

Molecular dynamics simulation of the ferroelectric phase transition in GeTe: Displacive or order-disorder character

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Experimental investigations of the phase transition in GeTe provide contradictory conclusions regarding the nature of the phase transition. Considering growing interest in technological applications of GeTe, settling these disputes is of great importance. To that end, we present a molecular dynamics study of the structural phase transition in GeTe using a machine-learned interatomic potential with *ab initio* accuracy. First, we calculate the asymmetric shape of the radial distribution function of the nearest-neighbor bonds above the critical temperature, in agreement with previous studies. However, we show that this effect is not necessarily linked to the order-disorder phase transition and can occur as a result of large anharmonicity. Next, we study in detail the static and dynamic properties of the order parameter in the vicinity of the phase transition and find fingerprints of both order-disorder and displacive phase transition.

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I. INTRODUCTION

The phase transition in ferroelectric materials is usually discussed in terms of two distinct mechanisms, which determine whether the phase transition has order-disorder or displacive character [1–6]. The distinction between these two mechanisms comes from the analysis of a simplified Landau model of ferroelectric materials [7]. In the displacive limit of the phase transition, the frequency of a soft phonon mode becomes zero in the higher-symmetry structure at the critical temperature. The soft phonon mode freezes in the lower-symmetry structure driving the structural phase transition [1–4]. On the other hand, in the order-disorder limit of the phase transition, the local ferroelectric distortion persists above the critical temperature. In this case the paraelectric nature of the high-symmetry phase stems from the lack of the long-range spatial correlation of the polarization [5,6].

Germanium telluride, GeTe, is an important thermoelectric material that is also ferroelectric below 600–700 K [8–12]. The Landau model of ferroelectric phase transitions places GeTe at the boundary between materials exhibiting order-disorder and displacive characters of the ferroelectric phase transition [13]. This is further confirmed by a number of experimental studies with contradictory conclusions [1–6]. Depending on the spatial resolution of the experimental method, the phase transition in GeTe is found to be either order-disorder or displacive. This ambiguity suggests that a computational, first-principles-based study of the phase transition would provide useful insights.

Our recent works have been able to explain a number of interesting properties of GeTe at the ferroelectric phase

transition, primarily negative thermal expansion [14] and an increase in the lattice thermal conductivity [15]. However, both of these studies relied heavily on a phonon picture of GeTe, implying a displacive character of the phase transition. There is an open question of whether the inclusion of order-disorder character in the calculations would lead to different results and conclusions.

Molecular dynamics (MD) simulations are probably the most direct tool for classical simulations of materials [16–18]. In principle, they can capture all relevant physical effects at high temperatures, where quantum corrections are negligible. However, MD simulations for systems containing many atoms when forces are determined by density functional theory (DFT) are extremely computationally expensive [19,20]. To circumvent this issue, researchers usually rely on a simple analytic form of interatomic potentials which have limited accuracy and transferability [21–23]. Recent works on machine learning interatomic potentials aim to correct this and provide interaction models of quality similar to DFT, at a much more modest computational price [24–28]. These interatomic potentials were recently used to describe phase transitions in a variety of materials [29–33].

In this paper, we present a molecular dynamics study of the ferroelectric phase transition in germanium telluride. To calculate atomic forces and energies along MD trajectories, we used our recently developed interatomic potential for GeTe using the Gaussian approximation potential (GAP) framework [24,25]. Our model of interatomic interactions in GeTe, based on DFT energies and atomic forces, reproduces the experimental structural parameters and negative thermal expansion at the phase transition. The radial distribution function of the nearest-neighbor bonds in GeTe was found to be strongly non-Gaussian even at temperatures above the phase transition. We show that this does not necessarily mean that the phase transition has an order-disorder character and that this

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effect could arise as a consequence of strong anharmonicity. Furthermore, we present a detailed investigation of the order parameter behavior at the ferroelectric phase transition, which is found to exhibit fingerprints of both order-disorder and displacive character.

II. COMPUTATIONAL DETAILS

Molecular dynamics simulations were performed using the LAMMPS code [34]. To calculate the atomic forces and energies, we used our previously fitted GAP for GeTe [15,35]. This interatomic potential was fitted to DFT energies and atomic forces. More details about the fitting procedure and the potential are given in Ref. [15]. To obtain the equilibrium values of structural parameters at different temperatures, we first run a 10 ps simulation using the *NVT* ensemble to equilibrate velocities at the given temperature, followed by a 20 ps *NPT* simulation to equilibrate the structure [36,37]. We then run a 200 ps *NPT* simulation while collecting data every 0.1 ps. The time step is taken to be 1 fs. For a convergence study with the size of the simulation region, see the Supplemental Material [38]. At each temperature we start from the zero-temperature equilibrium structure of GeTe and set random initial atomic velocities sampled from the normal distribution with the variance corresponding to the target temperature.

To compute the order parameter at different temperatures, we perform 300 ps *NVT* simulations on a 512-atom cell while collecting atomic positions every second time step. A time step of 1 fs was used in all simulations. Prior to data collection, we equilibrate the system for 50 ps in the *NVT* ensemble.

III. STRUCTURAL PARAMETERS AND THERMAL EXPANSION OF GeTe

Germanium telluride crystallizes in a rhombohedral structure below 600 K (see Fig. 1), which is described by the following lattice vectors:

$$\begin{aligned}\vec{R}_1 &= a(b, 0, c), & \vec{R}_2 &= a\left(-\frac{b}{2}, \frac{b\sqrt{3}}{2}, c\right), \\ \vec{R}_3 &= a\left(-\frac{b}{2}, -\frac{b\sqrt{3}}{2}, c\right).\end{aligned}\quad (1)$$

Here a is the lattice constant of the primitive unit cell of GeTe, $b = \sqrt{\frac{2}{3}}(1 - \cos\theta)$, and $c = \sqrt{\frac{1}{2}}(1 + 2\cos\theta)$. θ is the angle between the lattice vectors and can be regarded as a secondary order parameter since in the cubic phase it has a fixed value of 60° and a lower, temperature-dependent value in the rhombohedral phase. The atomic positions in reduced coordinates are taken to be Ge (0,0,0) and Te ($0.5 + \tau$, $0.5 + \tau$, $0.5 + \tau$).

We calculate the structural parameters of GeTe (the lattice constant a and the rhombohedral angle θ) at several temperatures. At each time step we calculate the instantaneous values of the lattice constant and rhombohedral angle from the geometry and volume of the simulation region. Following that, we find the structural parameters at a given temperature as a simple arithmetic mean of the instantaneous values along the MD trajectory. The results are given in Fig. 2 and compared with a number of available experiments [2,40,41]. In Fig. 2,

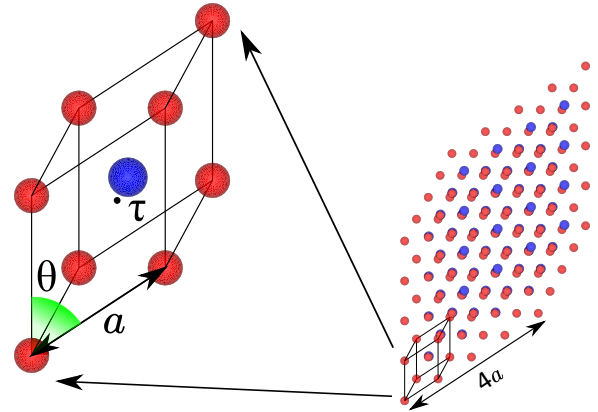


FIG. 1. Primitive unit cell of GeTe. Red (blue) spheres are germanium (tellurium) atoms. a is the lattice constant, θ is the rhombohedral angle, and τ is the order parameter (the vector from the center of the unit cell, the black point, to the tellurium atom). The side image shows the simulation cell in molecular dynamics simulations. For presentation purposes we show the $4 \times 4 \times 4$ supercell, instead of the $10 \times 10 \times 10$ used in our calculations. The image was made using the VESTA software [39].

we show the relative change of the structural parameters compared to their 300 K values (V is the volume of the primitive cell):

$$\begin{aligned}\alpha_u &= \frac{u_T - u_{300\text{K}}}{u_{300\text{K}}}, & u &= a, V, \\ \alpha_\theta &= \frac{\theta_T - \theta_{300\text{K}}}{60^\circ - \theta_{300\text{K}}}.\end{aligned}\quad (2)$$

Our calculations reproduce the experimental results very well. All studies show negative expansion of the lattice constant at intermediate temperatures (above 300 K and below the critical temperature) and positive expansion in the cubic phase. We find that the lattice constant has a positive thermal expansion coefficient for temperatures below 300 K, as measured in the experiment. The rhombohedral angle tends to the cubic value of 60° at high temperatures. From the behavior of the rhombohedral angle, we can infer that the critical temperature in our study is 634 K (the middle point between the last rhombohedral structure at 631 K and the first cubic structure at 637 K), which is in the range of experimental results (600–700 K) [8].

We also calculate the volumetric thermal expansion of GeTe [see Fig. 2(c)]. Again, our results follow closely experimental findings, both showing negative thermal expansion at the phase transition. In the cubic phase, GeTe regains positive thermal expansion, in agreement with experiment. We do not see a discontinuity in the calculated thermal expansion of GeTe. To be precise, we see a decrease in the volumetric thermal expansion coefficient as we approach the phase transition from lower temperatures, which eventually becomes negative thermal expansion at 631 K. For a more elaborate discussion of negative thermal expansion near the phase transition, see the Supplemental Material [38].

Finally, we compute the Ge-Te nearest-neighbor bond lengths. A number of experimental [5,6] and theoretical

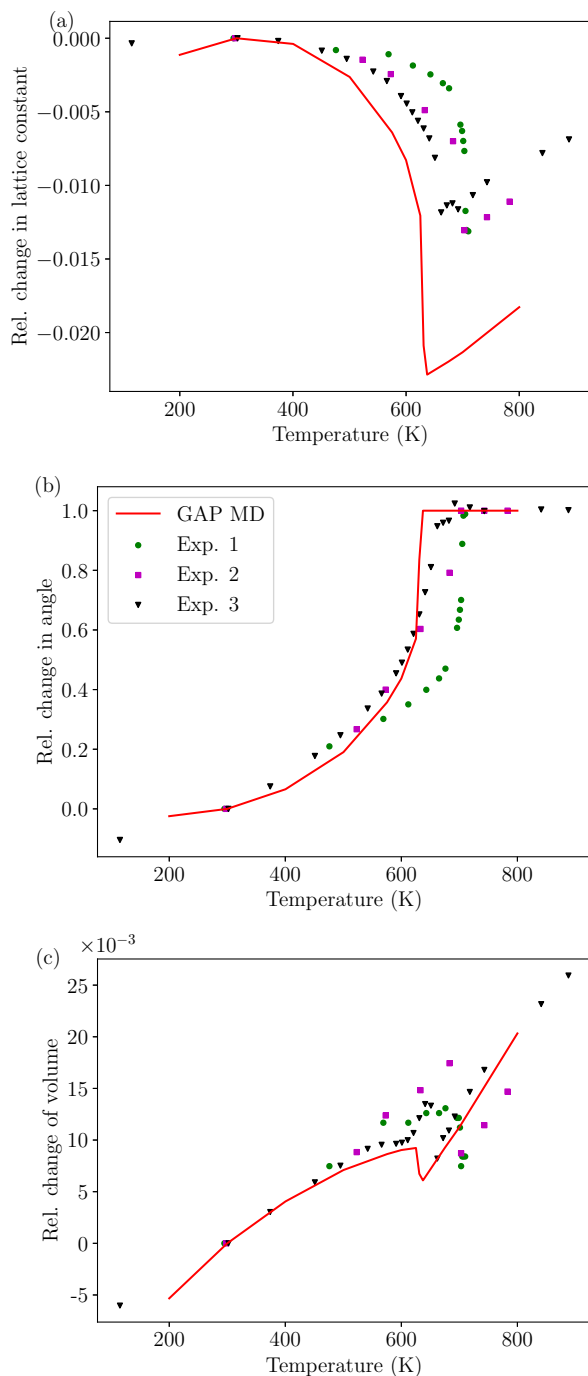


FIG. 2. Relative change of (a) the lattice constant, (b) the rhombohedral angle, and (c) the volume of GeTe with temperature. The red lines are our MD results, while the points represent experimental data taken from Refs. [2] (green), [40] (magenta), and [41] (black).

studies [19,20] claim that they observed persistence of unequal bond lengths in the cubic phase. Previous theoretical studies inferred this effect from the distorted Gaussian shape of the radial distribution function (RDF) for these bond lengths (≈ 3 Å). If the interatomic interaction is perfectly harmonic, one would expect bond lengths to be normally distributed around some mean value which is the reported bond length. A distortion of this Gaussian shape is usually

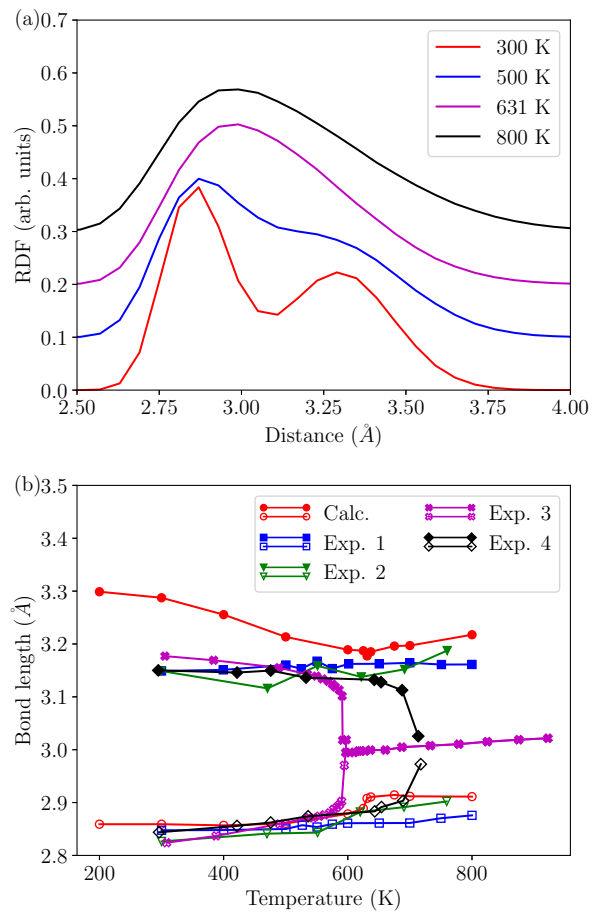


FIG. 3. (a) Radial distribution function of GeTe for the nearest-neighbor bonds at different temperatures. (b) Nearest-neighbor bond lengths in GeTe. Our calculations are in red, Ref. [5] is in blue, and Ref. [6] is in green (experiments reporting the order-disorder character of the phase transition). Ref. [3] is in magenta, and Ref. [2] is in black (experiments reporting the displacive character of the phase transition). The solid symbols represent longer bond lengths, while the open symbols represent shorter bond lengths. The lines are guides to the eye.

attributed to the presence of two Gaussians, which means that we have two different bond lengths in the considered length scale. Like in the previous theoretical studies, we also find two different bond lengths if we try to fit our data with two Gaussians [see Fig. 3(a)]. Figure 3(b) shows the fitted bond lengths using two Gaussians in our calculation compared to experiments [2,3,5,6]. The experiments that could probe local structure obtained unequal bond lengths in the cubic phase [5,6] [labeled Exp. 1 and Exp. 2 in Fig. 3(b)], while the experiments that saw the average structure saw equivalent bond lengths [2,3] [labeled Exp. 3 and Exp. 4 in Fig. 3(b)]. Our results obtained by fitting the RDF with two Gaussians are in overall agreement with experimental results that saw the local structure. However, contrary to those experiments, we see an interesting behavior near the phase transition, a noticeable increase in the short bond length and a noticeable decrease of the larger bond length. This change in bond lengths does not make them equal, however, and the local rhombohedral phase seems to persist in the cubic phase as well.

From the analysis above, it is clear why the non-Gaussian shape of the nearest-neighbor bond length has been interpreted as a fingerprint of the order-disorder phase transition [20]. However, we observe the same non-Gaussian behavior even in the case of other rocksalt compounds modeled using interatomic potentials, such as PbTe [23] and MgO [42] (see the Supplemental Material [38]). These two materials are undoubtedly rocksalt and still have the distorted Gaussian shape for the nearest-neighbor RDF. The deviation from the simple Gaussian shape of the RDF is stronger in PbTe compared to MgO, probably because PbTe is more anharmonic. The reasoning for this assumption is as follows. First, we assume that the bond length is determined solely due to pairwise interactions between atoms. Then the probability distribution of that bond length would be proportional to $\exp[-U(R)/k_B T]$, where $U(R)$ is the energy of that two-atom system. If this energy is purely harmonic, we would have a Gaussian distribution of the bond length. However, in the case that the bond has an anharmonic term, there will be a skewing of the distribution in one of the directions, which is what we observe in all three systems (MgO, PbTe, and GeTe). Additionally, we find that the fitting procedure fails to correctly reproduce the “static” bond lengths in the rhombohedral phase of GeTe (see the Supplemental Material [38]). Hence, our results show that the non-Gaussian shape of the RDF is not proof of the order-disorder behavior in GeTe, and we are more inclined to believe it is a consequence of the large anharmonicity of the Ge-Te nearest-neighbor bond.

IV. ORDER PARAMETER

We calculated properties of the order parameter at various temperatures in order to understand the driving mechanism for the phase transition in GeTe. We calculate the local order parameter $[\tau_i(t)$ for the i th unit cell inside the supercell] as

$$\tau_i(t) = \vec{x}_{\text{Te},i}(t) - \vec{x}_{\text{Ge},i}(t) - 0.5 \sum_j \vec{R}_j, \quad (3)$$

where $\vec{x}_{\text{Te}/\text{Ge},i}$ is the instantaneous position of the tellurium/germanium atom in the i th unit cell and \vec{R}_j are the primitive lattice vectors at a given temperature. The average over all unit cells inside the MD simulation region at a certain time step represents the instantaneous order parameter. The average of the instantaneous order parameters over the entire MD trajectory represents the order parameter for that temperature (see the Supplemental Material [38] for additional information).

Figure 4(a) shows the total order parameter calculated at different temperatures compared with available experimental literature [2,40,41]. We can see that the overall agreement is good and that the differences mostly come from different values of the critical temperature. The inset shows the temperature dependence of the soft TO (A_{1g}) phonon mode frequency. We have calculated the phonon frequencies using the temperature-dependent effective potential method [43–45]. We can fit the temperature dependence of the order parameter and the soft TO mode to a simple functional dependence:

$$f(T) = A(T_C - T)^\gamma,$$

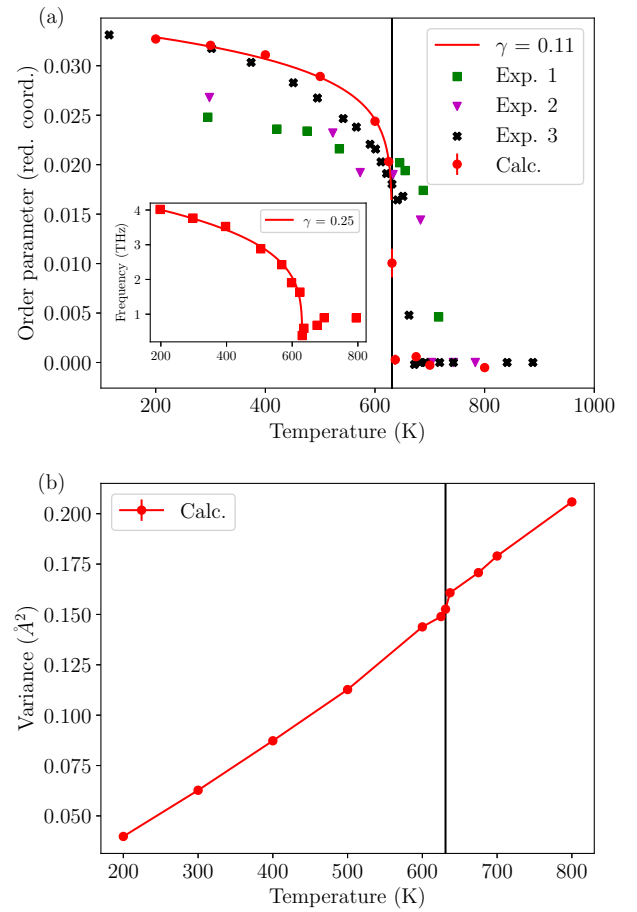


FIG. 4. Temperature dependence of (a) the average order parameter and (b) the variance of the order parameter as extracted from the probability distribution functions of the order parameter at different times and temperatures (see Supplemental Material [38] for more explanation). The experimental points are taken from Refs. [2,40,41]. The red points denote the results from our calculations, while the bars are the standard errors of the averaged quantity. The vertical black line shows the phase transition boundary. In (a), the red solid lines correspond to the power law fit to our calculated results, where γ is the exponent. The inset in (a) shows the calculated soft transverse optical phonon frequency versus temperature.

where T_C is the critical temperature and A and γ are the fitting parameters. A simple Landau approach to the displacive phase transitions predicts that the γ parameter for the soft TO mode should have the same value as the γ exponent for the order parameter [7] (see the Supplemental Material for clarification). This is not what we find in our calculations: γ for the order parameter is around two times smaller than γ for the soft TO mode. The possible reason for this is that the effects of the degrees of freedom other than the order parameter (such as large strain-order parameter coupling or disorder of the local order parameter) make a straightforward consideration of the Landau model inapplicable.

The procedure we used to calculate the average order parameter at a certain temperature allows us to calculate the time average variance of the local order parameter (see the Supplemental Material [38] for clarification), which is shown in Fig. 4(b). We notice a small jump at the phase transition.

The standard errors are shown, and they are much smaller than the size of the step in variance at the phase transition (the standard errors are smaller than the points). This increase is similar to the increase observed for the Debye-Waller factor in experiments. In experiments, this increase is explained by the ambiguity in determining the crystallographic phase of the system, i.e., whether the system is in a unique phase or a mixture of the two phases [41].

We suggest that the increase in the variance in Fig. 4(b) is due to a weak order-disorder character of the phase transition. The model for this behavior is as follows. The unit cell polarizations in our simulations are distributed according to a normal distribution centered around the instantaneous order parameter. The variance of that distribution should be a smooth function of temperature. In the displacive phase transition, the instantaneous order parameter becomes zero, and there should be no abrupt change in the variance. However, in the order-disorder phase transition, the unit cell's polarization would be normally distributed around two values of the instantaneous order parameter that have the same absolute magnitude but opposite signs. If these two mean values are sufficiently close, the distributions of the unit cell order parameter would overlap and yield a single-peak behavior, obscuring the order-disorder character. However, in this scenario the variance of the unit cell polarization distribution may abruptly change, which is what we calculate in our simulations. Hence, we interpret the observed step in the variance as the signature of a weak order-disorder character of the phase transition.

Finally, we look at the dynamics of the order parameter at different temperatures. We define the order parameter correlation function as

$$\begin{aligned} G_{\alpha\beta}(\vec{r}, t) &= \langle \tau_{\alpha}(0, 0) \tau_{\beta}(\vec{r}, t) \rangle \\ &= \iint d\vec{r}' dt' [\tau_{\alpha}(\vec{r}', t') - \langle \tau_{\alpha} \rangle] \\ &\quad \times [\tau_{\beta}(\vec{r}' + \vec{r}, t' + t) - \langle \tau_{\beta} \rangle]. \end{aligned} \quad (4)$$

Here α and β denote the Cartesian coordinates, and \vec{r} is the position vector of the unit cell. We can find the Fourier transform of this quantity, $\Gamma_{\alpha\beta}(\vec{q}, \omega)$.

First, we discuss the behavior of $\Gamma_{zz}(\vec{q} = 0, \omega)$ at different temperatures, as shown in Fig. 5(a). We oriented our simulation cell so that the order parameter is polarized along the z Cartesian direction. We can see that at low temperatures (300 K), the peak of this quantity is around 4 THz, which is the frequency of the soft optical mode [see Fig. 4(a)]. Additionally, we find that the order parameter correlation function in the other two Cartesian directions has a peak at the frequency of other optical modes (see the Supplemental Material [38]). This peak softens as we approach the transition temperature and disappears at the phase transition, leaving only a quasielastic peak (i.e., peak at the zero frequency, corresponding to zero energy transfer in scattering experiments). Interestingly, in the cubic phase, only the quasielastic peak persists, and the oscillations of the order parameter cannot be associated with any phonon. This behavior shows there is no persistent correlation among unit cell polarizations throughout the simulation region, suggesting a displacive character of the phase transition. On the other hand, in the case of the

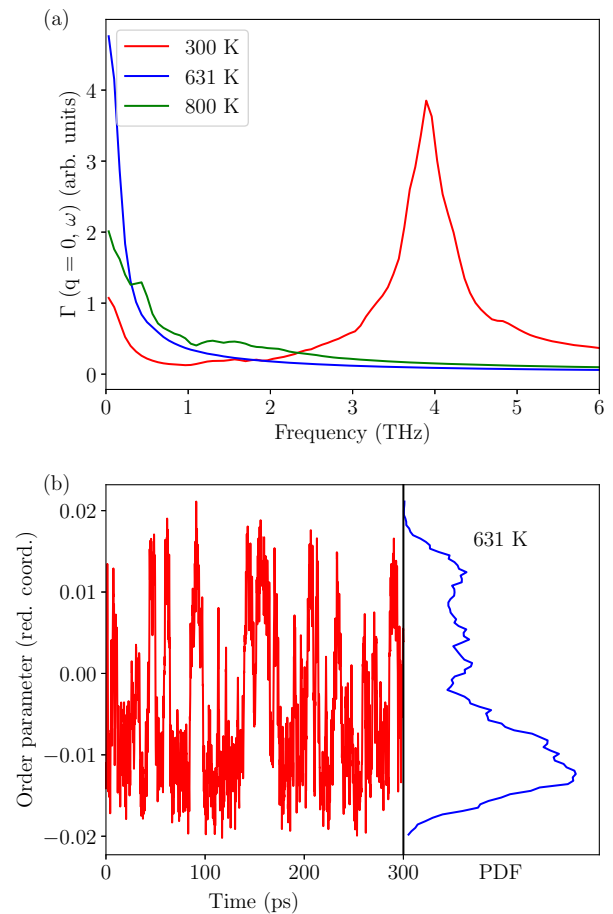


FIG. 5. (a) Frequency dependence of the Fourier transform of the order parameter correlation function [see Eq. (4)] at different temperatures. (b) The time evolution of the order parameter at 631 K. The side plot shows the probability density function of the instantaneous order parameter at this temperature.

order-disorder phase transition, the thermal oscillations of the polarization around local minima, although in opposite wells and out of phase, would still oscillate with the same frequency, leading to a nonzero signal in Fig. 4(a).

To understand better the dynamics of the order parameter at the phase transition, we show the instantaneous order parameter $\langle \tau_z \rangle(t)$ at 631 K in Fig. 5(b). We can see that although the spatial correlation persists and the order parameter is nonzero (the system is still in the rhombohedral phase), the value of the order parameter starts to switch between plus and minus signs. This switching leads to an exponentially decaying correlation function and, ultimately, to the quasielastic peak observed in Fig. 5(a). The switching behavior is dependent on the simulation cell size, with larger cells having lower frequencies of switching. This indicates that in the thermodynamic limit there would be no switching, and thus, this behavior cannot be interpreted as the order-disorder phase transition.

We also calculated the order parameter correlation length at different temperatures. We observed a large jump in the correlation length at the phase transition (see the Supplemental Material [38]), which suggests that the phase transition is of the second order. However, due to the small size of our simu-

lation cell, we could not observe whether the divergence of the correlation length follows a specific power law dependence.

V. CONCLUSIONS

In summary, we used molecular dynamics simulations to model the structural phase transition in GeTe using our recently developed Gaussian approximation potential for GeTe that mimics density functional theory results very well. First, we confirmed the results of our recent study on negative thermal expansion at the phase transition.

Second, we calculated the radial distribution function of the nearest-neighbor bonds in GeTe for both crystallographic phases. We observed a strongly non-Gaussian shape of the radial distribution function in the cubic phase in accordance with previous *ab initio* MD simulations. However, we showed that this effect is most likely due to the strong anharmonicity of the Ge-Te bonds and not due to a persistent local rhombohedral distortion in the cubic phase.

Next, we discussed in detail the behavior of the order parameter at the phase transition. We found fingerprints of both order-disorder and displacive phase transitions. Both the order parameter and the soft TO mode frequency continuously fall to zero at the phase transition, pointing to the displacive character of the phase transition. However, the variance of the order parameter probability distribution function exhibits a small step at the phase transition, which can be explained by the order-disorder phase transition.

Finally, we investigated the dynamics of the order parameter at the phase transition and found that in the low-symmetry phase it closely follows the behavior of the soft TO mode. This correlation disappears in the cubic phase, suggesting a possible displacive character of the phase transition. We showed the emergence of switching behavior at the phase transition, where polarization retains spatial correlation but loses temporal correlation. In the end, we calculated the order parameter correlation length for different temperatures and found that it diverges at the phase transition, suggesting that the phase transition is of the second order.

The distinction between the displacive and order-disorder phase transitions comes from the limiting cases of the simple Landau model of the second-order phase transition. As simple ground state calculations show [13], GeTe does not belong to either of these limiting cases, although it can be shown to be closer to the displacive model. The lengthy and detailed investigation that we carried out using molecular dynamics confirms this conclusion. The displacive character of the phase transition is supported by the disappearance of the temporal correlation of the order parameter with the persisting spatial correlation. A weak order-disorder character of the phase transition can be inferred from the temperature dependence of the variance of the order parameter.

Germanium telluride is a rare material in which both the order-disorder and displacive characters of the phase transition coexist. Similar behavior might exist in lead chalcogenides, where the off-centering of local dipoles has been claimed to be observed [18,46,47]. This effect could occur also in ferroelectric SnTe [48]. A detailed first-principles study has disproved the existence of off-centering in PbTe [18]. Clearly, IV-VI materials represent very interesting test subjects for this type of study. While there has been a fairly large number of papers on the properties of PbTe and GeTe, the other members of this group have not received as much attention. Finally, it would be interesting to see whether the coexistence of order-disorder and displacive characters of the phase transition has an influence on the phonon and transport properties of GeTe, specifically lattice thermal conductivity. While our previous study [15] resolved the enigma of the lattice thermal conductivity enhancement at the phase transition, it did not capture the influence of the order-disorder character.

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