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A chemical link between Ge–Sb–Te and In–Sb–Te phase-change materials[†]

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We identify a similar feature in the chemical-bonding nature of seemingly different phase-change materials (PCMs) for data storage. This affords new insight into the "next-generation" material In₃SbTe₂, establishes a hitherto missing link to the more ubiquitous Ge–Sb–Te alloys, and encourages the search for new PCMs beyond established electron-counting schemes.

PCMs are leading candidates for novel data storage and processing technologies,¹ including promising applications in energy-efficient nanoscale devices² or in brain-like computing.³ Many PCMs are found on the GeTe–Sb₂Te₃ (GST) quasi-binary tieline, such as $Ge_8Sb_2Te_{11}$ (the "Blu-Ray material"), or $Ge_2Sb_2Te_5$, which is used in nonvolatile electronic memories.¹ Beyond this quasi-binary system, the search for new PCMs with attractive properties is a very active field of research. It is thus highly desirable to devise microscopically guided design rules and predictive "fingerprints" to find better-performing PCMs, rather than relying on serendipity alone.⁴

The ternary alloy In₃SbTe₂ ("IST" in the following) has been explored as a possible PCM⁵ and shown to possess attractive features: amorphous IST is stable at distinctly higher temperatures than GST,⁵ and its crystallisation was reported to proceed *via* multiple distinct stages which exhibit different resistivities.⁶ In chemical and physical terms, however, IST differs strongly from GST compounds: its composition is devoid of Ge, and crystalline IST is metallic,^{6a} whereas GST alloys are semiconductors in both crystalline and amorphous forms.⁷ A simple electroncounting argument further emphasises the difference: most PCMs have an average valence p-electron count (N_p) of three per atomic site,¹ whereas in IST there are only 2.3 p-electrons per site. By definition, IST does not belong to the previously suggested "treasure map"^{4b} for $N_p = 3$ phase-change alloys. The material does not seem to "fit in" with the others, plainly spoken.⁸

In this light, the structural preferences in the In-Sb-Te system are even more surprising. IST was first reported in 1964 as a metastable quasi-binary alloy (InSb + 2 InTe ⇒ In₃SbTe₂).⁹ Both binary constituents are characterised by tetrahedral nearest-neighbour environments for the indium atoms: InSb is a typical III-V semiconductor with a zincblende type lattice, and InTe takes the TlSe structure type (Fig. 1a).¹⁰ By stark contrast, IST is structurally similar to GST in the crystalline state: it exhibits a cubic rocksalt (NaCl) type structure,⁹ as recently corroborated by combined state-of-the-art diffraction techniques¹¹ and, independently, by high-resolution transmission electron microscopy.¹² Indium atoms form one face-centred cubic sublattice, whereas the second, interpenetrating one is randomly occupied by Sb and Te; disorder hence exists on the anion sublattice in IST, while it is found on the cation sublattice in GST.13

In this Communication, we explore why IST crystallises in the rocksalt type whereas binary InSb and InTe do not. Starting from this specific question, we will arrive at a more general bonding "fingerprint", and a bond-optimisation mechanism that we argue exists in PCMs. We continue and expand upon bonding studies in the GST system;¹⁴ there, and here, crystal orbital Hamilton populations (COHPs)¹⁵ serve to identify stabilising and destabilising interactions between pairs of neighbouring atoms. For the sake of argument, we start by looking at the binary parent compound, InTe, and explain why it does not crystallise in the rocksalt type at ambient conditions.

Fig. 1a shows the experimentally determined structure of InTe,¹⁰ which exhibits 1D chains of $In[Te_4]$ tetrahedra in

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[†] Electronic supplementary information (ESI) available: Supercell models as used for pCOHP analyses (given in CIF format) as well as two supplementary movies. See DOI: 10.1039/c5tc02314a



Fig. 1 (a) Crystal structure of binary InTe.¹⁰ Indium atoms are drawn as light green spheres; tellurium atoms are larger and blue. (b) Densities of states (DOS) and crystal orbital Hamilton population (COHP) analysis‡ for In-Te bonds in these tetrahedra ("Expt."). (c) Same but for the octahedra in rocksalt-type InTe. COHPs are drawn such that stabilising interactions fall to the right of the energy axis, and destabilising ones to the left. *x*-Axis values are omitted for clarity, as they are irrelevant to the discussion here.

c direction; between these chains, formally univalent In atoms are located. The bonding within the In[Te₄] tetrahedra is fully optimised (Fig. 1b): the filled bands up to the Fermi level $\varepsilon_{\rm F}$ all make positive contributions to –COHP (thus, lower the total energy); this indicates stable covalent In–Te bonds. On the contrary, a similar computation for InTe in a rocksalt-type structure¹⁶ shows filled antibonding levels (–COHP < 0), as seen in Fig. 1c. We emphasise that electron-counting arguments would not have revealed the differences between the two competing structures, and *ab initio* descriptors are needed instead; we have recently observed, and argued similarly for the orthorhombic and rocksalt-type polymorphs of GeSe.¹⁷ In summary, COHP analysis provides a simple, if unsurprising, explanation for the stability of the experimentally observed structure with In[Te₄] tetrahedra.

What happens upon the transition from InTe ($N_p = 2.5$) to quasibinary IST ($N_p = 2.33$)? We start by considering the simplest model compatible with stoichiometry: we therefore describe the rocksalt-type structure of InTe in the hexagonal unit-cell setup,¹⁸ which contains three cation and three anion sites (In₃Te₃). In this cell, we then place Sb on the (0, 0, 1/2) position, and the relaxed model is shown in Fig. 2a. It is used here not only for its simplicity, but also because large supercells with hundreds of atoms are practically inaccessible to the standard COHP implementation employed so far.

Fig. 2b provides COHP curves for this IST model. Antibonding In–Te interactions (–COHP < 0) below $\varepsilon_{\rm F}$ are evident, very similar to those in rocksalt-type InTe. For the In–Sb bonds, however, such destabilisation is almost completely absent. This can be understood through a "quasi" rigid band model: the substitution Te \rightarrow Sb reduces the local valence electron count by one (going from a group-VI to a group-V element); accordingly, $\varepsilon_{\rm F}$ is lowered and depopulates antibonding regions. Such arguments of Fermi level tuning have been invoked before to understand vacancy formation¹⁴ and vacancy diffusion¹⁹ in PCMs.

At this point, the question emerges why one would not start a similar *Gedankenexperiment* from the stable phases of InSb



Fig. 2 (a) The simplest possible structure model for rocksalt-type IST, using the hexagonal unit-cell setup. Sb atoms are drawn in red. (b) Bonding analysis for In–Sb and In–Te contacts in this cell (the latter curve has been averaged over the two inequivalent contacts). Note the clearly different locations of the low-lying Sb s and Te s bands (\approx -10 and -12 eV, respectively), whereas the In s levels mainly contribute to the higher-lying bands around -6 eV.

and InTe. Indeed, as both binary compounds are characterised by tetrahedrally coordinated In atoms (recall Fig. 1a), one might expect similar structural features for the quasi-binary phase.⁹ To probe this question, supercell models of stable InSb and InTe were constructed; subsequently, the anion sublattices were randomly occupied with Sb and Te atoms (1:2 ratio)



Fig. 3 (a) Structural model of hypothetical zincblende IST, and pCOHP curves for the initial model (averaged over all nearest-neighbour In-Sb and In-Te contacts, respectively). Upon releasing the atomic positions, the system amorphises. (b) Structural model of InTe-type IST, with pCOHP curves as above

and the density of the cells was scaled accordingly.§ The simulation cell derived from InSb contains 216 atoms in total, and that based on InTe holds 192 atoms.

Our aim is to elucidate the bonding nature in these more "realistic" supercell models, but the large system size prohibits the use of traditional COHP analysis for technical reasons (e.g., the space group of the model is lowered to P1, significantly increasing computational demands). Instead, bond-analytical data for the large supercells are obtained by projection from plane-wave based density-functional theory (DFT) results onto a local auxiliary basis, which yields a quantity dubbed "projected COHP" (pCOHP).²⁰ The interpretation of the latter is no different from traditional COHP analyses.

We first discuss the hypothetical zincblende-type model of IST (Fig. 3a). Here, both the In-Sb and the In-Te contacts display strongly destabilising interactions, evidenced by large negative -pCOHP peaks directly at $\varepsilon_{\rm F}$ (arrows). This effect is most pronounced for the In-Te bonds, which agrees well with the expectation that substituting $Sb \rightarrow Te$ will increase the valence electron count compared to InSb and push $\varepsilon_{\rm F}$ up into antibonding regions of the electronic band structure. Consequently, when released according to Hellmann-Feynman forces, the atoms in this model are displaced so strongly as to lead to amorphisation (Fig. 3a, bottom left). To rule out a spurious pressure-induced effect, we repeated the simulation using the lattice parameter of pure InSb (and thus a much lower atomic density and internal pressure); nonetheless, the model still emerged as unstable. We also confirmed that such



Fig. 4 (a) Representative structural fragment from the unrelaxed InTetype IST model (Fig. 3b), emphasising the "interstitial" indium atoms between chains of edge-sharing tetrahedra (cf. Fig. 1a). Here, In...Sb and In...Te contacts are marked by dashed lines, exemplarily so; in total, each interstitial In atom has eight anionic neighbours. (b) Bonding analyses as in Fig. 1-3, but for the "long" contacts in binary InTe (left) and for the ternary InTe-type IST model (right).

-pCOHP

-pCOHP

-12

long bond

-COHP

structural instability is not a spurious finite-size effect: the DFT relaxation of a large 1728-atom model is shown in the ESI⁺ (Movie S1). In summary, zincblende-type IST is clearly unstable, which explains why this phase has never been experimentally observed.

For the InTe-type model, the situation is slightly more complex (Fig. 3b). Here, the In-Te contacts appear almost fully optimised, with bonding levels filled and antibonding levels empty, like in the stable binary phase (Fig. 1b). The In-Sb bonds experience a slight undersupply of electrons but no significant instabilities. Instead, we must now consider those In atoms between the tetrahedra (Fig. 1a) which have been tacitly ignored so far.

Fig. 4a provides a structural close-up: the interstitial In atoms lie between chains of tetrahedra. In pure InTe, these interstitial atoms thus have only Te neighbours; in the randomised ternary model, some Sb atoms are present, too. These longer contacts, in the binary phase, give rise to a minor fraction of filled antibonding levels (Fig. 4b, left), outweighed, however, by the fully optimised bonds within the In[Te₄] tetrahedra (dashed lines). In the ternary IST model, the situation is clearly different: especially for the In $\cdot \cdot$ Sb contacts, $\varepsilon_{\rm F}$ resides in a region of strongly destabilising interactions (arrows in Fig. 4b). Hence, the InTe structure is no stable alternative for IST, either, and relaxation likewise leads to significant distortions (Fig. 3b).

As above, large-scale (1536-atom) simulations were performed for validation and are shown as ESI⁺ (Movie S2). Interestingly, in the latter case, local distortions towards octahedral environments are observed. Clearly, crystalline IST favours the rocksalt structure as the most acceptable compromise, and exhibits octahedral coordination at variance with both binary phases. The key role of local structural fragments (in particular, tetrahedral- *vs.* octahedrallike) has been a recurring theme in the study of PCMs and their properties.²¹ It has also been discussed in a careful moleculardynamics study of amorphous In₃SbTe₂ to which we may refer the interested reader.²²

Finally, let us address a question posed before: is there a link between IST and the aforementioned GST materials family?^{12,23} In Fig. 5, we compare the electronic structures of metastable crystalline GST and IST; the latter is modelled in a 216-atom supercell with randomly occupied Sb/Te sublattice. Both GST and IST exhibit antibonding COHPs directly below $\varepsilon_{\rm F}$, more pronounced so for the more electron-rich bond type (*viz.*, Sb–Te in GST, and In–Te in IST). Fig. 5 also suggests mechanisms for how the rocksalt phases are stabilised. The starting points are compounds that are unstable in the cubic phase (InTe)⁹ or nonexistent at all (Ge₂Sb₂Te₄).¹⁴ Two different mechanisms, vacancy formation and Te \rightarrow Sb substitution, then "heal" the electronic instability and lead to experimentally observable crystal structures.¶

We reiterate that the antibonding interactions below $\varepsilon_{\rm F}$ are not fully removed, only partially, as noted for crystalline GST¹⁴ and for crystalline and amorphous GeTe.^{21*b*,24} Further extensive work will be required to understand why IST needs an Sb:Te ratio of exactly 1:2 to reach the electronic "sweet spot". Unambiguously, however, the control of $\varepsilon_{\rm F}$ is the crucial argument in both materials classes. This microscopic similarity is in line with a previous experimental study by Oeckler and

Fig. 5 Qualitative schemes for stabilisation mechanisms in metastable crystalline GST and IST alloys, respectively. Left: Stabilisation of $GeSb_2Te_4$ as revealed in ref. 14; figure adapted from there. Right: Proposed mechanism for IST (this work).

co-workers, who already noted "comparable real structure effects and properties" in GST and IST.¹¹

In conclusion, we argue that the electronic structures of rocksalt-type GST and IST phase-change materials exhibit similar features with regard to the chemical-bonding nature, despite their different p-electron counts. In both, the location of the Fermi level is tuned intrinsically, such as to reduce (yet not completely nullify) antibonding interactions. In general, our results provide impetus for the further exploration of In_3SbTe_2 , and beyond this particular material, they stress how the search for new PCMs should include even those compounds which do not seem to "fit in" according to simple electroncounting arguments.

Computational methods

First-principles computations were performed in the framework of gradient-corrected DFT.²⁵ Large models of up to 1728 atoms were fully relaxed with QUICKSTEP,²⁶ a mixed-basis code implemented in CP2K.²⁷ Thereby, Gaussian basis sets (triple- ζ plus polarisation quality) were employed to expand the Kohn-Sham orbitals, while plane waves (cutoff 300 Ry) were used to compute the charge density; the pseudopotentials were of the scalar-relativistic Goedecker type.²⁸ Structural models of rocksalt-type IST were relaxed using the VASP code²⁹ and projector augmented-wave³⁰ potentials. In all these computations, the Brillouin zone was sampled at Γ .

COHPs¹⁵ for small structural models were computed based on tight-binding linear muffin-tin orbital (LMTO) theory in the atomic spheres approximation (TB-LMTO-ASA program).³¹ To analyse bonding in large supercells, projected COHPs²⁰ were retrieved from VASP single-point computations on $2 \times 2 \times 2$ *k*-point grids.³² An atom-centred minimal basis of Slater type orbitals (STOs) was employed for projection as implemented in the LOBSTER program.^{20b}

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Notes and references

[‡] Technically similar COHP computations, albeit with different purpose and interpretation, have previously been reported by one of us in ref. 8. § The lattice parameters were scaled to correspond to a mass density of 7.0 g cm⁻³ (ref. 33), which is in good agreement with the single-crystal XRD density given by Oeckler and co-workers.¹¹ We note in passing that the pycnometric density⁹ and that of sputtered thin films³³ is lower; the reasons (*e.g.*, possible void formation) need further study but are likely not relevant to the focus of this work.



¶ One might assume that further Te \rightarrow Sb substitution would make the lattice even more stable; however, structural optimisation of a 216-atom supercell of In₃Sb₂Te₁ (hence with inverted Sb:Te ratio) did not succeed but led to strong distortions away from the rocksalt structure. This agrees with the fact that In₃Sb₁Te₂ is the only experimentally known phase in the ternary system.

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