Dynamic crystallography reveals spontaneous anisotropy in thermoelectric GeTe

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Peak performance in energy materials is associated with high symmetry and atomic fluctuations.[1][2] Indeed cubic thermoelectrics, phase change memories, photovoltaics etc are often claimed to be highly disordered.[3][4] In GeTe and related IV-VI compounds, this is said to provide the low thermal and high electronic conductivities needed for thermoelectric applications[5]. However, a general theory linking these empirical observations to transport properties is lacking. Since conventional crystallography cannot distinguish between disorder and atomic motions, we develop the energy-resolved variable-shutter pair distribution function (vsPDF) technique. We show that the atomic lattice of GeTe is nearly perfectly crystalline at all temperatures, but hosts remarkably large and anisotropic dynamics. Along the (111), direction, motion is almost uncorrelated, however, interactions are strengthened along the (100), direction. We show that this anisotropy naturally emerges from a Ginzburg-Landau model which couples polarisation fluctuations through long-range elastic interaction.[6] We propose that the liquid-like optical phonons screen charge carriers from scattering, as found in the lead halide hybrid perovskites.[7][8][9][10][11][12] This explains the contradictory properties of c-GeTe, which conducts heat like a glass, yet electricity like a crystal.[13] Coupling of the resultant ferroelectric large polarons to elastic anisotropy is likely ubiquitous in the IV-VI materials, ferroelectrics and photovoltaics, allowing strain engineering of novel optoelectronic properties.[13][14][15][16][17]

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The spectacular[13][14][15][16][17] thermoelectric properties of the binary IV-VI group materials reflect their proximity to ferroelectric instabilities.[18] GeTe is actually polar and rhombohedral at room temperature, with optimum (lowest) thermal lattice conductivity ($\kappa_L$) found in the high-temperature cubic phase.[19] However, even the structure of pristine (undoped) c-GeTe is strongly debated. Local probes claim atomic disorder,[19][20] in apparent disagreement with spectroscopy and diffraction.[21][22] Our X-scattering measurements highlight the disagreement between average and local probes. Diffraction shows that the $R\bar{3}m$ ferroelectric phase disappears at ~650 K, converting to the cubic rock-salt $Fm\bar{3}m$ structure (S1). The split ($\Delta r \approx 0.3$ Å) Ge-Te distances in r-GeTe, change to a single, symmetry-enforced, value in c-GeTe, which is nearly as crystalline as silicon (S2). However, our total scattering measurements support the contradictory results of other local probes.[21][22] Above 650 K, the nearest-neighbour peak in the pair distribution function (PDF) remains asymmetric (Fig. 1a). Fitting this requires breaking the Ge point-group symmetry, with a disordered 8-fold split site (Fig. 1b). In Fig. 1c, we plot the mean squared displacements, $\langle \sigma^2_{C} \rangle$, along the principle ADP axis of r-GeTe, and the size of the apparent (111)$c$ displacements in c-GeTe as a function of temperature. This ‘flattening’ of a
double well potential is consistent with Landau theory. However, we find that polarisation fluctuations grow beyond 7 meV, in contrast to the Curie-law behaviour of simple ferroelectrics. Curiously, we also noticed that the 6 Å Ge-Ge/Te-Te peak is anomalously sharp at all temperatures (Fig. 1a), behaviour which is also seen for other polarisable IV-VI materials (S3). In fact, the presence of local symmetry breaking is also debated for e.g. PbTe and SnTe, and the microscopic origins of their thermoelectric properties are also controversial. Energy-integrated crystallography cannot distinguish static disorder from dynamic motions. However, time-of-flight neutron spectrometers may be used to generate 'dynamic' pair distribution functions (vsPDF). Classically, cuts through $S(Q, \omega)$ space at fixed energy transfer are individually Fourier transformed. Unfortunately, normalising the inelastic signal is non-trivial, and the resulting real-space signal is not directly comparable to the time-average PDF, $G(r, \tau = \infty)$ determined by the elastic scattering. In addition, the energy and real-space resolutions of chopper spectrometers are inversely correlated. Here, in analogy to photography, we therefore develop the variable-shutter PDF method (vsPDF). By varying the energy integration window ($0 < E_{max} < \infty$), we extrapolate between the blurred time-average PDF, $G(r, \tau = \infty)$, and the instantaneous snapshot PDF, $G(r, \tau = 0)$. Note that all inelastic scattering is captured, ranging from sharp phonons, to broad features reflecting short-range correlations.

The raw data for c-GeTe at 720 K highlight the effect of 'shutter speed' on the reciprocal space structure factors (Fig. 2a). This data was collected using our highest incident energy ($E_i = 300$ meV), and shows striking differences between the structure factors, $Q_i [S(Q) - 1]$, generated from the total and elastic-line signals. The clear high-Q inelastic oscillation (Fig. 2a) can be parameterised as $\sim \sin(Qr)$ with $r \approx 2.88$ Å, which is the nearest-neighbour Ge-Te distance in our split-site model for c-GeTe (Fig. 1b). This is also exactly the predicted high-Q limit for the monophonon cross section, and rules out uncorrelated Einstein oscillators, which would not contribute to this structure in $S(Q)$.

In real-space the elastic-line PDF nearly recovers the undistorted NaCl structure seen by diffraction (S4). However, a trace of distortion remains in the first coordination sphere due to the energy resolution of $\sim 14$ meV in this configuration (S5). We therefore used data collected with $E_i = 120$ meV, which sacrifices real-space resolution for much better energy resolution ($\Delta \sim 4.5$ meV), to guide a principle component analysis (S6). This yielded a clean time-average PDF and inelastic component, while improving the energy resolution by a factor of $\sim 3$ (without reducing $r$-resolution). An excellent ($R_w = 0.12$) fit to the elastic component was achieved with an undistorted NaCl structure (Fig. 2b,c). We hence recover the structure seen by diffraction, with a well-defined average Ge position. In general, correlated motion acts to sharpen, broaden, or displace peaks in $G(r, \tau)$. This inelastic signal appears as a 'modification function', with an integral of zero over $G(r)$, and a characteristic $W$-shape under peaks in the residual $G_{obs}(r) - G_{calc}(r)$. This can be seen in the fit of the NaCl model (Fig. 2b,c) to the instantaneous PDF, where the first coordination sphere distortions and the 6 Å $\langle 100 \rangle$ feature are proven to reflect dynamical correlated motion. The former is a direct result of the high-Q signal seen in Fig. 2a. The success of our PCA analysis is reflected in the similarity between the fit residual and the inelastic component. Energy-dependent linear combination shows (S6) that the crossover between time-average and instantaneous structures occurs at $\sim 6$ meV.

Next, we build a consistent picture of the diffuse scattering, atomic motion and phonon dynamics using $ab initio$ molecular dynamics (MD) calculations. These were performed at 720 K, and as reported previously the X-ray weighted radial distribution function (S7) reproduces the asymmetry seen in experiment. The temperature dependent effective potential mode (S8) was

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**FIG. 1:** Local distortion in GeTe and fits to X-ray pair distribution functions in the $R3m$ and $Pm3m$ phases. a, (top) Fit to the room temperature pair distribution function (PDF) of GeTe using the $R3m$ structure ($R_w = 0.087$). Peaks corresponding to several important distances are highlighted. (bottom) Best fit of our split-site model for c-GeTe at 825 K ($R_w = 0.104$); b, Apparent disorder in c-GeTe, note the splitting of the purple Ge sites; c, Extrapolated mean square (111) displacements as a function of temperature. The average Ge position is shown as solid symbols, and the horizontal bars represent thermal motion.
FIG. 2: Time-averaged and instantaneous neutron scattering results for c-GeTe at 720 K using $E_I = 300$ meV neutrons. a, Structure factors, $Q\times[S(Q)-1]$, determined for the elastic (time averaged) and total (instantaneous) scattering of GeTe at 720 K using ARCS. These were normalised and filtered using the procedure described in the methods. Note that the former contains a small ad-mixture of inelastically scattered neutrons due to the finite ($\Delta E \sim 14$ meV) energy resolution. A significant extra oscillation is present in the total integrated structure factor, which implies 2.88 Å real-space correlations. b, Elastic PDF extracted using PCA analysis, and the instantaneous (total) PDF. Both are fitted using the rock-salt c-GeTe structure (red line). A significant increase in peak splittings and sharpening are found at low-$r$ when including the inelastic signal. c, Enhanced view of the low-$r$ fits for the two data sets. The peak splitting of the first coordination shell is completely removed by the PCA analysis.

used to extract phonon dispersions for c-GeTe and simulate the thermal diffuse scattering (TDS) and phonon density of states (PDOS). Excellent agreement between the simulated and measured TDS is found at 720 K (Fig. 3a), where we show our highest Q-resolution data ($E_I = 40$ meV). This supports our assignment of the local structure to correlated motion. The corresponding phonon dispersion is shown in Fig. 3b, and we find c-GeTe to be dynamically stable, with a zone center energy of 7 meV for the $\Gamma_4$ soft mode. This energy scale matches our experiments (S6), and the eigenvalues of this model also match the $\langle 111 \rangle_c$ anisotropic motion identified by our X-ray scattering results. The results of a Debye function calculation are also shown in Fig. 3a. This simulates snap-shots of uncorrelated distorted octahedra, confirming the proximity of c-GeTe to an order-disorder scenario, as well as the size of the displacements.

In other IV-VI rocksalt materials, the effect of temperature on the PDOS may be accounted for using the quasi-harmonic approximation where the low-temperature PDOS is convoluted by an energy dependent damped harmonic oscillator. For r-GeTe, this is the case between 300 and 550 K, using a quality factor, $1/Q \sim 0.21$. However, much larger changes are found in the cubic phase (Fig. 3c), with the emergence of a peak at 11.5 meV. The position of this feature matches the calculated optic DOS, however, this (harmonic) calculation produces a very sharp peak due to the lack of lifetime broadening. In contrast, extracting the incoherent PDOS using the velocity autocorrelation function not only reproduces the peak position, but also the energy envelope of the PDOS. Given the agreement between the calculated phonon moment and observed TDS, this shows that the ‘disorder’ in c-GeTe is the result of anharmonic optical modes of mainly Ge character, with strongly reduced lifetimes. The associated large fluctuations also explain the giant enhancement of dielectric constant and mimic symmetry-breaking when orientationally averaged probes are used.

The above results show that c-GeTe is highly crystalline, and that all local structure is dynamic in origin. We therefore return to our synchrotron X-ray PDF measurements (Fig. 1a) and attribute all local structure and sharpening effects to TDS, and thus dynamic displacements. For an ideal Debye solid at $T \gg \Theta_D$, the PDF peak widths have an isotropic $r$-dependent sharpening of $\sigma_{ij} = \sigma_{ij}' \sqrt{1 - \delta_1/r_{ij}}$, where $\sigma_{ij}'$ is the uncorrelated value. The parameter $\delta_1$ is freely refined. Although good fits are achieved with the rhombohedral or split-site cubic model, $\delta_1$ is strongly correlated with structural parameters, and never fits some features like...
FIG. 3: Calculated thermal diffuse scattering and phonon dispersion for c-GeTe a, Comparison of the energy integrated ($E_i = 40$ meV) scattering and simulation at 720 K. Note the excellent agreement of the background thermal diffuse intensity. The black line shows the result of calculating the scattering of an isolated distorted GeTe octahedron using the Debye function. b, Phonon dispersion extracted from ab-initio MD simulations. In contrast to $T = 0$ K DFT, the structure is found to be dynamically stable. c, Observed and calculated phonon densities of state for c-GeTe at 720 K. Results are shown for a harmonic calculation from the phonon dispersion, and directly from the MD simulation using the velocity autocorrelation function.

FIG. 4: Temperature dependence of real-space dynamics in GeTe a, Temperature dependence of the anisotropic correlated motion in GeTe. The plot shows the peak height of selected features in the residual $(G(r,0) - G_{obs}(r)$ as shown in S9, lines are guides to the eye. b, Wave-vector dependence of the strain-mediated coupling between polar degrees of freedom. The anisotropy is clear from the butterfly pattern.

the $(100)_c$ 6 Å peak. By refining the average structure at long range (20-50 Å), and fixing $\delta_1$ at zero, the true magnitude of its affect may be appreciated. The residual oscillations represent the X-ray weighted TDS integrated over multiple Brillouin zones, and extend to at least 1 nm at 300 K, before damping upon heating (S9). The temperature dependence of this signal is a model-independent measure of real-space dynamics in GeTe. Plotting the peak heights as a function of temperature (Fig. 4a) reveals a clear directional anisotropy, not captured by the simple isotropic sharpening model. Correlated motion in the $(111)_c$ direction begins to fall well before the R-C phase transition, and is swamped by random displacements in the cubic phase. This drastic softening is consistent with DFT calculations which show that the Ge-Te bond order is only 0.566 in c-GeTe. In contrast, correlations along $(100)_c$ stiffen approaching the phase transition, becoming nearly temperature independent at $T > T_C$. This matches theoretical predictions with an increased Born effective charge ($Z^*$) activating the fourth nearest-neighbour $(100)_c$ coupling. In accordance with metavalent bonding theories, $Z^*$ is highly predictive (S3). The $(100)_c$ peak is misfit for PbTe, SnTe, and possibly also metallic Bismuth. The sharpening is notably weaker in PbSe, and absent in PbS, confirming the scaling with $Z^*$. This prompted us to develop a generic model for cubic ferroelectrics which couples polarisation fluctuations to elastic strains. The dominant coupling is to the rhombohedral shear, and we imposed an elastic compatibility condition. This generates an anisotropic and long-range interaction (not found in classic Landau theory) between polarisation fluctuations, mediated by the strain degrees of freedom (Fig. 4b, S1). The local physics favours disorder, while the elastic interactions produce anisotropic couplings that suppress fluctuations but in certain directions only. This model explains the counter-intuitive properties of thermoelectrics like GeTe, where the effect of instantaneous disorder on electrical and thermal conductivities is rather decoupled. In the case of the cubic IV-VI materials, the 'stiff' $(100)_c$
direction corresponds to the direction of maximum $p$-orbital overlap, which forms the conduction band\cite{53}. Meanwhile, a snapshot of the structure along $(111)_c$ reveals dynamic correlations over no more than 1-2 unit cells. We therefore propose that charge carriers are protected by a "ferroelectric large polaron"\cite{18} as found in lead halide perovskites. This is supported by the very similar phenomenology seen in these materials classes, which include apparent local disorder\cite{20} and evidence for anisotropy\cite{21,22}. At the same time, the length scale of instantaneous disorder is optimum for scattering the long-wavelength acoustic phonons which carry heat\cite{40}.

Our results also explain the empirical correlation between high symmetry and performance in energy materials\cite{41,42}. This arises because spontaneous elastic anisotropy is naturally stronger in cubic systems, as long-range strains are rapidly quenched by crystallographic degrees of freedom/ flexibility\cite{43}. High symmetry materials are hence more likely to host the highly anisotropic fluctuations which enhance transport properties as described above. The coupling between fluctuations and strain is also strong, opening up the possibility of controlling optoelectronic properties by this route. Indeed, in ferroelectric BaTiO$_3$, lattice strain increases\cite{24} the Curie temperature by $\sim$650 %. Strain engineering has also improved the performance of perovskite solar absorbers\cite{29}. The Ginzburg-Landau model developed above explains how this is achieved, through coupling to the fluctuations which improve charge separation through Rashba spin-orbit coupling\cite{44}. Finally, carrier mobility in thermoelectrics is strongly influenced by polaron formation and dynamics\cite{50}. Strain engineering hence also provides an attractive route to improve device performance.

In summary, thermoelectric GeTe is highly crystalline at all temperatures, and previous reports of disorder reflect highly anisotropic and anharmonic phonons. Polarisation fluctuations induce anisotropic elastic strains, explaining the phonon-glass electron-crystal contradiction, and opening up new routes to tune physical properties. We conclude by acknowledging the historical importance of soft-mode theory, and the measurement of vibrational frequencies using neutrons\cite{51}. Varying the ‘crystallographic shutter speed’ to measure time-dependent atomic displacements, is naturally complimentary. The techniques described here will benefit from advances in neutron super-resolution spectroscopy\cite{52} and may become a standard characterisation tool.

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Materials and Methods

We used two different samples of GeTe for X-ray and neutron scattering respectively. For the X-ray scattering experiments, we used a finely ground part of a single crystal which originated in the department of Prof. H.G. von Schnering in the Max Planck Stuttgart ca. 1980. This is part of the same sample used for early neutron scattering experiments. For the inelastic neutron scattering experiment, a ca. 20 g powder sample was prepared from elemental Ge and Te.

We collected data on two former beam lines of the European Synchrotron radiation facility (ID15B and ID31). On ID15B, we used an incident energy of 87 keV and a Mar345 image plate. The sample was placed in a quartz capillary and heated with a hot air blower. At each temperature point, we collected data with two sample-detector distances, thus data optimised for both Rietveld and PDF analysis were generated under identical conditions. The data were azimuthally integrated using PyFAI, and converted into real space using PDFGetx. For the conversion to real space, we used a Q-range of \(1 < Q < 19.5 \text{ Å}^{-1}\) and subtracted an experimentally determined background at each temperature point. Fits to the PDFs were performed using PDFGui. On ID31, we collected data in the cubic phase using the high-resolution analyser crystal stage and an incident energy of 31 KeV. Rietveld analysis was performed using the GSAS-EXPGUI package.

Inelastic neutron scattering data were collected on the ARCS spectrometer at the Spallation Neutron Source, ORNL. The sample was placed in a vanadium can, and data collected at \(E_i = 40, 120\) and \(300\) meV incident energies and at temperatures of 300, 550 and 720 K. We first normalised the detector solid angle and efficiencies to a white beam vanadium measurement, performed outside the sample environment. We then used a monochromatic \(E_i = 300\) meV vanadium measurement to correct for transmission through the MICAS-III furnace. We measured an empty vanadium can at 300 and 720 K for a background, and test measurements using a B4C mask in place of the sample showed that scattering of the incident beam from the sample environment were efficiently removed by the radial oscillating collimator. The background and absorption corrections were performed using the Paalman-Pings macro implemented in MANTID. Finally, the spectrometer has two small detector gaps at high angle. These can be removed by extrapolation in \(S(Q, \omega)\) space, as their trajectories are curved, and the signal at high-Q is relatively flat.

To normalise the structure factors as a function of energy transfer for Fourier transformation into real space, we used two approaches. These were: 1) adding a structure-less [1-Debye-Waller] factor; and ad-hoc PDF extraction using PDFGetN3. Both gave equivalent results. For the structure factors shown in Fig. 3, we performed a Fourier filtering in r-space at distance of 1.75 Å and below, then back-transformed to reciprocal space. As described in the main text, we used Principle Component Analysis (PCA) to analyse the dynamic PDFs (dy-PDF). This was performed using Igor Pro, and we used either linear combination or varimax rotation to separate the static and inelastic components.

For finite-temperature phonon calculations of the rocksalt phase, we employed the temperature-dependent effective potential method as implemented in the ALAMODE software. To incorporate long-distance interaction effects, a \(2 \times 2 \times 2\) conventional cell with 64 atoms was prepared. For the sampling of displacement-force data sets and the calculations of interatomic force constants (IFCs), 2,000 ab initio molecular dynamics (AIMD) steps with a time step of 1 fs were performed by VASP in the NVT ensemble at 720 K. In our VASP calculations, the electron-ion interaction and exchange-correlation functional were described by the projector-augmented wave (PAW) method and the generalized gradient approximation (GGA) with the parametrization of Perdew-Burke-Ernzerhof (PBE), respectively. First-order Methfessel-Paxton scheme with a smearing width of 0.05 eV was employed to integrate total energy in the Brillouin Zone (BZ), with \(4 \times 4 \times 4\) Monkhorst-Pack k-point grid. The energy cutoff in the plane-wave functions was set to be 228 eV. Valence electron configurations in Germanium and Tellurium were \(s^{2}p^{2}\) and \(s^{2}p^{4}\), respectively. INS simulation was performed using the OCLIMAX software. The \(S(Q, \omega)\) map was calculated using the frequencies and polarization vectors from the DFT phonon calculations. Powder averaging, coherent scattering, temperature effects, and higher order excitations (up to \(n=10\)) are included. A resolution function consistent with the experiment was applied.
Extended theory results

The purpose of this note is to derive an effective elastic coupling between polar degrees of freedom in a model for cubic ferroelectrics such as GeTe.

We consider a Ginzburg-Landau model with polarization \( P_\alpha(x) \) \((\alpha = x, y, z)\) coupled to the following elastic degrees of freedom as secondary order parameters: volumetric strain \( \phi_v(x) = (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \), deviatoric stains \( \phi_0(x) = (\epsilon_{xx} - \epsilon_{yy})\), \( \phi_1(x) = (2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})/\sqrt{3}\), and shear strains \( \phi_4(x) = \epsilon_{yz}, \phi_5(x) = \epsilon_{xz}, \) and \( \phi_6(x) = \epsilon_{xy}, \) where \( \epsilon_{\alpha\beta} = (1/2)(\partial u_\alpha / \partial x_\beta + \partial u_\beta / \partial x_\alpha) \) is the linear strain tensor.

The Ginzburg-Landau Hamiltonian is as follows,

\[
H = H_{\text{pol}} + H_{\text{elastic}} + H_{\text{pol-elastic}},
\]

where,

\[
H_{\text{pol}} = \int d^3x \left[ \frac{r}{2} \sum_\alpha P_\alpha^2(x) + \sum_{\alpha,\beta} [u + v \phi_0] P_\alpha^2(x) P_\beta^2(x) \right]
+ \frac{1}{2} \int d^3x' \sum_{\alpha,\beta} F_{\alpha\beta}(x - x') P_\alpha(x) P_\beta(x'),
\]

\[
H_{\text{elastic}} = \int d^3x \left[ \frac{1}{2} C_v \phi_v^2(x) + \frac{1}{2} C_d \left( \phi_0^2(x) + \phi_1^2(x) \right) + \frac{1}{2} C_s \left( \phi_4^2(x) + \phi_5^2(x) + \phi_6^2(x) \right) \right],
\]

\[
H_{\text{pol-elastic}} = \int d^3x g_\alpha \phi_4(x) P_y(x) P_z(x) + \phi_5(x) P_z(x) P_x(x) + \phi_6(x) P_x(x) P_y(x) \right].
\]

Here, \( r = r_0(T - T_0) \), \( u \) and \( v \) are quartic temperature independent quartic aharmonicities, and \( F_{\alpha\beta}(x) = (x^2 \delta_{\alpha\beta} - 3x_\alpha x_\beta)/x^3 \) is the dipole interaction. \( C_v, C_d, \) and \( C_s \) are elastic moduli and \( g_\alpha \) is an electrostrictive coupling constant to between polarization and shears. For our purposes (GeTe), we have assumed in (3) that the electrostrictive couplings to shears are dominant and ignore the couplings to volumetric and deviatoric strains.

We supplement the Hamiltonian (1) with the Saint-Venant condition (2),

\[
\nabla \times (\nabla \times \epsilon)^T = 0,
\]

which ensures compatibility between strains. In the absence of Eq. (1), the Hamiltonian (1) provides a standard long-wavelength description of the ferroelectric transition (21) in which the effect of the electrostrictive coupling is to generate a local quartic interaction between the polar degrees of freedom. By imposing compatibility, the coupling becomes non-local (22).

Assuming the system reaches mechanical equilibrium much faster than the polarization, we integrate out the strains in Eqs. (2) and (3) with the constraint (4) in favor of a quartic interaction between the polar degrees of freedom,

\[
H_{\text{eff}} = -\frac{g_\alpha^2}{2C_s} \int d^3q \sum_{\mu,\nu=4,5,6} K_{\mu\nu}(q) \Gamma_\mu(q) \Gamma_\nu(-q).
\]

Here, \( \Gamma_4(q), \Gamma_5(q) \) and \( \Gamma_6(q) \) are the Fourier components of \( \Gamma_4(x) = P_y(x) P_z(x), \Gamma_5(x) = P_z(x) P_x(x), \) and \( \Gamma_6(x) = P_x(x) P_y(x) \), respectively. The kernels \( K_{\mu\nu}(q) \) are non-analytic, e.g., consider \( K_{66}(q) \) at \( q_z = 0, \)

\[
K_{66}(q) = \frac{(q_y^2 - q_x^2)^2 + (4/3)(C_t/C_s)(q_x^4 + q_y^4 + q_z^4)}{(q_y^2 - q_x^2)^2 + 4(C_t/C_s)q_x^2q_y^2 + (4/3)(C_t/C_s)q_x^4 + q_y^4 + q_z^4)(C_s + C_t)/C_s}.
\]

For \( q || (110), K_{66}(q) = C_s/(C_s + C_v + C_t/3), \) while \( K_{66}(q) = 1 \) for \( q || (100). \) Away from \( q_z = 0, K_{66}(q) \) exhibits a butterfly pattern, as shown in Fig. 4b. Non-analytic behavior is characteristic of elastic forces and is a consequence of their long-ranged and anisotropic nature (28). Explicit expressions for \( K_{\mu\nu}(q) \) are very elaborate and are not provided here, nonetheless they also exhibit non-analytic behavior.
Fig. S1: Results of fitting local and average structure of GeTe from synchrotron X-ray scattering. **a**, Ge-Te bond lengths from Rietveld refinement of the average structure. Also shown are bond-lengths extracted by fitting two Gaussian curves to the first peak in the pair distribution functions as a function of temperature. **b**, Refined primitive unit cell volume from Rietveld refinements as a function of temperature. Note the excellent agreement with the data points extracted by fitting the PDFs at high-$r$. **c**, Atomic displacement parameters extracted from the high-$r$ PDF fits. Similar results are obtained from the Rietveld refinements (not shown).

**Supplementary figures**
Fig. S 2: Comparison of very high resolution synchrotron powder X-ray diffraction data for c-GeTe and Si. Data were collected on the ID31 instrument at the European Synchrotron Radiation Facility, the highest resolution instrument in the world at the time. Silicon is used as a line shape reference due to its essentially perfect lattice coherence. The peaks from c-GeTe are nearly as sharp, showing that this phase is highly crystalline. Note the log scale and the co-existence of structured diffuse scattering for c-GeTe. The featureless background on the Si data is more intense due to a shorter counting time.
Fig. S 3: Ubiquity of $\langle 100 \rangle_{c}$ correlations in binary chalcogenides and hR6 structured materials. This figure reproduces figures from published work. Red circles have been added to highlight the residual around the $\langle 100 \rangle_{c}$ peaks. Permissions have been acquired as detailed for each panel, and full citations are included in the main manuscript text.

a, Neutron PDFs for PbTe at 10 K (top) and 300 K (bottom). Fits to a rocksalt structure are shown. Figure reproduced with permission from Figure 1 of Bozin et al, Science, 330, pp. 1660-1663 (2010). See: DOI: 10.1126/science.1192759.

b, Fit of a rocksalt structure to the X-ray PDF of SnTe in the cubic phase. Figure reproduced with permission from Knox et al, PRB 89 014102 (2014). See: https://journals.aps.org/prb/abstract/10.1103/PhysRevB.89.014102.

c, X-ray PDF and fit for Bismuth metal (top curve). Figure reproduced under the terms of a creative commons license from Li et al, Advanced Science, 3, 1600108 (2016). See: https://doi.org/10.1002/advs.201600108.

d, Fit of a rocksalt structure to the X-ray PDF of PbSe in the cubic phase. Figure reproduced with permission from Yu et al, PRB 98 144108 (2018). See: https://journals.aps.org/prb/abstract/10.1103/PhysRevB.98.144108.
Fig. S 4: **Fit to elastic line PDF of α-GeTe at 720 K.** Observed, calculated and difference profiles for the fit of the NaCl structure to the elastic line PDF at 720 K. Note that a small ad-mixture of inelastically scattered neutrons is still present due to the finite 14 meV energy resolution. This results in a trace of first-coordination sphere distortion.

Fig. S 5: **Calculated energy resolution function of the ARCS spectrometer.** The energy resolution function of ARCS was calculated for $E_i=120$ and 300 meV using the Carpenter approximation for time of flight instrumentation, as implemented by Doug Abernathy (details on request).
Fig. S 6: Details of the principle component analysis applied to the dynamic PDF data. a, Applying PCA analysis to the dy-PDF data sets at 720 K generated two significant Eigenvalues. As shown in the top panel, these correspond to the elastic line PDF, and the inelastic modification function. The former has been overlaid with a calculation for rocksalt GeTe with no peak sharpening factor applied. Note the similarity of the inelastic component to the fit residual for the instantaneous PDF shown in Fig. 2. b, The separation between the two components was determined by linear combination for the 120 and 300 meV data sets. Both show the same trend, but the former (with much higher energy resolution), allows complete separation. c, Reconstructed PDF’s using the weights from the 120 meV data applied to the 300 meV data at 550 and 720 K. d, Results of fitting the first coordination sphere using a two-Gaussian approach. Note the weak shift seen in the rhombohedral phase. In the cubic phase, a single peak was fitted when the position error from a two Gauss fit was greater than the refined peak splitting.
Calculated X-ray weighted radial distribution functions from MD simulations, and comparison to X-ray PDF data. a, partial PDFs for $c$-GeTe from our ab initio MD simulation at 720 K. b, Comparison of the total X-ray weighted radial distribution function to experimental data at 720 K. Note the excellent agreement between simulation and data in the first coordination sphere.

Effect of temperature on the phonon density of states of $r$-GeTe. These data sets were generated using our 40 meV $E_i$ data. Note that our setup was not optimised for this energy, and that only a simple incoherent approximation was used to extract the PDOS. The 550 K data can be largely reproduced by modifying the 300 K data using a quasi-harmonic approximation with a quality factor, $1/q = 0.21$. Full details can be found in the main text references.
Fig. S 9: **Real-space thermal diffuse scattering in GeTe.** (top) Observed, calculated and difference fits to the X-ray PDFs of GeTe at 300 and 825 K. Two residual curves are shown for each fit, that arising from the fits discussed in the text, and the result of fitting the average-structure at 20-50 Å; (bottom) Colour map showing the raw residuals after fitting all the X-ray PDF data sets with the average structure over the range 20 \( \leq r \leq 50 \) Å. Each residual was normalised by the fitted scale factor.
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