

Bond constraint theory and the quest for the glass computer

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Abstract. Electronic switching in amorphous chalcogenide semiconductors has been observed and studied for nearly forty years. Technological exploitation of this phenomenon has most recently emerged in DVD's where GST, a compound of germanium, antimony, and tellurium, is used to store information. We explain how GST behaves as a switch and how X-ray absorption fine structure can be used to unlock the specifics of the switching process. The tool that leads to this deeper understanding is the bond constraint theory. We explain how this theory leads to an explanation of switching and of the behavior and properties of amorphous materials in general. Finally, the prospects for developing GST-related materials into non-volatile memory media that could be the basis for glass computers are discussed.

Keywords. Switching; chalcogenide glass; bond constraint theory.

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1. Introduction

Ever since the electronic switching in chalcogenide glasses was reported in 1968 [1], people have been dreaming of computers based on these glasses. Recent interest has been rekindled by the discovery of certain compositions that can be reversibly and repeatedly switched between the amorphous (a-) and crystalline (c-) states by light or current pulses of the appropriate intensity and duration [2]. A dramatic difference in reflectivity and resistivity between the a- and c-states (designated 0 and 1) has allowed the use of these compositions in DVD devices.

Ge₂Sb₂Te₅ (GST) has been found to be a particularly robust and reliable material for use in optical and electrical switching applications. While the compound's properties and performance are well-documented [2–4], a fundamental explanation of the suitability of GST for these applications has not been identified. That is the purpose of our study: Why does it behave so well as a switch? Such information will

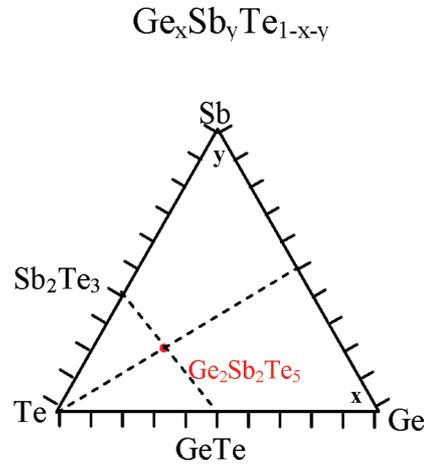


Figure 1. GeSbTe composition diagram, showing the location of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ at the Sb_2Te_3 and GeTe tie line.

not only satisfy our scientific curiosity, but will also help in solving an important technological problem.

The problem is that while GST switches beautifully between the a- and c-states, it does not do so forever. After about ten million cycles or so, it no longer works. If we could push this to about 10^{14} cycles, we could replace CPU. Therefore, the goal is to find a better material that will switch up to this many times without degrading. One of the advantages of GST-based CPU will be that it would be non-volatile. That is, the system would hold zeroes and ones with no current necessary to hold the state. A glass computer would not require booting! Nor would it draw power when not calculating!!

2. GST as a glass

We propose to focus on a region of the ternary composition diagram of the $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ system near the material of greatest technological interest, $\text{Ge}_2\text{Sb}_2\text{Te}_5$, commonly called GST or 2-2-5. Here is how glass technologists look at GST (figure 1). It lies on the intersection of two lines: the bisector of the Te vertex angle and the line joining GeTe and Sb_2Te_3 . These are stable molecular solids. In this sense GST can be thought of as a mixture of these two molecular solids. We shall presently show, however, that this view of GST is incorrect, as it is not consistent with the analysis of our EXAFS data.

As we go from Te to Ge, the material goes from floppy to rigid. Bond constraint theory (BCT) couches the balance between rigid and floppy materials in terms of average number of constraints per atom in interatomic force field space and the number of degrees of freedom in real space. BCT and EXAFS data allow us to identify this compound (GST) as an unstressed-rigid material and in the final analysis [5–7] explains why GST behaves so well in switching applications.

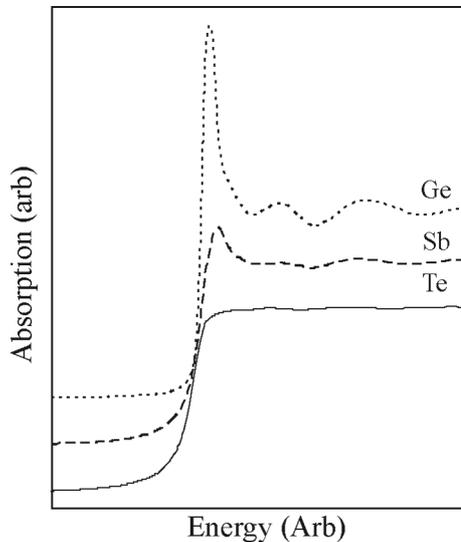


Figure 2. Normalized K_1 absorption spectra for all three atomic species, shifted in energy for comparison. Spectra are displayed on the same energy axis for ease of comparison.

The key to the understanding of the switching process is the knowledge of local bonding arrangements of the material in both the amorphous and rock-salt crystalline phases. The extended X-ray absorption fine structure or EXAFS results provide precisely the microscopic information one needs to obtain this knowledge for GST.

3. EXAFS

Here is how EXAFS works. When a photon is absorbed by an atom, the photoelectron associated with the absorption interferes with the neighboring atoms. The interference associated with the local environment gives rise to wiggles (fine structure) on the absorption edge (see figure 2).

We analyze these interference wiggles to decipher the local environments of constituent atoms.

Figure 3 shows, as an example, the analysis of the data for the Ge edge. We do similar analysis for all three edges (i.e., Sb and Te also). The blue line is the data. The red line is the model. We construct a model in real space that gives us a blue curve in the lower plot that matches the data of the red curve. Then we transform back to k-space to see how well our model fits the data. We do this iteratively for all three edges (for details, please see ref. [5]).

Table 1 shows all the pairs for the three atoms Ge, Sb, and Te, which have been used to fit the EXAFS data. Note that there are several pairs missing, namely, Ge–Sb, Sb–Sb, Te–Te (for which there is no evidence). It is comforting that the data are self-consistent. That is, in the Ge edge we find no evidence for Sb neighbors,

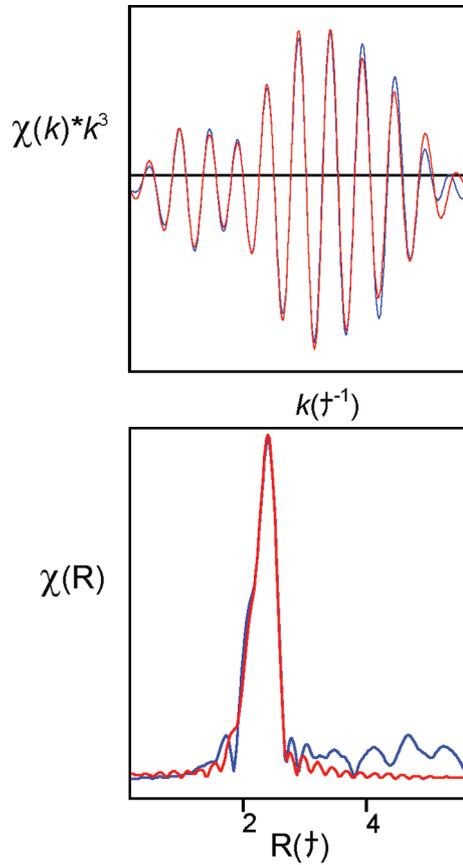


Figure 3. Artemis/IFEFFIT fits of Ge-K edge data using small cluster model. Fit includes Ge-Te and Ge-Ge path contributions. No acceptable fits were found with Ge-Sb bonding.

Table 1. Coordination numbers and the nearest neighbor distances for the constituent atoms Ge, Sb and Te, as inferred from the EXAFS data.

Atom	Bond	Coordination	R (Å)
Ge	Ge-Te	3.3 ± 0.5	2.63 ± 0.01
	Ge-Ge	0.6 ± 0.2	2.47 ± 0.03
Sb	Sb-Te	2.8 ± 0.5	2.83 ± 0.01
	<i>Sb-Te(e)</i>	0.5 ± 0.3	2.51 ± 0.01
Te	Te-Ge	1.2 ± 0.3	2.62 ± 0.01
	Te-Sb	1.2 ± 0.3	2.83 ± 0.01

N.B.: *Sb-Te(e)* is the electrostatic bond, as discussed in ref. [5].

and at the Sb edge we find no evidence for Ge neighbors. Further, note that the Te nearest neighbor distances ($R_{\text{Te-Sb}} = 2.83 \text{ \AA}$ and $R_{\text{Te-Ge}} = 2.62 \text{ \AA}$) are found to be the same, within the error, regardless of whether they were determined from Te-edge data or from the neighboring atom data (Sb and Ge respectively). Also note that the reported bond lengths agree with tabulated covalent radii for each species [8]. The values of the coordination numbers (N) obtained indicate fully coordinated Ge and Sb with $N_{\text{Ge}} = 3.9 \pm 0.8$ and $N_{\text{Sb}} = 2.8 \pm 0.5$ and slightly over-coordinated Te with $N_{\text{Te}} = 2.4 \pm 0.6$.

4. Bond constraint theory (BCT)

The simple physical requirement that the number of constraints in an amorphous material equals the number of degrees of freedom in the space that material occupies (or network dimensionality) defines a relatively simple criterion for an ideal, strain-free thin film or bulk material [9]. For an ideal glass in three dimensions, the bond constraint metric is 3, so that the average number of bonds/atom C_{av} is given by

$$C_{\text{av}} = 3. \quad (1)$$

This simple criterion provides the basis for the application of BCT for discriminating between materials with different degrees of ideality in the context of the ease of ‘glass formation’. When it is met, $C_{\text{av}} = 3 \pm 0.1$, a material may be considered to be a ‘good glass-former’. This criterion will be important in identifying the ease of reversible optical or electrical switching in thin film amorphous materials for memory applications. We start with the basic assumption [9] that for an ‘ideal’ glass the average number of constraints is 3. Then we expand the number of constraints in terms of the stretching and bending constraints. Defining $\langle r \rangle$ as the average coordination, we get an important relation between the number of constraints and the average coordination:

$$C_{\text{av}} = (5/2)\langle r \rangle - 3. \quad (2)$$

So now the ‘ideal’ glass has an average coordination

$$\langle r \rangle = 2.4. \quad (3)$$

This is equivalent to an average number of constraints per atom of 3.

An alternative approach that arrives at the same conclusion (eq. (3)) is provided by rigidity theory, as developed originally by LaGrange [10], Maxwell [11] and later by Thorpe and co-workers [12]. This approach considers rigidity in systems with 2-, 3- and 4-fold coordinated atoms in a material with local molecular units of N atoms. In calculating the total number of modes of vibration of such a system, they identify modes that require energy (i.e. constraints) and those that do not. The latter are the so-called zero-frequency or floppy modes, and given the symbol F . F can be expressed as the difference between the total possible number of vibrational modes of the system, $3N$, and the modes determined by constraint counting. Proceeding in this way, F is given by

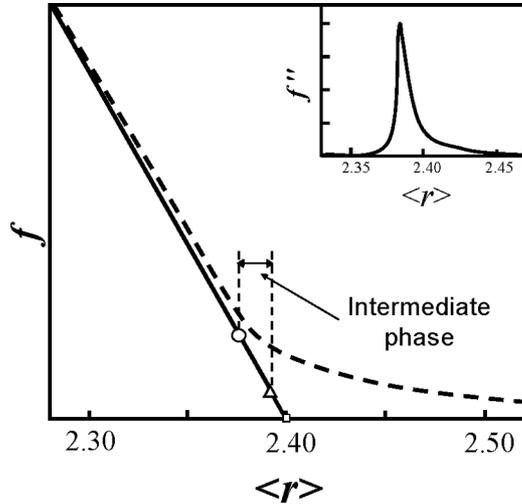


Figure 4. Plot of f as a function of $\langle r \rangle$. Theory is shown by the solid line and the model by dashed line. Inset shows second derivative of f as a function of $\langle r \rangle$.

$$F = 3N - \sum_{r=2}^4 n_r \left(\frac{r}{2} + [2r - 3] \right). \quad (4)$$

The fraction of zero-frequency modes, $f = F/3N$, may then be calculated and is given by

$$f = 2 - \frac{5}{6} \langle r \rangle. \quad (5)$$

With increasing average network coordination, $\langle r \rangle$, the fraction of zero-frequency modes f decreases, and is exactly equal to zero at the condition given in eq. (3). The relationship between f and $\langle r \rangle$ for $\langle r \rangle \leq 2.4$ is given by the solid line of figure 4. The equivalence of the approach based on the assumption inherent in BCT (eq. (1)) and the approach of rigidity theory (eq. (3)) is manifest in the fact that both identify a material with $\langle r \rangle = 2.4$ as lying at a nexus dividing materials that are floppy from those that are stressed-rigid with respect to material properties.

Results obtained by the Thorpe group go beyond the simple analytical treatment outlined above [13]. This research also includes computer modeling of large networks of atoms. Such modeling provides a numerical determination of the fraction of zero-frequency modes, f . Plots of f as a function of $\langle r \rangle$ reveal three distinct composition regions. One such plot is shown as the dashed line in figure 4.

There is an intermediate region where the system is neither floppy nor is it stressed-rigid. This is the region where the ideal glass is formed. The inset shows the second derivative of f . It accentuates the fact that there is a material intermediate between floppy and stressed-rigid. It is this intermediate material that Feng *et al* [14] showed exists, experimentally. The question is: does GST belong to this stress-free rigid regime? For this we must do constraint counting.

5. Counting constraints

Let us now count constraints using group theory. For Ge, we find five bending constraints and two stretching constraints (figure 5). That is a total of $C_{\text{Ge}} = 7$ constraints.

Similarly, we get $C_{\text{Sb}} = 4.5$ and $C_{\text{Te}} = 2$. These give, for GST, $C_{\text{av}} = (2C_{\text{Ge}} + 2C_{\text{Sb}} + 5C_{\text{Te}})/9 = 3.66$, which in turn yields (using eq. (2)) $\langle r \rangle = 2.7$.

Note that this is different from the value 2.4 for an ideal glass. So it appears, from this calculation, that GST is not an ideal glass. Perhaps we should look at our constraint counting, a bit more carefully.

6. Removal of constraints

It turns out that if homopolar bonds are present, the counting of constraints needs more attention. The reason is that when two neighboring atoms are identical a constraint against bending exists, because of Pauli exclusion principle. When a homopolar bond is allowed, this constraint is removed (see figure 6). Using EXAFS data we can count constraints correctly, taking into account homopolar bonds.

The EXAFS data show a significant number of homopolar Ge–Ge bonds in GST. Let us now, once again, count the number of constraints with homopolar bonds in the mix.

As shown in figure 7, 2.67 constraints out of 7 are removed for the four-fold tetrahedral configurations with homopolar Ge–Ge bonding, leaving only 4.33 constraints behind.

So, the number of constraints for germanium $C_{\text{Ge}} = 4.33$.

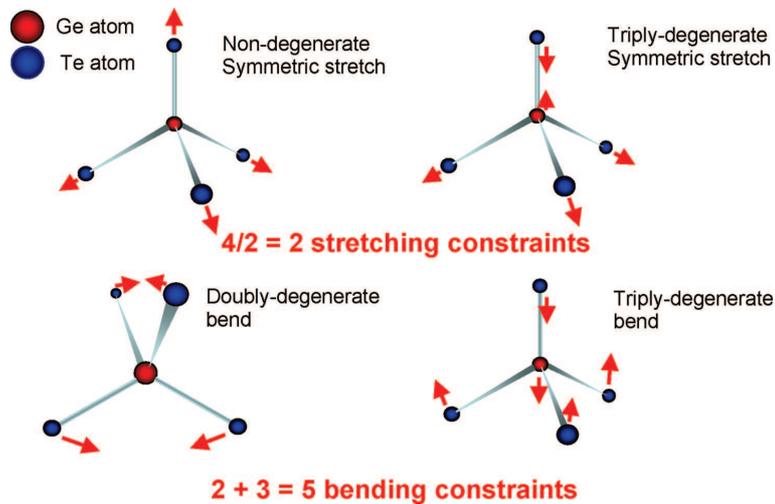


Figure 5. Constraint analysis for germanium.

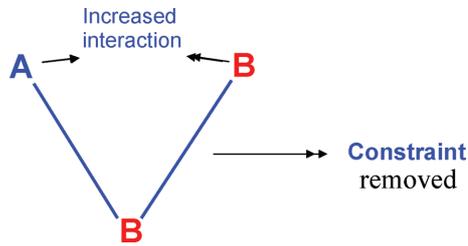
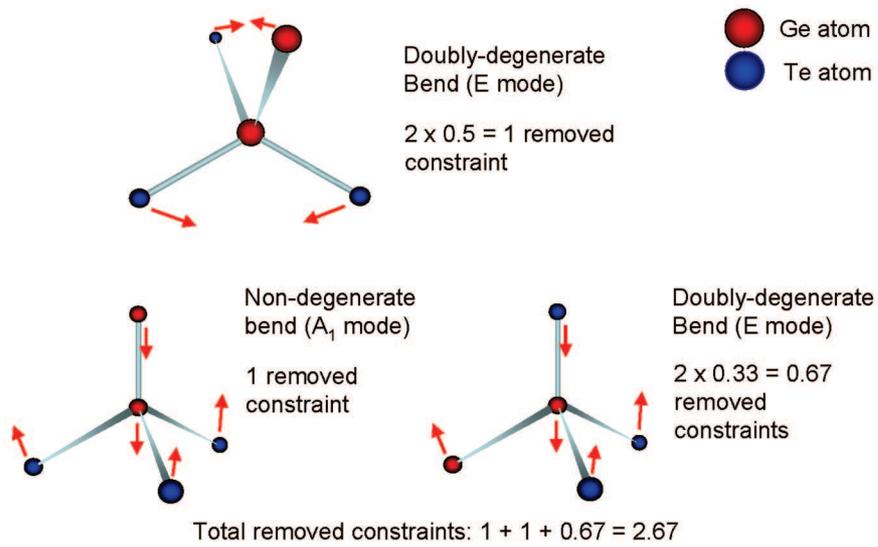


Figure 6. Homopolar bonding allows interaction between differing atomic species and removal of constraints.



Therefore, total number of constraints for Ge_2Te_3 configuration: $7 - 2.67 = 4.33$

Figure 7. Constraint counting for Ge in Ge_2Te_3 allowing homopolar bonding of Ge.

A similar analysis for Sb and Te gives, $C_{\text{sb}} = 4.5$ and $C_{\text{Te}} = 2$.

Now we add (with appropriate weightage), constraints for all three atoms in GST and calculate the average number of constraints per atom, as before. This then gives the effective average coordination for GST as

$$\langle r \rangle_{\text{effective}} = 2.4.$$

So GST is indeed an ideal glass, i.e., it lies in the stress free-rigid regime.

7. Thermodynamics of switching

Let us now look at this intermediate material from another point of view. In switching from the a- to the c-state, we have a balance such that the lowest free energy

state is always obtained. Whether the state is a- or c- is a kinetic consideration. The thermodynamically minimal state is determined in terms of a balance between enthalpy and entropy. If the system were over-constrained, repeated cycling would result in the system locking into a free energy minimum determined by enthalpy. If, on the other hand, the system were under-constrained, repeated cycling would find the system going down an entropy hill into an a-state that would not return to the c-state.

Finally, we consider the over-coordinated Te. There are some three-fold coordinated Te atoms. The EXAFS data show this to be 17%. If we consider the intersection of the Sb_2Te_3 - Ge_2Te_3 tie line with the Te vertex bisector, we have a material that might be considered a combination of these molecular solids blended to give the proper composition for 226. Now add 17% over-coordinated Te to this material and one has 225. But this is exactly what the EXAFS signal gave us.

So, we now have a model for GST. It is a material with molecular units of equal amounts Ge_2Te_3 and Sb_2Te_3 embedded in a matrix of a-Te where 17% of the Te are three-fold coordinated.

8. Summary and conclusions

EXAFS studies of the nearest-neighbor bonding of Ge, Sb and Te in as-deposited $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films indicate significant concentrations of both Ge-Ge and Ge-Te bonds, but no Ge-Sb bonds. Additionally, this analysis of the three EXAFS spectra yields internally self-consistent atomic coordination numbers and bond lengths. Combined with bond energies for the system, the EXAFS-determined bond parameters give the following molecular structure:



with 17% of the Te-atoms 3-fold, rather than 2-fold coordinated. The over-coordinated Te-atoms are assumed to have a positive formal charge of 1, and a subsequently smaller atomic radius, thereby accounting for the reduced distance associated with the Sb-Te electrostatic bond [5]. The average bond coordination, $\langle r \rangle$, and average number of bond-stretching and -bending constraints/atom, C_{av} , have been determined using bond constraint theory. The inclusion of Ge-Ge bonding in Ge_2Te_3 groups provides microscopic basis for (i) the different systematic variations in C_{av} along the two tie-lines identified by Yamada *et al* [2]; (ii) the important role of 3-fold Te in the amorphous-to-crystalline transition exploited in optical memory applications and (iii) the ability of GST to form a good glass and its propensity for repeatable phase change transitions.

Finally, we discuss the prospects of making a glass computer. To do so, we have got to be sure we have a material that balances enthalpy and entropy exactly. The best way to determine this is to do EXAFS on some of the dead cells. If we find them to have $\langle r \rangle$ significantly larger than 2.4, we would tweak the composition to add a bit more Te. Conversely, if $\langle r \rangle$ were less than 2.4, we would make the composition less Te-rich. The problem is to get a sample of a dead cell that is large enough to do EXAFS on it. For now, the cells are too small and so it is not possible. We are working on the problem from both ends: we are trying to get a large dead cell and are developing ways to do EXAFS on smaller samples.

Acknowledgement

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References

- [1] S R Ovshinsky, *Phys. Rev. Lett.* **21**, 1450 (1968)
- [2] N Yamada, E Ohno, K Nishiuchi and N Akahira, *J. Appl. Phys.* **69**, 2849 (1991)
- [3] T Nonaka, G Ohbayashi, Y Toriumi, Y Mori and H Hashimoto, *Thin Solid Films* **370**, 258 (2000)
- [4] B Lee, J R Abelson, S G Bishop, D Kang, B Cheong and K Kim, *J. Appl. Phys.* **97**, 093509 (2005)
- [5] D A Baker, S C Agarwal, G Lucovsky, M A Paesler and P C Taylor, *MRS Proc.* (Spring Meeting, San Francisco, April 2006), Invited paper
- [6] D A Baker, M A Paesler, G Lucovsky, S C Agarwal and P C Taylor, *Phys. Rev. Lett.* **96**, 255501 (2006)
- [7] M F Thorpe, D J Jacobs, M V Chubynsky and J C Phillips, *J. Non-Cryst. Solids* **266–269**, 859 (2000)
- [8] F A Cotton and G Wilkinson, *Advanced inorganic chemistry*, 3rd Edition (Interscience Publishers, New York, 1972), Chap. 3, p. 117 (Table 3.4)
- [9] J C Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979)
- [10] J L LaGrange, *Mécanique Analytique* (Paris, 1788)
- [11] J C Maxwell, *Philos. Mag.* **27**, 294 (1864)
- [12] M F Thorpe, *J. Non-Cryst. Solids* **57**, 355 (1983)
- [13] D J Jacobs and M F Thorpe, *Phys. Rev. Lett.* **75**, 22 (1995)
- [14] X Feng, W J Bresser and P Boolchand, *Phys. Rev. Lett.* **78**, 23 (1997)