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Phase transition in crystalline GeTe: Pitfalls of averaging effects

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For the case example of GeTe, we demonstrate that the use of techniques that probe the average structure may lead to misleading conclusions regarding the nature of phase change. GeTe is a narrow band-gap semiconductor and a ferroelectric with the simplest conceivable structure that—according to previous studies—undergoes a ferroelectric-to-paraelectric displacive phase transition at ~705 K. In this work, we provide direct experimental evidence that, contrary to the existing paradigm, the local distortion remains essentially unchanged with temperature and argue that the previous conclusion about the displacive nature of the ferroelectric-to-paraelectric transition was due to misinterpretation of Bragg diffraction, a technique that is only sensitive to the average structure and does not "see" random local distortions. The reported results have far-reaching implications for other materials exhibiting displacive phase transitions where conclusions have been reached based on results obtained using averaging techniques.

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I. INTRODUCTION

Phase transitions constitute a vast and important field of solid-state physics from both academic and applied viewpoints. In many cases, conclusions about phase transitions and their nature are drawn based on Bragg-diffraction studies and/or Raman scattering. For the case of GeTe, we demonstrate that diffraction techniques, despite being very powerful, rely on average rather than local structure. This intrinsic limitation (spatial averaging) can lead to erroneous interpretation of the experimental results.

GeTe is a narrow band-gap semiconductor and also a ferroelectric with the simplest conceivable structure containing just two atoms in the unit cell. In the low-temperature ferroelectric phase GeTe (α-GeTe) possesses a rhombohedral structure with the space group $R3m$. This structure can be viewed as a rocksalt structure slightly distorted along the $\langle 111 \rangle$ direction with a subsequent shear relaxation along the $\langle 111 \rangle$. The driving force for the formation of the rhombohedral phase has been a subject of various studies in the past.[1] In this phase, Ge and Te atoms are sixfold coordinated by each other with subsets of three shorter (2.83 Å) and three longer (3.15 Å) bonds often described as a Peierl distortion due the reduced coupling between the p-type orbitals that constitute the basis for bonding in GeTe.[2]

Apart from presenting significant academic interest as a model IV-VI ferroelectric, GeTe presents a high technological interest being an end point of the GeTe-Sb_2Te_3 pseudobinary tie line that describes the so-called phase-change materials used in various memory applications.[3] The unusually large difference in material properties between the amorphous and crystalline phases of phase-change materials has been used in rewritable optical memory such as digital versatile disks (DVD) as well as in electrical memory applications with switching speeds on the order of a nanosecond.[4] In these materials, the local distortion around the Ge atoms is similar to that in the binary GeTe.[3] As a large fraction of the current rewritable DVD market as well as the now coming-to-market next generation of nonvolatile electrical memory devices are based on compositions along this tie line, understanding of the structural behavior of the simpler binary system holds the promise of giving deeper insight into the more complicated alloys used for commercial devices.

It should be noted that conventional dielectric techniques to measure susceptibility across the transition temperature are not possible for GeTe due to the very high electrical conductivity that precludes the formation of large electrical fields across the material.

Based on Bragg-diffraction studies, mainly neutron diffraction,[5] it was concluded that GeTe undergoes a displacive ferroelectric-paralectric transition with the Curie temperature, T_c, around 705 K transforming to the rocksalt structure (space group $Fm3m$) with concomitant disappearance of the Peierls distortion. Experimental bond lengths calculated from unit-cell data obtained from neutron-diffraction data[5] show an apparent symmetrical convergence of the two bond lengths present in the rhombohedral phase to the average value near T_c (Fig. 1, upper panel).

Interestingly, neutron-diffraction studies on *liquid* GeTe have revealed the presence of shorter and longer bonds in this material above the melting point and the term "reentrant Peierls distortion" was coined to describe this behavior.[8] The reentrant Peierls distortion has been attributed by the authors to partially remaining chemical order in the liquid phase.

Based upon the observation of phonon-mode softening with temperature, the displacive nature of the transitions has been also suggested by Raman scattering,[6] although the highest temperature studied was approximately 150 K lower than their estimated T_c.

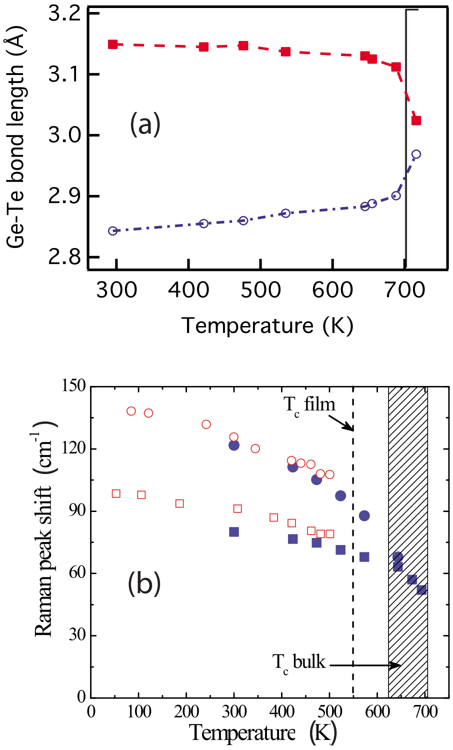

FIG. 1. (Color online) (a) Experimental evidence for the displacive nature of the phase transition. Ge-Te bond lengths calculated from unit-cell data obtained from neutron-diffraction data on bulk GeTe samples (Ref. 4). (b) Raman phonon-mode frequencies, filled symbols represent data from the present work on GeTe sputtered thin films; open symbols stand for data from Ref. 6 on bulk GeTe single crystals. The hatched area spans over the temperature range in which the critical temperature values T_c for the ferroelectric phase transition of GeTe have been reported in the literature. The dashed line represents the T_c of thin films (Ref. 7).

In a one-dimensional analog of a displacive phase transition, below T_c each atom resides on one side of a double-well potential and the positions of the atoms collectively change in all unit cells identically; the spacing between the minima decreases as temperature is increased. At T_c, the spacing between the well minima vanishes and the second derivative of the potential goes to zero giving rise to a soft mode. The orthogonal orientation of the lattice axes in the cubic phase allows application of this description, as well as the concept of a Peierls distortion, to the three-dimensional case.

In this paper, we report a detailed investigation of the structure of GeTe from 10 K to above the melting point and provide evidence that the macroscopical ferroelectric-paraelectric phase transition observed by diffraction is not of a displacive nature as has been believed to date but arises from an order-disorder transition with local distortions preserved across the transition temperature and also as the material melts. We argue that the misinterpretation of the nature of the phase transition arises from the use of Bragg diffraction that probes the ensemble average structure and is insensitive to random local distortions. We also argue that the obtained results may have significant implications for other cases when the reported phase transition were obtained by techniques relying upon average structure and where similar misinterpretation could have been made.

II. EXPERIMENTAL DETAILS

Stokes-side Raman spectra were recorded for a polycrystalline GeTe film with a transparent protective $(ZnS)_{0.85}(SiO_2)_{0.15}$ capping layer over a broad temperature range from room temperature to above T_c. The use of a capping layer is crucial as even small changes in composition due to Te sublimation at high temperature can lead to changes in the ferroelectric transition temperature; such considerations limited the temperature range of the earlier Raman study[6] and the resultant reliability of the conclusions drawn.

Micro-Raman spectra (×50 objective) were recorded with the aid of triple monochromator (Jobin-Yvon T64000) in the double subtractive mode using a Ti:Sapphire laser (pumped by an Ar^+-ion laser) as an excitation source ($\lambda = 763$ nm). The sample temperature was controlled using a hot stage (Linkam THMS600) with the accuracy of 1 K. More details can be found in Refs. 9 and 10. The Raman spectra were analyzed quantitatively by fitting each spectra to a damped harmonic oscillator model from which the Raman peak shift ω_0 and the damping coefficient γ were determined.[11]

In order to obtain reliable information on the local structure and its evolution at T_c, we have employed x-ray absorption fine structure (EXAFS) observations to directly observe the changes in the Ge-Te bond length with temperature. The characteristic time of EXAFS measurements is 10^{-15} s, i.e., EXAFS is capable of taking a true snapshot of the structure. Samples for EXAFS measurements were sputtered GeTe films deposited on both sides of Al foil with a thickness of 2 μm. The samples were annealed in inert atmosphere to induce crystallization. Measurements were taken as a function of temperature from 10 K to above the melting point at both Ge K and Te K edges. The obtained spectra were analyzed simultaneously using ARTHEMIS and ATHENA packages.

X-ray appearance near-edge structure (XANES) spectra were calculated using the *ab initio* real-space full multiple-scattering code FEFF8.[12] FEFF8 is a fully relativistic, all-electron Green's-function code that utilizes a Barth-Hedin formulation for the exchange-correlation part of the potential and the Hedin-Lundqvist self-energy correction. In our FEFF calculations, the cluster radius was set to 9 Å around the central atom, which corresponds to about 100 atoms in the model. Prior to the XANES simulations, the rhombohedral GeTe structure was relaxed at 0 K using density-functional-theory simulations.

III. RESULTS AND DISCUSSION

The results of Raman spectra analysis are shown in Fig. 1 (lower panel). Group theoretical calculations of the irreducible representation of the distorted rocksalt structure of GeTe show the presence of two modes that are Raman active, $\Gamma_1(A_1)$ at 122 cm^{-1} and $\Gamma_3(E)$ at 80 cm^{-1}. The frequencies of both modes can be observed to decrease with increasing temperature while the corresponding bandwidth increases.

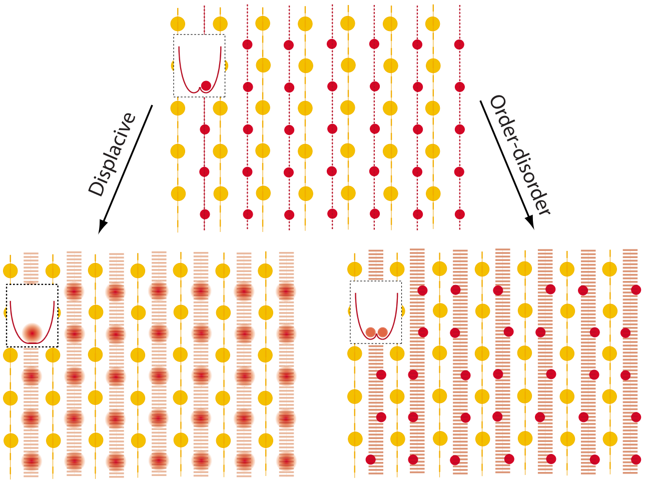

FIG. 2. (Color online) Schematic illustration of ferroelectric-paraelectric displacive (left) and order-disorder (right) transitions from the starting rhombohedrally distorted phase. In both phases after the transition the interatomic planes appear equidistant with apparent plane "broadening."

The Γ_3(E) appears to shift at a higher rate, merging into the spectral envelope of the Γ_1(A_1) peak at about 573 K.

Strong-mode softening is clearly visible (Fig. 1, lower panel). The extension of the temperature range in the present study clearly shows that the soft-mode frequency is still far from zero even in the hatched region that corresponds to the transition temperature. It should also be noted that thin GeTe films exhibit the transition at temperatures almost 100° lower than the bulk material,[7] further emphasizing the fact that the vibrational frequency does not become zero.

The above results do not agree with the conclusions about the displacive nature of the transition drawn previously. To address this issue, we would like to stress that Bragg (as opposed to total) scattering measures the average value of the electron distributions in diffraction planes making it impossible to distinguish between stochastic variation in the directionality of the long and short bond axis and the convergence of the long and short bonds to a single value.[13,14] Thus from the point of view of Bragg-diffraction real-mode softening resulting from a displacive transition is indistinguishable from an order-disorder transition when the multiwell potential minima become (quasi)equally populated: both manifest themselves as structures with equidistant plane spacing and a large isotropic thermal factor (Fig. 2).

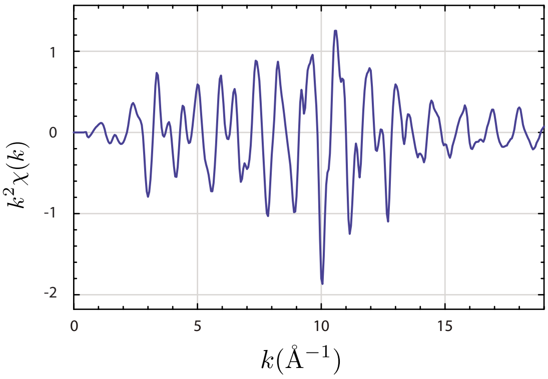

FIG. 3. (Color online) Raw EXAFS oscillations measured at Ge K edge at T=50 K.

In order to obtain reliable information about the local structure, EXAFS spectra were measured over a broad temperature range across T_c. Use of highly uniform samples resulted in a high-quality signal up to large k values (Fig. 3). The obtained spectra were analyzed simultaneously at both Ge K and Te K edges. An example of fitting is shown in Fig. 4. The fitting results (shown for the real part in R space) demonstrate the high quality of the fits for both the magnitude and the phase.

The results of the fitting of the Ge-Te distances for the shorter and longer bonds obtained from an analysis of the measured EXAFS spectra are shown in Fig. 5 (upper panel). The above results unambiguously demonstrate that *locally* the structure remains distorted above T_c in essentially the same manner it is distorted at lower temperatures. The fact that GeTe becomes paraelectric macroscopically means that the local distortions become stochastic at T_c, i.e., the ferroelectric-to-paraelectric transition is of order-disorder type illustrated by the lower-right panel in Fig. 2.

The above results may seem to be in contradiction with the previous conclusion—drawn from neutron diffraction—that the volume of GeTe shrinks at T_c as the temperature increases. This apparent disagreement is yet another pitfall. There is no direct correlation between the actual interatomic distances (probed by a local-structure technique) and the vol-

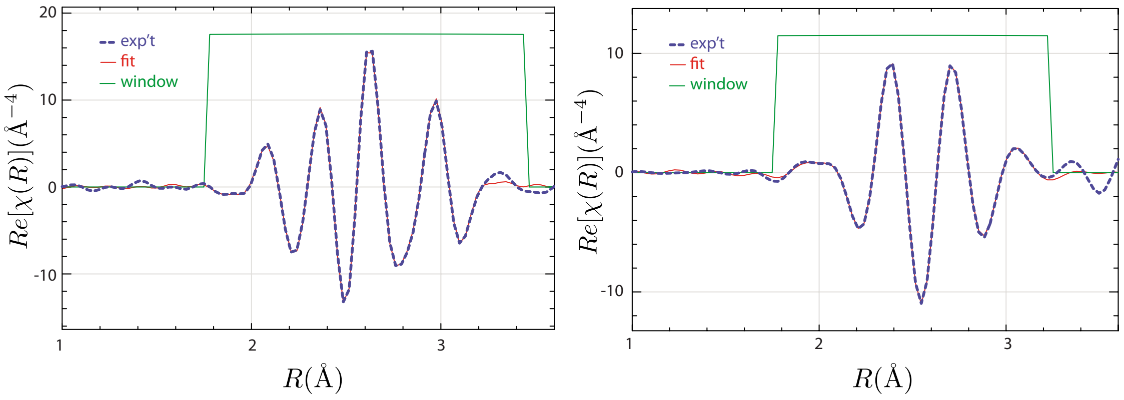

FIG. 4. (Color online) An example of fitting results (for the real part in R space) for the Ge (left) and Te (right) K edges.

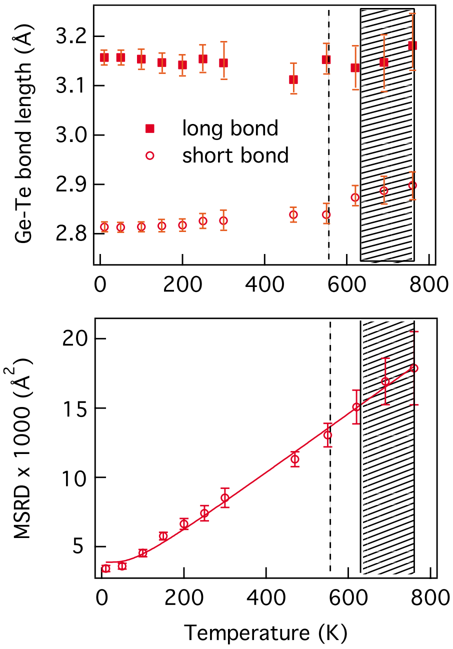

FIG. 5. (Color online) Temperature dependence of the shorter and longer Ge-Te bonds across the phase transition (upper panel) and a similar dependence for MSRD for the shorter Ge-Te bonds (lower panel). As in Fig. 1(b), the hatched area spans over the temperature range in which the critical temperature values T_c for the ferroelectric phase transition of GeTe have been reported in the literature. The dashed line represents the T_c of thin films, Ref. 7. One can see that properties change *monotonically* across T_c. See text for more details.

ume determined from the average-structure measurements. A well-established example of such a situation is silica where pair-distribution analysis demonstrates a continuous *increase* in the actual Si-O distance with temperature, in sharp contrast with the neutron powder diffraction that "sees" a *decrease* in the average Si-O bond length.[15]

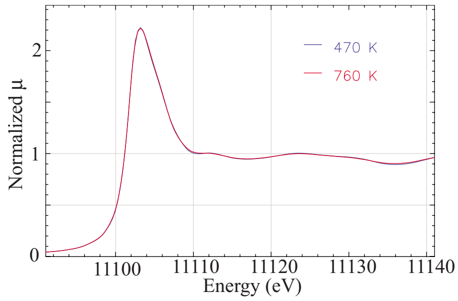

FIG. 6. (Color online) Comparison of XANES spectra measured at Ge K edge below and above T_c. The two spectra are identical indicating the unchanged local structure

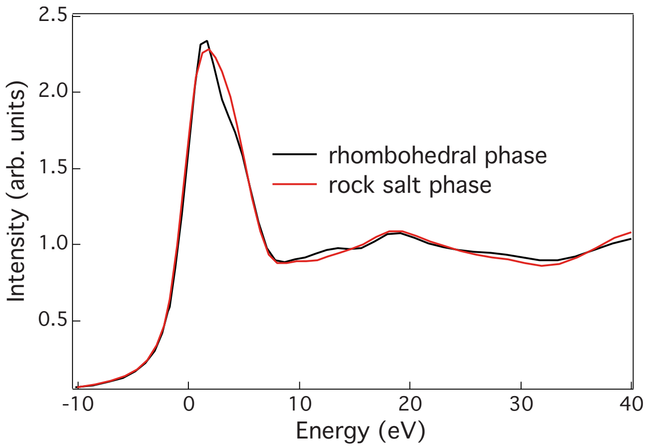

FIG. 7. (Color online) Simulated XANES spectra of the rhombohedral and rocksalt structures. The spectrum of the rhombohedral phases has features at approximately 12 and 30 eV that are similar to those observed experimentally

Further grounds for the unchanged local structure come from consideration of the bond stiffness as a function of temperature. Figure 5 (lower panel) shows temperature dependence of mean-square relative displacement (MSRD). The extent to which MSRD increases with temperature as well as its absolute value are determined by the bond strength usually represented by an Einstein temperature Θ_E that is related to MSRD, σ, through the following equation:

$$\sigma^2 = \frac{\hbar^2}{2\mu k_B \Theta_E}\coth\left(\frac{\Theta_E}{2T}\right) + \sigma_0^2.$$

Here, μ is the reduced mass, k_B is Boltzmann's constant, and σ_0 is the static disorder. The Einstein temperature is typically around 300 K for tetrahedrally bonded semiconductors, around 120–150 K for Se and Te that form helical chains with only two first-nearest neighbors, and in a 30–60 K range for clathrates.[16] Should the Ge atom become located within a soft-mode potential in the center of the rocksalt cell, there should be a noticeable increase in MSRD above T_c.

One can see that the MSRD for GeTe in the entire temperature range can be fitted with a *single* value of Θ_E demonstrating again that there is no change in the Ge-Te bond strength (i.e., the first derivative of the interatomic potential) and hence the local potential relief remains unchanged as the material is heated above T_c.

While EXAFS is essentially only sensitive to pair correlations, i.e., interatomic distances, XANES, on the other hand, involves multiple scattering which makes it a sensitive probe for the three-dimensional arrangement of atoms within a cluster of around 1 nm in diameter and centered around the absorbing atom.[17] Figure 4 shows experimental XANES spectra taken below and above T_c. The spectra are identical which further demonstrates that there is no change in the local arrangement of atoms. To obtain further insight, we have simulated XANES spectra using FEFF (Ref. 12) for the rocksalt and rhombohedral phases of GeTe (Fig. 6). The much stronger features in the simulated spectra arise from perfect order in the simulated structure. The shoulder observed in the experimental spectrum around 11112 eV and the feature at around 30 eV above the edge are in agreement with the rhombohedrally distorted structure (Fig. 7).

One might ask the question why the Peierls distortion in earlier work was visible by diffraction in the rhombohedral phase at low temperatures[5] and in the melt at high temperatures[8] but not in the intermediate-temperature "rocksalt" phase. We argue that this apparent conflict is a direct consequence of the averaging effects of Bragg diffraction. At low temperatures when atoms are displaced coherently, there are well-defined shorter and longer interplane distances in the rhombohedral crystal structure properly detected by Bragg diffraction. At temperatures above the phase transition, on the other hand, when the distortions are random the interatomic planes appear equidistant with apparent plane "broadening" which was interpreted as a large isotropic thermal factor due to increased amplitude of atomic vibrations associated with mode softening (see Fig. 2).

In the study of molten GeTe, on the other hand, a neutron-scattering technique was also used but the crucial difference is that due to absence of sharp diffraction peaks the authors had to use a more complicated pair-distribution analysis of the total scattering factor.[8] As the total scattering observations take into account all two-body correlations, they do not suffer from the site averaging effect that occurs for Bragg diffraction. As a result, the local distortion in the liquid phase was properly detected. We suggest that the Peierls distortion that reappears in the melt should more appropriately be called "revisualized" rather than "reentrant" since it never disappears in the first place.

IV. CONCLUSIONS

We conclude that despite the currently accepted consideration that GeTe exhibits a ferroelectric transition of displacive nature, the present experimental results (both EXAFS and Raman) provide evidence for the order-disorder character of the transition since the local distortions do not disappear at the Curie temperature. The previous misconception about the displacive nature of the transition has arisen from a misinterpretation of Bragg-diffraction data and more specifically was due to the neglect of site averaging effects involved in Bragg diffraction. Our results demonstrate that the Peierls distortion that allegedly "reenters" upon melting, never disappears in the first place but simply becomes invisible in the temperature range between the Curie temperature and the melting point due to the above-mentioned averaging effects of Bragg diffraction.

We suggest that the described intrinsic inability of techniques, which measure an average structure, to reliably detect random local distortions has far-reaching implications. In particular, our results invite reconsideration of other cases where conclusions about displacive phase transitions were reached based on Bragg-diffraction studies without considering an alternative possibility of an order-disorder transition.

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