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# Structural and electronic phase changes in GaGeTe with pressure

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Chalcogenide-based compounds are an important part of the family of layered materials, extensively studied for their two-dimensional properties. An interesting line of investigation relates to the evolution of their properties with hydrostatic pressure, which could lead to structural transitions and itinerant electronic behavior. Here we investigate the evolution of a layered ternary compound GaGeTe as a function of pressure with X-ray diffraction, Raman and infrared spectroscopy, and *ab initio* calculations. The Ge layer retains a germanene like vibration though enveloped in Ga and Te layers. We show experimental and theoretical evidence of metallization in two steps. At  $\sim 6$  GPa Raman and infra-red spectroscopic data undergo changes compatible with delocalized charge carriers. Calculations ascribe this to the Fermi level crossing of a valence band. At  $\sim 16$  GPa infra-red transmission and Raman modes disappear and X-ray diffraction signals a structural transition to a phase which is metallic according to our calculations. We obtain consistent agreement between experiment and theory concerning the structural, vibrational and electronic structure evolution with pressure.

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In layered chalcogenide compounds, variation of the metal and the chalcogenide species allows for a wide range of properties and structures. Gallium germanium telluride (GaGeTe), a ternary compound, is of interest because of possible topological states which may exist in view of the eventual small band-gap in its electronic structure [1, 2]. The rhombohedral  $R\bar{3}m$  structure of GaGeTe consists of hextuple layers (Te-Ga-Ge-Ge-Ga-Te) bound by van der Waals interactions. In each layer, the Ge atoms form a buckled hexagonal sheet. The buckling is substantial and this atomic plane can also be visualized as a double Ge layer in the armchair configuration. The Ge plane is sandwiched by two GaTe layers with the  $\beta$ -GaSe structure. This suggests that GaGeTe may actually be a natural germanene analog packaged in GaTe. However, the layers cleave at the Te-Te interface which implies that Ge-Ga bonds are relatively strong. An interesting direction is to study the evolution of the GaGeTe structure and electronic states as a function of pressure as has been done for layered materials like MoS<sub>2</sub> [3, 4] or BiTeI [5] in the recent past. Some questions that are pertinent for GaGeTe include the following. Can metallization be observed with pressure? Are there structural phase transitions with pressure? We examine the pressure phase diagram of GaGeTe with Raman and IR spectroscopy, synchrotron X-ray diffraction (XRD) and *ab initio* calculations. A zone center Raman mode [6] linked to the in-plane vibrations of germanium atoms does exist with  $E_g$  symmetry. Its frequency is very

close to the germanene mode analogous to the G-mode of graphene [7, 8], despite the large buckling of the germanium plane and the bonding with the neighbouring Ga atoms. We find through our XRD measurements that a structural transition intervenes at  $\sim 16$  GPa. At this pressure Raman and IR signals vanish and do not reappear even at the highest measured pressure of 49.5 GPa. Electronic structure calculations show that this vanishing can be ascribed to the completely metallic nature of the new phase with damping of Raman modes and loss of IR transmission. However itinerant charge carriers already appear at a lower pressure at  $\sim 6$  GPa as seen by changes in both Raman and IR signals, with calculations indicating a Fermi level crossing of the valence band.

## EXPERIMENTAL DETAILS

GaGeTe single crystals were made in a Bridgman furnace from polycrystalline GaGeTe synthesized from high-purity Ge, Ga and Te. In all experiments, freshly cleaved GaGeTe was loaded in a membrane diamond anvil cell (DAC) [9] with neon as the pressure transmitting medium [10] and a ruby [11] for pressure calibration [12]. The powder XRD experiments under pressure (up to 17GPa) were performed using an 80  $\mu\text{m}$  beam at 25keV ( $\lambda=0.4957$  Å) on the Xpress beamline at the Elettra Sincrotrone (Trieste, Italy). Le Bail refinements (Fig. 1) were performed using Fullprof28.

Raman scattering was performed in backscattering with a 514.5 nm Ar laser focused to a  $2\ \mu\text{m}$  spot with incident power limited below 40 mW. The  $10\ \text{cm}^{-1}$  low frequency cut-off was achieved with three volume Bragg filters. A remnant low energy tail was subtracted using a polynomial background. Data was recorded in the  $10 - 1200\ \text{cm}^{-1}$  range and a normalised count-rate obtained. IR transmission was measured through a GaGeTe flake in a DAC using an in vacuum Fourier transform infrared spectrometer. Spectra were recorded in the  $4000-11000\ \text{cm}^{-1}$  range with a tungsten source and spectral resolution of  $4\ \text{cm}^{-1}$ . Fabry-Perot oscillations in the transmission spectra were filtered out with Fourier transform filtering for each spectrum. All measurements are at room temperature.

All simulations were performed with the Quantum ESPRESSO [13, 14] codes using the local gradient approximation with the PBE [15] parametrization. Atoms were modeled with scalar-relativistic norm-conserving pseudopotentials from the Pseudo DOJO project [16] with a kinetic energy cutoff of 80 Ry. Charge density was integrated over a reciprocal space grid of  $8 \times 8 \times 8$  points. When required, electronic occupations were modelled with a Methfessel-Paxton broadening of 0.02 Ry [17]. Phonon calculations were performed at the  $\Gamma$  point using density functional perturbation theory and Raman-active modes were identified by symmetry. Electronic bands are plotted along some high symmetry directions.

## RESULTS AND DISCUSSION

In Fig. 1a), powder XRD data is shown from ambient pressure to 16.1 GPa. The ambient pressure phase persists almost throughout and is well fit with the  $R\bar{3}m$  structure as shown in Fig. 1b) for 7.5 GPa. At 16.1 GPa the XRD pattern undergoes a significant change and is compatible with the  $P\bar{3}m1$  structure (Fig. 1c). We will discuss this structural change with respect to electronic structure calculations below. XRD data [18] show that with increasing pressure the sample undergoes texturing, degrading the quality of measurement [19]. At 16.1 GPa the new phase seems to be composed of only a few crystalline grains [18]. Spectroscopic measurements help to correlate the change in structure to the change in electronic properties.

In Fig. 2 we present results of Raman and IR measurements as a function of pressure. Six Raman peaks with non-negligible intensity are visible up to 14.3 GPa in Fig. 2a). The spectrum at 15.5 GPa is considerably damped and above 16 GPa the Raman spectrum is a featureless flat background until the highest measured pressure of 49.5 GPa. The disappearance of the Raman signal at 16 GPa can be linked to the structural change found in the XRD measurements at the same pressure while the continuous presence of the 6 Raman peaks is coherent

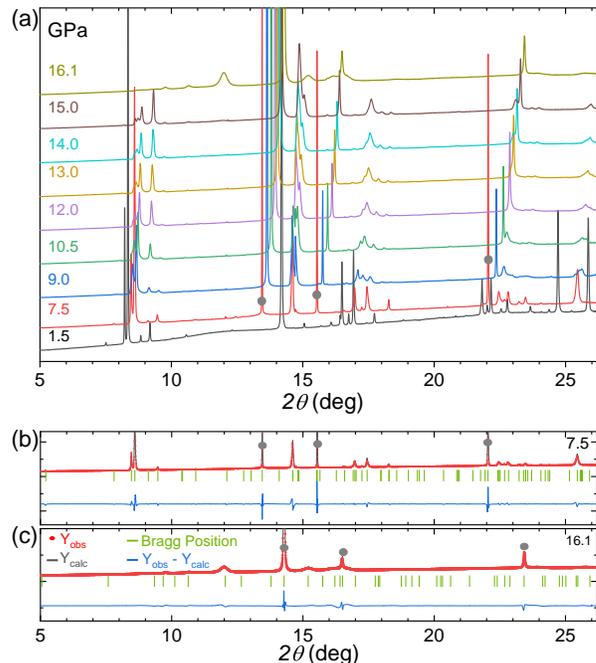


FIG. 1. a) X-ray diffraction patterns of GaGeTe as a function of pressure. While the  $R\bar{3}m$  structure remains unchanged till 15 GPa, at 16.1 GPa a new structural phase appears. b) LeBail fit to the data at 7.5 GPa with the  $R\bar{3}m$  structure. c) LeBail fit to the data at 16.1 GPa with the  $P\bar{3}m1$  structure. The sharp Bragg peaks (Grey solid circles) are from the crystallization of the pressure transmitter (Neon).

with the persistence of the ambient pressure phase below  $\sim 16$  GPa. Indeed in this regime all peak frequencies expectedly harden with pressure to varying degrees. There are considerable variations of intensities for the peak at  $78.7\ \text{cm}^{-1}$  and the one at  $280\ \text{cm}^{-1}$  (ambient condition frequencies) as pressure is increased. To confirm the nature of the transition at  $\sim 16$  GPa we also performed IR transmission measurements in the  $0.4 - 1.4\ \text{eV}$  range ( $4000-11000\ \text{cm}^{-1}$ ), Fig. 2 b). The lowest pressure (0.9 GPa) transmission spectrum is in good agreement with an earlier ambient pressure measurement [21]. Up to a pressure of 8 GPa (left panel) the spectrum is characterized by decreasing transmission as energy increases, a minimum at around 1 eV and a small peak in transmission around 1.2 eV. When the same transmission data is plotted as a function of pressure for a given wavenumber it reveals an anomaly at 6 GPa [18]. Above 8 GPa (right panel) the transmitted intensity decreases with pressure over the whole energy range and above 15 GPa the transmission is zero. This zero transmission pressure also corresponds to the disappearance of the Raman signal.

In Fig. 3 the measured (solid circles) and calculated (empty circles) variation of the Raman mode frequencies is plotted against the applied pressure. The side panels show the atomic movements of the corresponding zone

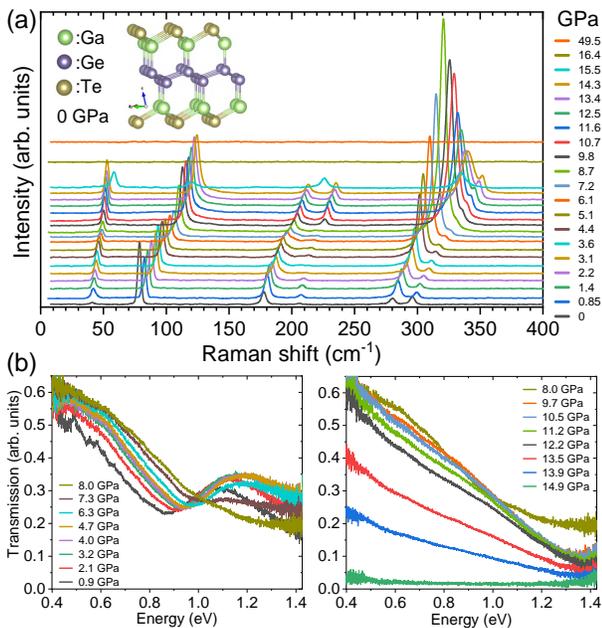


FIG. 2. a) Raman spectra of GaGeTe as a function of pressure. Above 15.5 GPa the Raman signal disappears, signalling a strongly damped metallic state. The insets show the ambient pressure GaGeTe crystal structure. b) IR transmission for GaGeTe over the same pressure range. Left panel: transmission from 0.9 to 8 GPa pressure. Right panel: transmission from 8 GPa to 15 GPa.

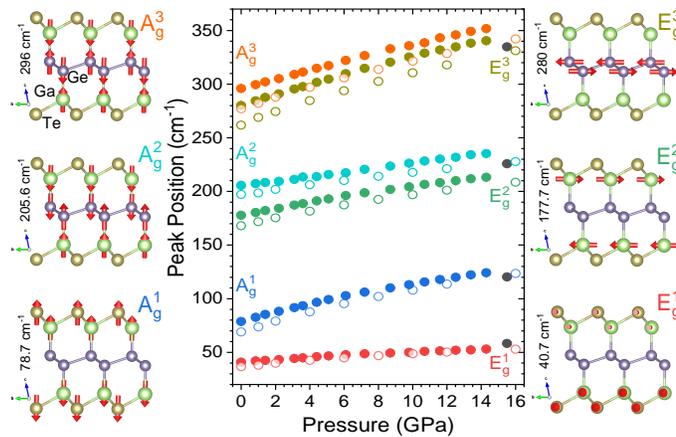


FIG. 3. The variation of the Raman modes with pressure. The measured frequencies (solid circles) are compared to the calculated *ab initio* values (empty circles). The side panels show the atomic movements of the corresponding zone center phonons. Three modes with out-of-plane vibrations of atoms ( $A_g$  symmetry) and three more with in-plane vibrations of atoms ( $E_g$  symmetry) can be observed.

center phonons [20]. The six modes are roughly grouped in three pairs of modes [6]. In these pairs, the lower frequency mode is an in-plane vibration with  $E_g$  symmetry while the higher frequency one is an out-of-plane vibration with  $A_g$  symmetry. The calculated *ab initio*

frequencies as well as their variation with pressure are in excellent agreement with the experiment. No significant change either in the number of modes or the slope of the dispersion with pressure is observed, indicating that there is no structural phase transition in the measured range. At 15.5 GPa (solid black circles) the measured spectrum changes as the phonon modes are strongly damped and reduced in number. For higher pressure and up to the highest measured pressure of 49.5 GPa Raman modes are no more observed. Between 3 and 4 GPa the  $A_g^1$  mode at  $78.7 \text{ cm}^{-1}$  evolves to an asymmetric line shape with an increasing linewidth as the pressure increases. This mode involves out-of-plane vibrations of Ga and Te atoms. Below (Fig. 5) we will show that the asymmetric line shape is a consequence of interference between the vibrational mode and continuum scattering from low energy electron-hole pair excitations generated by a band crossing the Fermi level with additional pressure. The second mode of interest is the  $E_g^3$  mode at  $280 \text{ cm}^{-1}$ . This mode involving in-plane vibrations of the Ge atoms is the analog of the graphene G mode for germanene [7, 22]. The Ge plane in GaGeTe can be considered to represent buckled germanene. The mode shows considerable variation of intensity and width which we will examine in the light of the changes in the electronic structure of GaGeTe with pressure.

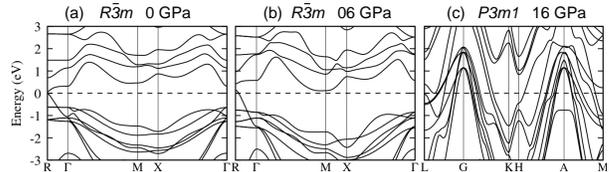


FIG. 4. Evolution of the first-principles-calculated electronic structure at three key values of the pressure: a) ambient, b) 6 GPa and c) 16 GPa.

As we have seen earlier, the *ab initio* Raman frequencies are in excellent agreement with the measurements. In Fig. 4 a) we show the evolution of the electronic structure as given by calculations at three key values of pressure: ambient, 6 GPa, and 16 GPa. The ambient-pressure electronic structure [22] shows a small direct band-gap at the R point of the BZ where both the dispersive valence band and the conduction band are close to the Fermi level. An indirect gap can be defined from the top of the valence band at the R point to two other points of the BZ, the bottom of the conduction band at  $\Gamma$  and at M. As pressure increases the Fermi level inducing delocalized charge carriers Fig. 4b). At 16 GPa our calculations indicate that both the  $R\bar{3}m$  structure and a new  $P3m1$  structure [23] are energetically possible, separated only by 40 meV. While the XRD data is incompatible with the  $R\bar{3}m$  structure, we successfully fit-

ted the data at this pressure with the  $P3m1$  structure. As can be seen in Fig. 4c), this phase is completely metallic. The vanishing Raman signal at 16 GPa and the total loss of the IR transmission can now be explained by strong damping with the sudden increase in carrier density after the phase transition.

We now discuss both the Raman and the IR data in more detail. The Raman response may become inactive because of the symmetry of the new phase if the transition is to a rock salt structure [24]. This is ruled out by our XRD data and also by our calculations. Between 6 GPa and 16 GPa the Raman signal persists even though free carriers exist (see Fig. 5) but it is completely damped by the transition to a strongly metallic phase at 16 GPa. Such damping has been observed in other systems showing metal-insulator transitions [25–27]. It may be argued that the non-zero IR transmission shown in Fig. 2b) indicates an electronic structure with an ambient pressure gap of the order of an eV instead of a much smaller gap as found by calculations. However the absolute transmission depends on the sample thickness which was not measured to avoid possible contamination by ambient exposure. Instead, several samples were tested till one with sufficient transmission was obtained. This sample is estimated to be less than a  $\mu\text{m}$  thick, consistent with the thickness estimation for a sample with a similar spectrum [21]. Indeed, even a sufficiently thin sample of graphite can transmit in the same range of energy [28] despite graphite having a vanishing gap. A final word of caution concerns the value of this direct gap at  $\Gamma$ . For GaGeTe it has been shown [1] that the calculated value can depend on the energy functional used and can vary between nearly zero to more than 0.5 eV.

We now examine the variation with pressure of the two Raman modes discussed briefly above. In Fig. 5 a) we show the variation of the  $A_g^1$  mode. The line shape is symmetric and narrow at low pressure but becomes asymmetric and widens at higher pressures. This change is analyzed using an asymmetric Breit-Wigner-Fano line shape (Eq. 1) to fit the measured peak [29].

$$I(\omega_s) = I_0 \left[ \frac{1}{q^2} + \frac{1 - 1/q^2}{1 + s^2} + \frac{2s/q}{1 + s^2} \right] \quad (1)$$

where  $s = (\omega_s - \omega_G)/\Gamma$ , and  $\omega_s$ ,  $\omega_G$ ,  $q$ ,  $\Gamma$ , and  $I_0$  are the Raman shift, the spectral peak position, the asymmetry factor, the spectral width, and the maximum intensity of the peak, respectively. The lower the asymmetric factor  $q$ , the higher the interference with the continuum excitations. Fig. 5 b) shows that the  $q$  factor suddenly drops by a factor of 4 between 5 and 6 GPa, corresponding to the valence band crossing the Fermi level at the BZ R point in our calculations. In Fig. 5 c) the electronic structure at 6 GPa is shown around the Fermi level with the corresponding partial density of states of Ge, Ga and Te. The states with the highest density around the Fermi level are those from Te. The  $A_g^1$  vibration involves out-

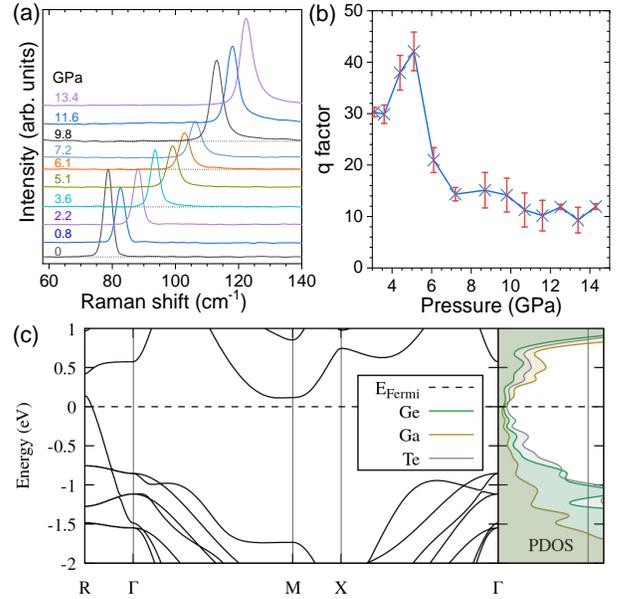


FIG. 5. a) Variation of the  $A_g^1$  mode with pressure showing the mode becoming wider and asymmetric at higher pressure. The baseline is shown for a few pressures b)  $q$  factor (signalling asymmetry) extracted from a Breit-Wigner-Fano line shape fit. c) Electronic structure and partial density of states at 6 GPa

of-plane movements of Te and Ga, confirming that this particular mode couples to the relevant electronic states to generate the interference and modified line shape.

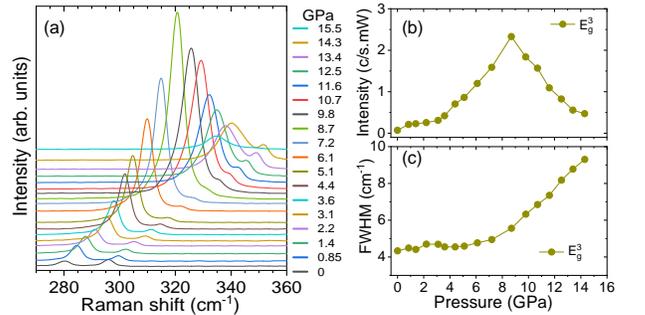


FIG. 6. a) Variation of the  $E_g^3$  mode with pressure. The  $E_g^3$  mode for the Ge plane ('germanene') is analogous to the graphene G mode. b) Intensity and c) Linewidth variation of the  $E_g^3$  mode.

Finally in Fig. 6 a) we show the variation of the  $E_g^3$  mode with pressure. The  $E_g^3$  mode is due to the in-plane vibration of Ge atoms and constitutes the germanene analog of the G mode for graphene [7, 8]. The fact that this mode is seen throughout the pressure range implies that despite the large buckling the Ge plane retains its character, though the mode undergoes variations of intensity and width (Fig. 6 b and c). The intensity variations can be ascribed to resonant effects as the electronic

structure varies with pressure. Lopez *et al.* [6] have shown that most Raman modes in GaGeTe at ambient pressure vary in intensity with the energy of the incident Raman light. In their work, the  $E_g^3$  mode is non-resonant at the incident energy of 2.41 eV, corresponding to our incident energy, but shows a remarkable increase in intensity for an incident energy of 2.6 eV. In our experiment, the incident energy is constant but the electronic structure varies with pressure as seen in Fig. 4. It is probable that at 9 GPa, an electronic transition is resonant with our incident energy resulting in the maximum of intensity for the  $E_g^3$  mode seen in Fig. 6 b). In Fig. 6 c) we observe that the linewidth of the  $E_g^3$  mode is constant at low pressure but above 5-6 GPa it steadily increases. This can be due to increased anharmonicity or due to enhanced electronic scattering through electron-phonon coupling [30]. The simpler explanation is the latter since charge carriers which could scatter phonons become available at this pressure.

In conclusion, in this work we examine the pressure phase diagram of GaGeTe using X-ray diffraction, Raman and IR spectroscopy and *ab initio* calculations. Earlier work has shown the advantages of studying the evolution of electronic structure in layered compounds such as MoS<sub>2</sub> [3, 4] or BiTeI [5] with pressure. GaGeTe is a chalcogenide containing a germanene plane and an unusual rhombohedral structure. Under pressure, GaGeTe undergoes both electronic and structural transitions. Calculations indicate that delocalized charge carriers become available at  $\sim 6$  GPa as the valence band approaches the Fermi level, a phenomenon that explains changes seen in the spectroscopic measurements. Above this pressure Raman data indicates Fano coupling between a Raman mode and the charge continuum and IR spectra show uniformly decreasing transmission. At 16 GPa, the Raman signal disappears, IR transmission goes to zero and diffraction data signal a transition to the  $P3m1$  structure which calculations confirm to be completely metallic.

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