Acoustic-Soft Optical Mode Coupling Leads to Negative Thermal Expansion of GeTe near the Ferroelectric Phase Transition

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GeTe is a well-known ferroelectric and thermoelectric material that undergoes a structural phase transition from a rhombohedral to the rocksalt structure at ~ 600 – 700 K. We present a first principles approach to calculate the thermal expansion of GeTe in the rhombohedral phase up to the Curie temperature. We find the minimum of the Helmholtz free energy with respect to each structural parameter in a manner similar to the traditional Grüneisen theory, and account for the temperature dependence of elastic constants. We obtain the temperature variation of the structural parameters of rhombohedral GeTe in very good agreement with experiments. In particular, we correctly reproduce a negative volumetric thermal expansion of GeTe near the phase transition. We show that the negative thermal expansion is induced by the coupling between acoustic and soft transverse optical phonons, which is also responsible for the low lattice thermal conductivity of GeTe.

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I. INTRODUCTION

Most materials expand upon heating, while those that shrink are much less common. Recent interest in these materials with negative thermal expansion (NTE) is also driven by technological applications that require materials with zero thermal expansion across a desired temperature range [1–3]. Even though NTE is an unusual phenomenon, it is relatively common for materials near structural phase transitions, and is typically associated with soft phonons and strong anharmonicity [1–3].

GeTe is the simplest ferroelectric material that exhibits NTE near the phase transition [4–7]. This makes it an ideal test case for identifying the physical effects leading to NTE. At low temperatures, GeTe crystallizes in a rhombohedral structure [4–8], characterized by the Te internal atomic displacement along the [111] direction from its high symmetry position in the rocksalt phase, (0.5,0.5,0.5) in reduced coordinates, as illustrated in Fig. 1. The angle between the primitive lattice vectors of the rhombohedral structure also differs from 60° for the rocksalt phase. GeTe experiences a structural phase transition from a rhombohedral to the rocksalt structure at ~ 600 – 700 K depending on the carrier concentration [4]. This phase transition is mediated by softening of the zone center transverse optical (TO) mode [9, 10], which corresponds to the frozen-in Te internal atomic displacement along the [111] axis.

The proximity to the ferroelectric phase transition also makes GeTe a very good thermoelectric material, either in the pure [12–17] or alloyed form [18–26]. Its soft TO modes interact strongly with acoustic modes which carry most heat, thus leading to the low lattice thermal conductivity [26] and the high thermoelectric figure of merit.

The same mechanism is responsible for the exceptionally low lattice thermal conductivity of PbTe [27–30]. GeTe can be driven closer to the soft TO mode phase transition not only by changing the temperature but also by alloying with PbTe [31]. We have recently shown that the acoustic-TO coupling is strongest for those (Pb,Ge)Te alloy compositions that are very near the phase transition, and leads to the minimal lattice thermal conductivity when mass disorder is neglected [26].

In this paper, we present a first principles method to compute the thermal expansion of the rhombohedral phase of GeTe up to the Curie temperature. We calculate the structural parameters by minimizing the total free energy with respect to each structural parameter in the spirit of the Grüneisen theory. Related standard approaches do not minimize the free energy with respect to the internal atomic position [32–36], which is critical to correctly describe the thermal expansion at the...
phase transition, as we will show. We further improve on the standard Grüneisen theory by implementing a simple scheme to determine the temperature dependence of quantities related to elastic constants. We show that our calculated thermal evolution of the structural parameters of GeTe agrees well with experiments. Negative volumetric thermal expansion of GeTe near the phase transition is also well described in our model. We find that the coupling between acoustic and soft TO modes is the dominant mechanism leading not only to the low lattice thermal conductivity of GeTe, as shown previously, but also to its NTE.

II. METHOD

We model the thermal expansion of rhombohedral GeTe using the ideas of the Grüneisen theory within the elastic and harmonic approximations for the mechanical and vibrational properties of solids, respectively. A rhombohedral unit cell is defined with the primitive lattice vectors $a(b, 0, c)$, $a(-\frac{b}{2}, \frac{\sqrt{3}b}{2}, c)$ and $a(-\frac{b}{2}, -\frac{\sqrt{3}b}{2}, c)$. Here $a$ is the lattice constant, and $b$ and $c$ are defined as:

$$b = \sqrt{\frac{2}{3}(1 - \cos \theta)},$$

$$c = \frac{1}{3}(1 + 2 \cos \theta),$$  

where $\theta$ is the angle between the primitive lattice vectors. The reduced atomic positions of GeTe within this unit cell are: $(0, 0, 0)$ for Ge atom and $(\tau, \tau, \tau)$ for Te atom. The temperature dependence of these structural parameters is implicit. The Helmholtz total free energy of a rhombohedral crystal per unit cell is defined as [37]:

$$F(a, \theta, \tau, T) = E_{el}(a, \theta, \tau) + F_{vib}(a, \theta, \tau, T),$$  

where $E_{el}(a, \theta, \tau)$ and $F_{vib}(a, \theta, \tau, T)$ correspond to the static elastic and vibrational free energy at temperature $T$, respectively. The values of all the structural parameters at a certain temperature can be found by minimizing the total free energy with respect to each structural parameter $u, u \in (a, \theta, \tau)$:

$$\frac{\partial F}{\partial u} = \frac{\partial E_{el}}{\partial u} + \frac{\partial F_{vib}}{\partial u} = 0. $$  

Within the harmonic approximation, vibrational free energy is given as [37]:

$$F_{vib} = \sum_{q, s} \left[ \frac{\hbar \omega_s(q)}{2} + k_B T \ln \left( 1 - \exp \left( -\frac{\hbar \omega_s(q)}{k_B T} \right) \right) \right],$$

where $\omega_s(q)$ is the phonon frequency of mode $s$ and wave vector $q$, and $k_B$ is the Boltzmann constant. The derivative of vibrational free energy with respect to one of the structural parameters $u$ reads:

$$\frac{\partial F_{vib}}{\partial u} = -\frac{1}{u} \sum_{q, s} \hbar \omega_s(q) \left( n(\omega_s(q)) + \frac{1}{2} \right) \gamma^u_s(q),$$  

where $n(\omega_s(q))$ is the Bose-Einstein occupation factor at temperature $T$ for a phonon with frequency $\omega_s(q)$. We define the generalized Grüneisen parameters with respect to each structural parameter as:

$$\gamma^u_s(q) = -\frac{u}{\omega_s(q)} \frac{\partial \omega_s(q)}{\partial u}. $$

We calculate phonon frequencies and generalized Grüneisen parameters for the values of the structural parameters $a$, $\theta$ and $\tau$ at 0 K. This is a reasonable approximation since only the soft TO modes close to the zone center will have a considerable temperature dependence in GeTe [38].

The static elastic part of total free energy can be expanded in a Taylor series as:

$$E_{el} = E_0 + \sum_u K_u \Delta u + \sum_{u,v} K_{uv} \Delta u \Delta v. $$

$\Delta u$ and $\Delta v$ represent the small deviations of the structural parameters $u$ and $v$ from their equilibrium values for temperature $T$ ($u, v \in \{a, \theta, \tau\}$). We define the first and second order coefficients as the changes of $E_{el}$ with respect to the changes of structural parameters: $K_u = \frac{\partial E_{el}}{\partial u}$ and $K_{uv} = (1 - \frac{1}{\gamma^u} \frac{\partial^2 E_{el}}{\partial u \partial v})$. The relationship between these coefficients and elastic constants is discussed in Appendix A. The final form for the derivative of static elastic energy with respect to one of the structural parameters reads:

$$\frac{\partial E_{el}}{\partial u} = K_u + \sum_v (1 + \delta_{uv}) K_{uv} \Delta v. $$

Coefficients $K$ change with temperature due to the contribution of the higher order terms in the Taylor expansion of static elastic energy. If we label the changes of the structural parameters at temperature $T$ with respect to their values at 0 K as:

$$\delta a = a - a_0, $$

$$\delta \theta = \theta - \theta_0, $$

$$\delta \tau = \tau - \tau_0, $$

we can expand static elastic energy as:

$$E_{el} = \sum_{u,v} K_{uv}^0 (\Delta u + \delta u)(\Delta v + \delta v) + \sum_{u,v,w} K_{uvw}^0 (\Delta u + \delta u)(\Delta v + \delta v)(\Delta w + \delta w) + (\Delta w + \delta w)(\Delta t + \delta t). $$
$K_{uv}^0$, $K_{uw}^0$ and $K_{uwu}^0$ are the second, third and fourth order coefficients defined for the changes of structural parameters calculated at 0 K, and $\delta u \in \{\delta a, \delta \theta, \delta \tau\}$. From Eqs. (7) and (10), we obtain coefficients $K_u$ and $K_{uv}$ that depend on changes $\delta u$ from the 0 K values, e.g.:

\[
\begin{align*}
K_a &= 2K_{aa}^0 \delta a + K_{a\theta}^0 \delta \theta + K_{a\tau}^0 \delta \tau + 3K_{aa\theta}^0 \delta a \delta \theta + \\
&+ 2(K_{aa\tau}^0 \delta a + K_{a\theta\theta}^0 \delta a \delta \theta + K_{a\theta\tau}^0 \delta a \delta \tau + K_{a\tau\tau}^0 \delta a \delta \tau).
\end{align*}
\]

Substituting Eqs. (5) and (8) into Eq. (3), we obtain:

\[
\Delta u = \sum_v S_{uv} \left[ \sum_{\omega_i} \hbar \omega_i(q) \left( n(\omega_i(q)) + \frac{1}{2} \right) \frac{v_i^v(q)}{v} - K_v \right].
\]

(12)

$S_{uv}$ are the elements of the matrix defined as an inverse of the matrix of coefficients $\hat{K}$:

\[
\hat{K} = \begin{bmatrix}
2K_{aa} & K_{a\theta} & K_{a\tau} \\
K_{a\theta} & 2K_{\theta\theta} & K_{\theta\tau} \\
K_{a\tau} & K_{\theta\tau} & 2K_{\tau\tau}
\end{bmatrix}.
\]

(13)

The matrix $\hat{S}$ is related to the compliance matrix which represents an inverse of the elastic constants matrix. We note that coefficients $K_u$ and $K_{uv}$ are functions of the structural parameters changes, $\delta a$, $\delta \theta$ and $\delta \tau$, see Eq. (11). We solve Eq. (12) for $\delta a$, $\delta \theta$ and $\delta \tau$ at each temperature by requiring that $\Delta u = 0$, which gives the thermal equilibrium structure. To do this, we construct an iterative solution as $\Delta u_{i+1} = \Delta u_i + \Delta u_i (\delta a_i, \delta \theta_i, \delta \tau_i)$, where $\Delta u_i$ is given by Eq. (12). This is iterated until $\Delta u_i \approx 0$.

We note that the presented method to calculate thermal expansion is inexpensive and straightforward to implement. Its implementation requires: (i) the density functional theory (DFT) calculations of the phonon frequencies and generalized Grüneisen parameters for the 0 K values of the structural parameters, (ii) the calculation of the DFT energy surface for a range of structural parameter values, whose fitting gives coefficients $K^0$ (Eq. (10)), and (iii) the iterative solution for $\delta a$, $\delta \theta$ and $\delta \tau$ in Eq. (12) until $\delta a$, $\Delta \theta$ and $\Delta \tau$ become zero for a range of temperatures.

Our approach for obtaining the thermal expansion of rhombohedral materials near soft optical mode phase transitions can be linked to the standard method based on the Grüneisen theory \cite{32,33}, as shown in Appendix A. This approach finds the minimum of the total free energy of the system with respect to strain, rather than structural parameters. Far from the phase transition, our method fully corresponds to the standard one. However, the standard approach typically neglects elastic constant variations with temperature, which are important for the accurate description of thermal expansion near the phase transition. Furthermore, the standard method does not track the thermal evolution of internal atomic position, and thus cannot capture the phase transition, as we will show. On the other hand, establishing the precise relationship between our method and statistical mechanics approaches \cite{39,40,41} is less straightforward and requires further study.

### III. COMPUTATIONAL DETAILS

DFT calculations were performed using the plane wave basis set, the generalized gradient approximation with Perdew-Burke-Ernzerhof \cite{12} parametrization (GGA-PBE) for exchange-correlation potential and the Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials \cite{43} as implemented in ABINIT code \cite{44}. For the ground state and static elastic energy calculations, we used a 32 Hartree energy cutoff for plane waves and a four shifted $12 \times 12 \times 12$ k-point grid for Brillouin zone sampling of electronic states. Harmonic interatomic force constants at zero temperature were calculated from Hellmann-Feynman forces obtained by the finite difference supercell approach using PHONOPY code \cite{45}. Forces were computed using 128-atom supercells ($4 \times 4 \times 4$ rhombohedral unit cells) with a 24 Hartree cutoff and a four shifted $3 \times 3 \times 3$ k-point grid. Phonon frequencies were calculated using a $20 \times 20 \times 20$ q-point grid for vibrational modes. We obtained generalized Grüneisen parameters using a finite difference method, taking the finite displacement to be smaller than 1% for $a$, and smaller than 1% of the difference between the 0 K rhombohedral and high temperature rocksalt structures for $\theta$ and $\tau$. For the calculation of coefficients $K^0$ in Eq. (10), we parametrized the energy surface on uniform grids for the values of structural parameters $a$, $\theta$ and $\tau$, from the 0 K rhombohedral structure to the high temperature rocksalt structure.

### IV. RESULTS AND DISCUSSION

We calculated the structural parameters of GeTe at 0 K using DFT and two different exchange-correlation functionals, local density approximation (LDA) \cite{13} and GGA-PBE, see Table I. To our knowledge, the measured values of the structural parameters at zero temperature are not available. Nevertheless, it is likely that, as the temperature is reduced from 295 K to 0 K, the angle and internal atomic position would deviate further from the high-symmetry (rocksalt) values, and would agree better with the GGA-PBE calculation than with the LDA. Since our goal is to describe the temperature dependence
of structural parameters near the phase transition, where internal atomic position plays a crucial role, we use the GGA-PBE functional in all further calculations. Our values of structural parameters are also in good agreement with previous DFT calculations \[10, 16\].

|            | $a$ [Å] | $\theta$ [deg] | $\tau$ | $V_0$ [Å$^3$] |
|------------|---------|----------------|--------|--------------|
| LDA        | 4.207   | 58.788         | 0.524  | 51.193       |
| GGA-PBE    | 4.381   | 57.776         | 0.530  | 56.420       |
| Experiment (295 K) | 4.299   | 57.931         | 0.525  | 53.513       |

TABLE I. Lattice parameters of GeTe at 0 K, calculated using LDA and GGA-PBE functionals, and compared with experimental results \[4\]. $a$ stands for lattice constant, $\theta$ for angle, and $\tau$ for internal atomic coordinate.

The phonon dispersion of GeTe at 0 K is given in Fig. 2(a), together with the experimental results for the frequencies of the Raman active zone center modes \[9, 47\]. Large intrinsic concentrations of charge carriers in real GeTe samples (1-20×$10^{20}$ cm$^{-3}$) completely screen long range interactions \[9\]. We roughly estimate this effect by setting Born effective charges to zero in the calculation of phonon frequencies (see dashed red lines in Fig. 2(a)). To evaluate the importance of screening, we also neglect this effect in the phonon calculation by using Born effective charge values obtained using density functional perturbation theory (DFPT) (solid black lines in Fig. 2(a)). Using both approaches, our calculated phonon frequencies at the zone center agree very well with experimental results \[9, 47\]. Fig. 2(b) illustrates that our computed phonon frequencies at the zone center agree very well with experimental results \[9, 47\]. We compare our results with those of Ref. \[9\] (green triangles). The integral of the density of states of GeTe calculated neglecting and including screening (solid black line and dashed red line, respectively) are no appreciable differences in the calculated phonon DOS if we exclude or roughly include screening effects, we neglect screening in all further calculations. Our phonon dispersion of GeTe also agrees well with a previous DFPT calculation \[10\].

The temperature dependence of all structural parameters of rhombohedral GeTe (lattice constant, angle and internal atomic coordinate $\tau$) are illustrated in Fig. 3. Solid lines represent our calculations, while symbols show the measurements of Refs. \[4, 5\]. The experimental values were transformed from the pseudocubic to the rhombohedral unit cell for comparison with our results. The computed temperature variation of structural parameters is in good agreement with experiments, despite the small discrepancy between the GGA-PBE and the room temperature experimental structural parameters (see Table 1). Dashed lines in Fig. 3 represent our calculations shifted by the difference between our values and the experimental values of Ref. \[4\] at 300 K. The calculated temperature dependence of the zone center TO mode frequency (see Appendix B) is also in very good agreement with experiment \[9\]. We highlight that all these agreements are obtained fully from first principles, without any empirical parameters.

Our calculated structural parameters of rhombohedral GeTe show clear indications of the ferroelectric phase transition near 700 K, see Fig. 3. As temperature increases, the angle $\theta$ and the internal atomic coordinate $\tau$ tend to their high symmetry values, 60° and 0.5, respectively. Moreover, the temperature dependence of all structural parameters diverges from a linear behavior at high temperatures (500-700 K), which signals the proximity to the phase transition.

The thermal evolution of the structural parameters of GeTe is correctly captured only when the total free energy is minimized with respect to all structural parameters, and the temperature dependence of coefficients $K_u$ and $K_{33}$ defined in Eq. \[8\] is taken into account. Fig. 4 shows the comparison between the calculations obtained using our approach and the standard approach \[32, 33\].
where the free energy is not minimized with respect to the internal atomic coordinate \( \tau \) and elastic constants do not vary with temperature. Even though internal atomic position is relaxed as strain is applied in the standard method, this approach gives qualitatively very different trends compared to our model and experiments [4, 5]. These results highlight the importance of improving the standard method, to include the critical physical effects occurring near the phase transition, as shown here.

Most interestingly, GeTe exhibits negative volumetric thermal expansion near the phase transition at \( \sim 700 \) K, which has been observed experimentally [4–7] and reproduced in our calculations, see Fig. 5(a). The volumetric contraction close to the phase transition is due to the NTE of the lattice constant shown in Fig. 3(a). We note that the sign of the volumetric thermal expansion de-
pends strongly on the exact composition of samples, as does the Curie temperature. Positive volumetric thermal expansion occurs in samples with more than 50.6% Te, as measured in Refs. [6, 7]. Samples with less than 50.6% of Te exhibit NTE at the phase transition [6, 7], which is in agreement with our calculation for stoichiometric GeTe (50% Te).

Analyzing all the physical quantities that determine the structural parameters (coefficients $K$ and generalized Grüneisen parameters entering Eq. (3)), we found that only $K_{a\tau}$, $K_{\theta\tau}$ and $K_{\tau\tau}$ change substantially near the phase transition. (Elastic constants also vary considerably close to the transition, see Appendix C). $K_{a\tau}$ and $K_{\theta\tau}$ reflect static elastic energy variations with respect to simultaneous changes of the structural parameters related to acoustic strain ($a$ and $\theta$) and the TO mode ($\tau$). Consequently, $K_{a\tau}$ and $K_{\theta\tau}$ quantify acoustic-TO coupling, and indicate its large variation close to the phase transition.

Acoustic-soft TO mode coupling that increases considerably near the phase transition causes the negative thermal expansion of GeTe. In our computational method, we can artificially turn off this coupling by setting $K_{a\tau}$ and $K_{\theta\tau}$ to zero, as shown in Fig. 5(b). The volume calculated by neglecting acoustic-TO coupling does not exhibit a negative thermal expansion. We thus conclude that strong acoustic-TO phonon coupling is the origin of the NTE of GeTe at the phase transition.

FIG. 5. (a) Volumetric thermal expansion of GeTe: our calculation (solid black line), experiment [4] (red circles), and our calculation shifted by the difference between our and the experimental value at 300 K (dashed black line). (b) Computed volumetric thermal expansion including and neglecting acoustic-soft optical mode coupling, shown in solid black and dashed red lines, respectively.

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The most commonly cited cause of negative thermal expansion in the literature is a negative Grüneisen parameter [49–52]. Here we investigate the role of generalized Grüneisen parameters in establishing the NTE of GeTe. We define average generalized Grüneisen parameters for $u \in \{a, \theta, \tau\}$ as:

$$\langle \gamma^u \rangle = \frac{1}{\hbar \omega_D} \sum_{q,s} \hbar \omega_s(q) \left( n(\omega_s(q)) + \frac{1}{2} \right) \gamma^u_s(q),$$

where $\omega_D$ is the Debye frequency [53]. The temperature dependence of $\langle \gamma^u \rangle$ is shown in Fig. 6(a). Fig. 6(b) illustrates the compliance elements that determine the value of lattice constant in Eq. (12), normalized as $S^*_a = S_{a\sigma}/a^2$, $S^*_\theta = S_{\theta\sigma}/a\theta$, and $S^*_\tau = S_{\tau\sigma}/a\tau$. The linear temperature dependence of the average generalized

FIG. 6. Temperature dependence of: (a) average generalized Grüneisen parameters defined for each structural parameter ($a$ - lattice constant, $\theta$ - angle, $\tau$ - internal atomic coordinate), and (b) normalized compliance matrix elements (see text for full explanation).
Grüneisen parameters stems from the Bose-Einstein occupation factor. In contrast, the compliance elements change dramatically with temperature near the phase transition, due to large temperature variations of $K_{\alpha\tau}$, $K_{\theta\tau}$ and $K_{TT}$. Since the lattice constant expansion is proportional to $S_{aa} \langle \gamma^a \rangle + S_{a\theta} \langle \gamma^\theta \rangle + S_{aa} \langle \gamma^\tau \rangle$ (Eq. (12)), its negative sign is partially due to negative $\langle \gamma^\tau \rangle$, which physically corresponds to the anharmonicity of the TO mode. Nevertheless, negative $\langle \gamma^\tau \rangle$ is not the main reason for the negative volumetric thermal expansion between acoustic and soft transverse optical modes, i.e. large acoustic-TO coupling so that the expansion becomes negative. Furthermore, $S_{a\theta}$ is also negative and its absolute value increases more rapidly at the phase transition, resulting in an additional negative contribution to thermal expansion. This analysis confirms the dominant role of acoustic-TO coupling in establishing the NTE of GeTe near the phase transition. We expect that this conclusion will remain valid even when the temperature dependence of phonon frequencies and generalized Grüneisen parameters $\gamma_i^a(q)$ is accounted for. This would make the temperature changes of $\langle \gamma^\tau \rangle$ near the phase transition somewhat larger than those calculated here, due to the temperature variations of the frequencies of soft TO modes close to the zone center.

V. CONCLUSION

We developed a first principles method that accurately describes the temperature dependence of all structural parameters for the rhombohedral phase of GeTe up to the Curie temperature of $\sim 700$ K. The key new features of our approach with respect to the standard method based on the Grüneisen theory are the minimization of free energy with respect to all structural parameters and the temperature dependence of elastic constants. Our computed thermal expansion is in very good qualitative agreement with experiment. We showed that the coupling between acoustic and soft transverse optical modes is the main reason for the negative volumetric thermal expansion of GeTe near the phase transition.

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Table II. Calculated elastic constants of GeTe using density functional perturbation theory (DFPT), and density functional theory (DFT) combined with a finite difference method. $C_{11} + C_{12}$, $C_{13}$ and $C_{33}$ were calculated directly using DFPT, and transformed into $K_{aa}$, $K_{a\theta}$ and $K_{\theta\theta}$ using Eq. (16). $K_{aa}$, $K_{a\theta}$ and $K_{\theta\theta}$ were computed using DFT, and transformed into $C_{11} + C_{12}$, $C_{13}$ and $C_{33}$ by inverting Eq. (16).

**APPENDIX B: SOFT OPTICAL MODE FREQUENCY**

Since $K_{\tau\tau}$ is the second derivative of total energy with respect to the internal atomic coordinate, we can calculate the TO mode frequency using [37]:

$$\omega_{T O}^2 = \frac{2K_{\tau\tau}}{\mu a_{||}}$$

where $\mu$ is reduced mass of the unit cell and $a_{||}$ is the length of the unit cell in the [111] direction. This makes it possible to track the softening of this mode and compare it to measurements [9], as shown in Fig. 7. We find a very good agreement between our calculated TO frequency and experiment.

![Graph showing TO mode frequency versus temperature](image)

**APPENDIX C: ELASTIC CONSTANTS NEAR THE PHASE TRANSITION**

In our calculations, the values of all elastic constants have a steep change at the phase transition, which is in agreement with experimental observations in Sn$_x$Ge$_{1-x}$Te [55] and Pb$_x$Ge$_{1-x}$Te [56]. Fig. 8 shows how $C_{11} + C_{12}$, $C_{13}$ and $C_{33}$ vary with temperature. $C_{11} + C_{12}$ increases rapidly at the phase transition, as observed in [55, 56]. Experimental values of $C_{13}$ and $C_{33}$ were not reported, but our calculations correctly capture their expected behaviour. At the high symmetry rock-salt phase, $C_{33}$ and $C_{11}$, as well as $C_{12}$ and $C_{13}$, should have the same values. In the low symmetry rhombohedral phase, $C_{33}$ has lower value than $C_{11}$ (Table I), so we would expect that $C_{33}$ will increase towards the phase transition to become equal to $C_{11}$. On the other hand, $C_{13}$ is larger than $C_{12}$, and it will decrease towards the phase transition to become equal to $C_{12}$. Both of these trends are observed in our results.

![Graph showing elastic constants versus temperature](image)
We calculated the Debye frequency of GeTe by fitting the analytical expression for the specific heat capacity obtained using the Debye model to that calculated using the phonon dispersion computed using density functional theory. Our calculated value of the Debye frequency is 3.8 THz.

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