

## Bonding origin of optical contrast in phase-change memory materials

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The large optical contrast between crystalline and amorphous phases of phase change memory materials is shown to arise from a large difference in the optical matrix elements. These are enhanced in the crystal by aligned rows of resonantly bonded  $p$  orbitals. Amorphous phases have normal-sized matrix elements due to an absence of this order, irrespective of coordination number. This is a more general description of local order differences between the crystalline and amorphous phases, which applies even when coordinations in the amorphous phases exceed the  $8-N$  value.

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Phase-change materials (PCMs) are typically GeSbTe alloys characterized by rapid reversible transition between their crystalline ( $c$ -) and amorphous ( $a$ -) phases of surprisingly different optical and electrical properties.<sup>1</sup> The optical band gap of the amorphous phases is  $\sim 50\%$  larger than the crystalline phase. More importantly, the optical dielectric constant  $\epsilon_\infty$  of the crystalline phase is typically two to three times that of the amorphous phase.<sup>2</sup> There is so far no simple explanation of this difference. Presently, the difference in bonding of  $c$  and  $a$  phases is generally discussed in terms of nearest-neighbor coordination numbers. The extended x-ray fine structure (EXAFS) data of GeSbTe alloys of Kolobov<sup>3</sup> and Baker<sup>4</sup> suggest that the Ge coordination falls from 6 to 4 in the amorphous phase. This is rationalized as a transition to  $8-N$  rule bonding, typical of amorphous semiconductors.<sup>5</sup> The different coordinations might cause each phase to have a different electronic density of states (DOS) and thus different optical properties. However, photoemission finds the DOS of the crystal and amorphous phases to be quite similar,<sup>6</sup> as do the *ab-initio* molecular-dynamics simulations.<sup>7-9</sup> Thus, neither experiment nor modeling really explains the twofold to threefold optical contrast.

A second point is that the  $8-N$  rule exaggerates the bonding difference between  $a$  and  $c$  phases. Molecular-dynamics simulations actually find less difference, with Ge occupying distorted fourfold and sixfold sites as well as tetrahedral sites in  $a$  phase,<sup>7-9</sup> while EXAFS finds Te coordinations well over 2 in  $a$ -GeSbTe.<sup>4</sup> It is therefore valuable to have a more general model of bonding in the  $a$ -phase, beyond the simple  $8-N$  rule.

We show here it is possible to lose medium range order in a  $p$ -bonded amorphous phase, while retaining the *same* coordination number. In the crystalline phase, resonant bonding leads to ordering and alignment of  $p$  orbitals on adjacent molecular units. This alignment is lost in the amorphous phase, irrespective of whether the coordination changes. We show that this has a large effect on the *optical matrix elements*, which are roughly twice as large for resonantly bonded  $p$  states, while they revert to a smaller molecular bonding value in the amorphous phase. This causes the optical contrast and difference in  $\epsilon_\infty$  or  $\epsilon_1(0)$ . Medium range disordering is thus more critical than coordination in controlling optical properties. It therefore provides a more general rule of the bonding differences between PCM phases, beyond the  $8-N$  rule.

The bonding in most amorphous semiconductors ( $a$ -Si,  $a$ -III-Vs,  $a$ -As<sub>2</sub>Se<sub>3</sub>) follows that in their crystalline phases so that the electronic DOS is similar to that of the crystal, except for a loss of van Hove singularities. Hence, as the dielectric function is given by a matrix element times the integral over the joint DOS,<sup>10</sup> and the matrix elements are similar, their  $\epsilon_\infty$  values are the same,<sup>11</sup> see Table I. Robertson *et al.*<sup>13</sup> and Shportko *et al.*<sup>2</sup> suggested empirically that the optical contrast might arise from a loss of *medium-range* order (MRO) and resonant bonding in the amorphous phase, which substantially reduces the optical matrix element, without much change in the DOS. We verify this idea here with calculations on model periodic structures.

As an example, Fig. 1 compares the experimental  $\epsilon_1$  and  $\epsilon_2$  spectra of GeTe in its crystalline (rhombohedral) and amorphous phases.<sup>2</sup> The main  $\epsilon_2$  peak of  $c$ -GeTe is much stronger and lies at lower energy than in  $a$ -GeTe. By Kramers-Kronig analysis, this translates into a smaller  $\epsilon_1(0)$  for  $a$ -GeTe.

To understand what is happening, consider Se. The most

TABLE I. Optical dielectric constants  $\epsilon_1(0)$  for crystal ( $c$ ) and amorphous ( $a$ ) phases, experimental (Refs. 2, 5, 11, and 12), some from Wemple using his Eq. (1) and Table IV. Calculated  $\epsilon_1(0)$  values for polymorphs with resonant and nonresonant bonds (aligned and unaligned  $p$  orbitals). Si, Ge, and GaAs values for reference. The calculated  $\epsilon_1(0)$  value may be overestimated due to the usual underestimate of band gap in local-density formalism.

	Experiment		Calculated	
	Crystal	Amorphous	Resonant	Nonresonant
Se	9.7	5.77	11.4	9.27
Te	29.5	12.4	49	17
GeTe	33.2	13.2	58	20
GeTe 4-2 bonded				8.1
Ge <sub>2</sub> Te <sub>3</sub>				11.9
As	26	19		
Sb			230	28
Si	11.6	11.6		
Ge	16	16		
GaAs	12	12		

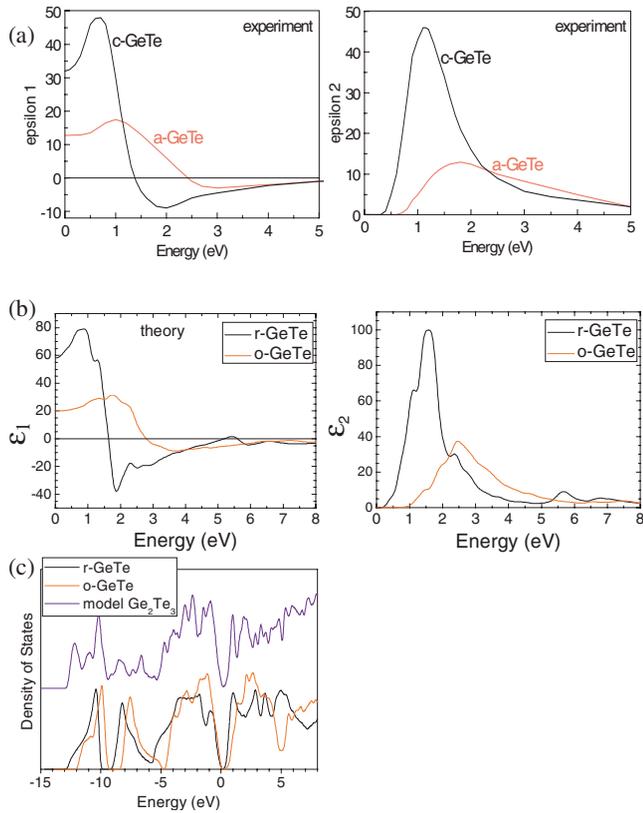


FIG. 1. (Color online) (a) Experimental dielectric functions of crystalline and amorphous GeTe (Ref. 2). (b) Calculated dielectric functions of *r*- and *o*-GeTe. (c) Calculated density of states for *r*-GeTe, *o*-GeTe, and  $\text{Ge}_2\text{Te}_3$  with 8-N bonding.

stable phase is trigonal Se (*t*-Se) whose atoms form spiral chains. This has a distorted simple cubic lattice with two short intrachain bonds and four longer interchain bonds so that the *p* orbitals on each site align along interchain bonds<sup>14</sup> [Fig. 2(a)]. The second crystalline phase of Se is monoclinic Se (*m*-Se), consisting of eightfold rings. Although crystalline, its *p* orbitals no longer align between molecules [Fig. 2(b)]. Amorphous Se consists of chains but with ring-like dihedral angles.<sup>15</sup> Locally, *m*-Se is a reasonable model of *a*-Se. We calculated the band structures and dielectric functions of *t*-Se and *m*-Se in the local-density approximation and find that  $\epsilon_1(0)$  of *t*-Se is 20% larger in *m*-Se (Table I). Thus, the change in intermolecular order explains the different  $\epsilon_\infty$  values of *t*-, *m*- and *a*-Se.

We repeat this for Te using *m*-Te as a model of *a*-Te. Figure 3 shows the calculated DOS and dielectric functions of *t*-Te and *m*-Te, with the calculated  $\epsilon_1(0)$  of *t*-Te being 2.8 times that of *m*-Te. This is near the 3.0 factor between the experimental  $\epsilon_1(0)$  of *t*-Te and *a*-Te.

Now consider GeTe. Crystalline GeTe is stable in the A7 rhombohedral (*r*-) structure. A7 is also a distorted simple cubic structure, in which atoms move off-center to form three short bonds and three long bonds. The short bonds form a puckered layer. We calculated the optical spectra of *r*-GeTe by LDA and find  $\epsilon_1(0) \sim 58$ , compared to 33 experimentally (Table I).

Consider two different models of *a*-GeTe. First, we made

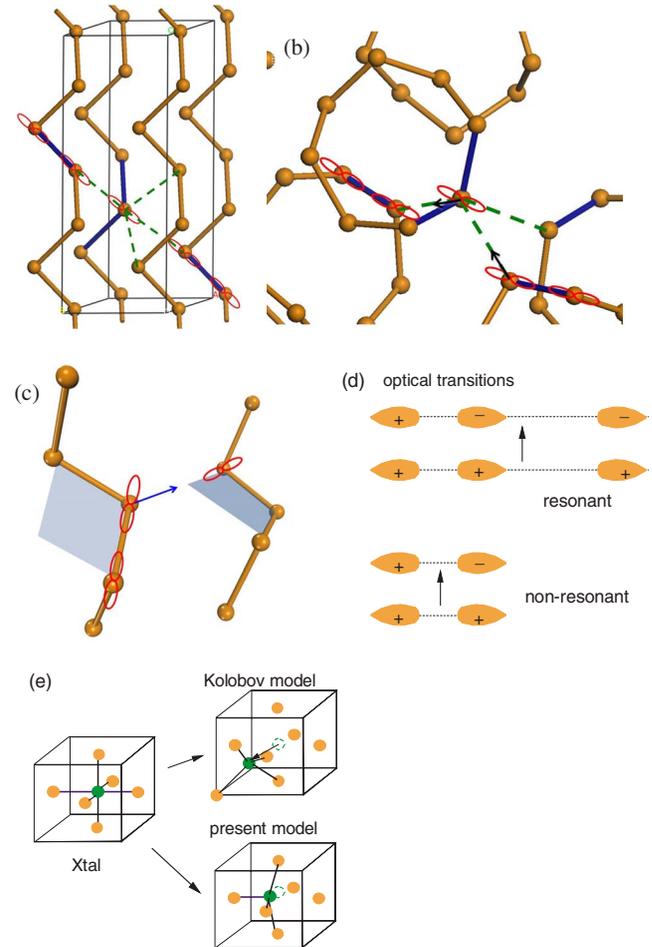


FIG. 2. (Color online) [(a) and (b)] Local order in trigonal and monoclinic Se, noting the *p* orbitals aligned in *t*-Se but not in *m*-Se, (c) how *p* orbital alignment is lost by displacement. (d) Optical transitions between bonding and antibonding orbitals in resonant and nonresonant cases. (e) Transition from sixfold to fourfold in Kolobov and our model.

various 4-2 coordinated structures obeying the 8-N rule containing Ge-Ge bonds. The calculated  $\epsilon_1(0)$  values vary from 5.8 to 11.1. A second model of *a*-GeTe is orthorhombic (*o*-) GeTe. It has the orthorhombic structure of GeSe and the 3-3 coordination of *r*-GeTe rather than the 8-N rule. The short bonds form puckered double layers, and there are long bonds both within and between the layers. (Its long bonds have similar length to those in *r*-GeTe.) The calculated  $\epsilon_1(0)$  of *o*-GeTe is 20.0, only 34% of *r*-GeTe. This replicates the factor 2.5 difference in experimental  $\epsilon_1(0)$  values of GeTe. Thus, *o*-GeTe is a phase with extreme optical contrast, *not obeying the 8-N rule* but retaining the 3-3 bonding of *r*-GeTe. This supports our more general model of bonding in amorphous phases, defined by a loss of aligned *p* orbitals, but which allows both 8-N and non-8-N bonding types.

These results show that strong optical contrast is possible for GeTe with the *same* coordination number of 3. How does this arise? In the isoelectronic Sb, the 5*s* electrons form a deep nonbonding state and its three *p* orbitals each contain one electron used for bonding. In simple cubic, the *p* orbitals

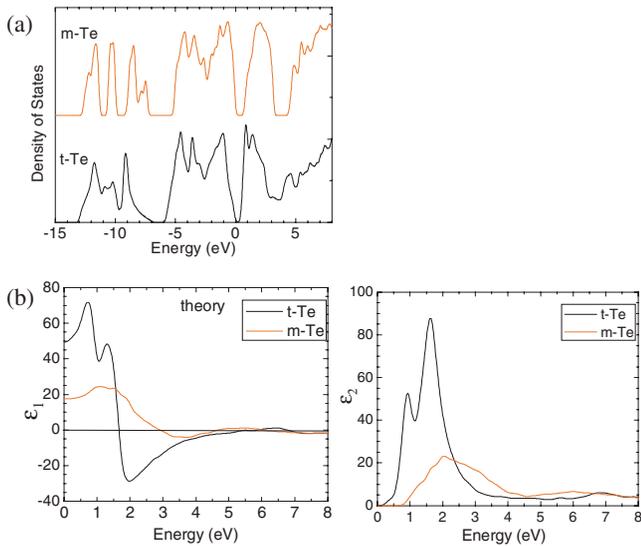


FIG. 3. (Color online) (a) Calculated density of states for *t*- and *m*-Te, and (b) calculated dielectric functions.

form three linear chains running along *x*, *y*, and *z* directions. This leads to a half-filled band with zero energy gap at the Fermi level  $E_F$ . This structure is unstable to a Peierls dimerization, which opens a gap at  $E_F$ , and creating the puckered layers of *r*-Sb. Despite this, the *p* orbitals retain linear alignment in the rhombohedral phase. The *p* bonding is called “resonant” because the valence electrons resonate between the three strong and three weak bonds of the original cubic lattice.<sup>16</sup> The same effect occurs in *r*-GeTe.

The amorphous phase retains some square bonding motifs of the cubic, such as fourfold atom rings.<sup>9,17</sup> However, the absence of MRO means that the squares are displaced perpendicular to their plane or rotated with respect to each other, losing *p* orbital alignment [Fig. 2(c)]. This displacement and rotation is the critical aspect that distinguishes the MRO of *c* and *a* phases. Loss of alignment of *p* orbitals changes the optical matrix elements from that of resonant bonding to that for molecular bonds, a much short dipole [Fig. 2(d)].

We calculated the electronic DOS for various GeTe polymorphs. Their DOS of polymorphs with aligned and non-aligned *p* orbitals are very similar (Fig. 3). However, the dipole matrix elements  $M = \langle i | x | f \rangle$  are very different, where *i* and *f* are the initial and final states. For normal two-center bonds, *M* is about one bond length. For resonant bonding, the aligned chains have *M* values of typically two bond lengths. This difference is the fundamental source of the optical contrast.

This leads to three general points. The amorphous phases have no MRO at the second-neighbor level. Second, PCMs often have two *crystalline* polymorphs, a high-symmetry one with aligned *p* orbitals, and a low symmetry one with no alignment. The nonaligned polymorph can be used as a simple model of the *a*-phase. Third, the effect of different MROs on optical properties is much greater for heavier Ge, Sb, and Te than Si, As, or Se phases because of the stronger interunit bonding and higher metallicity of heavier elements.

Generalizing this to GST, Kolobov<sup>3</sup> previously repre-

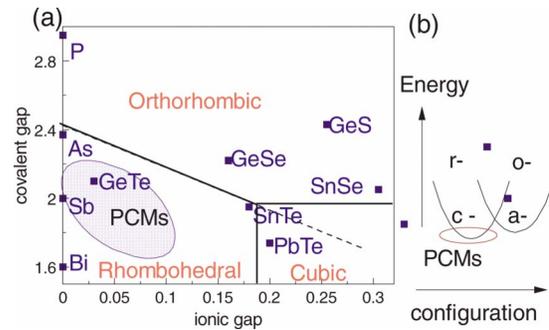


FIG. 4. (Color online) (a) Orbital ionicity plot of IV-VI phases, with good PCMs lying in the rhombohedral stability zone, (b) schematic of phase stabilities of good phase change materials.

sented the *c* to *a* transition as an umbrella flip of the Ge atom along the (111) direction, from octahedral to tetrahedral [Fig. 2(e)]. However, many Ge sites in GST are distorted fourfold sites,<sup>7–9</sup> and an alternative description of the transition is shown in Fig. 2(e). The Ge atom is displaced along (110) rather than (111), consistent with melting within a [111] plane, not along the (111) direction.<sup>18</sup> Generally, as Ge moves from sixfold to fourfold, the coordination distribution sharpens up, but the other two neighbors now form a boarder distribution, not seen by EXAFS.

Welnic<sup>19</sup> proposed a spinel model of *a*-GeSb<sub>2</sub>Te<sub>4</sub>, with fourfold Ge. The spinel has the smaller optical matrix element than the octahedral phase.<sup>20</sup> There, fourfold Ge sites break the resonant bonded Sb-Te chains, reducing  $\epsilon_1(0)$ . But we can break resonant bonding not only by inserting fourfold Ge but by simply misaligning *p* orbitals while retaining threefold coordination.

Thermodynamically, PCMs use weak glass formers Te, Sb, and Ge to give rapid phase transitions. Optical contrast is highest in these materials as they have more isotropic bonding—so when angular disorder disturbs intermolecular *p* orbital alignment, it strongly decreases  $\epsilon_1(0)$ . Good glass formers Se and As<sub>2</sub>Se<sub>3</sub> have weak interunit bonding, so disorder has less effect on  $\epsilon_1(0)$ . Thus, chemical trends give both rapid transitions *and* large optical contrast.

Which materials make the best PCMs. Lencer *et al.*<sup>21</sup> found that PCMs fall within the rhombohedral region of the Littlewood<sup>22</sup> phase diagram of IV-VI compounds [Fig. 4(a)]. This is consistent with our view. The stable crystalline phase of a good PCM should be a resonant rhombohedral phase, while the metastable amorphous phase should be nonresonant—orthorhombic—as in Fig. 4(b).

Our focus on MRO suggests that the crystalline to amorphous phase transition in PCMs generally involves a change in MRO and not simply a coordination change of single atoms, such as a proposed umbrella flip of Ge.<sup>3</sup> Experimentally, the energy barrier of the transition is quite high,  $\sim 2.4$  eV.<sup>23</sup> Indeed, the rate equation needs a large barrier and a large prefactor to give simultaneously a long (10 year) storage time at room temperature plus a fast phase transition at elevated temperature. The umbrella flip was calculated to have minimal barrier,<sup>24</sup> whereas a multi-atom MRO change would involve both a sizable barrier for multiple bond rearrangements plus a large entropy.

The effect of disorder on  $s$  or  $p$  states is very different. In  $s$  states, angular disorder has no effect; electron mobilities of  $10\text{--}30\text{ cm}^2/\text{V s}$  occur in amorphous oxide semiconductors.<sup>25</sup> In contrast, in  $p$ -bonded systems, angular disorder alone breaks the resonant bonding in PCMs, while dihedral angle disorder localizes the entire  $\pi$  band in  $a\text{-C}$ .<sup>26</sup>

In summary, angular disorder within  $p$ -bonded polymor-

phs with the same coordination number can cause large differences in optical functions. The key difference in bonding between the crystal and amorphous phases is not a reversion to 8–N rule bonding but loss of second-neighbor angular order.

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