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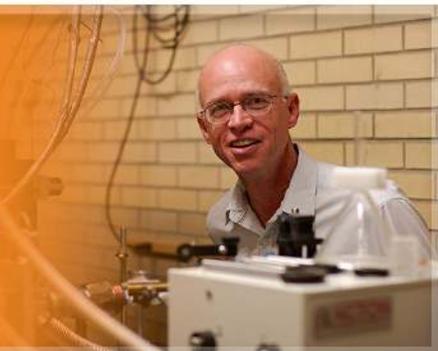Crystal morphology and nucleation in thin films of amorphous Te alloys used for phase change recording
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Structural study on amorphous and crystalline state of phase change material

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We report an inelastic (Raman) light scattering study on bulk crystalline GeTe (c-GeTe) and amorphous GeTe (a-GeTe) thin films and found to show pronounced similarities in local structure between the two states. In c-GeTe, the observed Raman modes represent the Ge atoms are in three different environments, namely, tetrahedral, distorted, and defective octahedral sites. On the other hand, in a-GeTe, Raman spectrum reveals Ge sites in tetrahedral and defective octahedral environment. We suggest that the structure of c-GeTe consists of highly distorted as well as defective Ge sites, which leads to the large concentration of intrinsic defects (vacancies). These random defects would act as topological disorder in the lattice and cause the bands to develop tails at the band edges, a continuum of localized levels appearing in the gap. The present study deepens the understanding of the local atomic structure, influence of defects and its close relation to the phase-change mechanism. © *2011 American Institute of Physics*. [doi:10.1063/1.3653265]

I. INTRODUCTION

Germanium telluride, GeTe, is the well known prototype phase change material (PCM) and is the basic ingredient of *pseudobinary* compound of GeTe-Sb$_2$Te$_3$ alloys, which are commercially used in rewritable optical memory (CD, DVD) and electronic non-volatile memory (NVM) technology.[1–3] These materials are largely found to show rapid and reversible transitions between the crystalline and amorphous state by an application of intense laser or electric pulse. Although the phase change phenomenon has been found by Ovshinsky about four decades back, the mechanism behind this behaviour is under debate. Most of the models involve in this topic are more specific or indirect assumptions about the microscopic structure in general and/or in the distribution of various structural units and the energy barriers between the two states in particular. Recently, significant progress has been made in this field by both experimental and theoretical simulation techniques.[4–8] Based on these results, it has been shown that the contrasts between the two states are largely characterized by considerable difference in their optical and electrical properties. These differences are largely ascribed to (1) change in the bonding character between the two states, consequently leads to change in the nearest-neighbour coordination numbers,[4] (2) presence of large concentration of intrinsic defects (vacancies) in the crystalline state,[5] and (3) a Peierls distortion in an octahedral Ge environment.[7] Most attempts to understand this phenomenon have been focused on the basis of structural aspects, as we do here.

Spectroscopic techniques provide much less information about the amorphous phases than in crystals. In spite of this, experimental work on amorphous GeTe (a-GeTe) and its alloys includes extended x-ray absorption fine structure (EXAFS), x-ray and neutron scattering, XPS, and Raman scattering measurements focused more on the local atomic structure and bonding nature.[9–14] All these techniques, in particular, EXAFS data suggests that the Ge coordination falls from 6 to 4 in the amorphous phase and the phase change in GeTe could be simply an octahedral-to-tetrahedral (umbrella) flip of Ge atoms, by assuming that all the Ge atoms are octahedrally coordinated in the corresponding c-GeTe.[13] In addition to the Ge coordination changes, there is controversy about the presence of homopolar Ge-Ge bonds in both states.[14] These discrepancies are due to the nature of the sample studied in the literature and the quality of absorption edge data fitting. Most of these studies have been carried out on crystallisation of vacuum deposited amorphous thin films. The formation of single phase α-GeTe by crystallization of amorphous thin film is strongly influenced by many factors such as thickness of the film, annealing temperature, aging effect, etc.[15] Thus, in order to neglect these factors, we have carried out experimental investigations on bulk c-GeTe sample.

In parallel with experimental work, theoretical *ab initio* molecular dynamics (MD) simulations have been performed to identify the origin of large contrast between the two states in terms of structural and dynamical aspects.[16–20] These studies mostly concentrated on a-GeTe and liquid GeTe. The main deceive results from these calculations has demonstrated that indeed majority of Ge atoms are in preferably tetrahedral environment, one third of Ge atoms are in defective octahedral sites (mostly four coordinated), and all Te atoms are three-fold coordinated.[16] Further, these MD simulation studies are supported by the recent theoretical *ab initio* calculation of Raman spectra of a-GeTe and c-GeTe by bond polarizability model (BPM).[20] Although the BPM provides more detailed picture of a-GeTe structure, failed to elaborate more about

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c-GeTe, by assuming that Ge atoms are in an octahedral sites in accordance with the Raman studies of single crystal α-GeTe.[21] More recently, it has been shown that resonance aspect of chemical bonding in the crystalline state is a unique fingerprint of PCMs.[22] The concept of "*resonance bonding*" addresses the case of covalent bonding with unsaturated bonds, that is, less than two electrons per bond. Following above concept, it has been suggested that the large contrast between the two states arise from a significant difference in the optical matrix elements, enhancement in the crystalline state by the aligned rows of resonantly bonded *p* orbitals and are absent in the amorphous state.[23] Therefore, a compelling experimental identification of cause for the phase change behaviour has not yet been provided.

In the present work, we have carried out inelastic (Raman) light scattering study on bulk crystalline α-GeTe and amorphous GeTe (a-GeTe) films and found to show pronounced similarities in the local atomic structure between the two states. More qualitatively, we show that the structural similarities between the two states can be directly related to the existence of nearly identical structural units and the electronic states accompanied by the intrinsic defects in the c-GeTe. Further, we identify that the influence of these defects on the structural stability of the c-GeTe and in the lattice would act as disorder, which causes the bands to develop tails at the band edges, a continuum of localized levels appearing in the gap. The disorder in c-GeTe is a direct consequence of the defects incorporated in the off-stoichiometric sub-lattice, which ultimately would lead to minimal barrier for multiple bond rearrangements.

II. EXPERIMENTAL

Bulk stoichiometric crystalline α-GeTe was prepared by slow cooling of the melt and then subsequently recrystallised at 708 K and 518 K for about 6 h. Crystallized phases were identified by the x-ray diffraction (XRD) and the nominal composition was examined by energy dispersive x-ray (EDX) analysis. a-GeTe thin films of about 500 nm thickness were deposited by dc sputtering directly onto glass substrates from a stoichiometric target of GeTe (99.99% purity). During the deposition, the background pressure of 5×10^{-5} mbar, 20 sccm Ar flow with deposition rate of 0.085 nm.s^{-1}, and operating in constant power mode of 20 W were maintained. As deposited thin film samples were characterized by XRD, TEM, and EDX and confirmed their amorphous nature and the stoichiometric. We did not find any nano/micro crystals in the as deposited amorphous thin films. The room temperature Raman spectra of α-GeTe and a-GeTe samples were recorded in the 180° back scattering geometry, using a 514 nm excitation of a air-cooled argon ion laser (Renishaw InVia Reflex Micro Raman Spectrometer). The incident laser power was adjusted to ∼0.1 mW for a-GeTe thin film and ∼2 mW for bulk α-GeTe sample in order to minimize heating effects on the illuminated sample region and, the spectral resolution was 1 cm^{-1}. To proceed for a quantitative determination of the various structural units in both states, it is necessary to use deconvolution procedure with the aim of separating individual vibrational modes from the composite line envelopes of temperature-reduced Raman spectrum in both cases.

III. RESULTS

The experimental powder XRD pattern (filled square) of bulk crystalline α-GeTe recrystallized at 708 K compared with the Rietveld-refined profile (solid line) and the difference curve is shown in Fig. 1. The Rietveld analysis shows that the obtained XRD pattern and the refinement converged with good statistics (JCPDS 47-1079; space group R3m). Furthermore, we have found that the Rietveld analysis on the recrystallized bulk GeTe sample at lower temperatures (518 K) resulted larger χ^2 (1.83) than recrystallized at 708 K sample with smaller χ^2 (1.66) represent a rather high reliability of the results.[24] Thus, the XRD results suggest that the structure of c-GeTe consists of highly distorted from the cubic rocksalt structure, i.e., it crystallizes in a distorted rocksalt (rhombohedral) structure with both Ge and Te atoms having only the opposite species as the nearest neighbours with two different bonding distances and there is no evidence of any other phases existence. Based on these results, we confirm that the obtained bulk recrystallized sample is single phase and the degree of local distortion strongly depends on the annealing conditions.

It is known that the Raman scattering by optical phonons of cubic phase of GeTe is forbidden by symmetry but is allowed in the low temperature phase of rhombohedral structure because of the lack of inversion symmetry. The Raman active vibrational symmetries and tensor components for α-GeTe structure would be of three optical phonon modes, i.e., $A_1(Z)$, $E(Y)$, and $E(-X)$, where X, Y, and Z denote the phonon polarization directions in the C_{3v} coordinate system and Z is the trigonal axis.[25] Experimentally, it has been observed that the Raman spectra of single crystal α-GeTe consists of both E and A_1 active modes at 93 and 127 cm^{-1} at room temperature and in parallel with lattice dynamical calculations, where the later one found to be as soft optical phonon

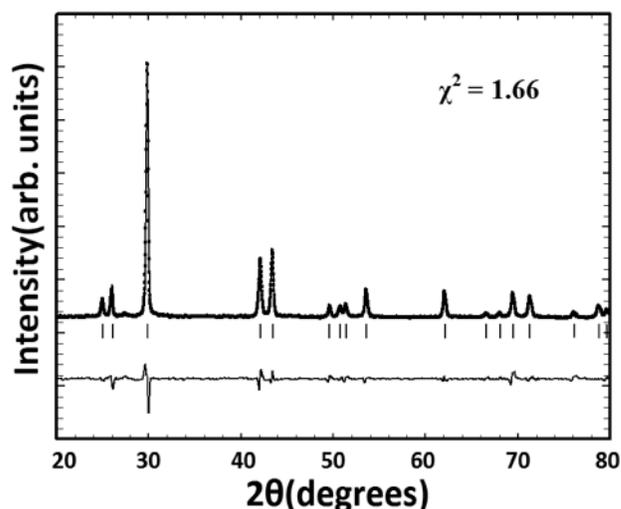FIG. 1. The experimental powder XRD pattern (filled square) of bulk crystalline α- GeTe (recrystallized at 708 K) compared with the Rietveld-refined profile (solid line) and the difference curve (bottom curve). The vertical spikes below the observed profiles indicate the predicted Bragg positions.

mode.[21] Based on the above assignments, we denote the observed E and A_1 modes solely due to the distorted octahedral environment of Ge atoms. The reduced Raman spectra of c-GeTe sample recrystallized at 708 K along with a-GeTe sample recorded at room temperatures are shown in Fig. 2. On a macroscopic level, there are significant differences between the c-GeTe and a-GeTe at high frequencies.

Remarkably, the Raman spectrum of c-GeTe in the present study is different from those reported in an earlier experimental study on crystalline thin film samples due to the lack of single phase α-GeTe.[13,14] In Fig. 3, we present the quantitative description of vibrational modes with the aid of a Gaussian line fitting procedure on bulk c-GeTe sample (recrystallized at 708 K) by using the four bands and are labelled C, E, G, and I in the frequency range of 50–275 cm^{-1}. The fitting parameters (peak position, width, and area) of the Raman data are summarized in Table. I. The frequency assignment of different species is based on comparisons of the experimental Raman spectra of isochemical crystals as well as theoretical calculations.[21,25] Based on the deconvolution procedure, we assign that Raman bands at 95 and 128 cm^{-1} correspond to the distorted octahedrally coordinated Ge atoms in accordance with the earlier reports.[20,21] In addition to these bands, we find a well defined Raman band at 156 cm^{-1} (band G) and at 233 cm^{-1} (band I) represent the vibrations of Ge atoms distinct from the distorted octahedral sites.

Recently, it has been shown by theoretical simulations and empirical bond polarizability model about the peculiar local structures of the a-GeTe and unravelled the presence of significant concentration of defective octahedral sites in a-GeTe in addition to the tetrahedral sites. Furthermore, these results are supported by the *ab initio* molecular dynamics studies on a-GST, where the one third of Ge atoms are in a tetrahedral position while the remaining Ge, Sb, and Te atoms shows a defective octahedral environment.[26] In this context, it is worthwhile to consider the experimental results obtained by coherent phonon spectroscopy, which provides the microscopic origin of ultrafast dynamics of coherent optical phonons occurring on ultrafast time scales. It is found
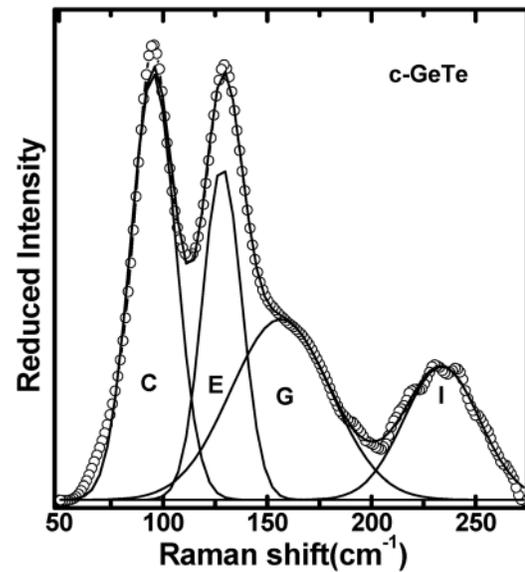
FIG. 3. Deconvoluted reduced Raman spectra of c-GeTe (recrystallized at 708 K) measured at room temperature (open symbols) and a representative fitting (lines) with four Gaussian bands to resolve the fine structure. The deconvolution procedure justified with the obtained R^2 of 0.99924.

that the appearance of the coherent vibrational modes significantly modified upon the phase change and in particularly, the motion corresponding to GeTe$_4$.[27] These results indicate that the peak at 4.8 THz (160 cm^{-1}) is due to the damping of the coherent phonons in a-GeTe and governed by the phonon-defect (vacancy) scattering rather than the anharmonic phonon-phonon coupling. Thus, we suggest that the vibrational mode at 156 cm^{-1} has different origin from the distorted octahedral sites and corresponds to defective octahedral sites (mostly in four coordinated sites) in accordance with those found in a-GeTe and a-GST (amorphous Ge$_2$Sb$_2$Te$_5$) (band at 165 cm^{-1}).[17,18] The Raman band at 128 cm^{-1} is composed of distorted and defective octahedral Ge atoms based on recent *ab initio* simulation studies and empirical bond polarizability model on a-GeTe.[20] Additionally, the theoretical calculation of phonon density of states for c-GeTe shows minimum at 112 cm^{-1} suggests that a pseudogap separating lower- and higher frequency optic like phonons.[20]

Insights on the phonons responsible for the defective and distorted octahedrally coordinated Ge sites are gained by carrying out Raman measurements in different polarization geometries. Fig. 4 shows the reduced Raman spectra of c-GeTe recrystallized at 518 K measured at room temperature with different polarization conditions. Strikingly sharp features appear in both the VV and VH Raman spectra of c-GeTe and more specifically the phonons above 190 cm^{-1} are mainly localized on the tetrahedral sites. The polarized VV spectrum emphasize phase coherence of atomic motions within the first coordination sphere or correlations in the motion of nearby atoms and are being reflected both by the distorted and defective octahedral coordinated Ge atoms. On the other hand, the polarized VH spectrum shown to resemble the density of states weighed by smoothly varying factors, where there is suppression of defective modes due to the localization. Using the above data, the degree of
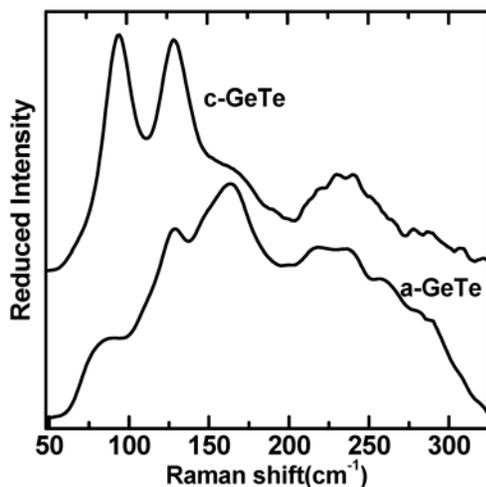

FIG. 2. Reduced Raman spectra of a-GeTe and c-GeTe measured at room temperature. The Raman spectra of c-GeTe represent the bulk sample recrystallized at 708 K.

TABLE I. Peak parameters (peak position, width, and normalised area) as determined through fits of the experimental data of bulk c-GeTe (recrystallized at 708 K) and a-GeTe. A possible assignment for individual peak has also been included in the second column.

		Crystal			Amorphous		
Peak assignment	Peak identity	Raman shift(cm)$^{-1}$	FWHM (cm)$^{-1}$	Normalised peak area	Raman shift(cm)$^{-1}$	FWHM (cm)$^{-1}$	Normalised peak area
A	3-fold coordinated Te				75	10.7	2.5
B	Symmetric bending mode of GeTe$_4$	—	—	—	87	17.8	8.3
C	Octahedral Ge	95	21.5	31.6	—	—	—
D	GeTe$_{4-n}$Ge$_n$ (n = 0)corner shared tetrahedra	—	—	—	112	18.3	11.4
E	Distorted octahedral Ge + defective octahedral Ge	128	18.9	21.8	—	—	—
F	Defective octahedral Ge	—	—	—	128	13.3	13.6
G	Defective octahedral Ge	156	47.8	29.9	160	23.4	30.9
H	GeTe$_{4-n}$Ge$_n$ (n = 1)Corner shared/isolated tetrahedra	—	—	—	189	25.3	11.0
I	GeTe$_{4-n}$Ge$_n$ (n = 1)isolated tetrahedra	—	—	—	218	22.4	10.4
J	GeTe$_{4-n}$Ge$_n$ (n = 2)Corner shared tetrahedra	233	36.1	16.7	238	11.2	3.0

depolarization is calculated by taking the ratio of the intensity of a Raman band measured with VH and VV geometry and it is sensitive indicator of symmetric properties of vibrational modes. In the present study, we find that depolarization ratio takes minimum value of 0.4 and correspondingly the Raman band at 128 cm^{-1} is attributed to the symmetrical vibration.[28] Thus, we conclude from the polarization measurements that the new band at 156 cm^{-1} coupled with band at 128 cm^{-1} is exclusively due to the defective octahedral sites. The spectral range above 190 cm^{-1} and below 275 cm^{-1} is due to the vibrations of different tetrahedral units, i.e., GeTe$_{4-n}$Ge$_n$ (n = 0–3) units.[20] The most recent experimental study on c-GST also reveals that the coexistence of both octahedral and tetrahedral Ge atoms and 35% of the total Ge atoms are in tetrahedral sites in their cubic phase.[29] Therefore, we suggest that in the crystalline state of α-GeTe structure, the Ge atoms are in three different environments, namely, tetrahedral, distorted, and defective octahedral sites.

The deconvoluted procedure has been adapted to reduced Raman spectrum of a-GeTe as shown in Fig. 5 and the corresponding peak assignments are summarized in Table. I. The important characteristic features of the obtained spectra of a-GeTe are similar to those reported in the literature.[13,16] More interestingly, in the case of a-GeTe, we do not observe a Raman band at 95 cm^{-1}, specific to the distorted octahedral Ge sites. In similar to c-GeTe, we assign the Raman bands at 125 and 162 cm^{-1} are corresponding to the vibrations of Ge atoms in defective octahedral sites. Further, we find that the significant fraction of Te atoms are three fold coordinated in addition to various tetrahedral GeTe$_{4-n}$Ge$_n$ units in a-GeTe, where these units are the main building blocks.[20] It is evident that the bands evolve above 200 cm^{-1} are higher intense than the c-GeTe due to the large concentration of various type of tetrahedral units. The distribution of these tetrahedral units has been discussed below and summarized in Table. I. Furthermore, we would like to mention that the presence of additional band in the deconvoluted spectrum at 144 cm^{-1} (peak X) may be due to the effect of aging.[16] Another interesting feature in the deconvoluted spectra of a-GeTe is that nearly 45% of Ge atoms are in the defective octahedral sites and in agreement with the theoretical *ab initio* calculation of Raman spectra of a-GeTe.[20] The Raman band above 218 cm^{-1} is assigned to be isolated tetrahedra with octahedral-like bonds, since they
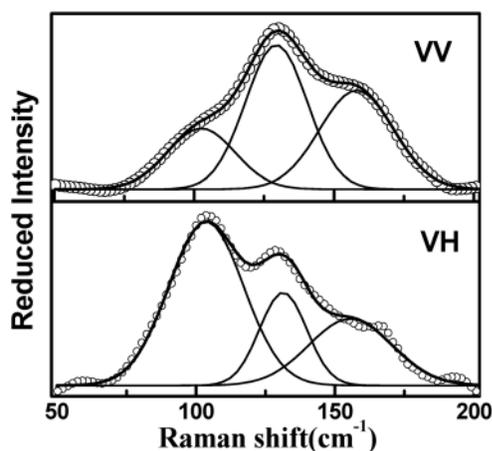
FIG. 4. Reduced Raman spectra of c-GeTe recrystallized at 518 K measured at room temperature with different polarization conditions.
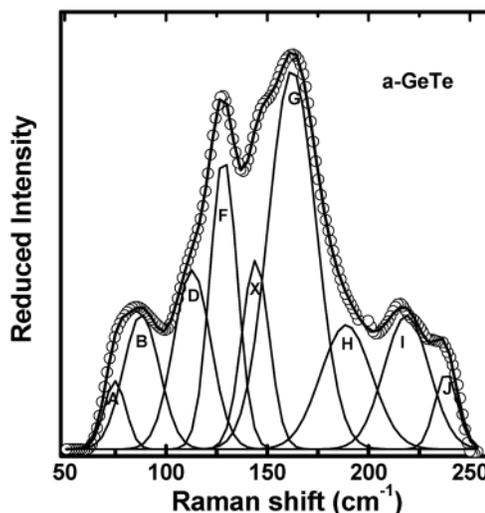
FIG. 5. Reduced Raman spectra of a-GeTe thin films (open circles) and a representative fitting (lines) with nine Gaussian bands to resolve the fine structure.

also belong to the neighbouring defective octahedral Ge atoms.[18,20]

IV. DISCUSSIONS

Finally, we analyse, in the following, the origin of local atomic structure on the phase change mechanism of GeTe. In spite of the Ge coordination change, there is significant amount of increase in the concentration of tetrahedral units in a-GeTe compared with c-GeTe. The presence of these tetrahedral units in the Raman spectrum between 198 and 240 cm^{-1} is very broad in the case of a-GeTe than c-GeTe. The broadening directly reflects the effect of disorder, which would lead to strong localization of these vibrational modes. The depth of this localization is expected to be comparable to the strength of the potential, i.e., to the amount of disorder present in the lattice. Thus, we suggest that the disordered defect states in the c-GeTe are originated from the different sources such as various types of tetrahedral units and defective octahedral coordinated Ge atoms.

Next, we would consider the relation between the type of structural units and the changes in the electronic states due to the defects. It has been shown that by using density-functional theory, the most stable crystalline phases of GeTe and GST with rocksalt-like structures are characterized by large vacancy concentrations and local distortions.[5,30] In crystalline IV-VI compounds, the absence of *sp* interaction is considered as semiconductors, with an average energy gap (E_g) equal to the energy difference ($\Delta\varepsilon$) between the *p* valance electron states of the anion and cation. Due to the *sp* interaction, the atomic orbital energies are lie within the bands and decrease the average gap and, therefore, destabilize the cubic structure. If the *sp* interaction becomes strong relative to $\Delta\varepsilon$, the crystal will be highly distorted (rhombohedral) and an increase in the average gap, while the *sp* interaction is small, the crystal will remain in the stable cubic structure. Further, small $\Delta\varepsilon$ indicates the gap would be less and there are states close to the Fermi energy. The rhombohedral distortion affects only such states and, therefore, affects the energy of the spectrum at the band edges.[31]

In this context, we use the idea of defect molecule[32] to understand more qualitatively the effect of vacancy on the electronic structure of GeTe. It has been shown that the vacancies in GeTe and GST alloys are predominantly due to the cation vacancies. First, let us consider a cation vacancy, where the defect molecules consist of six anion nearest neighbour. If the second-nearest-neighbour interactions are ignored, then, the eigenstates of the defect molecule will simply have energies equal to the anion atomic orbital energies and hence will be in deep resonance with valance bands. Similarly, if there is anion vacancy, then deep resonance states are found to be introduced in the conduction bands. Thus, the vacancies (ideal) in the GeTe and GST crystals induce states in resonance with the bands. Optical studies on bulk c-GeTe also indicate that the band edges have been strongly modified by the presence of defects.[33] Thus, the existence of the different type of defects and their random distribution in the sub-lattice ultimately leads to the bands to develop tails that stretch into gap and a continuum of localized levels in the gap. Furthermore, we suggest that the

larger number of pre-existing defects (vacancies) in c-GeTe would lead to minimal energy barrier and results the fast transition between the two states. In addition to this, different experimental and theoretical studies support that the band structure of amorphous GeTe would appear to be very similar to the band structure of crystalline GeTe.

V. CONCLUSIONS

In conclusion, we have shown that structural similarities between the crystalline and amorphous GeTe and their influence on the electronic structure. In c-GeTe, the Ge atoms are in three different environments, namely, tetrahedral, distorted, and defective octahedral Ge sites. On the other hand, in a-GeTe, the Raman spectra show only tetrahedral and defective octahedral sites. The present results directly support the *presence of large concentration of intrinsic defects (vacancies)* in c-GeTe due to the presence of various types of tetrahedral and defective octahedral units. These random defects in the lattice would act as disorder and cause the bands to develop tails at the band edges, a continuum of localized levels appearing in the gap. We believe that these correlations will bring more insights and better understanding for the optimization of phase change memory materials.

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