Elementary considerations on the local symmetry in optoelectronic materials and their phase change behavior

How the competition of ions in their attempt to increase local symmetry and electrons in their attempt to reduce it can lead to phase change behavior

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Abstract. Crystalline structures of elemental solids can be rationalized in terms of the competition between ions and electrons: Ions try to increase local symmetry and thus packing fraction, while electrons want to reduce it. If the latter win, layered structures, network, or molecular solids form and the opening of an electronic gap is favoured. In this work, it will be discussed how this competition can affect the thermodynamic behavior of phase change materials (PCMs), in particular that of Ge-Sb-Te alloys: Their technologically relevant metastable crystalline structures can be derived from (hypothetical, metallic) simple cubic crystals near half-filling via a symmetry breaking, such as a Peierls distortion in Sb-rich PCMs or ordering of chemical species onto sublattices on the GeTe-Sb_2Te_3 pseudo-binary line, leading to the formation of σ-bonded networks. Local symmetry and density become even smaller and the gap opens up even more in the glass, for example, when the group IV element germanium undergoes a coordination change from (distorted) octahedral in the crystal to tetrahedral. This coordination change leaves the σ-bonded network intact, as will be demonstrated by analysis of first-principle simulations. Based on local symmetry arguments, simple rules for the number of electron holes and/or vacancies in metastable crystalline structure of PCMs can be derived and the response of Ge-Sb-Te alloys to pressure be predicted: Crystalline alloys will amorphise under pressure when there are more Te than Ge atoms and increase their conductivity. Conversely, disordered alloys will crystallize if the number of Ge atoms exceeds that of Te. The possibility to switch the latter PCMs reversibly with pressure will be discussed. Lastly, unusual relaxation dynamics of PCMs are identified from first-principle calculations: When a solid is streched to its amorphisation point, the ionic energy (which is minimized in the crystal) increases with time as opposed to the dominating electronic energy. At the same time, coordination statistics become increasingly distinct with age from those in the crystal, i.e., the quenched fluid initially relaxes away from the crystalline phase.

1 Introduction

Rewritable optical media such as DVD-RW rely on the strong contrast of the optical properties that phase change materials (PCMs) exhibit between their ordered (metallic or more precise semi-metallic) and disordered (insulating or more precise semi-conducting) phase, representing 0 and 1 bits respectively [1]. Owing to many beneficial properties, e.g., fast switching [2] and low costs, PCMs are promising candidates for improved non-volatile memory cells [3], for which they have already been successfully tested [4], and for other applications such as programmable switches. The enormous economic relevance of memory cells, the slowing down of flash memory scaling, and the promise that the switching behavior of PCMs bears in this context has spurred an increased research activity on PCMs in the past few years [3] with an emphasis on unraveling the microscopic origin of their phase change properties [5–8].

The contrast in optical and electronic properties of PCMs between the crystalline and glassy phases is typically not observed in other materials [9]. Regular metallic glasses conduct electricity similarly well as their crystalline counterparts, and the band gap in disordered semiconductors, such as doped silicon, is similar but typically smaller than that of chemically identical systems with long-range order [10]. Therefore, it has long been a mystery why these generally observed trends do not apply to PCMs. Before recent answers to this mystery will be summarized, it may be beneficial to comment on the chemical composition of PCMs and their electronic structure in some crystalline phases.

Most commercially used PCMs are based on either ternary compounds made of Ge, Sb, and Te, [11] or quaternary alloys containing predominantly Ag, In, Sb, and Te. [12] Thus, the predominant constituents of PCMs are - not surprisingly - elements which form either semiconducting or semimetallic solids at ambient conditions. In high-symmetry (high-temperature) crystalline phases, the local order in typical representatives of the ternary and quaternary alloys, specifically $Ge_2Sb_2Te_5$ and $Ag_5In_6Sb_{59}Te_{30}$, have been found to be very similar to one another. [13] It is thus tempting to assume that similar mechanisms are responsible for the PCM behavior in both families and that it may suffice to focus on one of the two when rationalizing their properties on a fundamental level.

Here, we will be concerned with the simpler and better-studied ternary alloys. Their ambient temperature and pressure phases can be derived from a simple cubic reference crystal with random occupation of atoms on given lattice sites. This makes the discussion of their band structure particularly simple. As argued in more detail in the main text, commercially used PCMs are at or near half filling in their (hypothetical) simple cubic (s.c.) reference structure. From there, they can reduce their energy efficiently through a symmetry reduction, either by Peierls distorting (see, e.g., elemental Sb [14]) or by ordering the chemical species onto sublattices. The latter happens, e.g., for $Ge_2Sb_2Te_5$, where Te atoms reside on one sublattice

of the rock salt structure, while Ge and Sb as well as vacancies occupy the other sublattice. [15] Irrespective of the details in which the crystal symmetry is reduced, a gap in the electronic band structure starts to open. While this short discussion may make plausible why crystalline PCMs are poor conductors or small band-gap semiconductors at ambient conditions, it does not yet explain why the band gap opens up substantially more when they disorder.

The first plausible explanation as to why PCMs are special was given by Kolobov *et al.* in 2005 [5]: Unlike most materials, which have similar local order in the glassy and the crystalline phase, they found that the coordination of Ge atoms is tetrahedron like in the disordered phase of PCMs, while its local coordination in the crystalline phase is octahedral. The transition from one local coordination to the other was called the umbrella flip. Due to the umbrella flip, the number of neighbors that germanium has in the glass matches the number of its valence electrons (as is the case, e.g., for C in insulating diamond), whereas in the crystal, those numbers differ (as for C in conducting graphite). While counting the number of electrons of a single atom in an alloy is insufficient to ascertain its conductivity, it may yet provide some intuitive guideline. A more rigorous quantitative analysis certainly requires a full band structure calculation, as done, by Welnic *et al.*: [6] They set up a crystalline (spinel) structure mimicking the suggested local order of ternary PCMs and found that the coordination change on Ge induces the anticipated dramatic band gap increase. Thus, Welnic *et al.* have shown that a change in local structure as anticipated

by Kolobov [5] can indeed increase or open the electronic gap and renders a semimetal into a semiconductor.

Despite its appealing simplicity, the umbrella flip model cannot explain PCM behavior at large: Various alloys consisting of group V and group VI elements, such as $Sb_2Te_{3-x}Se_x$ [16] and Sb_xSe_{100-x} [17,18] show typical phase change behavior. Yet no group IV element is present, which would be required for the umbrella flip. This calls for an alternative or more generally formulated explanation of PCM behavior.

Recent theoretical approaches to PCM behavior [19–21] are based on the concept of resonant bonding which was adopted for solids by Lucovsky and White [22]: They suggested that the stark contrast in the dielectric constant of some semiconductors between their crystalline and amorphous phase, in particular that of IV-VI binaries or group-VI elemental solids, is due to the presence of resonance bonding in crystals and its absence in glasses lacking long-range order. Wuttig *et al.* [19–21] extended these ideas to PCMs and demonstrated that the dielectric constant of ordered PCMs distinctly exceeds that of disordered PCMs, even after the contribution of the conducting electrons had been subtracted off.

In the present context, it may be interesting to note that not only the dielectric properties but also mechanical transport properties can differ between crystalline and amorphous phase change - or related - materials: Quasi-circular Sb nano-particles (which tend to be amorphous - as opposed to the distinctly non-circular crystalline Sb nanoparticles [23]) glide essentially frictionless on graphite

surfaces in ultra high vacuum while crystalline particles show much enhanced static friction [24]. The latter, however, should pin less easily than their amorphous counterparts provided that local order and chemistry are similar [25]. This implies that the local order must sometimes differ between amorphous and crystalline in small band gap semi-conductors/metals - even when group-IV elements are absent.

A striking difference between the umbrella flip and the resonance bonding model are the specific features of the changes in the structural motifs between crystal and glass. However different the details of the mechanism behind the resonance bonding and the umbrella flip models may seem at first sight, one could argue that there is a unifying scheme behind both: Each time the crystal appears to have larger local symmetry than the glass. For example, resonance bonding can reduce a (predominantly) bimodal distribution of bond lengths to a unimodal one, be it, for instance, in the famous case of benzol or the example given for resonance bonding in figure 5 of Ref. [19]. Unfortunately, no specific local structural motifs for disordered group-IV-free PCMs have been suggested, which is one of the reasons why the focus in this work has been laid on Ge-containing PCMs.

In this paper, it will be demonstrated that the umbrella flip is a particular case of the well-known competition between ions and electrons [26–28]: Ions attempt to increase symmetry and thereby packing fractions, while electrons try to reduce symmetry and thus implicitly attempt to reduce packing fractions (potentially resulting in the formation of networks or even molecular solids) by opening up an electronic gap. Here, it will be shown in detail how this ion-electron competition drives the structural relaxation in both crystalline and glassy PCMs via the coordination change of group IV elements.

The reason why the competition between ions and electrons is particularly fierce when alloys consist of elements near tellurium and antimony is that these two elements are positioned in the periodic table of the elements (PTE), where (elemental) solids turn from being metallic to being insulators as one goes from the left to the right or the top to the bottom in the PTE. In addition, elements that are located near antimony in the PTE have flexible valency, e.g., the coordination of Sb changes easily between 3 and 5 involving an altered hybridization. The competition between ions and electrons can be visualized particularly easily when group IV elements are present, such as Ge, which can be either sp^2-hybridized when 3-coordinated or sp^3-hybridized when tetrahedrally coordinated.

This paper is organized as follows: The way in which symmetry reduction and pressure affect electronic gaps in crystalline materials will be sketched in section 2, mostly in terms of the tight binding model. In sections 3 and 4 numerical data on ordered and disordered PCMs will be presented, respectively. For the latter, unusual relaxation dynamics will be revealed. How pressure affects atomic and electronic structure of PCMs will be investigated in section 5 and it will be predicted which initially crystalline Ge-Sb-Te PCMs disorder upon densification and which ones order from an initially glassy state.

2 Elementary approach to the electronic structure in crystalline PCMs

In this section, the interplay of atomic and electronic structure in PCMs will be reviewed, in particular those that consist predominantly of Ge, Sb, and Te atoms. We feel that the recent theoretical discussion of PCMs has been largely concerned with providing a lot of quantum mechanical detail, but that many elementary, albeit instructive and thus useful considerations regarding PCMs have either not been made or been forgotten. In the sense of Eugene Wigner's famous quote, *"it is nice to know that the computer understands the problem. But I would like to understand it too"*, we want to provide a qualitative discussion at a much more elementary level than in Ref. [29], and support our arguments, which due to their simplicity are not always new, with simple, analytical calculations of one-dimensional model systems as well as with realistic ab-initio calculations. Overall, this work, in particular this section, is meant to foster an intuitive understanding for the investigated materials.

Rationalizing the atomic structure of solids from elementary principles, requires one to consider (i) atomic packing fractions, (ii) the octet or related rules, and (iii) electrostatic effects. The latter will be moderate in Ge-Sb-Te based alloys, because all three elements have similar electronegativity. Light atoms, such as silicon or germanium, tend to be a minority species in PCMs. For heavier atoms, it is important to realize that the degeneracy of the outer s and p electrons is increasingly lifted, i.e., one may consider the $5s$ electrons of Te and Sb to be core electrons that do not (significantly) contribute to chemical bonding and electronic conductance. One could thus argue that as far as the element Sb is concerned, one may rather be dealing with a sextet rule, $Z = 6 - N_p$, than with an octet rule, $Z = 8 - N_{sp}$. [30] Here Z is the number of (covalently) bonded neighbors while N_{sp} and N_p are the number of sp or p valence electrons respectively. Once the sextet rule is satisfied, those structures will have relatively large stability that have a high packing fraction, i.e., it will be beneficial to order the larger atoms on a closed-packed lattice and the smaller ones will occupy the sites with large volumes.

For many Ge-Sb-Te compositions, in particular those in which Te is the majority species, Te atoms occupy one sublattice of the simple cubic lattice (say the Cl positions of the NaCl structure), while Ge, Sb, and potentially vacancies occupy the other [15,31]. This ordering can be rationalized within quite simple geometric and electrostatic arguments. First note that the electron affinity of Te is 1.97 eV while those of Sb (1.05 eV) and Ge (1.25 eV) are noticeably smaller. As a consequence, Te will be negatively charged and thus its size be enhanced, while Sb and Ge will be positively charged and therefore have a reduced ionic radius. Like charges (as well as large spheres) will try to keep as far away from one another as possible, which - at fixed density - they can achieve by adopting a closed packed structure, e.g., face center cubic. Small ions can then occupy interstitial positions, in this case the Na sublattice in the rocksalt structure.

2.1 One-dimensional tight-binding model

Due to its importance in the present context, the effect that symmetry reduction has on the energy balance of non-interacting electrons will be reviewed. In addition to considering the effect of displacements, which are dealt with in standard text books [26,27], we will include the effect that chemical ordering has on the band structure in a mean-field approximation. The latter analysis shows in simple terms how ordering of atoms onto sublattices, as it happens for instance in the NaCl structure, can turn a metal into an insulator. This is easily done in the framework of the tight-binding approximation.

In addition to shedding insight on how symmetry reduction affects band structure, the following analysis will also allow us to rationalize the response of Peierls-distorted structures to pressure in section 2.2. A less qualitative and more quantitative analysis of the effect that pressure has on Peierls-distorted simple cubic structures was given by Gaspard *et al.* [30].

The one-dimensional tight-binding chain has much similarity with a one-dimensional elastic chain with nearest neighbor coupling. Its properties are quickly recapitulated here: A one-dimensional, mono-atomic linear chain with lattice constant a only has one acoustic branch and the wave numbers in the first Brillouin zone lie within $[-\pi/a, \pi/a[$. If we change either the mass of every other atom to another value or the spring stiffness of every other spring, then the system will double its lattice constant. The Brillouin zone (BZ) will only be half as large as before and there are now two branches that have zero slope at

the boundary of the BZ. Similar effects occurs in a tight-binding model for electrons, in which either every second on-site energy differs (chemical ordering), or bonds have alternating lengths (Peierls distortion), see Fig. 1.
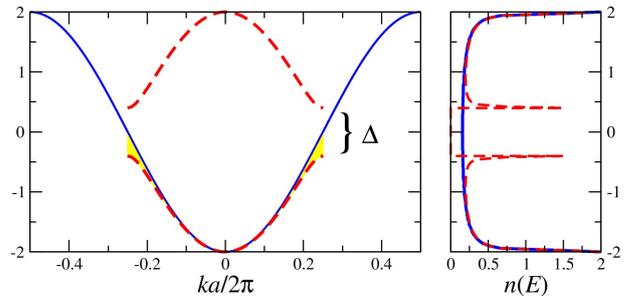

Fig. 1. Schematic representation of the effect that a symmetry reduction has on the dispersion, $E(k)$, in a one-dimensional chain and its effect on the density of states $n(E)$. Left: Solid (blue) and dashed (red) line represent the dispersion for a mono-atomic and di-atomic chain, respectively. The shaded (yellow) area is proportional to the electronic energy gained by the symmetry reduction. Right: Density of state for the diatomic chain.

The mean-field nearest-neighbor tight-binding Hamiltonian of a system with N pairs of atoms, e.g., Na atoms and Cl atoms on a line, can be written in real space as

$$H = \sum_{n=1}^{N} \left\{ \alpha_1 \Phi_1 \left(c_{n1}^\dagger c_{n1} - c_{n2}^\dagger c_{n2} \right) \right.$$
$$+ (t + \alpha_2 \Phi_2) \left(c_{n1}^\dagger c_{n2} + c_{n1} c_{n2}^\dagger \right)$$
$$\left. + (t - \alpha_2 \Phi_2) \left(c_{n2}^\dagger c_{n+1,1} + c_{n2} c_{n+1,1}^\dagger \right) \right\} \quad (1)$$

Here $c_{n\alpha}^\dagger$ is a creation operator for an electron in molecule or unit cell n. The index α enumerates the basis atom. $c_{n\alpha}$ is the corresponding annihilation operator. Φ_1 is an order parameter indicating to what extend the two molecules have separated onto sublattices, while Φ_2 is the average

value for the Peierls distortion, or in other words, twice the average difference between long bonds and short bonds. α_1 can be associated with the (differential) electronegativity. t is a tunneling amplitude for the electrons to hop from one atom to its neighbors when no Peierls distortion occurs. α_2 indicates how quickly t changes with bond length. In leading order, the dependence of the tunneling parameter on the bond length will be linear, which motivates the linear dependence of the hopping term with the order parameter in the mean field solution.

The Hamiltonian can be block diagonalized with the Fourier transform. For each (integer) wave number q, one can represent the block elements $\tilde{h}(q)$ as a $[2 \times 2]$ matrix:

$$\tilde{h}(q) = \begin{bmatrix} \alpha_1\Phi_1 & (t+\alpha_2\Phi_2)e^{-2\pi iq/N} + (t-\alpha_2\Phi_2)e^{2\pi iq/N} \\ \text{c.c.} & -\alpha_1\Phi_1 \end{bmatrix}, \tag{2}$$

where the (2,1) element of the matrix is the complex conjugate (c.c) of the (1,2) element. The eigenvalues of this matrix then are

$$E_{1,2} = \mp 2\sqrt{t^2 \cos^2\left(\frac{\pi q}{N}\right) + \alpha_1^2\Phi_1^2 + \alpha_2^2\Phi_2^2 \sin^2\left(\frac{\pi q}{N}\right)}. \tag{3}$$

In leading order, the gap that opens up at $q = N/2$ for half filling thus is

$$\Delta = 4\sqrt{\alpha_1^2\Phi_1^2 + \alpha_2^2\Phi_2^2} \tag{4}$$

and the electronic energy gained per particle at half-filling, ΔE_{HF} becomes

$$\Delta E_{\text{HF}} = \frac{1}{\pi/2} \int_{q=0}^{\pi/2} dq \left\{ E_1(q, \Phi_1, \Phi_2) - E_1(q, 0, 0) \right\}, \tag{5}$$

$$= -\frac{\alpha_1^2\Phi_1^2}{2\pi} \ln \frac{\alpha_1^2\Phi_1^2}{43.493t^2} - \frac{\alpha_2^2\Phi_2^2}{2\pi} \ln \frac{\alpha_2^2\Phi_2^2}{5.887t^2} + \cdots \tag{6}$$

where E_1 is the negative root from Eq. (3). The coefficients in Eq. (6) were obtained numerically from the data that is shown in Fig: 2.
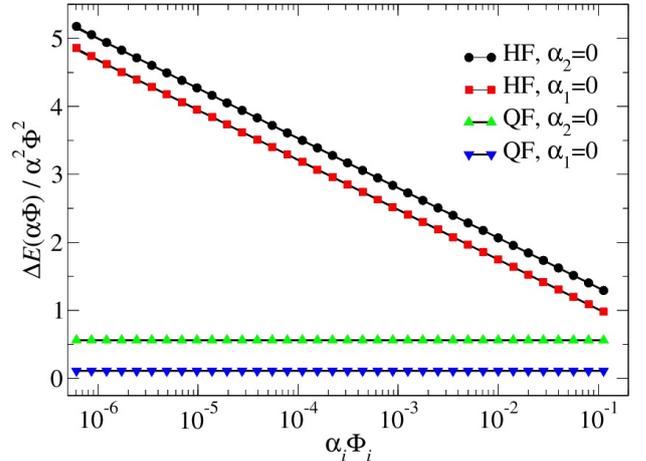

Fig. 2. Gain in energy (normalized by the square of the order parameter) due to ordering as a function of the order parameter. (Black) circles and (red) squares refer to half filling, while (green) triangles up and (blue) triangles (down) stand for quarter filling. HF and QF stand for half and quarter filling respectively. Lines represent data obtained via Eqs. (6) and (8).

An interesting aspect of Eq. (6) is that the energy gain is essentially quadratic in the order parameter, but that there is a prefactor that is logarithmic in the squared order parameter. This prefactor will make sure that the electronic contribution will always dominate the ionic contribution at small values of Φ_i, because in leading order, the ionic energy increases quadratically with the order parameter, i.e.,

$$\Delta E_{\text{ion}} = \frac{1}{2} \sum_{i=1}^{2} \beta_i \Phi_i^2 + \cdots \tag{7}$$

Here, β_2 can be interpreted as a spring or force constant related to the interaction between core ions, while β_1 is

essentially the (electrostatic) energy difference between a perfectly ordered and disordered arrangement of ions. Note that the sign of β_1 is not necessarily positive, e.g., when the ions have differing charge, Coulomb interactions will be minimized when different species are placed in an alternating fashion, so that a negative value of β_1 is to be expected. Conversely, β_2 should generally be positive, as the positive core ions repel each other with Coulomb potentials, which have positive curvature for like charges.

Due to the fact that ΔE_{ion} only increases quadratically with the order parameter, the considered, one-dimensional systems are unstable against a Peierls distortion and/or against ordering of chemical species onto sublattices within the tight-binding approximation. In other words, equidistant spacings in the linear chain are symmetry forbidden (zero temperature, classical ions) for half-filled systems due to the functional dependence of ΔE_{HF} on the order parameters, no matter how large β_i. Similar comments apply to the tripling of the lattice constant if the band is filled by one third or two third, etc., but energy reduction due to an increase of the linear size of the elementary cell is generally largest for half-filling [26]. Note, however, that equi-distant spacings in a (periodically repeated) chain can be recuperated when electron correlation can no longer be neglected and/or when the system is finite as for example in the case of a benzol ring, which adopts a resonant structure.

When the tight-binding chain is not at half-filling, the functional dependence of ΔE on the order parameters be-

comes simply quadratic, for example, at quarter filling:

$$\Delta E_{\mathrm{QF}} = -0.5611\alpha_1^2\Phi_1^2 - 0.11094\alpha_2^2\Phi_2^2 + ... \qquad (8)$$

Thus, when the systems are not at half-filling, it becomes a question of prefactors if the ions manage to establish symmetry or if the electrons keep the upper hand and break it. The logarithmic divergence of the prefactor in Eq. (6) also disappears for systems with dimensionality D greater than one, because the relative weight of the van Hove singularity becomes smaller in higher dimensions. In $D > 1$, it thus becomes again a question of prefactors if ions or electrons prevail.

Of course, the current model analysis cannot be used to make specific predictions on ordering in solids, e.g., when trying to ascertain what type of ordering onto sublattices occurs in higher dimensions. For example, determining which of the 36 possibilities [32,33] will be taken to Peierls distort away from the simple cubic lattice to another structure is a question of the number of valence electrons (halogens generally only form one short covalent bond per atom) and materials specific parameters: Heavy group V elements form three short bonds, while nitrogen with essentially degenerate s and p electrons, only forms one short bond in its cubic Pa3 phase [34,35], which may also be interpreted as a Peierls distorted simple cubic structure.

At the end of this section, it may be interesting to note that the only elemental solid with simple cubic structure at ambient conditions is polonium [36], which does not have a half-filled p-shell. Conversely, the elemental solids

formed by As, Sb, or Bi, all having half-filled p-shells, are all Peierls distorted at ambient conditions.

2.2 Effect of pressure in the tight-binding model

In this section, we will focus on the question of how pressure affects the Peierls distortion, which will be much more dramatic than the effect it has on ordering of elements onto sublattices. The rational is that β_1 cannot be expected to change signs. Thus ordering different chemical species onto sublattices will stay beneficial at large pressures.

Pressure increases the density and thus reduces bond lengths. This will affect the numerical values for the ion-related coefficient β_2 as well as the electronic coefficients t and α_2. The latter two terms may be expected to increase exponentially with decreasing bond length but to remain finite, while α_1 is an atomic property that should not depend on pressure. Conversely, β_2 is dominated by the Coulomb potential, which diverges at small separation. Upon densification one should thus expect β_2 to increase more rapidly in magnitude than the electronic terms and to become dominant.

Given the relatively rapid increase of β_2 with density, the ionic term must ultimately dominate the electronic one and consequently, the Peierls distortion will be squeezed out. For example, the group V elements P, As, Sb, and Bi, [37] become simple cubic under pressure. Likewise, density-functional calculations indicate relatively high stability of simple cubic structures for elemental sulfur [38] and tellurium [39] under pressure.

3 Electronic structure in crystalline PCMs

In this section we will analyze in more detail two important consequences of the analysis from section 2.1: (a) The reduction in electronic energy with increasing order parameter (be it Peierls or ordering) is largest when the systems are at half filling (in their hypothetical simple cubic reference state) upon doubling their periodicity, see Fig. 1. (b) The ordering of chemical species onto sublattices opens up a gap in the electronic density of states. For reasons of accuracy, it may be necessary to note that the opening can be incomplete for small order parameters, for example, in dimensions greater than one and/or in the presence of electronic couplings beyond nearest neighbors.

3.1 Electronic structure of GeTe-VacSb$_2$Te$_3$ and Sb-VacSb$_2$Te$_3$

What can we learn from consequence (a) mentioned in the previous paragraph? From an electronic point of view, it is energetically most beneficial for a simple-cubic system to have three p valence electrons per lattice site, where spin was implicitly allowed for. For the pair GeTe, each atom contributes on average three electrons, but the unit Sb$_2$Te$_3$ contributes three too many electrons for the sextet rule. Within the simple counting scheme, the desired balance can be reestablished if one vacancy (Vac) is introduced per Sb$_2$Te$_3$ unit. A well-relaxed $(GeTe)_{1-x}(Sb_2Te_3)_x$ crystal should thus approximately correspond to $(GeTe)_{1-x}$ $(VacSb_2Te_3)_x$. It may be tempting to compare this rule to simulation results of the formation energy of vacancies

such as those presented in figure 2 of Ref. [40]. Such a comparison, however, may not be unambiguous unless the calculations are done such that only the number of vacancies is varied at fixed stoicheometry of the real chemical constituents.

In order to shed more light onto the band structure of $(GeTe)_x(VacSb_2Te_3)_{1-x}$, let us consider a system of 58 atoms (14 Ge, 12 Sb, 32 Te) plus 6 vacancies, which were all randomly placed onto a simple cubic lattice. In our counting scheme, the system is at half filling as there are 18 more Te than Ge atoms, which are compensated for by six vacancies. Without any ordering onto sublattices, neither s-band nor p-band break up into sub-bands and the density of states (DOS) is large near the Fermi energy, as can be seen in Fig. 3. s- and p-bands still do not break up when the lattice is allowed to undergo local (thermal) distortions. However, once Te atoms are brought onto one sublattice and Ge and Sb atoms as well as vacancies onto the other sublattice, a deep dip occurs in the DOS close to the Fermi energy, in agreement with the reasoning that mainly bonding and no anti-bonding p-orbitals are occupied if for each 3 Te atoms exceeding the number of Ge atoms, one vacancy is introduced. (Remember that excited states are not reliable in DFT, but that trends in the DOS can be ascertained. Also, finite size effects due to disorder will be large for systems containing only 58 atoms.)

Introducing stoichiometric vacancies via the nomenclature $(GeTe)_x(VacSb_2Te_3)_{1-x}$ is in contradiction to a conclusion from Matsunaga *et al.* [31], who argued that the number of vacancies should be $x/(1 + 2x)$. (We may
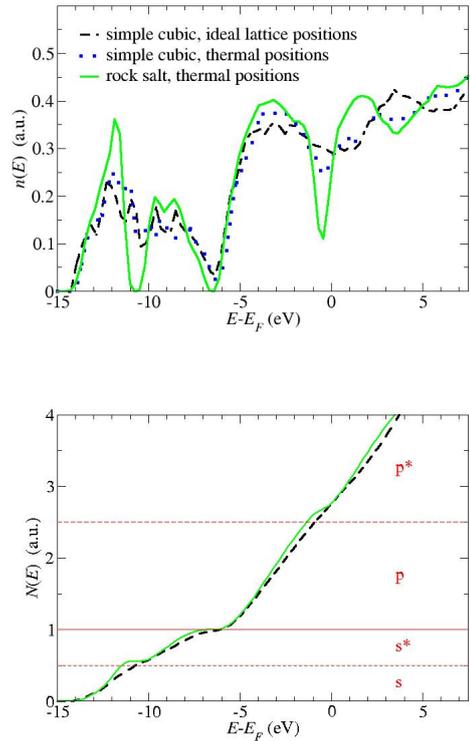

Fig. 3. (a) Electronic density of states $n(E)$ as a function of energy E for $Ge_2Sb_2Te_5$ under different constraints. Long-dashed (black) line: Different atoms and vacancies are placed randomly onto ideal, simple cubic lattice sites. Dotted (blue) line: Atoms are allowed to move away from ideal lattice positions. Solid (green) line: Te atoms occupy one sublattice, all other species occupy the other sublattice. (b) Integrated density of states $N(E) = \int n(E) \, dE$ as a function of energy E. Vertical straight (red) lines are drawn to separate bands that are dominated by s or p electrons, while vertical broken (red) lines roughly separate bonding from antibonding (*) orbitals.

have misunderstood the notation in Ref. [31] though). Differences may be subtle at small values of x, but for $x \to 1$ there can be a factor of up to three between the two results. We would still like to support our rationale with the following reasoning (and the arguments at the

end of this section): If one considers Sb_2Te_3 crystals, then it is possible to see that these structures are layers with strong (short) bonds within one Te-Sb-Te-Sb-Te unit and long bonds between two subsequent repeat units. [41] One could now make the case that the vacancies have condensed into the layer containing the long bonds, so that there would be one layer of vacancies for each Sb_2Te_3 slab.

We would like to conclude this section with a qualitative, graphical discussion of the number of vacancies in Sb-rich $Sb\text{-}Sb_2Te_3$. The considered compounds try to open the electronic gap predominantly via a Peierls distortion rather than by ordering of chemical species onto sublattices. For the sake of simplicity, let us reduce the dimensionality of the system from 3 to 2 and accordingly the number of valence electrons and degenerate valence states by one p-electron. In addition, we need to replace the sextet rule with a quartet rule, as we have dropped the number of degenerate valence states by one. When counting the number of atoms and electrons represented in Fig. 4, one can ascertain that it is necessary to introduce one vacancy for each pair of excess electrons in order to maintain the quartet rule. Generalization to 3 dimensions and 3 degenerate p-orbital states would make it necessary to compensate each 3 excess electrons with 1 vacancy, as suggested in the $(GeTe)_{1-x}(VacSb_2Te_3)_x$ nomenclature. Of course, the precise number of vacancies will be effected by additional system-specific energy and entropy arguments, for example it seems particularly beneficial to eliminate Ge-Te and Sb-Te bonds in Ge-Sb-Te compounds [40], but the current counting scheme should give at least a semi-quantitative guideline for the vacancy count.
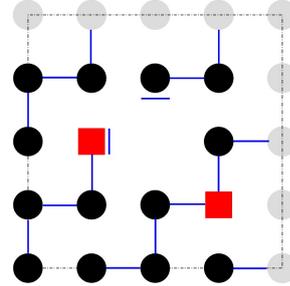

Fig. 4. Schematic representation of chemical bonding in a Peierls distorted system that contains predominantly atoms providing two valence electrons (black circles, to be associated with Sb atoms), two atoms each providing three valence electrons (red squares, to be associated with Te atoms), and one vacancy. Shaded, grey circles indicate periodic images of atoms. Thick blue lines represent short bonds or lone electron pairs on atoms. In the picture, one circular atom right next to the vacancy would have a formal negative charge, i.e., the circle with the lone electron pair, while one square atom would have a formal positive charge, i.e., the square without lone electron pair.

Given the formal charges that one may assign to atoms in Fig. 4, it is tempting to speculate that Te atoms tend to be located with increased probability next to a vacancy. This local structure would allow atoms to retain a zero formal charge. Conversely, if Te does not sit right next to a vacancy it will have a formal positive charge, which would not be particularly beneficial, because of Te's relatively large electron affinity. Specifically, in Fig. 4 it would appear energetically beneficial to swap the round atom with one lone pair (representing a negatively charged Sb

atom) with the square atom without lone pair (representing a positively charged Te atom). The current analysis thus predicts that vacancies should be generated predominantly close to Te atoms. An additional phenomenological argument for why Te should prefer to sit close to vacancies is that their slightly negative charge makes them have a larger effective radius, which induces an enhanced need for free volume. Due to the "nearsightedness" of chemistry [42] one may argue that similar statements hold when the systems are not exactly at half filling. Indeed *ab-initio* calculations of GeTe [43], $Ge_1Sb_2Te_4$ [40], and $Ge_2Sb_2Te_5$ [44] demonstrate that (also non-stoichiometric) vacancies preferentially sit close to Te.

3.2 Electronic structure of Sb and $Ge_{0.15}Sb_{0.85}$

While the quantitative analysis of the last section was mainly concerned with the electronic DOS of systems that are trying to open their gap with ordering of chemical species onto sublattices, we will now focus entirely on Peierls distorted systems. We start with the well-known analysis of the DOS of pure Sb both in its hypothetical simple cubic reference as well as in the Peierls distorted simple cubic phase, see Fig. 5. While similar analysis have been published before, e.g., in Refs. [39,45], it might be interesting to recalculate the data with the approaches used for this and our previous work [29].

It is interesting to note that the effects discussed in the theory section on the one-dimensional tight-binding model, are borne out much more clearly in Fig. 5 than in Fig. 3. An important reason certainly is that in the
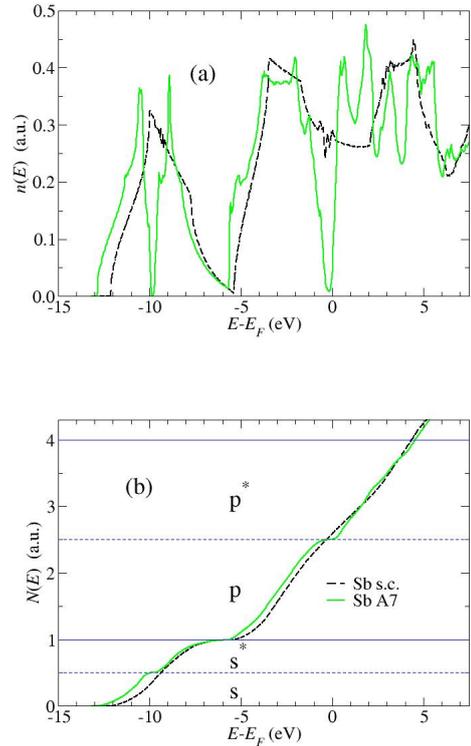

Fig. 5. (a) Electronic density of states, $n(E)$, of pure Sb and (b) integrated DOS, $N(E) = \int dE\, n(E)$. Dotted (black) lines refer to a hypothetical simple cubic reference phase at the experimental density while the solid (green) lines represent the Peierls-distorted A7 structure.

latter case, lines are smearing out due to the finite size of the disordered system and that k-point sampling does not lead to a better representation of the disorder.

The DOS of crystalline $Ge_{0.15}Sb_{0.85}$, which will be shown in the next section, is similar to the one of pure Sb. The main difference is that the gap due to the Peierls distortion is opening up below the Fermi energy, which is indicative of $Ge_{0.15}Sb_{0.85}$ being a hole conductor.

4 Disordered PCMs

4.1 Computational methodology

The computational aspects of this work are predominantly concerned with the post analysis of molecular dynamics simulations, which were presented in Ref. [29]. This post analysis is motivated by the author's partial disagreement with some interpretations given in Ref. [29]. (Publishing with many co-authors sometimes makes compromising necessary if one wants to see one's own ideas and results disseminated within reasonable time scales.) Details of the MD simulations, whose accuracy the author does not doubt, can be found in Ref. [29].

The post analysis was done with the plane-wave Quantum Espresso [46] and Abinit [47,48] packages. The exchange correlation was approximated with the BLYP density functional [49,50] and Troullier-Martins type pseodopotentials were employed [51].

4.2 Effect of umbrella flip on electronic structure

This section will be concerned with the question of how an isolated umbrella flip [5] affects the electronic structure of a solid whose original local structure is that of the ordered phase. As mentioned in the introduction, Welnic et al.: [6] demonstrated that the local umbrella flip of a Ge atom into the tetrahedral position indeed increases the electronic gap. Intuitively, one would have expected that the main change in the electronic charge density would be associated with the germanium atoms, as they would usually be expected to adopt an sp^3 hybridized state. How-

ever, in their calculation of a spinel model crystal with composition $GeSb_2Te_3$, Welnic et al. found that the hybridization changed more strongly on Te and Sb atoms than on Ge atoms. In contrast, Shakhvorostov et al. [29] confirmed the expected hybridization change on some Ge atoms for a fully relaxed structure of a quenched Ge-Sb liquid. Already Akola and Jones [52] had found that the $\approx 33\%$ sp^3-bonding Ge atoms can be made responsible for the narrowing of the π-band in amorphous $Ge_2Sb_2Te_5$ and the reduced weight of the density of states near the Fermi level in the disordered phase. At this point, I do not intend to claim that the changes in the DOS near the Fermi energy are (always) responsible for the contrast in optical and electric properties between ordered and disordered PCMs and that other effects, in particular Anderson localization are not of relevence. These issues can be material dependent.

In the following, Shakhvorostov et al.'s result will be used as starting point for our working hypothesis, namely that many Ge atoms adopt an sp^3 configuration when moving to its tetrahedral symmetry site and discuss how the electron count presented in Fig. 4 needs to be modified for this particular local configuration change. This picture implies that the 4s-electrons of Ge should no longer be considered core but valence electrons. For the heavier Sb atoms, let us keep considering the outer s electrons to be core electrons. Using these assumptions, I will speculate on the implications of the umbrella flip on the electronic structure.

For the sake of simplicity, let us furthermore assume that the crystal of consideration is Peierls distorted and close to half filling in its simple cubic reference state, e.g., an Sb crystal with a few Ge impurities. (Crystals such as cubic $Ge_2Sb_2Te_5$ would have to be interpreted within a resonance bond picture to satisfy the sextet rule, which in the present context is rather tedious.) The Ge-doped Sb crystal, when Peierls distorted, would be considered a hole conductor, because all Sb atoms contribute as many valence electrons as they have covalently bonded neighbors, while each Ge contributes one less electron, resulting in one hole per Ge. When the umbrella flip occurs, one additional bond between Ge and Sb is formed. The required electrons to form this bond are provided by the increased number of valence electrons, which come from the hybridization change of Ge. In this scenario the number of holes thus remains unchanged. In a real-space description, the hole (formally) moves from Ge, which is now sp^3-hybridized, to the Sb atom. The Sb atom is now trying to grasp on to the umbrella flipped Ge atom, for which it has to (partly) deploy electrons from already existing bonds. Similarly, when a Ge atom undergoes an umbrella flip in the vicinity of a Te atom, the original hole on the Ge and the original excess electron on Te would combine, leaving the balance of holes and excess charges per atom unaltered. This concept is consistent with the large changes in the electronic charge density on Te and Sb atoms found by Welnic *et al.* [6]. Lastly, when two Ge atoms bond there is one s-electron pair in excess, and the alloy may move away from half filling. It may be that for each three such

processes, the alloy is trying to create one vacancy, though this appears difficult in the solid phase. Of course, the current analysis cannot make any claims on the degree with which excess electrons and/or holes are localized near the atoms to which they were formally assigned.

When the "umbrella flipping" Ge atom grasps on to another Ge atom, then a new situation arises: Now it is possible that both atoms bring their s-electrons up to (formally) being valence electrons, which would be a mechanism to eliminate holes. Other possibilities to eliminate holes would be the formation of low-coordinated atoms, as they are found relatively frequently in liquid phases of Ge-Sb-Te compositions [53]. Despite the occurrence of a few "under-coordinated" atoms and Ge-Ge bonds of sp^3-hybridized Ge atoms, the most dramatic differences in the local structure between glass and crystal can be associated with the umbrella flip. Therefore, it will be meaningful to interpret changes in the electronic DOS predominantly in terms of the umbrella flip.

The electronic DOS of the glassy and the crystalline phase are compared in Fig. 6. One can notice that the electronic energy decreases with increasing disorder. This concerns in particular the s-electrons at the left end of the s-band. This effect can be taken as an indication that these electrons now participate in the bonding. Interestingly, the plateau indicative of the Peierls distortion in the crystal at $N(E) = 0.5$ has disappeared in the glassy phase.

In the further discussion of Fig. 6, let us assume that the dip in the electronic DOS near the Fermi energy, E_F, is underestimated in the DFT calculation, potentially be-
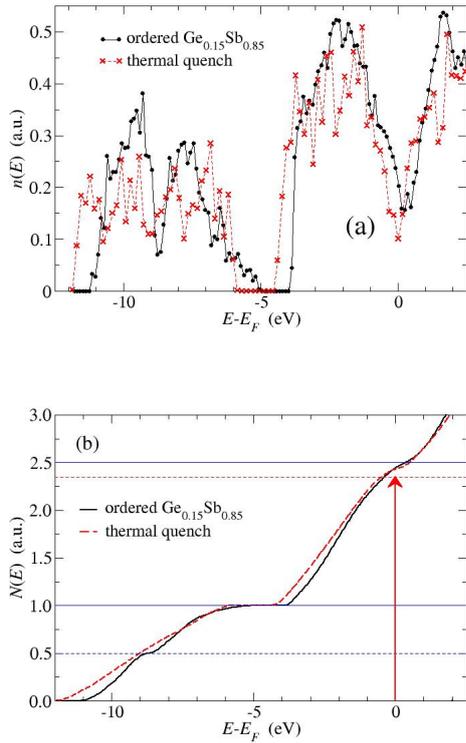
Fig. 6. (a) Electronic density of states, $n(E)$, of eutectic Ge-Sb and (b) integrated DOS, $N(E) = \int dE\, n(E)$. Solid (black) lines and circles refer to ordered alloys, while dashed (red) lines and crosses stand for alloys that were quenched from high to room temperature.

cause of the finite size of our system. In this sense, I would like to argue that the states left of the dip as p-valence band while those right to the dip belong to the conduction band. In this picture, crystalline eutectic Ge-Sb would be a hole conductor as the dip is located to the right of E_F: In the crystal, the slope in $N(E)$ is smallest near $N(E) = 2.5$, while due to the 15% Ge atoms, states are only occupied up to a value close to $N(E) = 2.5 - 0.15 = 2.35$. It seems plausible that the dip in the electronic DOS is shifted to the left, due to low-coordinated atoms and Ge-

Ge bonds. Moreover, the dip has become deeper, owing to the umbrella flip, as one may conjecture from Welnic *et al.*'s work [6].

4.3 Relaxation in Ge$_{0.15}$Sb$_{0.85}$ glass

When a liquid is supercooled, the common point of view is that the fluid structure becomes kinetically arrested during the quench so that the relaxation toward the solid does not take place on the relevant experimental time scales. In this section, I would like to argue that this view is not appropriate for the structural relaxation in disordered PCM alloys. Instead, it seems as though the glass relaxes *away* from the crystal, or in other words, the local structure in the liquid is closer to the local crystalline structure than that of the glass, which may be a new paradigm for relaxation in glassy systems. Conversely, the metal-insulator transition itself follows the well-known trends from the Peierls distortion, by which a structural change, such as the umbrella flip [5,6,54], induces a change in the band gap. Due to this argument, the claim in Ref. [29] that *the electronic driving force behind the phase change has the potential to change the interconversion paradigm in this material class* appears to be a gross overstatement.

In order to understand that the Peierls scenario applies on a qualitative level, let us examine the individual contributions to the net energy for the various structures in table 1: At ambient conditions (meaning temperature and density taken at the experimental density of eutectic Ge-Sb), the glass has a much reduced electronic energy and a much increased ionic energy as compared to the (already)

Table 1. Comparison of electronic, ionic, and total energies (all in eV) for a $Ge_{0.15}Sb_{0.85}$ system consisting of $N = 192$ atoms at different volumes per atom (in $\mathring{A}^3$). The ionic contribution contains the ion-ion interaction and the coupling to a constant-density and charge-neutralizing background. The ambient crystal is taken as reference.

system	electronic	ionic	total	V/atom
liquid, 973K	-25.32	25.67	0.348	29.64
annealed glass	-25.00	25.22	0.222	29.64
regular crystal	0.00	0.0	0.000	29.64
stretched crystal	-12.20	12.53	0.323	38.47
stretched glass	-20.51	20.74	0.231	38.47

Peierls-distorted crystal. This is exactly the same competition as for a regular Peierls instability: The electronic energy is decreased (and consequently the gap increased) at the expense of the ionic energy. Although a symmetry-argument, which is usually required for the Peierls distortion to be invoked, cannot be used in a straight-forward manner, it seems obvious that the creation of a tetrahedral Ge atom eliminates most previously allowed (local) symmetry transformations without adding new ones. (See also the first-principle work on reentrant Peierls distortions in liquid GeTe by Raty et al. [54]) Furthermore, it is not clear why electrons would only try to remove the degeneracy of occupied and unoccupied states at the Fermi energy, when the degeneracy is due to symmetry rather than accidental.

It may be important to mention that the ionic energies listed in table 1 contain the electrostatic energy of core ions with four elementary charges for Ge and five for Sb, within a neutralizing and homogeneous background. The latter only accounts for a constant offset that is independent of the ionic configuration. A more meaningful estimate of "true" ionic energies can be obtained by assigning more meaningful partial charges for the atoms. For an order-of-magnitude calculation, let us use the Bader ionic charges listed in figure 15 of Ref. [44], which are a little less than a factor of ten smaller than the "naked" charges. This would renormalize the estimates for the ionic energy differences by a little less than a factor of 100, e.g., at a volume of 29.64 $\mathring{A}^3$/atom, the ionic energy of the glass is a little more than ≈ 0.252 eV higher than that of the crystal. This in turn implies that the "true" electronic energy must have changed in a rather undramatic way given the 0.222 eV net difference between the two phases, which is consistent with frequently observed subtle differences in the electronic DOS between ordered and disordered PCMs.

It may also be worth investigating the relaxation dynamics that follows a simulation in which a crystal was stretched up to the point where it became unstable. This is done in figure 7. One can see that the ionic energy increases as a function of time (at fixed density!), while the electronic energy descreases. Thus, the ions must be adopting a structure which is less homogeneous and/or less closed packed and thus, the relaxation is driven predominantly by the electrons. In fact, there is an almost perfect correlation of the electronic energy with the net energy and anticorrelation with the ionic energy, as one

would expect from a Peierls-like scenario. Note that a similar relaxation scenario should also apply if the the presence of valence bonding in the crystal and its absence in the glass were the main distinguishing features between the ordered and disordered compounds.
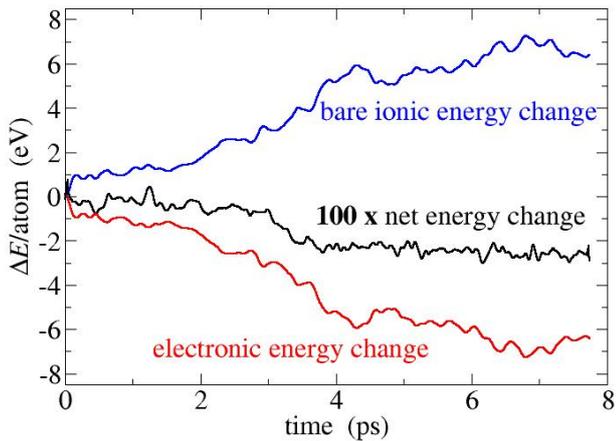

Fig. 7. Time dependence of ionic and electronic energy at fixed density after a stretched crystal became unstable and disordered.

Despite many similarities with a regular Peierl's instability, we suggest that the following three differences may be important when rationalizing the metal-insulator transition in PCMs: (a) There is an energy barrier that a Ge-atom has to overcome in order to move into the tetrahedral position, so that structural changes must be discontinuous, unlike those in the linear tight-binding chain, in which the atoms can move continuously. (b) The number of electrons that are involved in the formation of chemical bonds has changed through the umbrella flip. (c) When holes are present in the crystal (e.g. in Ge-Sb-Te when the Te-concentration exceeds that of Ge), chemical bonds

need to be eliminated in order to eliminate holes and to open up the gap.

When the glass is reached via tensile loading, see section 5, the eutectic Ge-Sb remains metastable up to $p = -4$ GPa, where each atom occupies on average a volume of 38.47 Å^3. At the corresponding density, the glass has again the lower electronic energy. Similarly, the ionic energy is again much enhanced in comparison to the metastable crystal, as can be seen in table 1. It is also interesting to note that the low-density crystal has the larger ionic energy than the high-density crystal. This is consistent with the discussion in section 2.2, where it was argued that electrons "win" at small densities while ions keep the upper hand at high pressure.

Lastly, it is interesting to compare the high-temperature liquid to the glass at ambient temperatures. From a purely energetic point of view, one might argue that the alloy has relaxed toward the crystal in both electronic and ionic energy. However, analysis of the structures bears an interesting observation [53]: At 973 K, the number of 4-coordinated Ge atoms in eutectic Ge-Sb is just a little below 50% versus 0% in the crystal and close to 70% in the room-temperature glass. Along the same lines, the number of three-coordinated Ge atoms (three short and six long bonds) in the crystal is 100%, which decreases to just above 40% in the 973 K melt and further to less than 30% in the relaxed glass. In these coordination statistics, the glass appears to relax away from the crystal to a different structure, in which the Ge atoms have different coordination than in the A7 structure.

5 Response of PCMs to pressure

When PCMs are compressed at ambient temperature, it is possible to observe amorphization of crystalline compounds, as is the case for $Ge_2Sb_2Te_5$ [55,56], while another PCM, namely $Ge_{0.15}Sb_{0.85}$ [29], undergoes a transition from amorphous to crystalline upon densification. In this section, I would like to discuss what leads to this different behaviour. Both types of behaviour can be understood in reasonable detail from simple free-volume type considerations.

If a compound contains stoichiometric vacancies, such as crystalline $Ge_2Sb_2Te_5$, is compressed, then its vacancies are going to be squeezed out before other processes occur [29]. A more refined picture was given by Cavarati *et al.* [56], who found that Te atoms preferentially fill the voids and that the umbrella flip is not induced through the densification. This behavior is easily rationalized within the developed picture: Te atoms are negatively charged, thus have the largest radius, and hence the largest need for free volume when pressure raises.

When vacancies are being squeezed out, new bonds are formed, which moves the system away from being half filled in the original reference structure, which implies that a doubling of lattice constant via Peierls or ordering no longer opens a gap at the Fermi level. Consequently, the number of electrons in the conduction band has increased after pressurization and the disordered system has enhanced conductivity.

Why does eutectic Ge-Sb respond different to pressure than $Ge_2Sb_2Te_5$? When no stoichiometric vacancies are present new mechanisms will be required to accomodate external pressure. Central to the reasoning presented here will be the coordination of Ge: The tetrahedral site has much smaller free volume than the (distorted) octahedral site. As a consequence, large pressures should make the Ge atoms favor the octahedral coordination while small or negative pressure should make the Ge atom move into the tetrahedral site. This is the reason why $Ge_{0.15}Sb_{0.85}$ does not behave the same way under pressure as $Ge_2Sb_2Te_5$ is that it contains no vacancies [29] and this is why the local order of amorphous Ge-doped Sb switches to the (local) order of crystalline Sb when the pressure is sufficiently high. Ref. [29] stressed Le Chateliers principle as an explanation for the phenomenon, which most certainly is an insufficient explanation: Many different solids, as diverse as silica, polyethylene, or regular metals, tend to have different densities in their glassy and amorphous phase, yet, they cannot be converted reversibly into one another at short time scales and room temperature via the application of tensile and compressive loads.

Central to the amorphous-to-crystalline transformation is the *local* structure of PCMs: If the umbrella-flip picture is true, then, as mentioned above, pressure will squeeze the Ge atoms from their tetrahedral coordination into the alternative octahedral location. The kinetics can be fast because the motion is quasi-displacive and non-cooperative. And the process can be reversed under tensile loads for the very same reason. These thoughts that follow in a natural fashion from Kolobov's results is what motivated me to initiate the pressure experiments on eutectic

Ge-Sb and not Le Chatelier's principle as falsely stated in Ref. [29].

As the crystal is lower in energy than the glass, the pressure-induced crystallization observed in Ref. [29] is irreversible for *positive* pressures, i.e., the crystal retains its long-range order after decompression to ambient conditions. In first-principle molecular dynamics simulations, it is easily possible to apply large tensile loads in the form of negative pressures. When this is done, the Ge atoms move back into the tetrahedral site and the system decreases its conductivity to similar values as those of thermally quenched fluids [29,53]. This means that including negative pressure, the system can be switched reversibly between being conducting and being insulating. It may be possible to achieve the required large negative pressure on very small scales, where materials tend to have larger hardness and toughness than on macroscopic scales.

If it were indeed possible to achieve the required positive and negative stresses at the nanoscale to switch PCMs, the question arises to what extent the materials would degrade, e.g., if the layered compounds would delaminate. After inspecting the structural evolution of the alloys during decompression, I would like to suggest that the systems are self-healing: The onset of delamination is required for the Ge atoms to find a tetrahedral site worth jumping into. Once the jump has occurred, the Ge atom moves the separating layers back together via strong sp^3 bonds.

This section will be concluded with a rule-of-thumb speculation on when pressure should lead to amorphization and when it should induce crystallization. Given the electron counts in the simple cubic reference phase of Ge-Sb-Te, the following rule should hold: If the the concentration of Te is higher than that of Ge, then vacancies will be present and crystals will become amorphous during densification. Conversely, when there are more Ge than Te atoms, amorphous compounds will crystallize under compressive stress. In the latter case, the process should be reversible, opening the possibility to switch PCMs via pressure.

6 Conclusions

In this paper, an attempt was made to rationalize the behavior of PCMs, in particular that of Ge-Sb-Te alloys, from elementary terms. This attempt shall be quickly recapitulated here. Starting point is the description of these solids from an undistorted simple cubic reference structure with random occupation of the elements on the lattice sites. From this reference structure, energy reduction during symmetry breaking is particularly large when the alloys are at half filling, i.e., if they create one vacancy for each three tellurium atoms in excess of germanium atoms. The symmetry breaking in the solid can be either a Peierls distortion in Sb-rich PCMs or ordering of species onto sublattices in compounds with large Te concentration. The symmetry breaking in the crystal opens up an incomplete or a small gap.

The developed picture allows one to argue that Te atoms like to sit close to vacancies as this makes them retain a neutral formal charge. Including charge transfer effects into the description (Te has slightly larger elec-

tronegativity than Ge and Sb) makes it plausible that Te atoms adopt a slightly larger radius, which enhances their need for free volume in comparison to that of Ge and Sb and thus makes these atoms move into the vacancies sites first when the pressure raises.

The main emphasis of this work, however, was laid on vacancy-free Ge-doped Sb and the umbrella flip of the Ge atom from its octahedral coordination in the crystal to the tetrahedral site in the glass. It was argued that this structural change does not move the alloys away from being the distorted structure of a formally half-filled crystal, as the outer s-electron of the Ge atom (or that of another group IV element) now participates more strongly in the bonding and thus provides the correct number of electrons for the newly created bond. Due to Ge now being in its natural coordination, the gap has opened up, or at least the DOS near the Fermi energy is reduced. Given that local structures differ between ordered and disordered Ge-doped Sb, it is doubtful that a comparison of participation ratios of electron near the Fermi energy is meaningful.

In this paper, it was also shown how the pressure-induced, amorphous-to-crystal transition in vacancy-free PCMs arises as a natural consequence from free volume arguments based on the umbrella flip picture: The group IV elements favor the larger (potentially distorted) octahedral coordination, while small or negative pressures bias in favor of the tetrahedral bonding. Using these arguments, it may be possible to fine tune the transition pressures via the atomic radius ratio of the group IV and group V elements composing the PCM.

Lastly, unusual relaxation dynamics were identified in the glassy phase of eutectic Ge-Sb: The number of four-coordinated Ge atoms increase with time and that of crystal-like three-coordinated atoms (three short and three long bonds) decreases. Likewise, ionic energy (which is minimized in crystalline Ge-doped Sb) *increases* with time (at constant density) as the glass ages. Thus, the local structures around Ge tend to become less crystal like with time, which may explain the relatively long life time of their amorphous state.

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