Amorphous structures of Ge/Sb/Te alloys: Density functional simulations

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Received XXXX, revised XXXX, accepted XXXX
Published online XXXX

Key words: Phase change materials, density functional simulations, Ge/Sb/Te alloys.

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Since their first development in the 1960’s, phase change (PC) memory materials have become essential components of optical memories (DVD-RW, Blu-ray Disc), ... used in countless households worldwide. They are now poised to play a decisive role in future non-volatile computer memories. PC memory materials are restricted to those with an extremely rapid and reversible transition between the amorphous and crystalline phases of an appropriate recording medium, and their development and optimization has been hindered by the inherent difficulties in determining amorphous structures.

1 Introduction

The era of phase change (PC) materials can be viewed as beginning with the much-cited paper of Stan Ovshinsky [1]. The 1960’s had seen a range of exciting developments concerning amorphous materials [2], and the second author heard seminars at Cornell University very soon after the publication of Stan’s work on resistive switching in semiconducting alloys. PC materials are based on the extremely rapid and reversible transition between the amorphous and crystalline form of nanosized “bits” in a very thin polycrystalline layer, whose states must show sufficient contrast in resistivity or optical properties to be identified. It is clear that most materials do not satisfy these criteria, and great efforts across more than 20 years were necessary to identify and develop appropriate alloys. The original paper discussed the alloy As₃₀Ge₁₀Si₁₂Te₄₈, and Te-based alloys have been well represented ever since.

Alloys of germanium, antimony, and tellurium (“GST” alloys) are among the most widely used in the above contexts, and there has been much speculation concerning their amorphous structures. Theoreticians were slow to appreciate the rich array of problems awaiting their attention, but the past few years have seen a dramatic change in this situation. Density functional calculations, which are generally free of adjustable parameters, have now been reported on numerous systems. We review here the information that has resulted about the amorphous structures of GST-alloys.

Since their first development in the 1960’s, phase change (PC) memory materials have become essential components of optical memories (DVD-RW, Blu-ray Disc), ... used in countless households worldwide. They are now poised to play a decisive role in future non-volatile computer memories. PC memory materials are restricted to those with an extremely rapid and reversible transition between the amorphous and crystalline phases of an appropriate recording medium, and their development and optimization has been hindered by the inherent difficulties in determining amorphous structures.
Central to our understanding of the properties of these materials is a knowledge of the structures of the different phases, but these are difficult to determine in binary or ternary alloys with significant numbers of vacancies. It was noted as late as 2005 that “the local structural order of glasses in the ternary system Ge$_x$Sb$_y$Te$_{1-x-y}$ is not well established” [6]. Even the structure of the metastable, ordered phase of GST is still open to question: Yamada [7] proposed that the metastable phase has a rock salt structure (as in GST), (c) Growth-dominated recrystallization. We hope that the following article, where we restrict our focus to GST (Group 1) materials, reflects the sense of excitement that has accompanied this work.

Figure 1: Phase diagram of PC materials and crystallization patterns. (a) The most commonly used materials for optical recording are in groups 1 and 2. (b) Nucleation dominated recrystallization (as in GST). (c) Growth-dominated recrystallization.

2 Density functional calculations

The density functional (DF) formalism [14] is the most widely used method for determining electronic and structural properties of condensed matter that does not require adjustable parameters. It is based on the electron density $n(r)$ and reduces the problem of determining ground state properties of an interacting system of electrons and ions to the solution of single-particle Schrödinger-like equations. An approximation for the exchange-correlation energy $E_{xc}$, one contribution to the total energy of the system, is unavoidable, but there has been substantial progress in this area in recent years [15]. Crucial to the success of applications to PC materials has been the coupling of DF calculations to molecular dynamics (MD) [11], since the DF energy surfaces and forces can be used to determine the motion of the ions at a known temperature.

Most simulations of amorphous materials are started with a liquid sample at high temperatures (typically above 3000 K), so that all memory of the initial solid configuration is erased. It is important that cooling to the melting point and to room temperature and below be carried out as slowly as possible, as energetically unfavourable configurations may otherwise be frozen in. In our calculations, we have used total simulation times of hundreds of picoseconds for samples of up to 630 atoms. DF calculations of this scale are extremely demanding of present computer resources, but they do allow definite statements to be made concerning the convergence of the simulation results as a function of sample size.

MD methods allow us to follow the coordinates $R_i$ and velocities $v_i$ of all atoms throughout the simulations, and insight into the local order can be found from the distributions of the bond ($\theta_{ijk}$) and dihedral angles ($\gamma_{ijk}$). The pair distribution function (PDF) $g(r)$ is a spherically averaged distribution of interatomic vectors,

$$g(r) = \frac{1}{\rho^2} \left( \sum_i \sum_{i \neq j} \delta(r_i) \delta(r_j - r) \right),$$

where $\rho$ is the density. Partial PDF $g_{\alpha\beta}(r)$ can be calculated by restricting the analysis to the elements $\alpha$ and $\beta$. The local structure can also be characterized by the average coordination numbers, which are found by integrating...
\( g_{\alpha \beta}(r) \) to the first minima \( R_{\text{min}} \)
\[
n_{\alpha \beta} = \int_0^{R_{\text{min}}} 4\pi r^2 \rho_{\alpha \beta}(r) g_{\alpha \beta}(r). \tag{2}
\]
The partial density \( \rho_{\alpha \beta} = \rho \sqrt{c_\alpha c_\beta} \), where \( c_\alpha \) and \( c_\beta \) are the concentrations of the elements. We calculate the structure factor \( S(Q) \) by Fourier transforming the \( g_{\alpha \beta}(r) \) to give the partial structure factors:
\[
S_{\alpha \beta}(Q) = \delta_{\alpha \beta} + \rho_{\alpha \beta} \int_0^{\infty} dr \ 4\pi r^2 [g_{\alpha \beta}(r) - 1] \frac{\sin(Qr)}{Qr}. \tag{3}
\]
These quantities can then be weighted according to the atomic fractions \( c_\alpha \) and form factors \( f_{\alpha}(Q) \) (for x-rays) or the \( Q \)-independent coherent scattering lengths \( b_\alpha \) (for neutrons) for direct comparison with experiment.

**Figure 2** Schematic form for 2D-vacancy.

The cavity analysis is performed by introducing the concepts illustrated in Fig. 2. A **vacancy domain** (I, Fig. 2) is a region where the minimum distance to a nearby atom is larger than a given cutoff (here 85% of the average Ge-Te distance, 2.8 Å), and each domain is characterized by the point where the distance to all atoms is greatest. We insert a **test particle** at the center of the largest sphere that can be placed inside the cavity (dashed circle in Fig. 2). This cavity centre can be used to calculate RDF, including cavity-cavity correlation functions. A **vacancy cell** (II, yellow in Fig. 2) is analogous to the Wigner-Seitz cell in crystals or Voronoi polyhedra in amorphous materials and are determined on an appropriate mesh with respect to the vacancy domains (I, Fig. 2). The importance of cavities and their relatively small number provide additional incentives for choosing large simulation cells.

Dynamical information includes the velocity autocorrelation function \( C_v \):
\[
C_v(t) = \frac{1}{N} \sum_{i=1}^N \frac{\langle v_i(0) \cdot v_i(t) \rangle}{\langle v_i(0) \cdot v_i(0) \rangle}, \tag{4}
\]
where \( N \) is the number of particles. The self-diffusion constant for all atoms or those of species \( \alpha \) can be determined from \( C_v \):
\[
D_\alpha = \frac{1}{3} \int_0^{\infty} \langle R_\alpha(t) - R_\alpha(0) \rangle^2 \frac{dt}{6t}, \tag{5}
\]
or directly from the coordinates \( R_\alpha \)
\[
D_\alpha = \lim_{t \to \infty} \langle \langle R_\alpha(t) - R_\alpha(0) \rangle^2 \rangle \frac{6t}{}, \tag{6}
\]
where the average is over all atoms of species \( \alpha \).

**3 Results and discussion** The structures and their changes with time and temperature provide a rich source of information for comparison with experiment, and we do this now for several Ge/Sb/Te compounds. We provide most details for GST-225, a prototype PC material that is often referred to simply as GST. In these materials it is convenient to separate the components into types \( A \) (Ge, Sb) and \( B \) (Te). More details of all calculations can be found in the original articles.

![Figure 3 System of 460 atoms and 52 vacancies in (a) c-GST and (b) a-GST. Red: Ge, blue: Sb, yellow: Te. Cavities are shown as light blue isosurfaces.](image)

### 3.1 Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (GST-225)

The amorphous (\( a \)-), liquid (\( l \)-) and crystalline (\( c \)-) phases of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} have been studied using a sample of 460 atoms and 52 vacancies in the unit cell over a total of 400 ps [16, 17]. The starting geometry [Fig. 3(a)] was a rock salt crystal structure, with the Na sites occupied randomly by Ge and Sb atoms (20% each), and the Cl sites by Te atoms [7]. At the end of the simulation (300 K), the amorphous structure in Fig. 3(b) was found. Cavities are shown by light blue isosurfaces, but we note that the multivacancy in Fig. 3(b) is just one of numerous cavities in \( a \)-GST.

The most striking (and unexpected) feature of the partial PDF (Fig. 4) is the medium-range order found among Te atoms up to 10 Å, with peaks at 4.16 Å and 6.14 Å, a minimum at 5.4 Å, and additional maxima at 7.8 Å and...
Figure 4 Partial PDF of α- (thick black) and ℓ-GST (red). Blue curve and bars are for c-GST at 300 K (with different scale).

9.8 Å. The weak maximum at 2.95 Å and the low coordination number (0.3) show that there are few Te-Te bonds, and there is no significant order at 900 K. Te atoms prefer coordination with Ge/Sb, with Te forming the second-neighbour shell. Thermal fluctuations in c-GST lead to broadening of the Bragg peaks. The “homopolar” Ge-Ge, Ge-Sb, and Sb-Sb bonds in the three phases are shown in Fig. 4. While these bonds are absent in c-GST, they occur in the amorphous phase (“wrong bonds”). Heating to 900 K results in significant changes in the Ge-Ge and Ge-Sb curves: the first peak now dominates, and the order between 4 and 7 Å moves to shorter range.

All coordination numbers for α-GST (Ge: 4.2, Sb: 3.7, Te: 2.9) are lower than in the crystal, but larger than the values (4, 3, 2) suggested by the oft-quoted “8 – N rule”, where N is the number of valence electrons. Liquid GST (900 K) is less ordered than the amorphous state. The similarities between ring statistics in α- and c-GST have been proposed as the basis for the structural phase change in GST [18]. The statistics of all irreducible loops (rings) in α- and ℓ-GST have been calculated using a bond cutoff of 3.2 Å and periodic boundary conditions (Fig. 5). Fourfold rings dominate the statistics at 300 K, and the contribution of “ABAB squares” is 86 % of the total. 52 % of atoms participate in at least one ABAB configuration. In Fig. 6 we show that alternating ABAB cubic structures also occur.

Cavities play an essential role in Ge/Sb/Te alloys. Since c-GST contains 10% vacancies, α-GST, whose density is 7% lower, must have empty regions (cavities or voids, see Fig. 3). Cavities comprise 11.8% of the total volume of α-GST (slightly more than in the crystal), and this increases to 13.8% at 900 K.

Figure 5 Ring statistics for α-GST (300 K) and ℓ-GST (900 K). ABAB refers to even-membered rings with bond alternation.

Figure 6 A cubic ABAB subunit in α-GST. A Ge-Ge bond (between the cube and its neighbours) and an Sb-Sb bond are evident. Cavities occur near the cube, and a threefold coordination is typical for Te.

Figure 7 (a) XPS valence band spectrum of c- (thick black) and α-GST (red) ([19], upper panel) and the calculated electronic DOS (lower panel). (b) Theoretical DOS of α-GST projected onto atom-centered s-, p-, and d-components and atomic types. (c) DOS difference between c-GST and α-GST [from (a), positive values imply a larger weight on α-GST]. (d) Electronic DOS of ℓ-GST. The vertical dashed lines mark the Fermi energy.

The energy eigenvalues in DF calculations cannot be related directly to the optical excitation spectra, but the electronic density of states (DOS) and its projections often lead to useful insight and are shown in Fig. 7. The former
are characteristic of materials with average valence five: the two lowest bands can be assigned to s-electrons (σ-band), and the broad band between −5 eV and the Fermi energy has p-character (π-band). The calculations for c- and α-GST show band gaps of around 0.2 eV at the Fermi energy. Photoemission measurements have shown that there are significant differences in the valence band DOS and the core levels of α- and c-GST and other Ge/Sb/Te alloys [19]. The differences measured by hard x-ray photoemission spectroscopy (XPS, [19]) are compared with our results in Fig. 7. The agreement is remarkably good, particularly for the DOS difference [Fig. 7(c)].

Figure 8 Calculated vibrational density of states for α-GST (VDOS, lowest curve), and power spectra from simulation trajectories for α-GST, for Ge, Sb and Te, and for fourfold coordinated Ge atoms (“4-Ge”). Curves have maxima at 1.3 (α-GST) or 0.65 (projections).

The distribution of vibration frequencies in condensed matter and molecules provides important structural information and can be calculated: (a) from the Fourier transform of the velocity-velocity autocorrelation function, calculated from trajectories of 6000 time steps of 3.025 fs each, and (b) from the dynamical matrix calculated from the second-order energy derivatives of a well-equilibrated structure at 0 K. The results for α-GST (Fig. 8) show that the agreement between the results for the two methods is very good. The most pronounced features are peaks near 60 cm−1 and 150 cm−1 and a tail for frequencies above 180 cm−1. Projections onto the vibrations of different elements and structural units show that the tail is associated with the vibrations of the lightest element Ge, particularly atoms that are fourfold coordinated.

The original DF calculations [16] agreed reasonably well with measured S(Q) and g(r) for GST, [18] but several details were open to improvement. In particular, we had used the approximation of Perdew, Burke and Ernzerhof (PBE) [20] for E xc, and the bond lengths that resulted were longer than those measured. A valuable collaboration between theory and experiment began when we discovered that the structure obtained in the original reverse Monte Carlo (RMC) fit to the x-ray diffraction (XRD) measurements [18] gave rise to a metallic density of states, i.e. no band gap at the Fermi energy. We combined the strengths of theory and experiment with the goal of finding a structure that:
- reproduces the measured S(Q) and the total pair distribution function g(r) for XRD and/or neutron diffraction,
- has bond lengths that are not artificially short and are consistent with EXAFS measurements,
- has an electronic structure with a band gap at the Fermi energy,
- has a DF total energy close to the minimum.

We do this by combining data from high-energy XRD [18] and XPS measurements on α- and c-GST [19] with DF simulations of a 460-atom sample over hundreds of picoseconds. This strategy is related to the “experimentally constrained molecular relaxation” (ECMR) of Biswas et al. [21].

We adopted the approximation of Tao et al. (TPSS) [15], which has orbital-dependent terms that increase the computing demands, but the resultant structures and energy differences are generally better for extended systems [15]. The structures of c- and α-GST [16] were re-optimized using the TPSS functional, and the PDF for c-GST agrees very well with XRD measurements (Fig. 9). Both EXAFS and XRD results indicate the presence of the double maximum in the PDF, and the calculated Ge-Te and Sb-Te bond distributions have double maxima that were not evident in the PBE results. The shorter Ge-Te and Sb-Te bond lengths (2.84 and 2.93 Å, respectively) agree very well with EXAFS values (2.83 and 2.91 Å) [8]. The longer bonds have maxima above 3.1 Å. TPSS bonds in α-GST are 1–2 % shorter than in the calculations using the PBE functional, and the coordination numbers (Ge: 3.9, Sb: 3.5, Te: 2.7) are lower than in [16] (4.2, 3.7, and 2.9). The cohesive energy is 2.62 eV, and c-GST is 58 meV/atom more stable than α-GST.

The re-optimized α-GST geometry was taken as input for RMC refinement using the experimental x-ray total structure factor S(Q). The experimental S(Q) can be reproduced very well with a range of input parameters,
but RMC simulations without constraints on the bond angles always led to a metallic DOS, even when the initial structure was semiconducting. A semiconducting structure that satisfies the x-ray structural information for $\alpha$-GST can be obtained in practice only by using an iterative scheme where the bond angle distributions Te-Ge-Te, Te-Sb-Te, Ge-Te-Ge, Ge-Te-Sb, and Sb-Te-Sb are constrained to have values close to those found in the DF calculations. The TPSS bond lengths are slightly shorter than PBE values, but the use of the PBE approximation instead of TPSS would lead with the present optimization scheme to very similar structures.

The RMC optimization of the TPSS structure yields a structure factor $S(Q)$ in excellent agreement with XRD results [Fig. 9(a)], with minor differences in amplitude near the first two peaks. The excellent description of the high-$Q$ region is important, because the short-range atomic correlations in the XRD pair distribution function $g(r)$ [Fig. 9(b)] is obtained by Fourier transforming $Q[S(Q) - 1]$ and is affected strongly by the high-$Q$ portion of $S(Q)$. The calculated $g(r)$ follows the experimental curve almost perfectly with small deviations near the first peak, and the total energy is only 79 meV/atom higher than that of the DF energy minimum. The electronic DOS shows a band gap at the Fermi level.

### 3.2 GeTe and Ge$_{15}$Te$_{85}$

Binary alloys of Ge and Te have fascinated experimentalists and theorists for decades. They were among the first to show real promise as phase change media [3], and there are striking changes on melting, particularly near the eutectic composition Ge$_{15}$Te$_{85}$. We have simulated $\alpha$-GeTe with 216 atoms in the unit cell and compared the results with those of $\alpha$-GST [22]. In both cases there is medium-range order of Te atoms and the crucial structural motif is a four-membered “$ABAB$ square”. The amorphous to crystalline phase change can then be viewed as a reorientation of such units to form an ordered lattice. The deviations from the “$8 - N$ rule” that are found for GST are also present in GeTe.

Simulations of the eutectic mixture Ge$_{15}$Te$_{85}$ [22,23] lead to partial PDF that again show signs of medium-range order. Amorphous GeTe has few Te-Te bonds, while Ge-Ge bonds are rare in Ge$_{15}$Te$_{85}$. The average coordination numbers are 4 for Ge and 3 for Te, and the most prominent configurations in GeTe and Ge$_{15}$Te$_{85}$ are Ge-GeTe$_3$ and Ge-Te$_4$, respectively. Ge atoms can be tetrahedrally and octahedrally bonded, and the former dominate in Ge$_{15}$Te$_{85}$. Atoms in GeTe favour octahedral or cubic bond angles, although sixfold coordination is found in only 3.4 % and 11.0 % of Ge atoms at 300 K and 1000 K, respectively. The GeTe network includes clusters of “$ABAB$ squares”. Corner and edge-sharing Ge-Te$_4$ tetrahedra are common in Ge$_{15}$Te$_{85}$. The threefold (cubic) coordination of Te in both GeTe and Ge$_{15}$Te$_{85}$ deviates from the predictions of the “$8 - N$ rule”.

As in GST, $ABAB$ squares are essential for the phase transition in GeTe. In $\alpha$-GeTe, 75 % of the atoms are involved. Even above the melting point (1000 K), 41 % of the atoms participate in $ABAB$ squares. The dominance of Te in the composition of Ge$_{15}$Te$_{85}$ means that there are fewer $ABAB$ squares, but cavities are characteristic of this alloy, occupying more than 25 % of the total volume in both amorphous and liquid states. The volumes and shapes vary widely, and the cavity distributions depend significantly on the temperature. There are more cavities in the liquid (680 K) and more that are smaller, whereas larger cavities (70 – 100 Å$^3$) are more abundant at 300 K.

### 3.3 Ge$_8$Sb$_2$Te$_{11}$ (GST-8211)

We have simulated 630 atoms (240 Ge, 60 Sb, 330 Te) of this GeTe-rich alloy in a cubic cell of dimension (27.19 Å) appropriate to the liquid density (0.03134 atoms/Å$^3$). After heating to 3000 K, the sample was cooled (120 ps) to the melting point (950 K), where data were collected (31 ps). During subsequent cooling to 300 K (melt-quench, 217 ps), there was a small adjustment of the density to that of the amorphous material. This was followed by data collection (30 ps) and cooling to 100 K (31 ps), where the structure was optimized by simulated annealing. The total simu-

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Figure 9 (a) Structure factor $S(Q)$ in $\alpha$-GST. Green: XRD [18]; black: calculated for RMC-optimized geometry. Inset: data for high $Q$ values. (b) Total PDF (XRD weights).
lation time of the melt-quench process was 429 ps. The optimized structure [Fig. 10(a)] shows a cubic column of 16 atoms that demonstrates $AB$ ordering, and Fig. 10(b) emphasizes the local coordination of Ge and Sb atoms.

The ring statistics of $\alpha$-$\text{Ge}_8\text{Sb}_2\text{Te}_{11}$, GeTe and GST-225 are compared in Fig. 11. There are many four-membered rings and few triangular configurations in all cases. As in GST-225, most of the four-membered rings in $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ show $AB$ alternation, confirming that the basic building blocks in the amorphous and crystalline phases are $ABAB$ squares [16,24,25]. A good example is the $ABAB$ column shown in Fig. 10. The odd-even alternation is apparent in GST-8211 and GST-225, and the ring distributions of these two materials are strikingly similar (Fig. 11). This may be surprising at first, since GST-8211 is much closer to GeTe on the pseudobinary line, but even a small increase in Sb content appears to change the properties of GeTe significantly.

Cavity shapes include facets, edges, corners, and protrusions. They are illustrated in Fig. 12 for the optimized structure of $\alpha$-GST-8211, where they occupy 12.4% of the total volume, i.e. the small increase in Sb content is accompanied by a dramatic increase in the number of cavities to a value near that in $\alpha$-GST-225. The coordination numbers around the cavity centers are Ge: 1.3, Sb: 0.4, and Te: 3.7, and other cavities: 0.2. Cavities are then surrounded mainly by Te atoms, and Ge is a more common neighbor than Sb. These features reflect the small Sb content and the underlying cubic structure that resembles the crystalline phase.

3.4 As-deposited vs. melt-quenched GST-225

Atomistic simulations on phase-change materials have focused on melt-quenched (MQ) samples, where a liquid sample is cooled rapidly. Experimental samples are often deposited on a substrate, and the structure is likely to differ. We have developed a method to generate an “as deposited” (AD) sample with 648 atoms at 300 K [26] and have compared the results with those for a 460-atom MQ sample, refined as described above with respect to XRD and XPS data [27]. The simulations were carried out at 300 K, beginning with a random template of 36 atoms in an area of $27.61 \times 27.61$ Å (layer thickness 1.4 Å). These atoms were
The electronic densities of states (DOS) in AD and MQ are very similar, with band gaps of 0.2 – 0.3 eV at the Fermi energy. The DOS profiles are in satisfactory agreement with XPS data [19], the most significant difference being near the DOS minimum around −10 eV between two $\sigma$-bands.

The PDF of both samples [26] show that Ge-Te and Sb-Te bonds dominate ($AB$ alternation). EXAFS measurements [8,29,30] have shown that Ge-Te distances shrink upon amorphization (2.61 – 2.63 Å), suggesting that Ge may have tetrahedral coordination. This differs from earlier DF simulations, which found mostly (distorted) octahedral configurations for Ge with Ge-Te bonds of 2.77 – 2.78 Å. Tetrahedrally bonded Ge atoms also occur. The discrepancies in the Ge-Te bond length appear to have two causes: (a) Most approximations for $E_{xc}$ tend to overestimate bond lengths by 2 – 3 %, but the use of the PBEsol functional here reduces this error (the Ge-Te PDF maximum is at 2.72 Å in MQ). (b) Sample preparation is crucial: AD has more tetrahedral Ge atoms, and the Ge-Te maximum shifts to 2.69 Å. Ge-Ge bonds (2.52 Å), which correspond mainly to tetrahedral Ge atoms here, agree well with experiment (2.47 ±0.03 Å) [29]. Sb-Te bond lengths change little upon amorphization, and the first maximum of AD and MQ is at 2.89 Å.

The other PDF show clear differences between the samples, since the number of “wrong bonds” is significantly larger for AD. This is reflected in the Ge-Te and Sb-Te PDF ($AB$ bonds) as weaker first maxima and emerging second maxima at 4.2 Å. The corresponding partial coordination numbers [26] show that Ge and Sb have twice as many wrong bonds (1.1 on average) as Te (including Te-Te bonds), although more than half of the atoms are Te. The total coordination numbers for AD are Ge: 4.2, Sb: 3.7, and Te: 2.8. Earlier work on MQ samples [16,27,24] indicated that the total coordination numbers of Sb and Te in $\sigma$-GST do not satisfy the “8 – $N$ rule” of covalently bonded networks, and additional support for this conclusion is found by calculating the bond orders (number of chemical bonds) for each interatomic connection [26].

The AD structure of $\sigma$-GST (648 atoms, over 200 ps) differs from MQ (460 atoms, [27]) in essential ways: (1) The environment of Ge atoms is predominantly tetrahedral in AD and disordered octahedral in MQ, and our results for the Ge-Te bond lengths agree with EXAFS measurements [8,29,30]. This resolves the contradiction between measured and bond lengths and those found in earlier DF calculations. (2) Homopolar and Ge-Sb bonds are more common and reduce the number of $AB\bar{A}B$ squares, which are needed for rapid crystallization. Sb and Te are more highly coordinated than expected from the “8 – $N$ rule”, so that $\sigma$-GST cannot be seen as a covalent network glass. The PBEsol functional gives improved results, and both samples tend to form fewer Te-Te bonds, and MQ is 11 meV/atom more stable than AD. Their structure factors
Figure 13 AD sample of a-GST at 300 K. (a) Top view after 17 added layers (648 atoms). The uppermost atoms within 1.2 nm are highlighted, and the red tetrahedra mark Ge atoms with tetrahedral coordination. Ge, red; Sb, blue; Te, yellow. (b) Side view of the final surface. (c-d) Two perspectives of final sample. Cavities (cyan isosurfaces) comprise 16.3% of the total volume.

Figure 14 (a) Structure factor \( S(Q) \) of AD (black) and MQ (blue) samples at 300 K, and XRD (red). The calculated \( S(Q) \) are shifted by 0.4. (b) Electronic DOS of AD and MQ samples. Vertical dashed line marks band gap separating the \( \sigma \)-band with Te-5s character.

...and electronic properties are similar, so that distinguishing between them using XRD alone remains a challenge.

4 Concluding remarks We have summarized here results of a range of simulations on Ge\(_2\)Sb\(_2\)Te\(_5\) (GST-225), GeTe, Ge\(_8\)Sb\(_2\)Te\(_{11}\), and Ge\(_{15}\)Te\(_{85}\). The availability of leadership class computers and efficient numerical algorithms make density functional calculations possible for systems with hundreds of atoms over time scales of hundreds of picoseconds, i.e. approaching the crystallization time of phase change materials. This is an immensely encouraging development, and the calculations have enabled us to identify the crucial pattern (“ABAB squares”) in the phase transition in GST [16], to study the differences between GeTe, GST, and Ge\(_{15}\)Te\(_{85}\), and to identify structural differences between as-deposited and melt-quenched structures of GST-225.

We have presented most details of our own work on GST alloys, but other calculations are important, as are other PC materials. Concurrently with Ref. [16], Caravati et al. [24] performed DF/MD simulations on a-GST-225 (270 atoms, cooling from 2300 K to 300 K in 58 ps). The simulated \( S(Q) \) was very similar to that in [16], and the authors noted the coexistence of tetrahedral and octahedral sites in a-GST: One third of Ge atoms were in a tetrahedral environment, while the remaining atoms showed a defective octahedral environment. The same authors studied the effects of stoichiometric defects [31] and pressure-induced amorphization in the same material [32]. Hegedüs and Elliott [25] have performed DF/MD simulations (63 atoms, 1.3 ns) of the crystallization process in \( a \)-GST-225. Crystallization is the time-limiting process in the write/erase cycle of PC materials and is the focus of much current research.

We have restricted our discussion to alloys on the tie line GeTe–Sb\(_2\)Te\(_3\) in Fig. 1(a), which are group 1 materials where crystallization of the amorphous bits proceeds by nucleation from within. We noted above that amorphous bits of Sb-based materials near the Sb\(_{70}\)Te\(_{30}\) eutectic (group 2), also used as PC materials, crystallize from the polycrystalline surroundings. We have simulated the amorphous structure of Ag\(_{3.5}\)In\(_{3.8}\)Sb\(_{75.6}\)Te\(_{17.7}\) and suggested a plausible scheme for its crystallization [33].

Some words of caution are, however, appropriate. One of the most remarkable results of this study was the discovery of medium-range order in Te atoms in a-GST and GeTe, and this would be impossible to detect in simulations of fewer atoms. This is also true for studies of cavities, which can occur as large multivacancies in these systems. Earlier simulations often considered less than 100 atoms. While they certainly aided our understanding of the
processes involved, they cannot be expected to give reliable predictions. It is also crucial that the liquid state be cooled over a time scale that is physically relevant. The use of Born-Oppenheimer MD with an efficient predictor-corrector scheme for converging the orbital eigenfunctions has been decisive in our own work, since the time steps are two orders of magnitude greater than possible with standard techniques. Furthermore, high temperatures favour metallic samples in many of these systems, and the absence of a gap in the eigenvalue spectrum often leads to instabilities in the Car-Parrinello approach. Similar findings were found in other work [24].

We have noted that the approximation used for the exchange-correlation is crucial to obtain an accurate description of the structures of several PC materials. Elemental Te provides an interesting material in this context, since experimental and calculated structure factors and pair distribution functions often disagree. The results of DF calculations of structural properties of Te were found to depend significantly on the choice of the exchange-correlation functional Te provides an interesting material in this context, since the time steps are two orders of magnitude greater than possible with standard resources and the effort required to analyze the results is enormous. Both in terms of computational resources and the effort required to analyze the results. This situation is unlikely to change in the short term, and it is indeed pertinent to ask whether simulations of “hundreds of atoms” are enough to answer the problems we face. The development of classical force fields that have DF accuracy is important, and the recent work of Sosso et al. [35] is an interesting development. These authors used a huge database of DF calculations on Ge/Te systems to develop a force field for GeTe that permits MD simulations with much longer time scales and up to several thousand atoms.

We return at the end of this review to where we began, by acknowledging the pioneering work of Stan Ovshinsky as beginning the field of PC materials. We wish him all the best as he begins his tenth decade.

Acknowledgements We thank all colleagues who worked with us on these problems, particularly J. Kalikka, K. Kobayashi, S. Kohara, T. Matsunaga, and N. Yamada. J. A. thanks the Academy of Finland for support. The calculations were carried out on IBM BlueGene and Intel Xeon computers in the Forschungszentrum Jülich and the John-von-Neumann Institute for Computing (NIC). The German Research School for Simulation Sciences is a joint venture of the FZ Jülich and the RWTH Aachen University.

References

[2] See, for example, N. F. Mott, Advan. Phys. 16, 49 (1967), and references therein.