

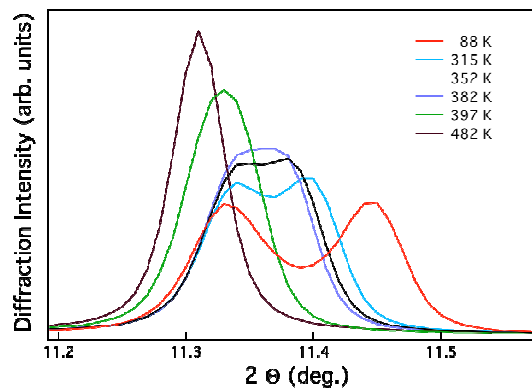
## Structure and bonding in phase-change alloys

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Properties of a material are determined by its structure. It is thus necessary to know the details of the structure in order to understand the materials' properties. 'Structure' means different things in different contexts. Thus the structure of crystals is usually determined from diffraction studies. It should be kept in mind, however, that Bragg diffraction (and in 99% of cases diffraction implies Bragg diffraction) occurs on planes of atoms in a solid, i.e. it is sensitive to average atomic positions. This said, Bragg diffraction cannot detect stochastic local distortions.

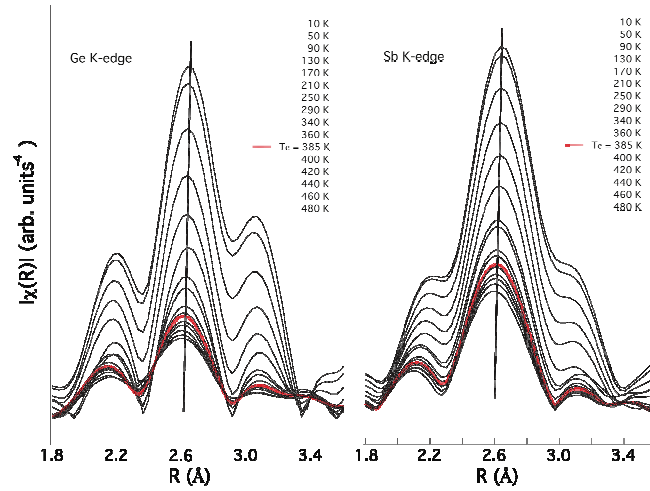
There are two examples relevant to phase-change materials. One is the ferroelectric transition in GeTe-based compounds. The general consensus is that GeTe is rhombohedrally distorted at low temperature (has three shorter and three longer Ge-Te bonds) and changes to the cubic rocksalt phase at temperatures above the Curie point. This transition, called displacive, has been originally derived from neutron diffraction but is also evident from X-ray diffraction (Fig. 1) [1]. The two peaks characteristic of a rhombohedral phase merge into a single peak characteristic of the cubic phase, leaving little doubt about the displacive nature of the transition.



**FIGURE 1:** Bragg diffraction spectra of GST-8211 at different temperatures indicating a transformation from a rhombohedral phase to the cubic phase, after [1].

At the same time, local structural probes such as EXAFS or total scattering have unambiguously demonstrated that shorter and longer bonds persist across the ferroelectric transition (Fig. 2) i.e. locally the structure *does not* change to the rocksalt phase [2,3]. In other words the transition is of order-disorder type. This situation is not unique to GeTe. There are numerous examples in the literature [4] when ferroelectric transitions, order-disorder in nature, were ascribed to displacive type when based on Bragg diffraction alone.

Along the same lines, while Bragg diffraction studies suggested that GeSbTe alloys in the metastable phase possess a cubic structure, EXAFS, and subsequently neutron scattering studies demonstrated that the structure is locally rhombohedrally distorted, similar to GeTe.



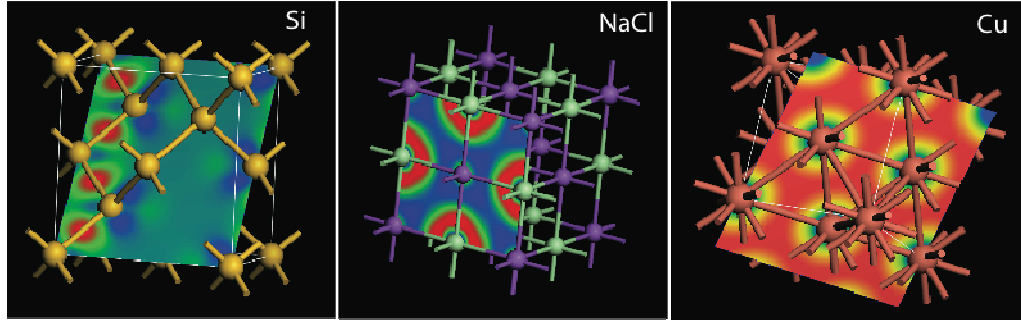
**FIGURE 2:** Fourier-transformed EXAFS spectra of GST-8211, measured across the ferroelectric transition [1].

These examples demonstrate that use of Bragg diffraction alone is insufficient for phase-change materials where the shorter and longer bonds co-exist and use of local probes is crucial to resolve the details of the structure.

While the existing stochastic distortions are irrelevant for some cases where the average structure determines the properties, in some other cases, the presence of distortions is crucial. Thus, when the longer bonds break during the amorphisation process, displacements of Ge atoms are also stochastic giving rise to large entropic losses. Confinement of Ge motion to one direction realised in iPCM resulted in a drastic (95 % !!!) decrease in energy consumption.

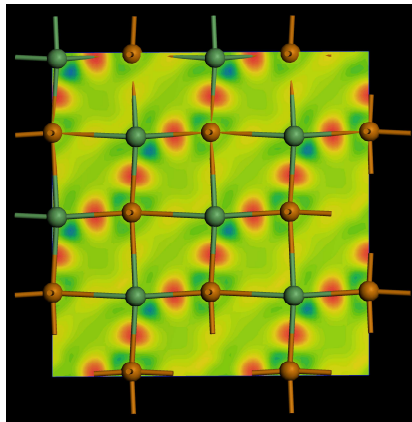
It should be also noted that both diffraction and EXAFS are one-dimensional probes. In order to get insights into three-dimensional arrangement of atoms, it is crucial to use 3D probes such as XANES spectroscopy. It was through use of XANES that differences between tetrahedral Ge sites and four-fold coordinated Ge sites with close to 90° bonding angles, were resolved experimentally [5]. It was also use of XANES that demonstrated that a significant fraction of Ge sites in the crystalline phase were not resonantly bonded [6].

According to Ioffe and Regel, properties of a material are determined by the short-range order. Here, again, it should be realised that the short-range order is determined *not only* by the atomic structure *but also by the nature of interaction between the atoms*. There are various ways of looking into this issue, such as electron localisation function, charge density difference (CDD), and localised Wannier orbitals, to name a few; each having its own advantages and disadvantages. We have chosen to use CDD as it directly shows the redistribution of electron density resulting from interatomic interaction. Shown in Fig. 3 are CDD maps for covalently bonded Si, ionically bonded NaCl and metallic Cu. A charge pile-up half-way between two atoms is a signature of a covalent bond. Below we apply the CDD analysis to phase-change alloys, starting with GeTe.



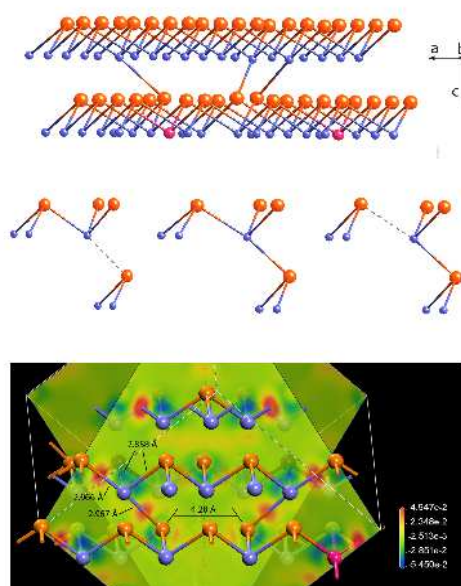
**FIGURE 3:** CDD maps for covalently bonded Si, ionically bonded NaCl and metallic Cu, after [7]

The description of GeTe as distorted cubic suggests its three-dimensional structure. At the same time, application of the CDD analysis demonstrates the presence of a strong bonding energy hierarchy and a better description of GeTe is a layered structure with covalent-like bonds within layers and a weaker interaction between the layers.



**FIGURE 4:** CDD map of ideal GeTe [8]

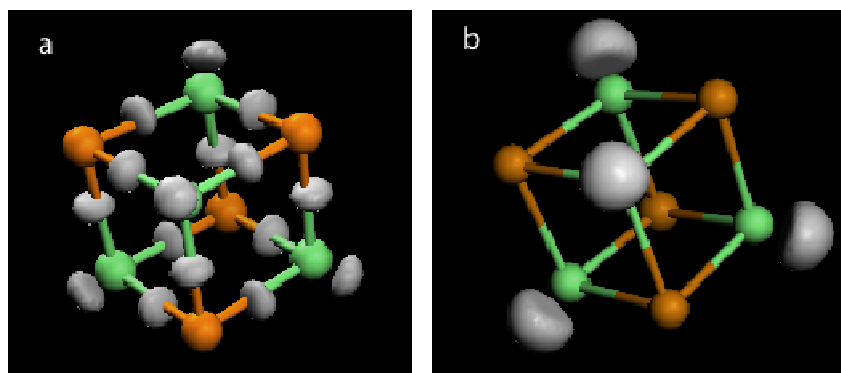
What is the nature of the weaker interaction? In the ideal GeTe the weaker bonds are formed using back-lobes of the same orbitals that are used to form stronger intralayer bonds. The back lobes have anti-bonding nature with respect to the shorter bonds but they have bonding nature for Ge-Te pairs with longer interatomic distances. Hence the *nature* of bonding is the same on both sides of any given Ge (or Te atom) but the *strengths* of bonding is different due to different interatomic distances in the Peierls-distorted structure. Bonding in GeTe can thus be referred to as partially resonant. The difference in the bonding strength is rather strong and has a significant impact on the stability of GeTe making it intrinsically fragile [8].



**FIGURE 5:** The formation of 3c-4e bonds using Te lone-pair electrons [7].

Upon Sb substitution, Ge-site vacancies and two-fold coordinated Te atoms are created, giving rise to three-center four-electron bonds, whose presence diminishes the hierarchy between the intra- and interlayer bonds resulting in a more symmetric cubic structure with a larger degree of resonance. The 3c-4e bonds in GeSbTe are softer than similar bonds in GeTe which may be a possible reason for the larger cyclability of GeSbTe and its different crystallisation mechanism [7].

The bonding nature, i.e. the distribution of electrons, is equally important in the amorphous phase. While some time ago it was proposed that local Ge(3):Te(3) bonding configuration with  $90^\circ$  bonding angles in GeTe is a result of p-type bonding combined with the formation of dative bonds [5, 7, 9], it was subsequently shown that Ge orbitals are in fact  $sp^3$ -hybridised, resulting in the presence of lone-pair orbitals subtended at Ge atoms. The presence of these orbitals facilitates the formation of tetrahedral sites, and is argued to be responsible for structural relaxation in the amorphous phase, including the drift phenomenon [10].



**FIGURE 6:** The increase charge density at Ge atoms along the GeTe cube diagonals (left: CDD, right: ELF) suggests that Ge atoms are  $sp^3$  hybridised despite the  $90^\circ$  bonding angles.

Finally, in the talk we discuss how the nature of interatomic bonding affects GeTe-Sb<sub>2</sub>Te<sub>3</sub> superlattices opening new possibilities for iPCM device fabrication.

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