# The phase-transition in GeTe revisited: Local Versus Average Structure

P. Fons[1,4] A.V. Kolobov[1,4], M. Krbal[1], J. Tominaga[1], K.S. Andrikopoulos[2], S. Yannopoulos[3], G.A. Voyiatzis[3], and T. Uruga[4]

[1]Nanodevice Innovation Research Center, National Institute of Advanced Industrial Science & Technology, Tsukuba Central 4, Higashi 1-1-1, Tsukuba, Ibaraki, 305-8562, Japan

[2]Department of Applied Sciences, Technological Educational Institute of Thessaloniki, 57400, Sindos, Greece

[3]Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Chemical Processes (FORTH/ICE-HT), P.O. Box 1414, GR-26504 Patras, Greece

[4]SPring-8, Japan Synchrotron Radiation Institute (JASRI), Kouto 1-1-1, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

## ABSTRACT

GeTe represents one endpoint of the technologically important GeTe-$Sb_2Te_3$ pseudobinary phase-diagram. As such, it is important to investigate and understand well the changes in local structure with temperature in the crystalline phase. GeTe is a semiconductor that has been reported to undergo a ferroelectric to paraelectric phase transition during the transformation from the room temperature R3m to the Fm3m phase at $\sim 705\,\mathrm{K}$ concomitant with the vanishing of the Peierl distortion present in the room temperature structure. This transition has long been described as being displacive in nature with more recent reports postulating the presence of a reentrant Peierl distortion above the melting point. We demonstrate that the transformation is not displacive, but is actually an order-disorder transition and that earlier reports of a reentrant Peierl transition are an artifact of the differing experimental techniques used. We discuss the implications of these observations on structural transitions in phase-change memory alloys that lie along the GeTe-$Sb_2Te_3$ pseudobinary tie line.

**Keywords:** GeTe,ferroelectric, structure

## 1. INTRODUCTION

GeTe lies at the end of the technologically important GeTe-$Sb_2Te_3$ pseudobinary tie-line and is currently experiencing a revival as a possible phase-change material due to its high crystallization temperature and recent improvements in understanding its growth properties[3, 13]. GeTe also exhibits bond length contraction upon transformation from the crystalline to amorphous phase [10, 9] that is characteristic of Te-based phase-change materials along with the concomitant large changes in optical and electrical properties. In the current paper, we focus on local structural changes in crystalline GeTe as a function of temperature in the hope of gaining deeper insight into the local structure of more complicated ternary phase-change alloys such as $Ge_2Sb_2Te_5$.

GeTe is a narrow band-gap (0.7 eV) 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 ( $\alpha$-GeTe) possesses a rhombohedral structure with a space group R3m. This structure can be viewed as a rocksalt structure slightly distorted along [111] direction with a subsequent shear relaxation along the [111]. The driving force for the formation of the rhombohedral phase has been a subject of various studies in the past [12]. In this phase, Ge and Te atoms are six-fold 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 to the reduced coupling between the p-type orbitals that constitute the basis for bonding in GeTe [7].

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 diffraction studies and/or Raman scattering.

For a case example 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 interpretations of the experimental results.

Based on diffraction studies, mainly neutron diffraction [4], it was concluded that GeTe undergoes a displacive ferroelectric-paralectric transition with the Curie temperature, $T_c$, around 705 K with the structure changing to the rocksalt structure (space group Fm3m) with concomitant disappearance of the Peierls distortion. A displacive transition is a phase transition in which small displacements of atoms within each unit cell collectively change in such a way that the symmetry of the crystal changes. These changes are not typically the result of significant bonding changes in the solid. As mentioned above, the lower symmetry of the $\alpha$-GeTe phase can be visualized as the presence of a shear along the $\langle 111 \rangle$ direction that vanishes at $T_c$ and the formation of the $\beta$-GeTe phase along with the extinction of the dipole moment. The change in symmetry is also associated with the softening of the shear mode corresponding to the distortion along the [111] direction in the $\alpha$-GeTe phase or a *soft-mode*.

Experimental bond lengths calculated from unit cell data obtained from neutron diffraction data [4] 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. The reentrant Peierls distortion was attributed by the authors to partially remaining chemical order in the liquid phase [14].

Based upon the observation of phonon mode softening with temperature, the displacive nature of the transition has been also suggested by Raman scattering [18], although the highest temperature studied was ca. 150 K lower than their estimated $T_c$.

In a one dimensional analog of a displacive phase transition, below $T_c$ an 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 the 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 the current work, we investigate the structure of GeTe from 10 K to above the melting point and provide evidence that the macroscopic 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. These findings may have significant implications for other cases when a reported phase transition is obtained by techniques relying upon the average structure where similar misinterpretation can be made.

To investigate more carefully for the presence of mode-softening, a series of Stokes-side Raman spectra were taken for a polycrystalline GeTe film with a transparent protective $(ZnS)_{0.85}(SiO_2)_{0.15}$ cap layer from room temperature to $\sim T_c$. The use of a capping layer is crucial as even small changes in composition due to Te sublimation can lead to changes in the ferroelectric transition temperature; such considerations limited the temperature range of the earlier Raman study and the resultant reliability of the conclusion drawn [18].

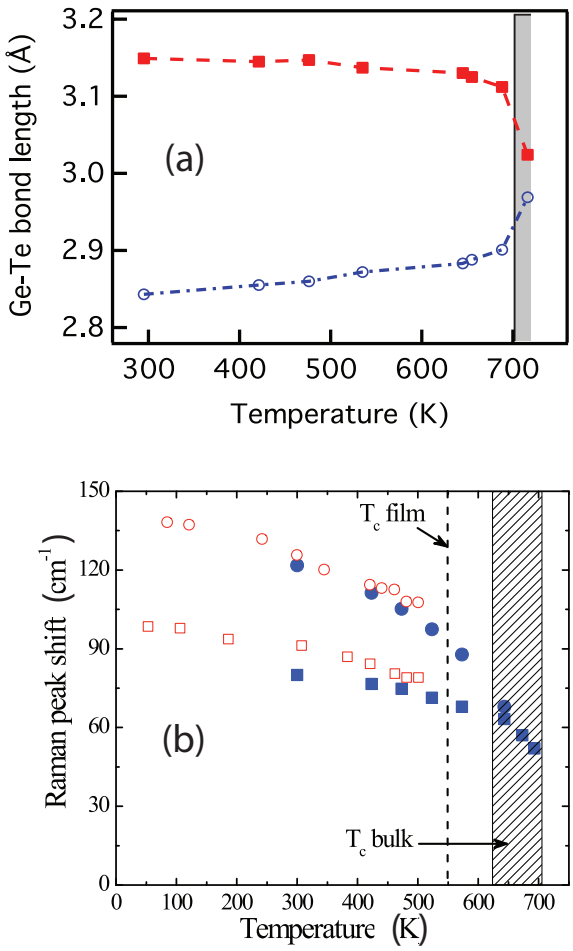


FIGURE 1. (a) Experimental evidence for the displacive nature of the phase transition. Ge-Te bond lengths calculated from unit cell data obtained from neutron diffraction data on bulk GeTe samples [4] (b) Raman phonon mode frequencies, filled symbols represent data from the present work on GeTe sputtered thin films; open symbols stand for data from Ref. [18] 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. [11].

Micro-Raman spectra (x50 objective) were recorded using a triple monochromator (Jobin-Yvon T64000) operated in double subtractive mode using a Ti:Sapphire laser (pumped by an $Ar^+$-ion laser) as an excitation source at 763 nm. The sample temperature was controlled by a hot stage (Linkam THMS600) with accuracy of 1 K. More details can be found in [1]. Group theoretical calculations of the irreducible representation of the distorted rock salt structure of GeTe show the presence of two modes that are Raman active, $\Gamma_1(A_1)$ at $122\,\mathrm{cm}^{-1}$ and $\Gamma_3(E)$ at $80\,\mathrm{cm}^{-1}$. The frequencies of both modes can be observed to decrease with increasing temperature while the corresponding bandwidth increases. The $\Gamma_3(E)$ appears to shift at a higher rate, merging into the spectral envelope of the $\Gamma_1(A_1)$ peak at about 573 K.

The Raman spectra were analyzed quantitatively by fitting each spectra to a damped harmonic oscillator model from which the Raman peak shift $\omega_0$ and the damping coefficient $\gamma$ were determined [5]. Strong mode softening is clearly visible (Fig. 1, lower panel). The extension of the temperature range clearly

shows 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 degrees lower than the bulk material [11], further emphasizing the fact that the vibrational frequency does not become zero.

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 [8, 19] as would be expected in a purely displacive transition. 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 multi-well potential minima become (quasi)equally populated; both manifest themselves as structures with equidistant plane spacing and a large isotropic thermal factor (Fig 2).

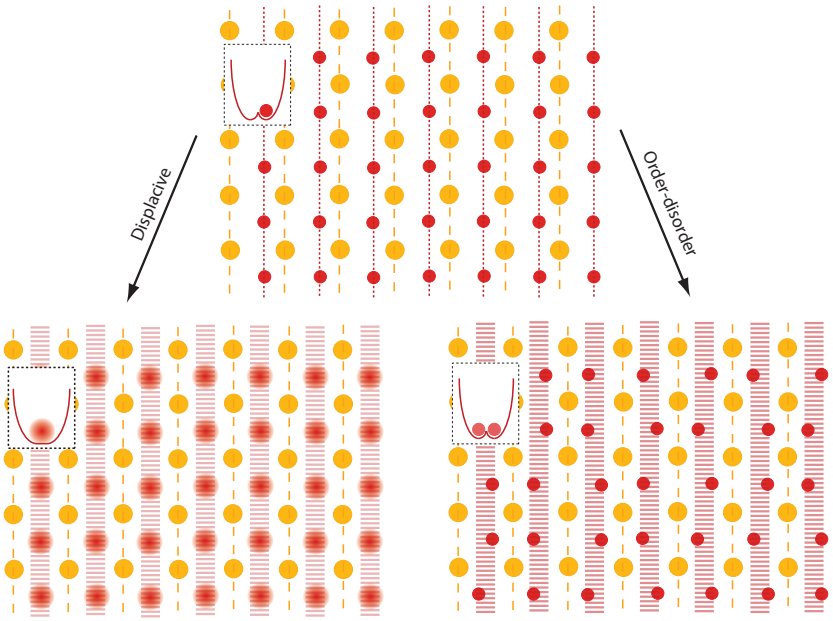


FIGURE 2. Schematic illustration of ferroelectric-paraelectric displacive (left) and order-disorder (right) transitions from the starting rhombohedrally distorted phase. In both phases after the transition the interatomic planes appear equidistant with apparent plane 'broadening'.

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 as determined by the uncertainty principle and the core-hole lifetime. EXAFS is thus capable of taking a true snapshot of the structure as EXAFS sampling is about three orders of magnitude faster than the characteristic time scale of lattice vibrations. Samples for EXAFS measurements were sputtered GeTe films deposited on both sides of Al foil with a thickness of 2 $\mu$m. 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 and Te K-edges and analyzed simultaneously using ARTHEMIS and ATHENA packages [15]. Typical raw $\chi$ data for the Ge and Te K-edges along with first shell fit traces can be seen in Fig.3.

The results of the fitting of the Ge-Te distances for the shorter and longer bonds are shown in Fig. 4 (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

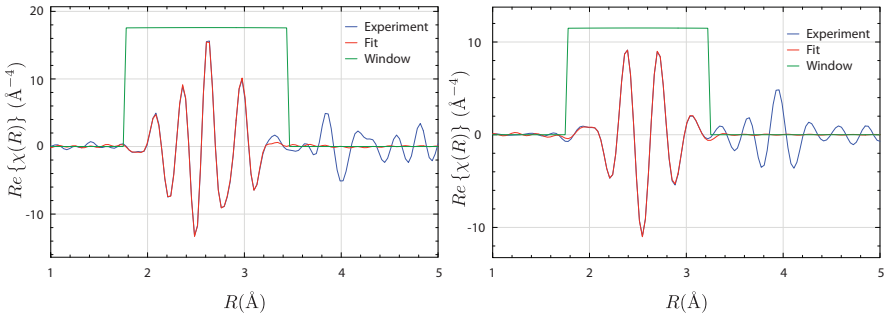


FIGURE 3. Typical raw XAFS $\chi$ data for Ge and Te K-edges, respectively, along with first-shell fit traces. A $k^3$ weighting has been used.

becomes paraelectric macroscopically means that the local distortions become stochastic at $T_c$, i.e. the ferroelectric-to-paraelectric transition is an order-disorder transition as illustrated by the low-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 of the technique. There is no direct correlation between the actual interatomic distances (probed by a local-structure technique) and the volume 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 [6].

Additional evidence for the local structure not changing with temperature comes from measurements of bond stiffness as a function of temperature. Fig. 3 (lower panel) shows the temperature dependence of the mean-square relative displacement (MSRD). The extent to which the MSRD increases with temperature as well as its absolute value are determined by the bond strength whose temperature dependence is often well approximated by the correlated Einstein model in which the influence of the projected phonon density of states is approximated by a delta function in energy. The Einstein temperature $\Theta_{\mathrm{E}}$ is related to the MSRD, $\sigma$, 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, $\Theta_{\mathrm{E}}$ is the Einstein temperature, $\mu$ is the reduced mass, $k_B$ is Boltzmann's constant, and $\sigma_0$ 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 K to 60 K range for clathrates [16]. If the Ge atom were located within a soft-mode potential in the center of the rocksalt cell, there would be a noticeable increase in the MSRD above $T_c$.

The MSRD for GeTe over the entire temperature range can be fitted with a *single* value of $\Theta_{\mathrm{E}}$ 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 $T_c$. The absolute value of $\Theta_E = 218 \pm 2$ K is in between that of tetrahedrally bonded and "linearly" bonded semiconductors and is in good agreement with the distorted rocksalt (or rhombohedral) structure where three shorter covalent bonds form the backbone of the network (the three longer bonds being relatively weak).

While EXAFS is essentially only sensitive to pair correlations, XANES, on the other hand, involves multiple scattering which makes it a sensitive probe for the spatial arrangement of atoms over a coherence length of around 1 nm centered on the absorbing atom [17]. XANES simulation using FEFF [2] reveal noticeable differences between the rhombohedral and rocksalt phases. Fig. 5 shows experimental XANES spectra taken below and above $T_c$. The spectra are identical which further demonstrates that there is no

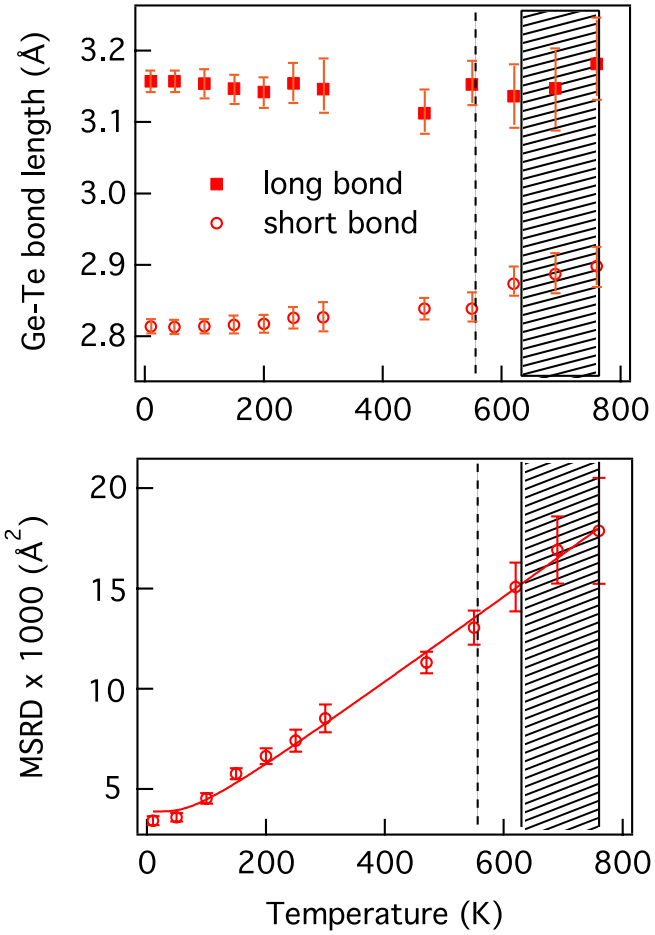


FIGURE 4. Temperature dependence of the shorter and longer Ge-Te bonds across the phase transition (upper panel) and a similar dependence for MSRD for the shorter Ge-Te bonds (lower panel). As in Fig. 1b, the hatched area spans over the temperature range in which the critical temperature values $T_c$ for the ferroelectric phase transition of GeTe have been reported in the literature. The dashed line represents the $T_c$ of thin films, Ref. [11]. One can see that properties change *monotonically* across $T_c$. See text for more details.

change in the local arrangement of atoms. A shoulder observed around 11130 eV is in agreement with the rhombohedrally distorted structure (not shown).

One might ask the question why the Peierls distortion reported earlier was observable by diffraction in the rhombohedral phase at low temperatures [4] and in the melt at high temperatures [14] but not in the intermediate-temperature "rocksalt" phase. We argue that this apparent contradiction 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 interplanar distances in the rhombohedral crystal structure giving rise to Bragg diffraction; the local and average structures are the same. 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 can be misinterpreted as a large isotropic thermal factor due to an increased amplitude of atomic vibrations associated with mode softening (see Fig. 2).

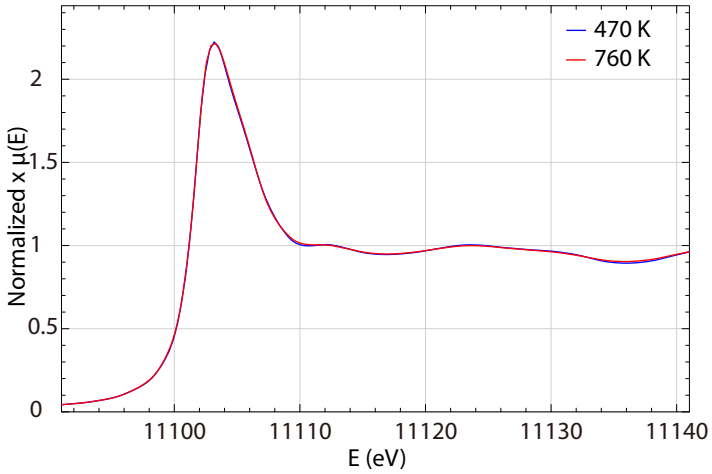


FIGURE 5. Comparison of XANES spectra measured at Ge K-edge below and above $T_c$. The two spectra are identical indicating an unchanged local structure.

In the study of molten GeTe, on the other hand, a neutron scattering technique was also used but crucially due to the absence of sharp diffraction peaks the authors had to use a more complicated pair-distribution analysis of the total scattering factor [14]. As the total scattering observations take into account all two-body correlations, they do not suffer from the site averaging effects that occur for Bragg diffraction. As a result, the local distortion in the liquid phase is properly detected.

We conclude that despite the currently accepted belief that GeTe exhibits a ferroelectric transition of a displacive nature, the present experimental results (both EXAFS and Raman) provide evidence the order-disorder character of the transition since 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 due to the neglect of site averaging effects involved in Bragg diffraction. We suggest that the intrinsic inability of techniques which measure the average structure to reliably detect random local distortions has far-reaching implications. In particular, our results invites 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.

Acknowledgements. XAFS measurements were done at beamline BL01B1 as part of 2007B0006 and 2009A1462 proposals. MK would like to thank JSPS for provision of a research fellowship.

**References**

[1] K. Andrikopoulos, S. Yannopoulos, A. Kolobov, P. Fons, and J. Tominaga. Raman scattering study of GeTe and $Ge_2Sb_2Te_5$ phase-change materials. *J. Phys. Chem. Solids*, 68(5-6):1074–1078, 2007.

[2] A. Ankudinov, B. Ravel, J. Rehr, and S. Conradson. Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure. *Phys. Rev. B*, 58(12):7565–7576, 1998.

[3] G. Bruns, P. Merkelbach, C. Schlockermann, M. Salinga, M. Wuttig, T. D. Happ, J. B. Philipp, and M. Kund. Nanosecond switching in GeTe phase change memory cells. *Appl. Phys. Lett.*, 95(4):043108, 2009.

[4] T. Chattopadhyay, J. Boucherle, and H. Von Schnering. Neutron diffraction study on the structural phase transition in GeTe. *J. Phys. C*, 20:1431–1440, 1987.

[5] M. DiDomenico, S. Wemple, S. Porto, and R. Bauman. Raman spectrum of single-domain $BaTiO_3$. *Phys. Rev.*, 174(2):522–530, 1968.

[6] T. Egami and S. J. L. Billinge. *Underneath the Bragg peaks: structural analysis of complex materials*. Pergamon, Kiddington, Oxford, UK, 2003.

[7] J.-P. Gaspard, A. Pellegatti, F. Marinelli, and C. Bichara. Peierls instability in covalent structures I. electronic structure, cohesion and the Z=8-N rule. *Philosophical Magazine B*, 77:727–744, 1998.

[8] C. Giacovazzo. *Fundamentals of crystallography*, volume 7. Oxford University Press, Oxford, 2002.

[9] A. Kolobov, P. Fons, J. Tominaga, A. Ankudinov, S. Yannopoulos, and K. Andrikopoulos. Crystallization-induced short-range order changes in amorphous GeTe. *J. Phys. Cond. Mat.*, 16:S5103–S5108, NOV 10 2004.
[10] A. V. Kolobov, J. Tominaga, P. Fons, and T. Uruga. Local structure of crystallized GeTe films. *Appl. Phys. Lett.*, 82(3), 2003/01/20/.
[11] T. Matsunaga, H. Morita, R. Kojima, N. Yamada, K. Kifune, Y. Kubota, Y. Tabata, J.-J. Kim, M. Kobata, E. Ikenaga, and K. Kobayashi. Structural characteristics of GeTe-rich GeTe-$Sb_2Te_3$ pseudobinary metastable crystals. *J. Appl. Phys.*, 103(9):093511, 2008.
[12] K. Rabe and J. Joannopoulos. Theory of the structural phase transition of gete. *Phys. Rev. B*, 36(12):6631–6639, 1987.
[13] S. Raoux, H.-Y. Cheng, M. A. Caldwell, and H.-S. P. Wong. Crystallization times of Ge–Te phase change materials as a function of composition. *Appl. Phys. Lett.*, 95(7):071910, 2009.
[14] J. Raty, V. Godlevsky, P. Ghosez, C. Bichara, J. P. Gaspard, and J. R. Chelikowsky4. Evidence of a reentrant Peierls distortion in liquid GeTe. *Phys. Rev. Lett.*, 85(9):1950–1953, 8 2000.
[15] B. Ravel and M. Newville. *ATHENA*, *ARTEMIS*, *HEPHAESTUS*: data analysis for X-ray absorption spectroscopy using *IFEFFIT*. *J. Synchrotron Radiat.*, 12(4):537–541, Jul 2005.
[16] B. Sales, B. Chakoumakos, D. Mandrus, and J. Sharp. Atomic displacement parameters and the lattice thermal conductivity of clathrate-like thermoelectric compounds. *J. Solid State Chem.*, 146(2):528–532, 1999.
[17] G. Smolentsev, A. Soldatov, and M. Feiters. Three-dimensional local structure refinement using a full-potential XANES analysis. *Phys. Rev. B*, 75(14):144106, 2007.
[18] E. Steigmeier and G. Harbeke. Soft phonon mode and ferroelectricity in GeTe. *Solid State Commun.*, 8:1275–1279, 1970.
[19] E. Stern and Y. Yacoby. Structural disorder in perovskite ferroelectric crystals as revealed by XAFS. *J. Phys. Chem. Solids*, 57(10):1449–1455, 1996.

**Biography**

Paul Fons received a M.S. in Physics and a Ph.D in materials science from the University of Illinois in 1990. He was a visiting research fellow at the Institute of Applied Physics at Tsukuba University from 1990-1992. He became a permanent staff member in the Optoelectronics division of the Electrotechnical Laboratory of the National Institute of Advance Industrial Research (AIST) and Technology in 1993. In 2003, he moved to the Center for Applied Near-Field Optics Research within AIST to work on materials characterization of Te-based alloys where he was head of the Nano-Optics Research Team. In 2010, he moved to the Nanodevice Innovation Research Center where is the group leader of the Functional Nano-Phase-Change Research Team.