Supplementary Material of

Layered topological semimetal GaGeTe: New polytype with non-centrosymmetric structure

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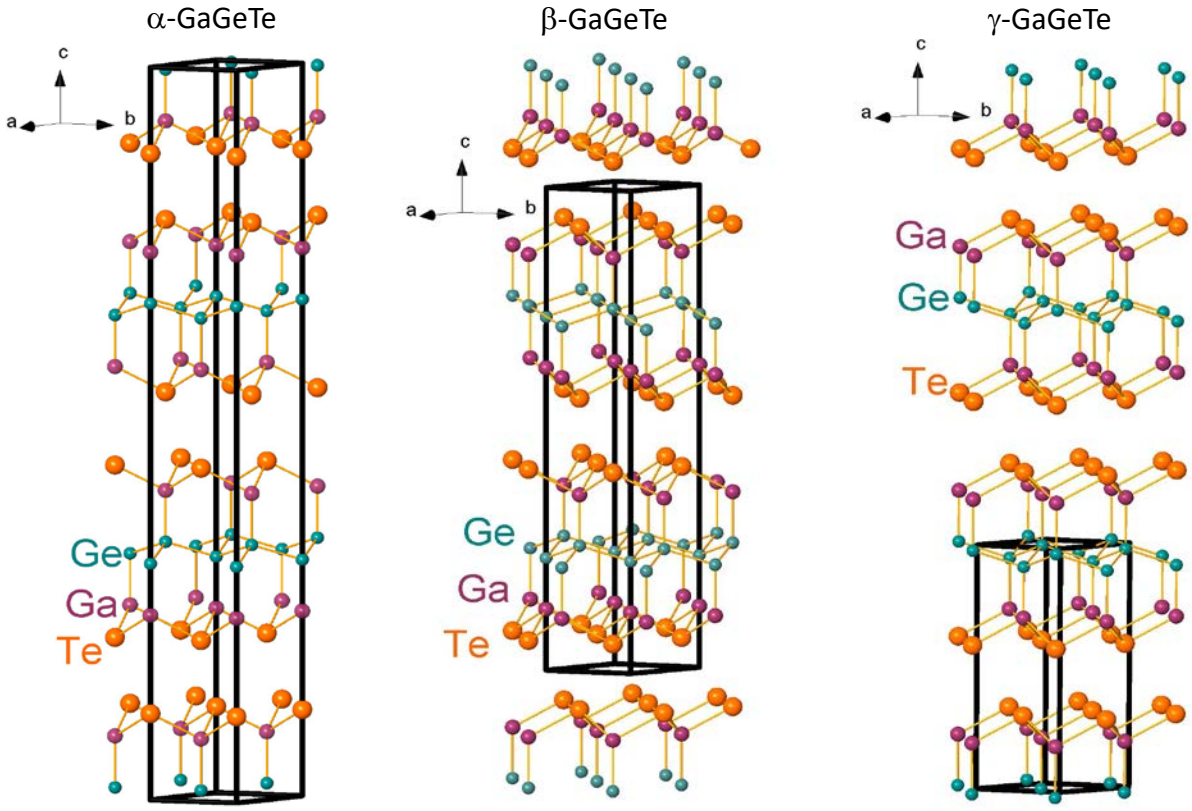

Figure S1. 3D view of the crystal structure of bulk α-GaGeTe, β-GaGeTe, and γ-GaGeTe.

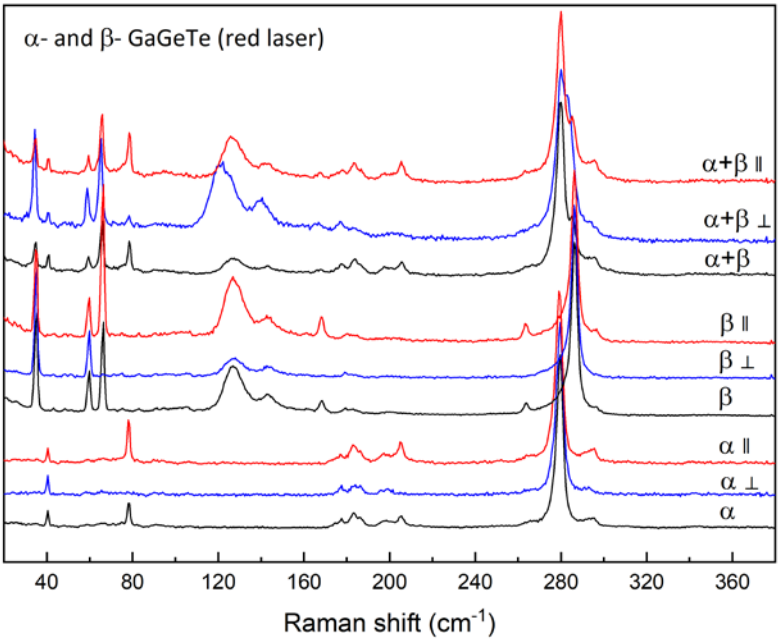

Figure S2. Unpolarized and polarized (parallel and cross polarizations) RS spectra of α-GaGeTe β-GaGeTe and a mixture of both polytypes at room conditions excited under non-resonant (632.8 nm) conditions.

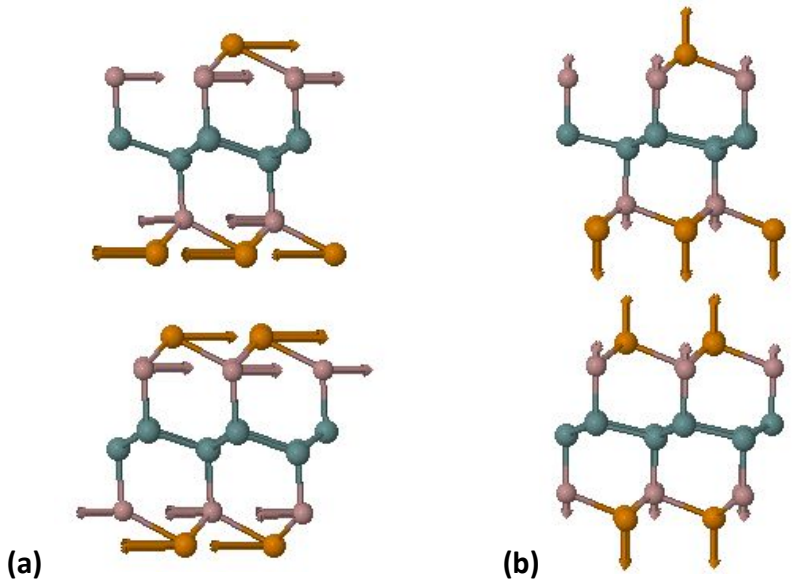

Figure S3. Atomic motion of E_g^1 (a) and A_{1g}^1 (b) vibrational modes of α-GaGeTe predicted at 40.1 and 76.1 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes show Ge atoms at rest and Ga and Te atoms in motion. These two modes are the rigid layer modes of α-GaGeTe where each layer vibrate against the neighboring layer. E_g^1 is the transversal or shear layer mode (with a pure Ga-Ge bending mode contribution) and A_{1g}^1 is the longitudinal or compressional layer mode (with small contribution of a Ga-Ge symmetric stretching mode).

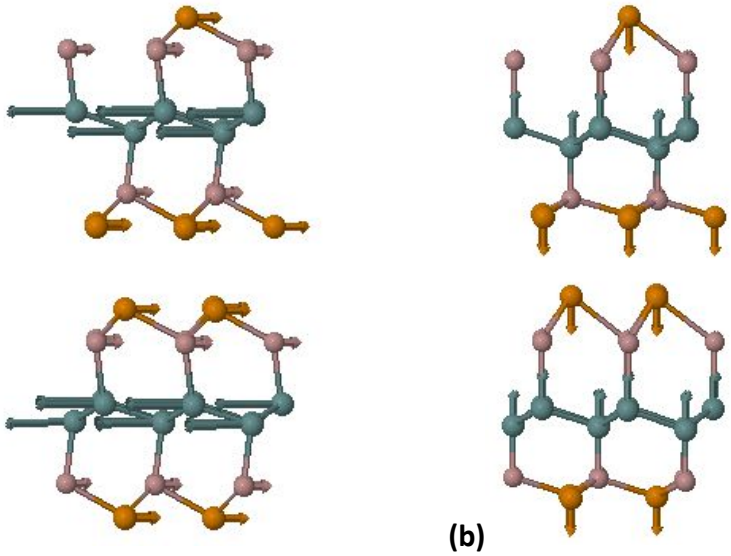

Figure S4. Atomic motion of E_u^1 (a) and A_{2u}^1 (b) vibrational modes of α-GaGeTe predicted at 52.5 and 138.6 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes show Ge atoms vibrating out-of-phase with respect to Ga and Te atoms. These two modes are rigid intra-layer modes of α-GaGeTe, where the germanene sublayer vibrate against the other two Ga-Te sublayers. E_u^1 is the transversal or shear intra-layer mode (a pure Ga-Ge bending mode) and A_{2u}^1 is the longitudinal or compressional intra-layer mode (almost a pure Ga-Te bending mode with small contribution of a Ga-Ge asymmetric stretching mode).

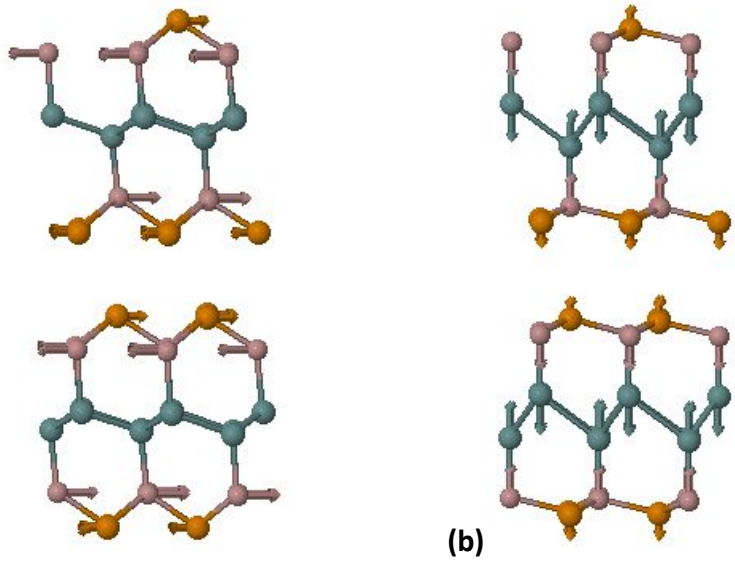

Figure S5. Atomic motion of E_g^2 (a) and A_{1g}^2 (b) vibrational modes of α-GaGeTe predicted at 177.0 and 197.9 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. The first mode shows Ge atoms at rest and Ga and Te atoms in motion. The E_g^2 mode is a mixture of a Ga-Ge bending mode, a Ga-Te stretching mode, and a weak interlayer shear mode. The A_{1g}^2 mode is a mixture of a Ge-Ge bending mode, a Ga-Te bending mode, and a very weak interlayer compressional mode due to the small amplitude of Te vibrations along the *c*-axis in comparison with the A_{1g}^1 mode.

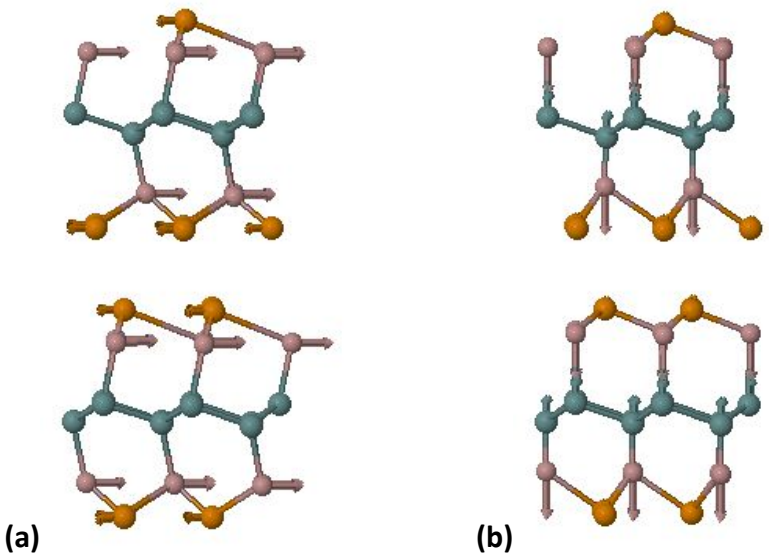

Figure S6. Atomic motion of E_u^2 (a) and A_{2u}^2 (b) vibrational modes of α-GaGeTe predicted at 177.1 and 267.3 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. The first mode shows Ge atoms at rest and Ga and Te atoms in motion. The E_u^2 mode is a mixture of a Ga-Ge bending mode and a Ga-Te stretching mode. The A_{2u}^2 mode is a mixture of a Ga-Ge asymmetric stretching mode and a Ga-Te bending mode.

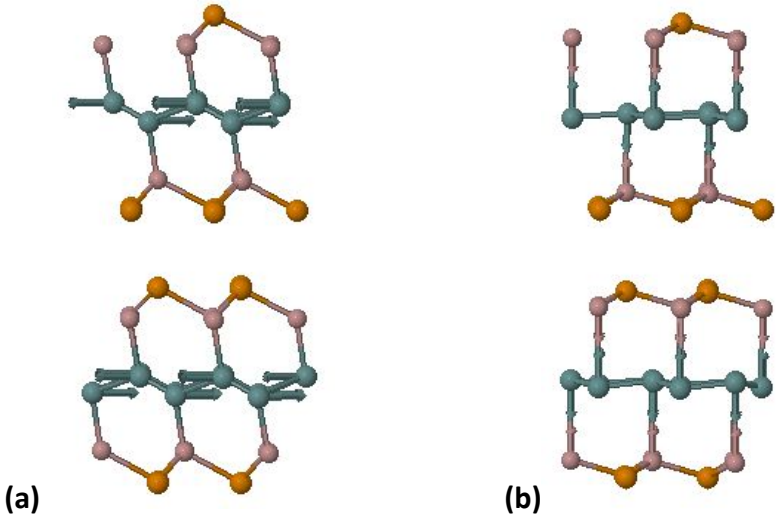

Figure S7. Atomic motion of E_g^3 (a) and A_{1g}^3 (b) vibrational modes of α-GaGeTe predicted at 276.0 and 282.6 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes show Te atoms at rest and Ga and Ge atoms in motion. In the E_g^3 mode, neighbor Ge atoms vibrate out-of-phase. This mode is a mixture of a Ge-Ge stretching mode and a Ga-Ge bending mode. On the other hand, the A_{1g}^3 mode is a mixture of a Ga-Ge symmetric stretching mode and a Ge-Ge bending mode. The close mass of Ga and Ge leads to a similar frequency of both stretching modes.

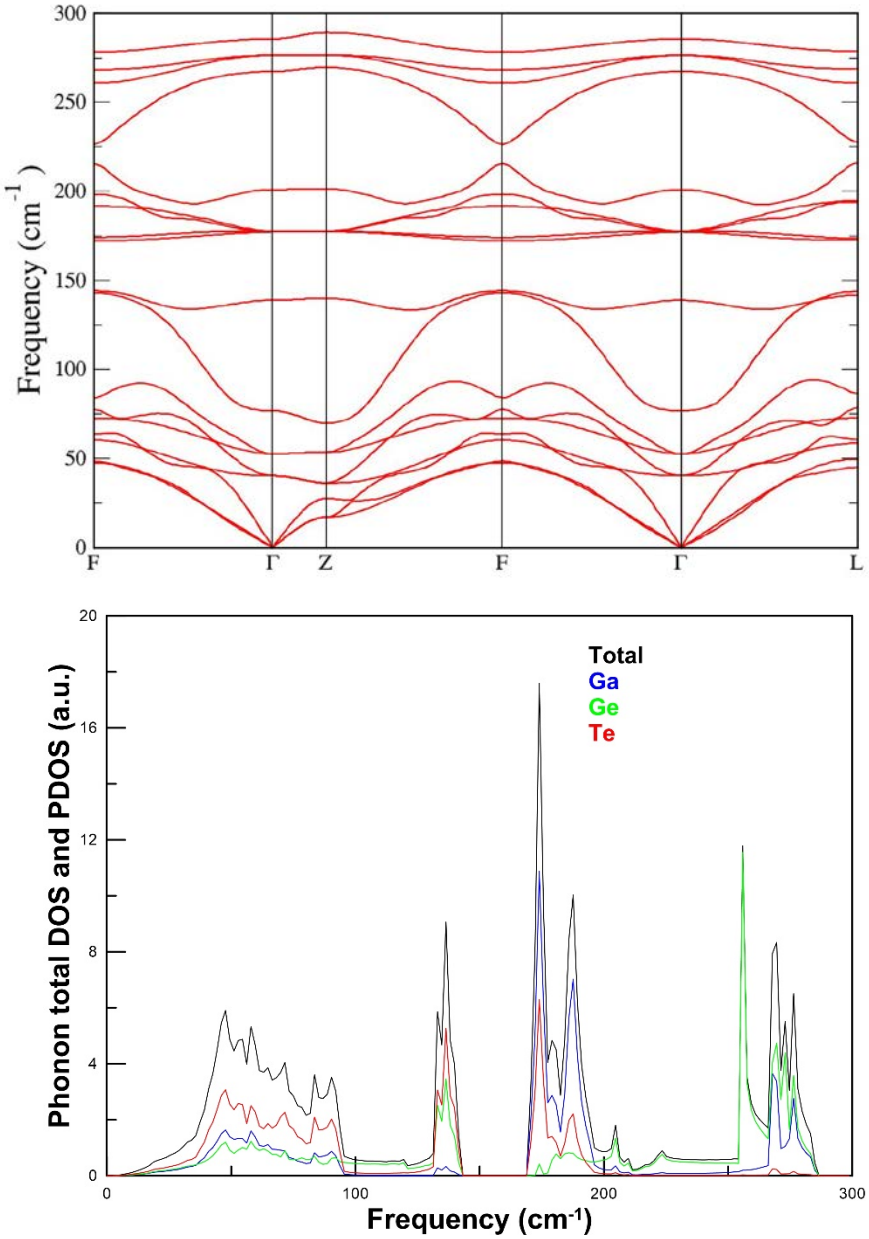

Figure S8. Top: Phonon dispersion curves of α-GaGeTe. Bottom: Total and partial (atom-projected) one-phonon density of states of α-GaGeTe.

The phonon dispersion curves of α-GaGeTe shows the typical phonon branches of a tetrahedrally-coordinated compound, like ZnO **[S1,S2]**, with phonon branches: i) related to transversal acoustic (TA) phonons (up to 75 cm^{-1}); ii) related to longitudinal acoustic (LA) phonons (from 75 up to 145 cm^{-1}); and iii) related to transversal optic (TO) and longitudinal optic (LO) phonons (from 165 up to 290 cm^{-1}). This means that TA phonons are in the region of the E_g^1 and E_u^1 modes, LA phonons include the region of A_{1g}^1 and A_{2u}^1 modes, and TO and LO phonons are mixed in the mid-frequency region of E_g^2, E_u^2 and A_{1g}^2 modes and in the high-frequency region of A_{2u}^2, E_g^3, and A_{1g}^3 modes. Additionally, we must note that there is a phonon gap between acoustic and optical branches (from 145 to 165 cm^{-1}). The most interesting feature of the phonon dispersion curves is the low-frequency values found for the TA and some LA modes at the Z point of the Brillouin zone. These low-frequency modes below 75 cm^{-1} suggest a very

low thermal conductivity in bulk GaGeTe along the *c*-axis, in agreement with what has been recently predicted for monolayer GaGeTe **[S3]**.

The one-phonon density of states shows that Te vibrations contribute to vibrational modes up to 200 cm^{-1}, while Ga and Ge contribute to all vibrational modes, with Ge modes contributing mostly to vibrations close to 135 cm^{-1} and above 250 cm^{-1} and Ga modes contributing mostly to vibrations between 165 and 200 cm^{-1} and above 265 cm^{-1}. In the one-phonon DOS, the highest contribution comes from the mid-frequency modes E_g^2 and E_u^2 between 170 and 200 cm^{-1} due to the low dispersion of the curves of these two modes along the BZ.

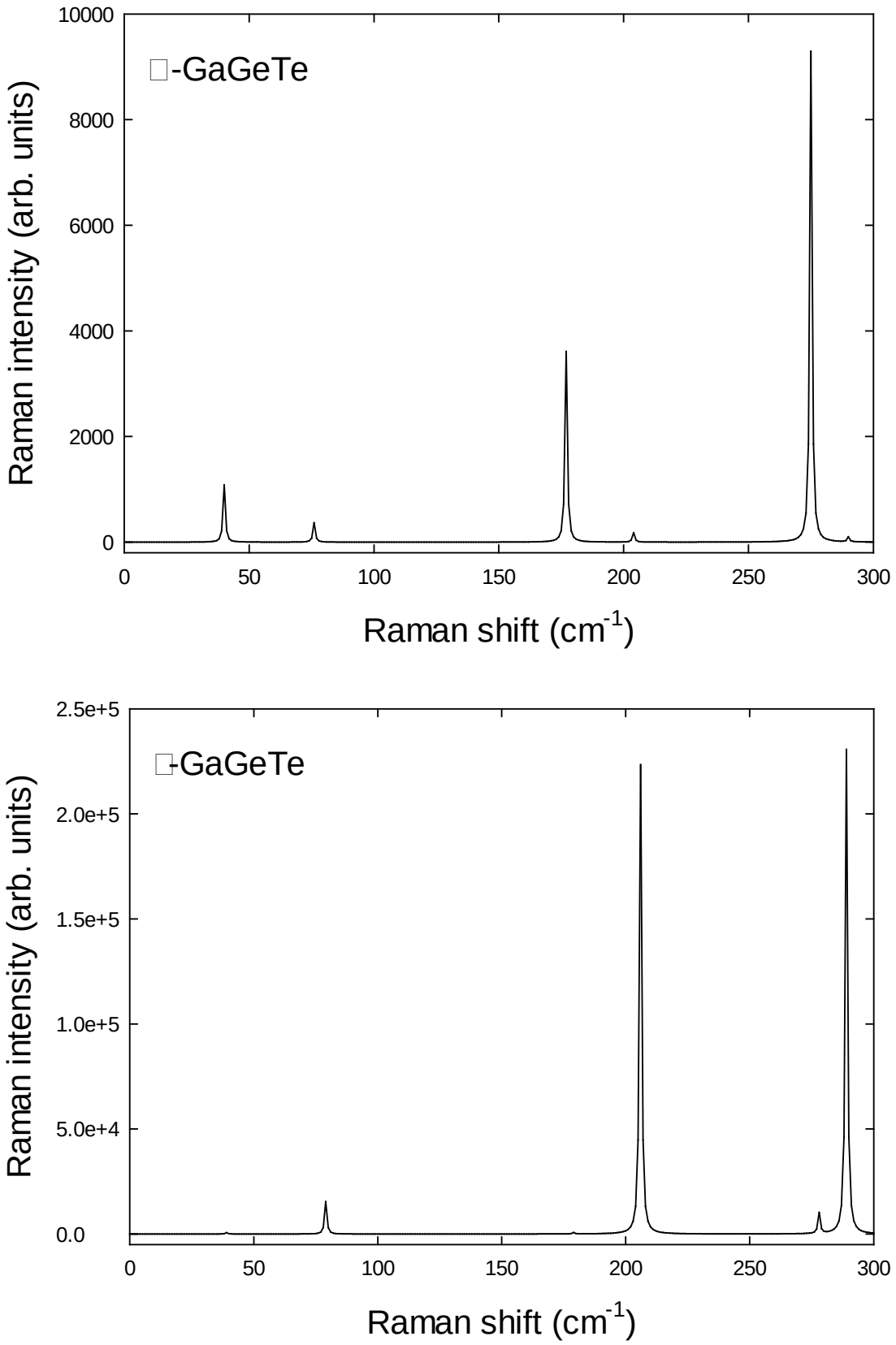

Figure S9. Simulated unpolarized RS spectrum of α-GaGeTe (top) and γ-GaGeTe (bottom) using Lorentzian lineshapes of 1 cm^{-1} linewidth.

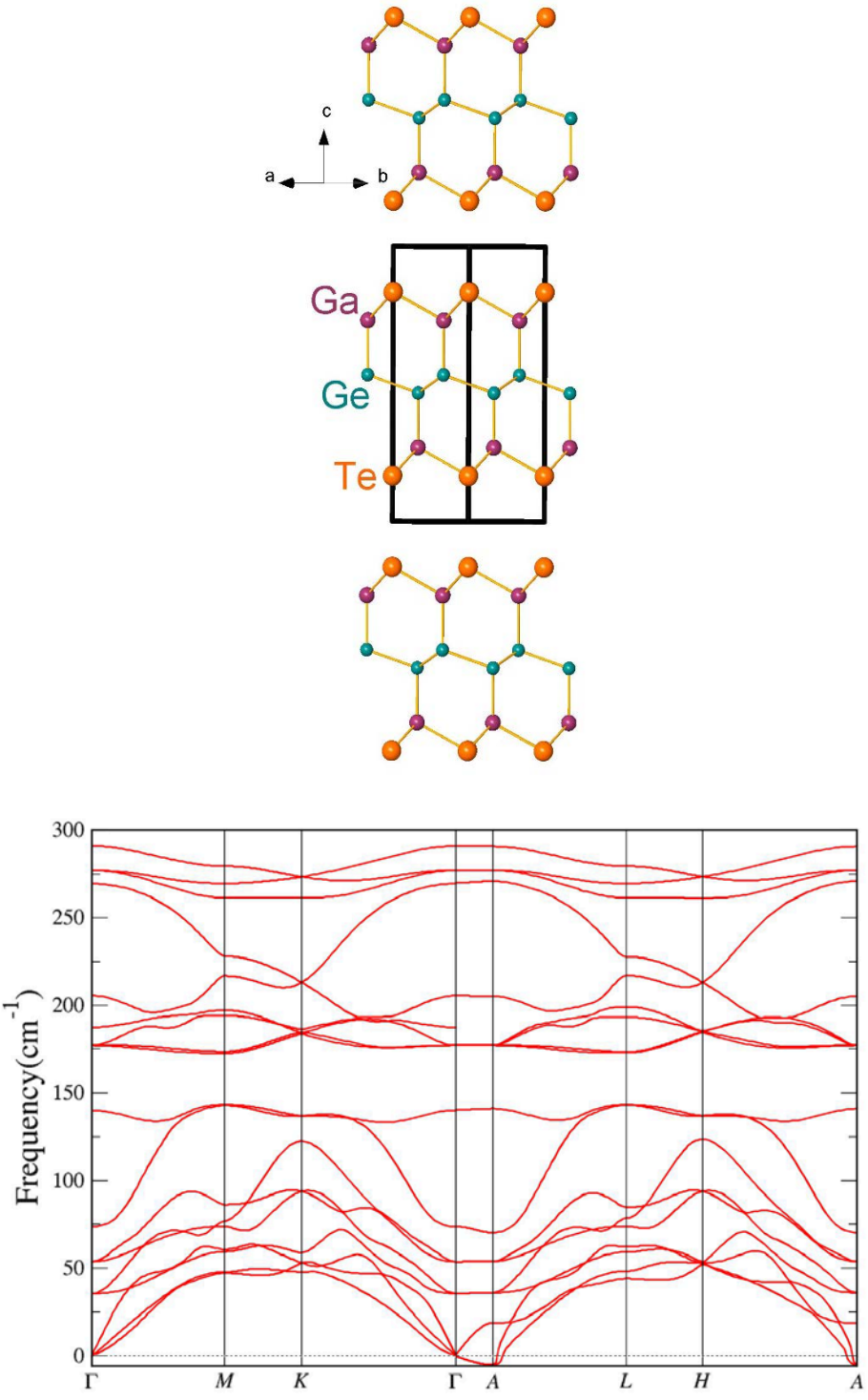

Figure S10. Detail of the crystalline structure of GaGeTe-mono (top) and theoretical phonon dispersion curves of GaGeTe-mono (bottom) along the main points (Γ—M—K—Γ—A—L—H—A) of the Brillouin zone. Note the imaginary frequencies near the A point.

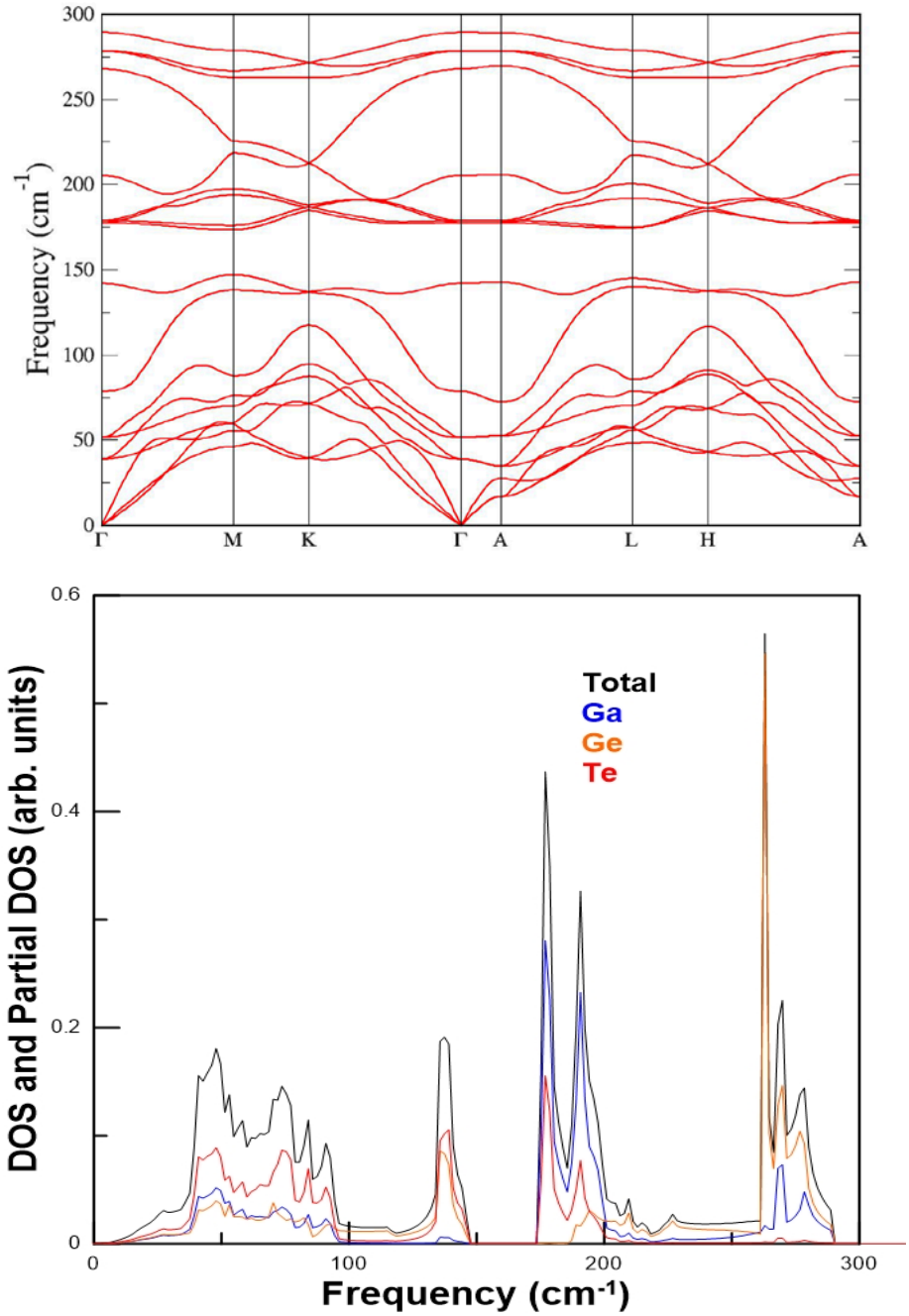

Figure S11. Top: Theoretical phonon dispersion curves of γ-GaGeTe along the main points (Γ—M—K—Γ—A—L—H—A) of the Brillouin zone. Bottom: Theoretical total and partial (atom-projected) one-phonon density of states of γ-GaGeTe.

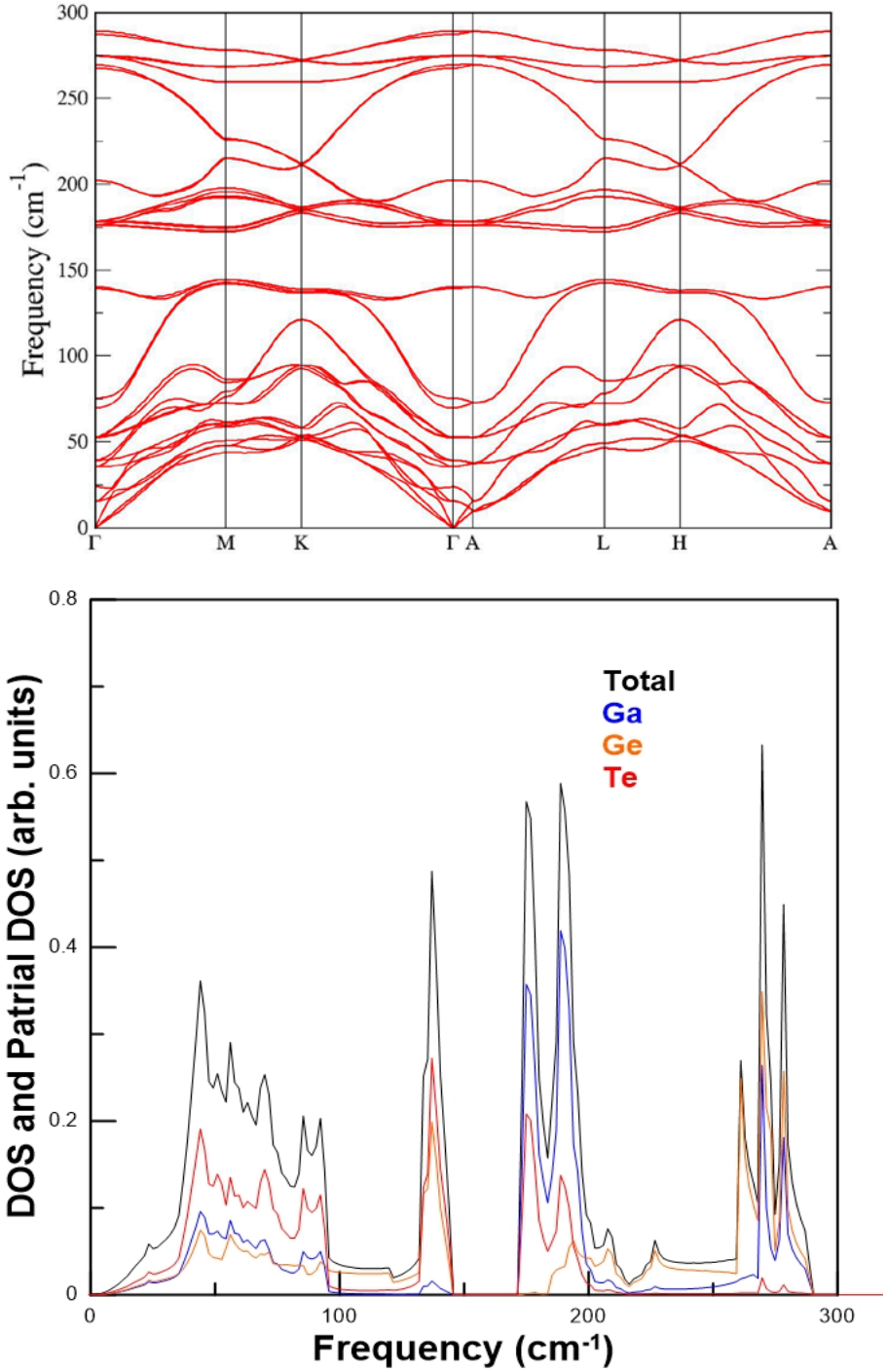

Figure S12. Top: Theoretical phonon dispersion curves along the main points (Γ—M—K—Γ—A—L—H—A) of the Brillouin zone of β-GaGeTe. Bottom: Theoretical total and partial (atom-projected) one-phonon density of states of β-GaGeTe.

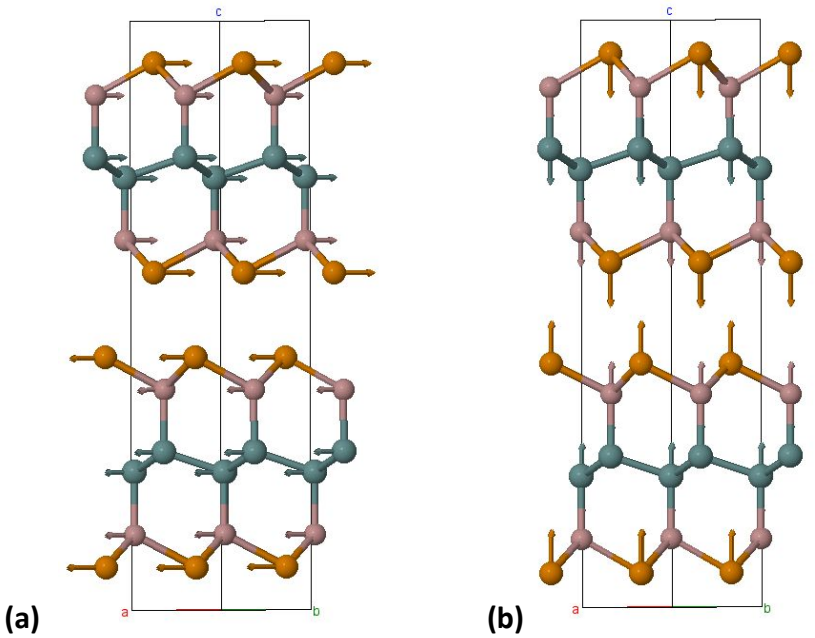

Figure S13. Atomic motion of E_2^1 (a) and B_1^1 (b) vibrational modes of β-GaGeTe predicted at 16.2 and 24.0 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are the rigid layer modes of β-GaGeTe where each layer vibrate against the neighboring layer. E_2^1 is the transversal or shear layer mode and B_1^1 is the longitudinal or compressional layer mode.

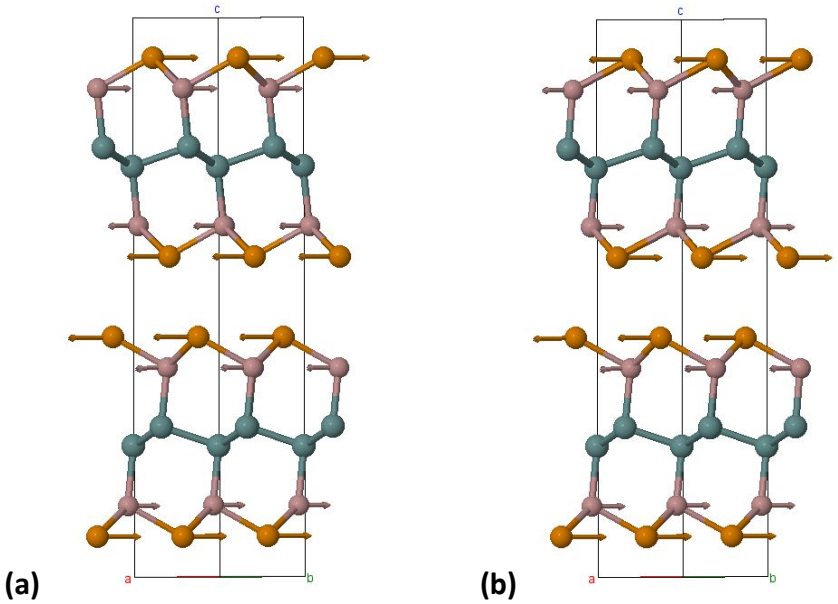

Figure S14. Atomic motion of E_2^2 (a) and E_1^1 (b) vibrational modes of β-GaGeTe predicted at 35.6 and 39.1 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are shear intra-layer modes of β-GaGeTe (pure Ga-Ge bending modes), where Ge atoms are at rest and the Ga-Te sublayers vibrate in opposite directions. In the E_2^2 mode, adjacent Ga-Te atoms of neighbour layers vibrate in-phase while in the E_1^1 mode, adjacent Ga-Te atoms of neighbour layers vibrate out-of-phase.

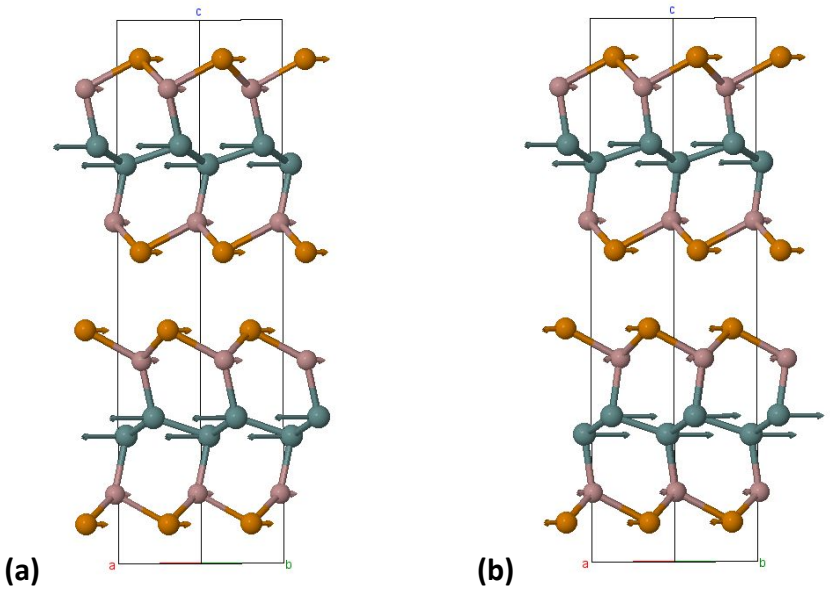

Figure S15. Atomic motion of E_1^2 (a) and E_2^3 (b) vibrational modes of β-GaGeTe predicted at 52.5 and 53.1 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are shear intra-layer modes of β-GaGeTe (also pure Ga-Ge bending modes), where Ge atoms vibrate in the opposite direction to the top and bottom Ga-Te sublayers. In the E_1^2 mode, adjacent Ga-Te atoms of neighbour layers vibrate in-phase while in the E_2^3 mode, adjacent Ga-Te atoms of neighbour layers vibrate out-of-phase.

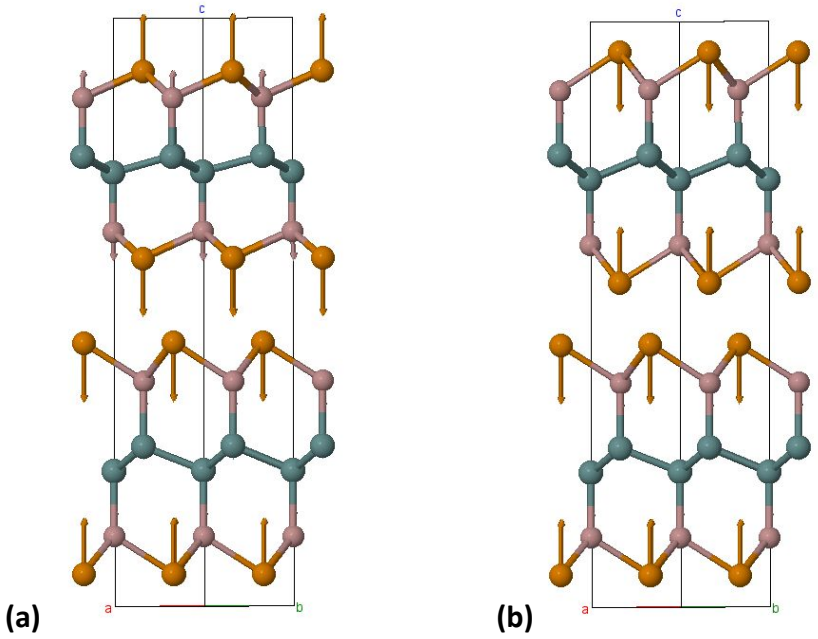

Figure S16. Atomic motion of B_1^2 (a) and A_1^1 (b) vibrational modes of β-GaGeTe predicted at 69.7 and 75.7 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are longitudinal intra-layer modes of β-GaGeTe where Ge atoms at rest and Ga and Te atoms vibrating against the Ge sublayer (partial Ga-Ge symmetric stretching mode). In the B_1^2 mode, the Ga-Te sublayers of neighbour layers vibrate in-phase, while in the A_1^1 mode the Ga-Te sublayers of neighbour layers vibrate out-of-phase.

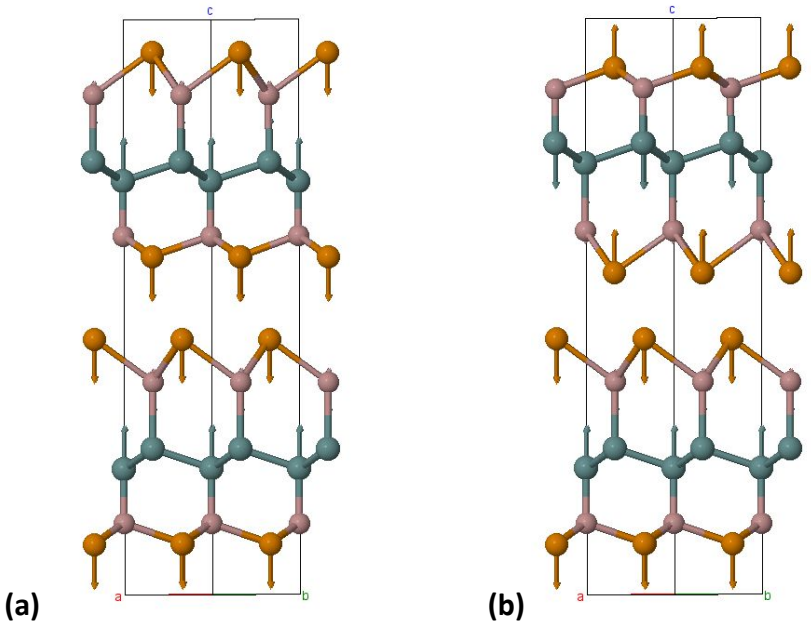

Figure S17. Atomic motion of A_1^2 (a) and B_1^3 (b) vibrational modes of β-GaGeTe predicted at 139.4 and 140.4 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are also longitudinal intra-layer modes of β-GaGeTe where Ge atoms vibrate in-phase with one Ga-Te sublayer and out-of-phase with the other Ga-Te sublayer (full Ga-Ge symmetric stretching mode). In the A_1^2 mode the Ga-Te sublayers of neighbour layers vibrate in-phase, while in the B_1^3 mode the Ga-Te sublayers of neighbour layers vibrate out-of-phase.

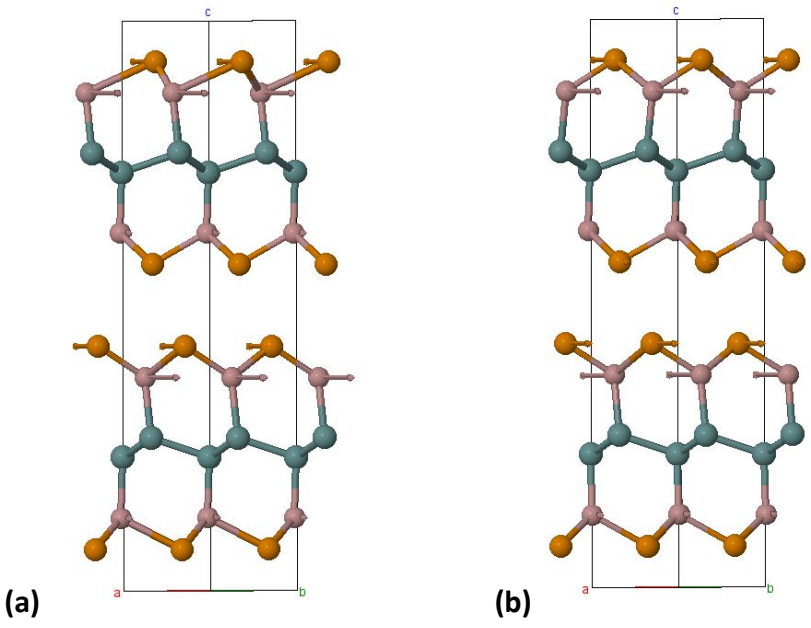

Figure S18. Atomic motion of E_1^3 (a) and E_2^4 (b) vibrational modes of β-GaGeTe predicted at 176.3 and 176.6 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are intra-layer modes of β-GaGeTe that are a mixture of a Ga-Ge bending mode and a Ga-Te stretching mode, where Ge atoms are at rest and Ga and Te atoms vibrate out-of pase in the a-b plane. In the E_1^3 mode, the same Ga and Te atoms of neighbour layers vibrate in-phase while in the E_2^4 mode, the same Ga and Te atoms of neighbour layers vibrate out-of-phase.

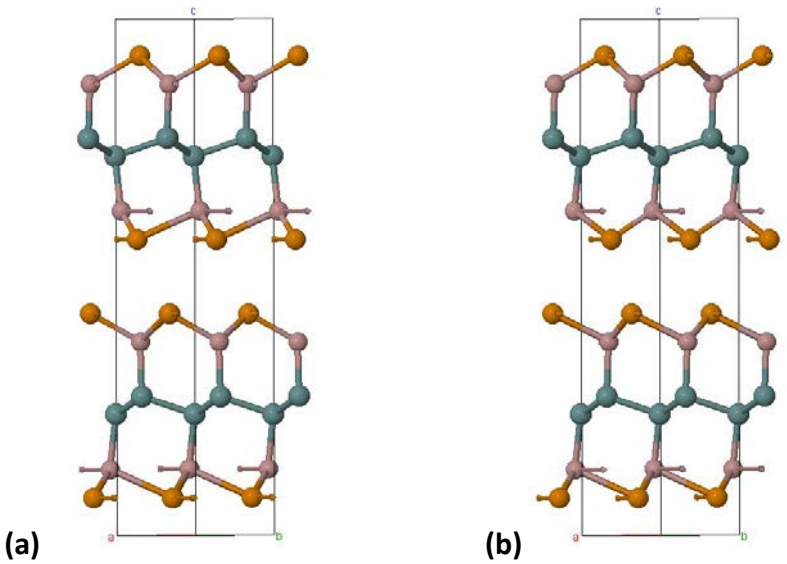

Figure S19. Atomic motion of E_1^4 (a) and E_2^5 (b) vibrational modes of β-GaGeTe predicted at 178.4 and 178.6 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are intra-layer modes of β-GaGeTe that are also a mixture of a Ga-Ge bending mode and a Ga-Te stretching mode, where Ge atoms are at rest and Ga and Te atoms vibrate out-of pase in the a-b plane. In the E_1^4 mode, the same Ga and Te atoms of neighbor layers vibrate in-phase while in the E_2^4 mode, the same Ga and Te atoms of neighbor layers vibrate out-of-phase. In the modes of Fig. S17 (Fig. S16), the amplitude of vibration is largest for the Ga and Te atoms of the bottom (top) of the layers.

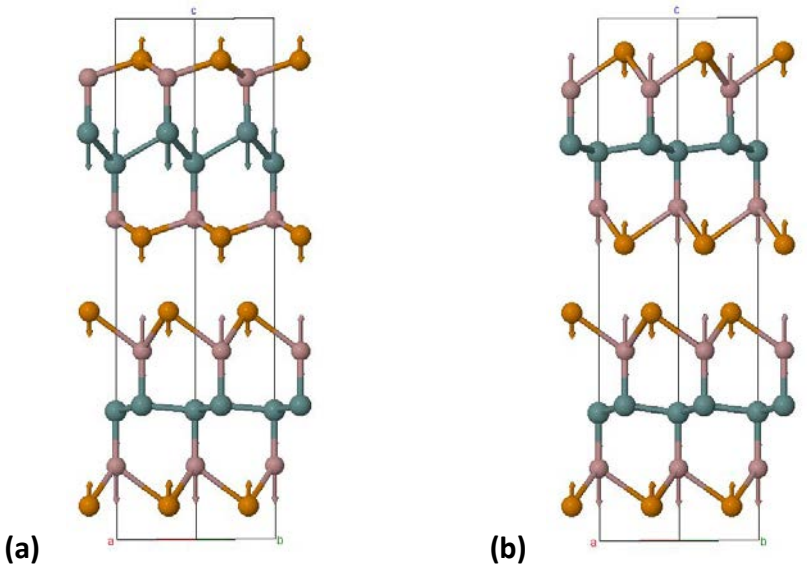

Figure S20. Atomic motion of B_1^4 (a) and A_1^3 (b) vibrational modes of β-GaGeTe predicted at 200.4 and 201.0 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are also longitudinal intra-layer modes of β-GaGeTe where Ge atoms vibrate in-phase along the c axis with neighbor Ga atoms in both bottom and top sublayers, which in turn vibrate out-of-phase with respect to Te atoms in their respective sublayers. Both modes are a mixture of a Ge-Ge bending mode and a Ga-Te bending mode. Additionally, the A_1^3 mode has a weak interlayer compressional mode due to the out-of-phase Te vibrations along the *c*-axis in the neighbor layers, that does not occur in the B_1^4 mode.

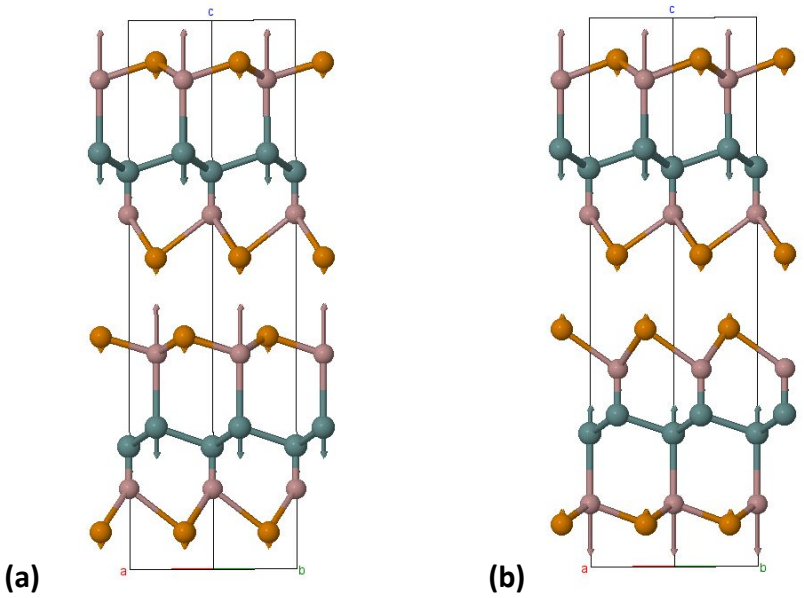

Figure S21. Atomic motion of A_1^4 (a) and B_1^5 (b) vibrational modes of β-GaGeTe predicted at 267.9 and 269.9 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are also longitudinal intra-layer modes of β-GaGeTe where Ge atoms vibrate out-of-phase along the c axis with respect to neighbor Ga atoms in both bottom and top sublayers, which in turn vibrate out-of-phase with respect to Te atoms in their respective sublayers. Both modes are a mixture of a Ge-Ge bending mode, a Ga-Te bending mode, and a Ga-Ge asymmetric stretching mode. In the A_1^4 mode, all atoms of one layer vibrate in-phase with those of the neighbor layer, while in the B_1^5 mode atoms of different layers vibrate out-of-phase.

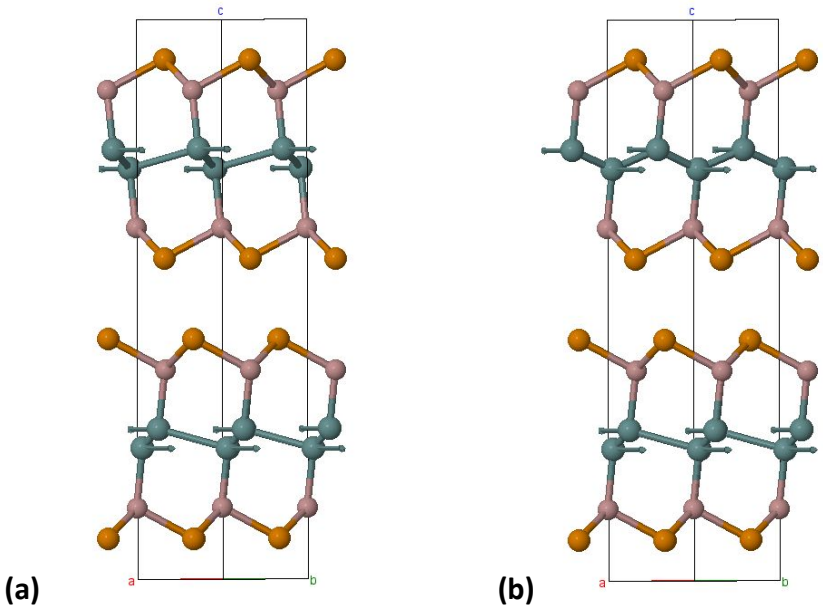

Figure S22. Atomic motion of E_1^5 (a) and E_2^6 (b) vibrational modes of β-GaGeTe predicted at 274.6 and 274.7 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes show Te atoms at rest and Ga and Ge atoms in motion along the a-b plane, but the Ge atoms vibrate with much larger amplitude than Ga atoms. In both modes, neighbor Ge atoms vibrate out-of-phase. These modes are a mixture of a Ge-Ge asymmetric stretching mode and a Ga-Ge bending mode.

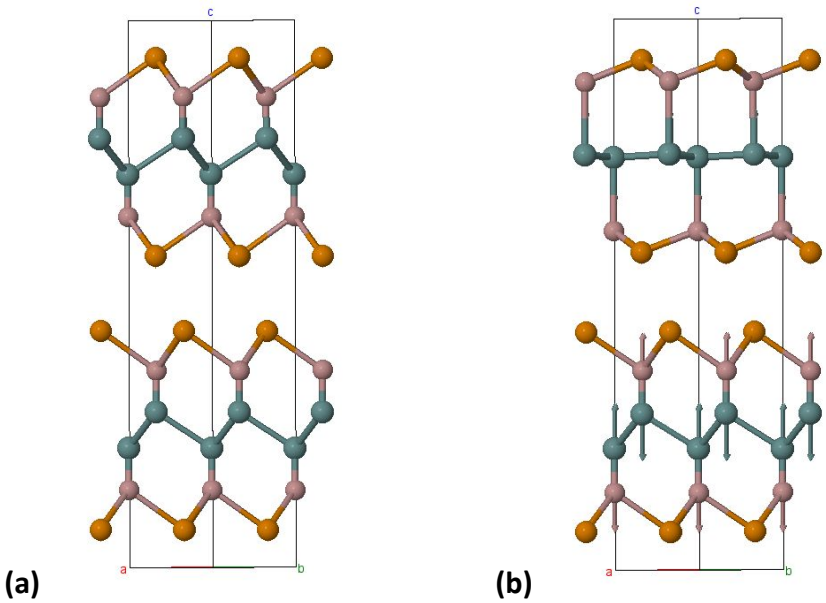

Figure S23. Atomic motion of A_1^5 (a) and B_1^6 (b) vibrational modes of β-GaGeTe predicted at 285.6 and 288.3 cm^{-1}. Ga, Ge, and Te atoms are depicted in pink, gray, and orange colors. These two modes are also longitudinal intra-layer modes of β-GaGeTe where Te atoms are at rest and neighbor Ge and Ga atoms vibrate out-of-phase along the c axis. These two modes are a mixture of a Ge-Ge bending mode, a Ga-Te bending mode and a Ga-Ge asymmetric stretching. In A_1^5 the vibrations in the two layers of the unit cell are in pase, while in B_1^6 the vibrations of the two layers are out-of-phase.

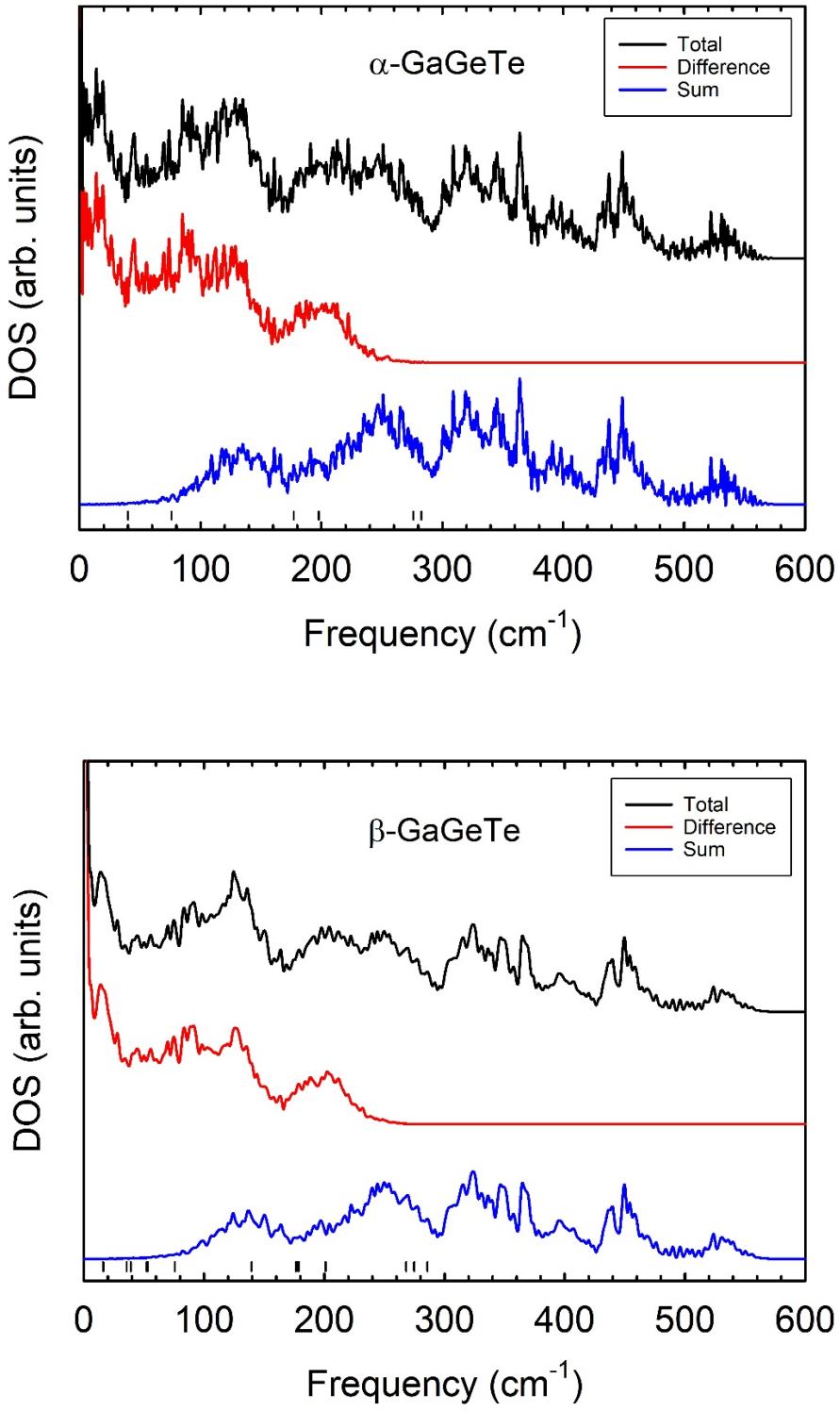

Figure S24. Theoretical total and partial two-phonon DOS of bulk α-GaGeTe (top) and bulk β-GaGeTe (bottom) at room conditions. Total, sum, and difference two-phonon DOS are plotted in black, blue, and red, respectively. The theoretical frequencies of the six first-order Raman-active modes of bulk α-GaGeTe and of the sixteen first-order Raman-active modes of bulk β-GaGeTe are represented as black bottom marks.

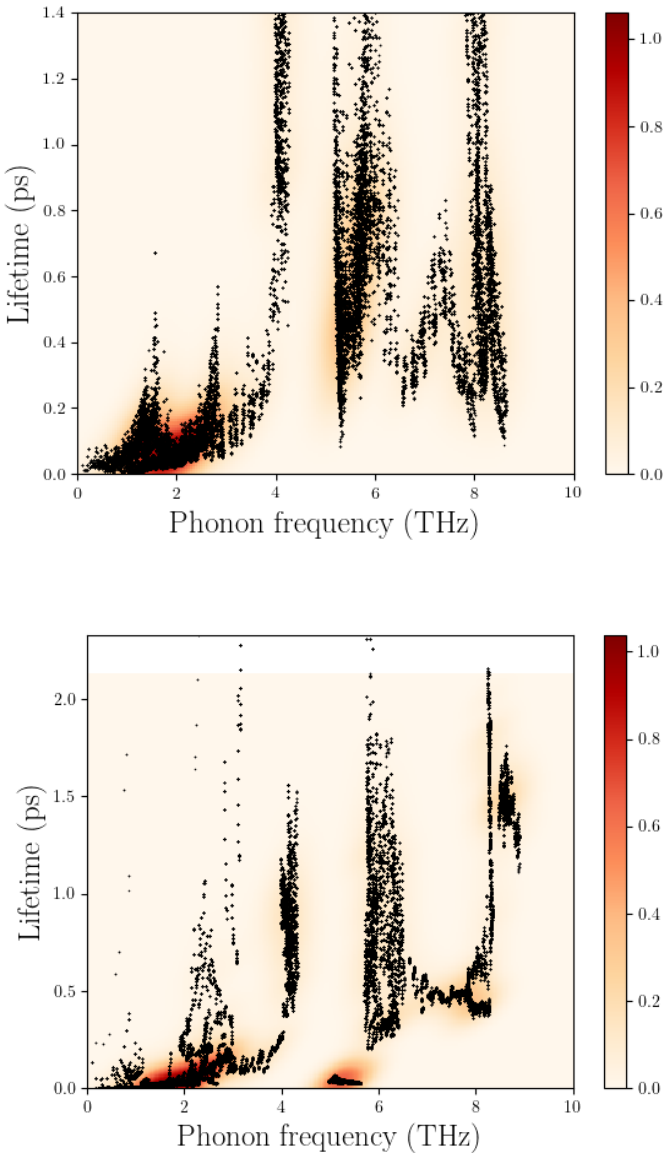

Figure S25. Calculated phonon lifetimes of α-GaGeTe (top) and β-GaGeTe (bottom) at 300 K. The color shades represent the phonon density, consequently darker shades refer to higher phonon densities.

Table S1. Theoretical PBEsol (PBE-D3) atomic coordinates of the *P-3m1* (s.g. No. 164) structure of GaGeTe-mono. The theoretical PBEsol (theoretical PBE-D3) lattice parameters of the hexagonal unit cell are: *a* = 4.0401 Å (4.0833 Å), *b* = 4.0401 Å (4.0833 Å), *c* = 12.4506 Å (12.3275 Å), and V_0 = 176.0000 Å^3 (178.0000 Å^3).

Atom	Wyckoff site	x	y	z
Ga	2d	1/3	2/3	0.2729 (0.2689)
Ge	2d	1/3	2/3	0.4678 (0.4673)
Te	2c	0	0	0.1708 (0.1660)

Table S2. Theoretical (PBEsol and PBE-D3) Raman- and infrared-active frequencies, ω, at ambient conditions for GaGeTe-mono. Theoretical (LDA) data from Ref. S3 for the α-GaGeTe monolayer (also with s.g. *P-3m1*) are also included for comparison.

Mode	ω (th.)[a] (cm^{-1})	ω (th.)[b] (cm^{-1})	ω (th.)[c] (cm^{-1})
E_g^1	35.6	34.4	39.0
E_u^1	53.8	53.8	57.1
A_{1g}^1	73.8	77.6	75.9
A_{2u}^1	140.1	138.5	149.0
E_g^2	177.2	172.9	186.9
E_u^2	177.3	173.2	186.9
A_{1g}^2	205.5	203.4	220.0
A_{2u}^2	269.4	266.4	284.7
E_g^3	277.1	270.5	284.7
A_{1g}^3	291.1	287.7	305.2

[a] PBEsol, [b] PBE-D3, [c] Estimated from Ref. S3.

Table S3. Theoretical PBEsol (PBE-D3) atomic coordinates of the *P-3m1* (s.g. No. 164) structure of γ-GaGeTe. The theoretical PBEsol (theoretical PBE-D3) lattice parameters of the hexagonal unit cell are: *a* = 4.0220 Å (4.0730 Å), *b* = 4.0220 Å (4.0730 Å), *c* = 11.5638 Å (11.6937 Å), and V_0 = 162.0000 Å^3 (168.0000 Å^3).

Atom	Wyckoff site	x	y	Z
Ga	2d	1/3	2/3	0.7545 (0.7553)
Ge	2d	1/3	2/3	-0.0351(-0.0348)
Te	2d	1/3	2/3	0.3567 (0.3540)

Table S4. Theoretical (PBEsol and PBE-D3) Raman- and infrared-active frequencies, ω, at ambient conditions for γ-GaGeTe. Theoretical (LDA) data from Ref. S3 for the α-GaGeTe monolayer (also with s.g. *P-3m1*) are also included for comparison.

Mode	ω (th.)[a] (cm^{-1})	ω (th.)[b] (cm^{-1})	ω (th.)[c] (cm^{-1})
E_g^1	37.7	38.1	39.0
E_u^1	52.4	53.0	57.1
A_{1g}^1	79.0	79.7	75.9
A_{2u}^1	142.3	140.6	149.0
E_u^2	177.3	173.5	186.9
E_g^2	178.5	174.7	186.9
A_{1g}^2	205.3	203.4	220.0
A_{2u}^2	268.1	264.3	284.7
E_g^3	278.1	270.5	284.7

A_{1g}^3	289.6	285.3	305.2

[a] PBEsol, [b] PBE-D3, [c] Estimated from Ref. S3.

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