substantial. This is shown in 17a,b. In the distorted geometry, one of these combinations (17a) is stabilized; the other one (17b) is pushed up in energy. The picture is, therefore, analogous to a pairing distortion, the prototype being a linear chain of hydrogen atoms that distorts to diatomic molecules.

The net result is a distortion from the TII to the GeS structure. Since as many bonds are broken in the transition as are formed, we expect the resulting energy change to be small. In the 2D calculations, we favor the low-symmetry structure by 0.135 eV per formula unit. For the experimental 3D structure the TII...
We think, however, that this contradiction can be resolved. The word "gap" as we used it in this connection should refer to the energy difference between the $\pi$ and $\pi^*$ type states in the solid-state materials. These are clearly the "in-plane" orbitals ($p_\alpha$ and $p_\beta$ in our coordinate system), which are responsible for making and breaking the bonds in question. In the interaction diagram in Figure 2, these orbitals are easily identified. With application of the electronegativity argument, the $\pi^*$ orbitals move to higher energies if one moves from Ge to Sn and Tl. Given a constant anion, the $\pi$ orbitals stay at approximately the same energy. In the solid-state materials, these orbitals spread out into bands, but the basic features of the dimer building block are still preserved. We could see this by comparing the tentative band structure in Figure 2 with its calculated counterpart in Figure 3.

A word about the electronegativity differences is still in order. The EN differences we are talking about are quite small (for Tl, Ge, and Sn, EN = 2.0; for S and Se, EN = 2.6; for I, EN = 2.7). Whereas for Tl the EN values immediately support a more ionic model and a larger "gap", one is not able to differentiate between GeS and SnS based on Pauling's EN scale. A number of well-known facts (e.g. gray and white Sn modifications, trends in ionization enthalpies, etc.) however, show that Sn actually is more metallic than Ge.

Similar reasoning can be applied for the tellurides. The GeTe structure, which is an ordered variant of the rhombohedral As structure, undergoes at 400 °C a transition to a rock salt structure type. In fact, the GeTe structure can be derived from the parent rock salt structure, just like the GeS structure type, by breaking three mutually orthogonal linkages around each octahedrally coordinated rock salt site. Black phosphorus has been reported to undergo a phase transition at 50 kbar to the $\gamma$77 structure. We do not want to dwell on this particular point, since this has been analyzed by Burdett and co-workers in some detail.

What about the lead chalcogenides? Let us recall that the action of the lone pair in 10-electron compounds causes a breaking of bonds in the rock salt parent structure, resulting in typical 10-electron structure types, such as TlI or GeS. For lead and other heavy elements, relativistic effects are well-known to contract the $5s$ orbital and to lower its energy. This is generally known as the inert-electron-pair effect. As a result, the lone pair repulsion in lead chalcogenides, e.g. PbS, is reduced and a rock salt structure is preferred.

The point still to be considered is the stacking of the 2D layer to the full three-dimensional structure. A detailed discussion of interlayer bonding in 10e compounds has been given by Trinquier and one of us in a study of PbO. We want to highlight only a few points here. When the layers are stacked together, the bands that have lobes pointing away from the layer will be perturbed. In simple terms, a symmetric and antisymmetric combination of these orbitals can be formed. This is shown schematically in a projection on the layers in and . At the $\Gamma$ point, the symmetric combination will be stabilized, the antisymmetric combination will be destabilized. Going along the different symmetry lines, we can predict the evolution of the bands from the phase of the lobes pointing up and down. We will not pursue this in further detail here, but the general result is a broadening of the highest occupied bands. We can pick up these features in the DOS curves for the GeS and TlI modification, but do not show those curves here.

For the experimental geometries, we calculate net charges of 0.98 (TlI) and 0.82 (GeS) on each tin atom. The resulting Sn-Sn

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overlap populations are 0.073 and 0.046 for interlayer distances of 3.455 and 3.405 Å, respectively. These numbers indicate that there is bonding to some degree between the Sn atoms of different layers. The corresponding COOP curves for intralayer Sn-S and interlayer Sn-Sn bonding are depicted in Figure 10. The lower bands up to -12 eV contribute to Sn-Sn bonding, whereas those above make an antibonding contribution. Contributions to Sn-Sn interlayer bonding will come from orbitals that point into the interlayer region. There are some low-energy bands with this characteristic, but the primary contribution to Sn-Sn bonding comes from the two highest bands. In these bands, in the region -9 to -13 eV, the lower portion is interlayer Sn-Sn bonding, with the upper portion antibonding. This pattern for the overlap population is similar to what has been observed in the PbO case, and we think that it describes the typical bonding situation in ten electron MX compounds.

The evolution of the overlap populations and the relative variation in the total energy when the layers are progressively brought together are shown for the TII modification in Figure 11. The largest change in the overlap populations corresponds to the interlayer Sn-Sn bond. The overlap population increases strongly if the layers are pressed together beyond the experimental distance. The intralayer Sn-S overlap populations decrease during this process; the intralayer Sn-Sn overlap population is negative and very small. The same holds for interlayer Sn-S and S-S overlap populations. The interaction between the layers is repulsive, as can be seen from the energy variation. The experimental geometry \( b = 11.48 \) Å is on the softly rising part of the energy curve.

Let us conclude this section with a brief comparison of the SnS structure types with the PbO structures, which were analyzed by Trinquier and one of us previously. PbO exists in two polymorphic forms: red tetragonal \( \alpha \)-PbO (litharge) and yellow orthorhombic \( \beta \)-PbO (massicot). Both structures are layer structures with 10 electrons per formula unit as SnS. Although the atoms in PbO are four-coordinated (instead of five-coordinated as in SnS), the bonding picture in PbO and SnS is—ever up to finer details—remarkably similar. Some of the points were mentioned in the text. Transitions between both PbO forms have been reported, but although they are “symmetry-allowed” (first Landau condition), they are not of second order type.

Interestingly enough, we encounter the double layers observed in the TII structure in the intercalation compound \((\text{Tc}_2)_2 \text{I}_2\) \(^{(20)}\) again. This truly remarkable material contains planar double layers of tellurium formed from \( \text{Tc}_2 \) units (if we follow the hierarchy of interactions), which are arranged along the c axis. As in the TII structure, this provides a 1+4 coordination for the Te atoms with Te-Te distances of 2.713 and 3.323 Å. Molecular planar layers of \( \text{I}_2 \) molecules are situated between the layers, the intramolecular bond length being 2.715 Å and the intermolecular contacts being more than 3.384 Å. Can we expect a distortion of the Te double layers similar to that observed in SnS?

On the basis of the experience we have accumulated up to this point, we can predict qualitatively the shape of the band structure of a Te 2D double layer. Since the geometries of the SnS (TII) and \( \text{Tc}_2 \) layers are very similar, we expect the shape of the bands to be alike in both cases. The important difference originates from the atom electronegativities. The interaction diagram in Figure 2 shows that the Sn- and S-centered orbitals are nicely separated, due to the different electronegativities of Sn and S. The orbitals for the \( \text{Tc}_2 \) fragment in \( \text{Te}_2 \) are those of a homonuclear diatomic unit. The level ordering is the familiar \( \sigma, \pi, \pi^*, \sigma^* \) sequence, and the splitting of the \( \sigma_p \) levels is ~6 eV, the \( \sigma_s \) splitting being ~14 eV for the given Te-Te distance.

In the next step the \( \text{Tc}_2 \) units are arranged to form a double layer, and the orbitals of the molecular unit spread out into bands. The \( \sigma_p \) bands have only a small overlap along any direction in the two-dimensional Brillouin zone. Therefore the resulting bands have to be rather flat. The \( \sigma_p \) orbitals, however, show substantial overlap, and the bands will show large dispersion. The situation is very similar to that for a square net of atoms. Because we discuss a double layer of atoms, the number of bands simply has


to be doubled by forming a symmetric and antisymmetric combination. The calculated band structure is shown in Figure 12. There is a striking similarity to the band structure of SnS in the TII modification; only the dispersion of the bands has changed. Let us discuss the band composition at $I'$. The lowest four bands are the 5$s$ bands. Bands 5 and 8 (22 and 23) are one of the $\pi/\pi^*$ combinations of the Te$_2$ fragment; they are bonding between the Te$_2$ units. The other $\pi/\pi^*$ combination, which is bonding between the Te$_2$ units, is composed of bands 7 and 9 (24 and 25). Bands 11/13 and 12/14 are the corresponding antibonding partners. These bands are involved in the basal bonding around Te. The $p_x$ combination (now bonding within but bonding and antibonding between Te$_2$ fragments), which is involved in the axial bonding, is given in bands 6 and 10 (26 and 27). The highest two bands, bands 15 and 16, are the corresponding antibonding partners ($p_y$, antibonding within and bonding/antibonding between the Te$_2$ units).

For Te double layers we have 24e/unit cell (12e/Te$_2$), and the corresponding Fermi level is indicated by an arrow at the left margin of Figure 12. Since the p bands overlap very efficiently,
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Figure 12. Band structure of a 2-dimensional Te₂ slab.

Whereas the Te double layer in (Te₂)₂I₂ could be related to the SnS (TII) structure by adding two electrons, one may equally well want to remove one electron (on paper). This leaves us with the nine-electron compounds, and the unpaired electron is taken care of by connecting two layers by a metal–metal bond, as in GaS. Alternatively one can break a bond in the NaCl structure, a nice example being GeP. In InS³ (29b) two GeS type layers (GeS given in 29a for comparison) are connected by an In–In bond. A corresponding high-symmetry version (due to the missing lone pair) is found in the tetragonal HgCl structure³⁴ (29c), where a Hg–Hg bond is formed.

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Appendix. The extended Hückel method²⁵,³⁶ in the tight-binding approximation²⁷ was used in all calculations. The parameters are listed in Table I. For Sn the exponents were contracted to match the experimental band structure, in particular the dispersion along the line Γ–X and at the Γ point. Sets of 27 or more k points were chosen according to ref 39 to calculate the DOS and COOP curves.

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