

Supplementary Material of

Structural, Vibrational, and Electronic Behavior of Two GaGeTe Polytypes under Compression.

E. Bandiello^{1,*}, S. Gallego-Parra^{1,*}, A. Liang,² J.A. Sans¹, V. Cuenca-Gotor¹, E. Lora da Silva³, R. Vilaplana⁴, P. Rodríguez-Hernández⁵, A. Muñoz⁵, D. Diaz-Anichtchenko², C. Popescu⁶, F.G. Alabarse⁷, C. Rudamas⁸, C. Drasar⁹, A. Segura², D. Errandonea², and F.J. Manjón¹

¹ *Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022 Valencia, Spain*

² *Departamento de Física Aplicada-ICMUV, MALTA Consolider Team, Universitat de València, 46100 Burjassot, Spain*

³ *IFIMUP, Institute of Physics for Advanced Materials, Nanotechnology and Photonics, Department of Physics and Astronomy, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal*

⁴ *Centro de Tecnologías Físicas, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain*

⁵ *Departamento de Física, Instituto de Materiales y Nanotecnología, MALTA Consolider Team, Universidad de La Laguna, La Laguna, 38205 Tenerife, Spain*

⁶ *CELLS-ALBA Synchrotron Light Facility, MALTA Consolider Team, 08290 Cerdanyola del Vallès, Barcelona, Spain*

⁷ *Elettra Sincrotrone Trieste, S.S. 14 - km 163,5 in AREA Science Park, 34149 Basovizza, Trieste, Italy*

⁸ *Escuela de Física, Facultad de Ciencias Naturales y Matemática, Universidad de El Salvador, San Salvador, El Salvador*

⁹ *Faculty of Chemical Technology, University of Pardubice, Pardubice 532 10, Czech Republic*

1.- Structural data

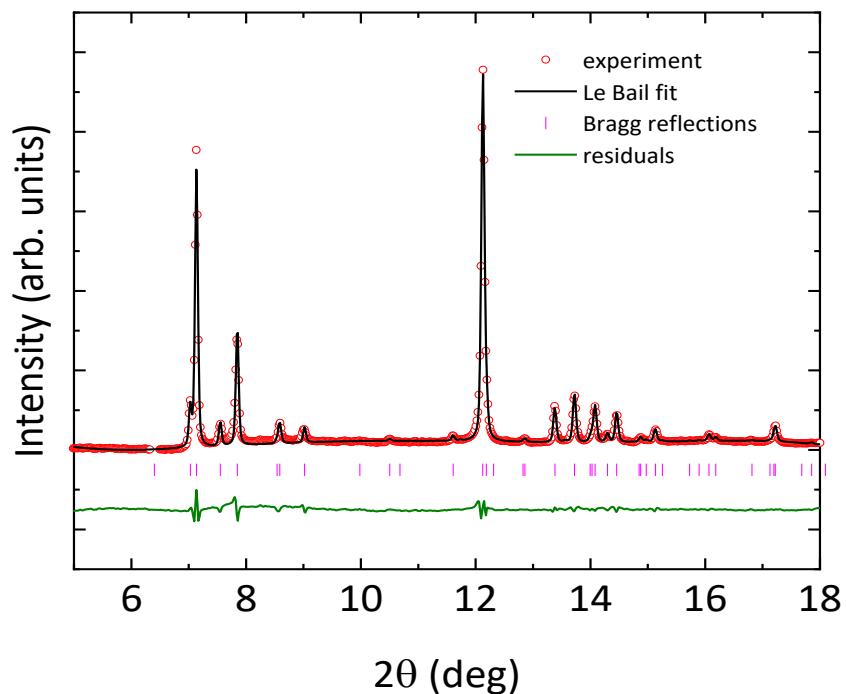


Figure S1. Experimental XRD pattern of α -GaGeTe at 1.2 GPa in the Alba-1 experiment (red circles, $\lambda=0.4246$ Å) and Le Bail refinement of the XRD pattern (black line). Magenta ticks show the position of Bragg reflections, while the green line represents the residuals of the Le Bail fit (difference between experimental and computer XRD patterns).

Table S1. Experimental and theoretical (PBEsol) unit-cell parameters for α - and β -GaGeTe at near RP pressure, except for the experimental cell parameters of the α polytype in the Alba-1 experiment that are shown at the minimum pressure of $P=1.2$ GPa.

Polytype		Experiment				Theory
		Alba-1 (1.2 GPa)	Alba-2	Elettra	Ref [1]	(PBEsol)
α $(R\bar{3}m)$	a (Å)	3.9924(1)	4.0454(4)	4.0459(1)	4.0480	4.0495
	c (Å)	34.592(2)	34.648(8)	34.789(2)	34.7340	34.4336
	V (Å ³)	477.50(5)	491.06(5)	493.18(5)	492.91	489.01
β $(P6_3mc)$	a (Å)	-	4.0320(5)	4.0350(1)	4.0379	4.04518
	c (Å)	-	22.2334(5)	22.274(5)	22.1856	23.00478
	V (Å ³)	-	313.024(5)	314.08(5)	313.27	326.00

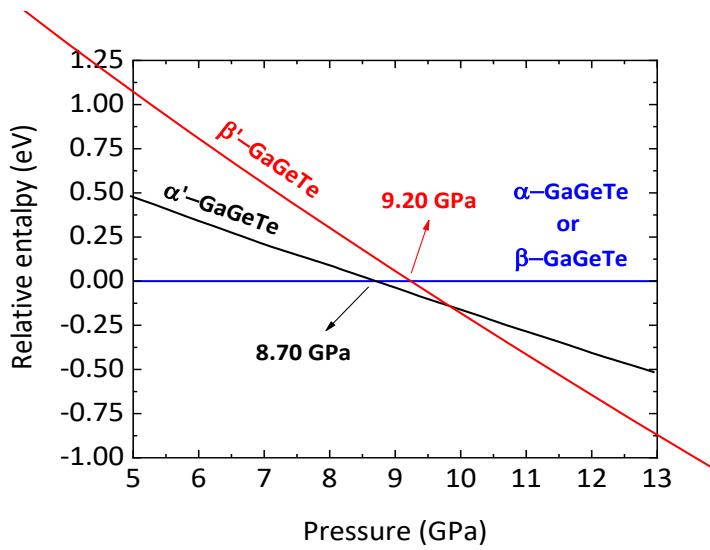


Figure S2: Theoretical relative enthalpy of the proposed high-pressure phases α' -GaGeTe (black line) and β' -GaGeTe (red line) with respect to those of the low-pressure phases α -GaGeTe and β -GaGeTe (blue line), respectively. The high-pressure phases become competitive above 8.70 GPa (α' -GaGeTe) and 9.20 GPa (β' -GaGeTe).

Table S2. Theoretical (PBEsol) atomic coordinates of the structure of α' -GaGeTe (s.g. $R\bar{3}m$, No. 166) at approximately 10 GPa. The theoretical PBEsol lattice parameters of the hexagonal unit cell are: $a = 3.6540 \text{ \AA}$; $c = 30.6151 \text{ \AA}$, and $V_0 = 354.00 \text{ \AA}^3$.

Atom	Wyckoff site	x	y	z
Ga	6c	0	0	-0.07287
Ge	6c	0	0	0.64364
Te	6c	0	0	0.20602

Table S3. Theoretical (PBEsol) atomic coordinates of the structure of β' -GaGeTe (s.g. $P6_3mc$, No. 186) at approximately 10 GPa. The theoretical lattice parameters of the hexagonal unit cell are $a = 3.6730 \text{ \AA}$, $c = 20.3705 \text{ \AA}$, and $V_0 = 238.00 \text{ \AA}^3$.

Atom	Wyckoff site	x	y	z
Ga1	2b	1/3	2/3	0.64062
Ga2	2b	1/3	2/3	0.3729
Ge1	2a	0	0	0.21627
Ge2	2b	1/3	2/3	0.28539
Te1	2a	0	0	0.44202
Te2	2b	1/3	2/3	0.06045

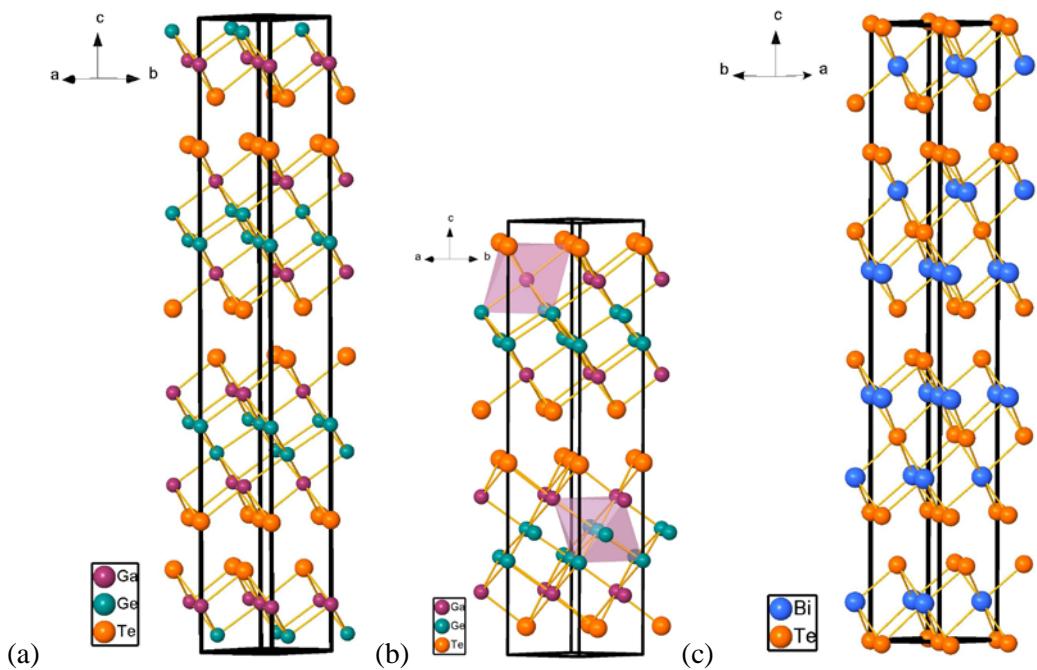


Figure S3. 3D view of the hexagonal unit cell of α' -GaGeTe (a) β' -GaGeTe (b), and Bi_2Te_3 (c). Ga, Ge, and Te atoms are represented in purple, green, and orange, respectively. The sixfold coordination of Ga and Ge atoms in both structures by the pink octahedra in the structure of β' -GaGeTe. Note that each monolayer of α' -GaGeTe and β' -GaGeTe is similar to that of the monolayer of Bi_2Te_3 where the central sublayer of Te is substituted by the germanene sublayer.

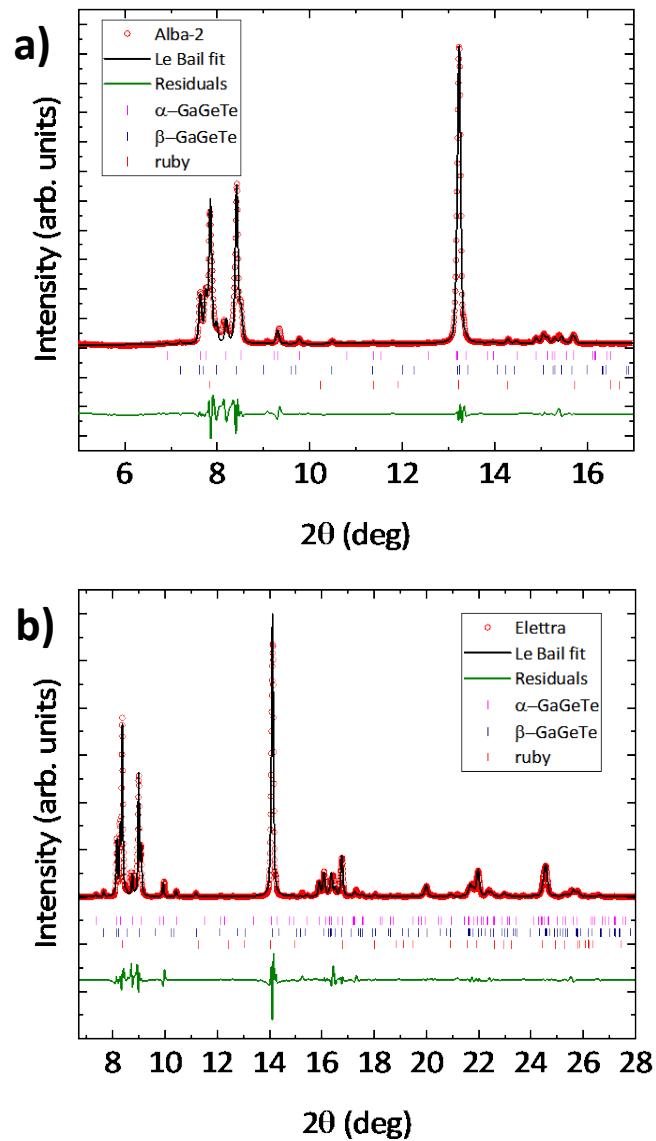


Figure S4. Experimental XRD data (red circles) and Le Bail fits (black line) for the (a) Alba-2, and (b) Elettra experiments. In both plots, residuals are represented by a green line. Bragg reflections for α -GaGeTe, β -GaGeTe, and ruby are shown (magenta, blue and red ticks, respectively).

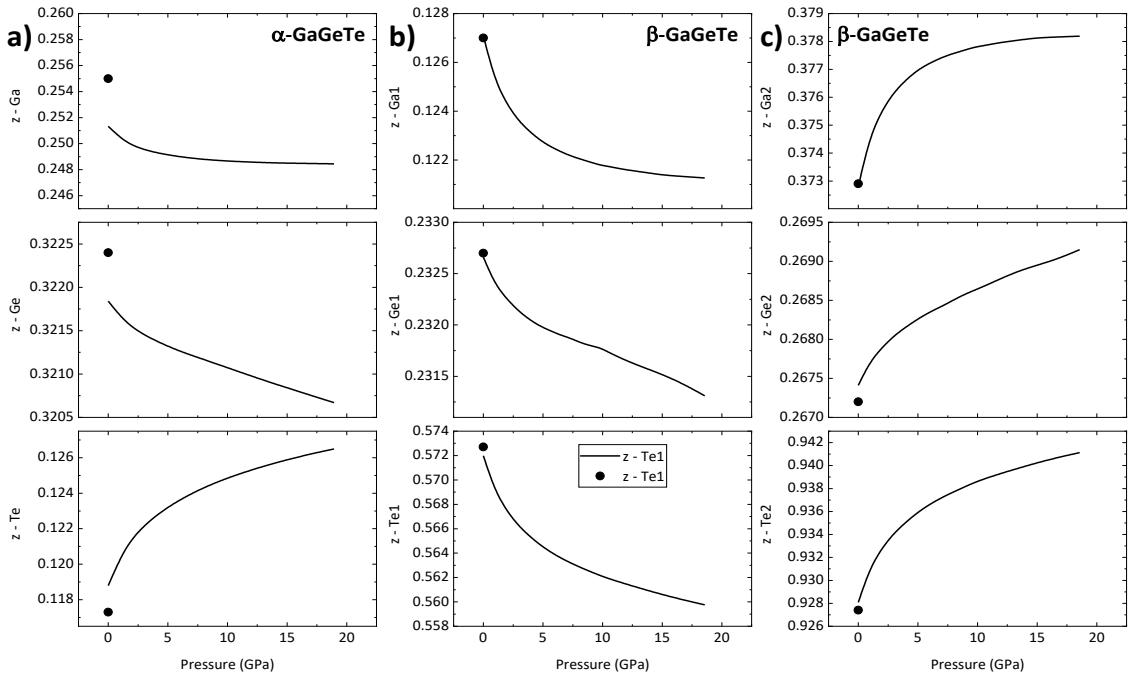


Figure S5. Theoretical pressure dependence of the z free atomic parameters of Ga, Ge and Te for a) α -GaGeTe and b) and c) β -GaGeTe. For comparison, experimental values at 0 GPa from Ref. [1] are plotted as symbols.

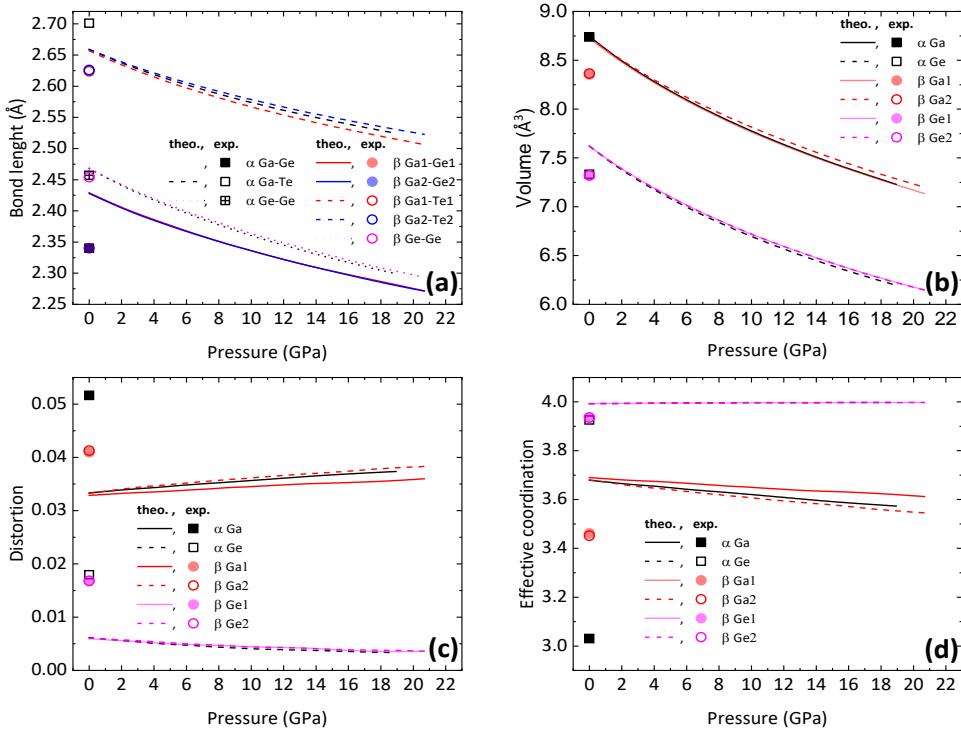


Figure S6. Theoretical (lines) pressure dependence of the bond lengths (a), polyhedral volumes (b), distortion index (c), and effective coordination (d) of Ga and Ge tetrahedra in α - (black lines and black symbols) and β -GaGeTe (red, blue and magenta symbols), respectively. Corresponding experimental values at room pressure, as measured from the data in Ref. [1], are shown as symbols. See legends for details. Ge-Ge distances are identical for Ge1 and Ge2 tetrahedra in β -GaGeTe. Additionally, due to their small experimental and theoretical differences, Ga-Ge distance in α -GaGeTe and the Ga1-Ge1 and Ga2-Ge2 distances in β -GaGeTe are graphically very close in panel (a), thus theoretical lines and experimental values at room pressure are superposed, respectively. The same happens for the volumes of Ge1 and Ge2 tetrahedra in β -GaGeTe in panel (b). For data with (partial) superposition, transparency was used (i.e., β Ga1-Ge1, β Ga2-Ge2 and α Ga-Ge in panel (a); β Ga1 (Ge1), and β Ga2 (Ge2) in panels (b), (c) and (d)). The low experimental value of the effective coordination for the Ga polyhedron in α -GaGeTe (panel (d)) is due to the fact that the calculated Ga-Te and Ga-Ge bond distances for this polyhedron are more similar to each other in theoretical calculations than in experimental data (see data in Table S5 for a numerical comparison).

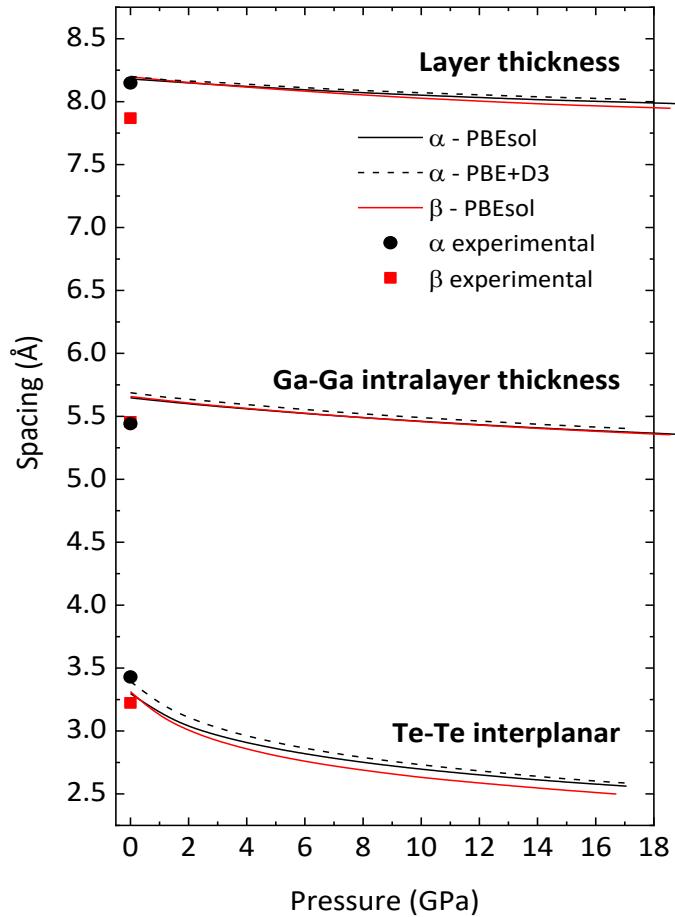


Figure S7. Theoretical (lines) pressure dependence of the thickness of a GaGeTe monolayer (layer thickness), interplanar distance between Ga planes inside a monolayer (Ga-Ga intralayer thickness) and interplanar distance (Te-Te interplanar) for α -GaGeTe and β -GaGeTe (in black and red, respectively). Experimental values of the corresponding magnitudes at room pressure, as reported in Ref. [1], are represented by black circles and red squares (α -GaGeTe and β -GaGeTe, respectively). Dashed black lines represent PBE+D3 calculations for α -GaGeTe and are shown to confirm the qualitative equivalence of PBEsol and PBE+D3 calculations, as mentioned in the main manuscript. Note that the calculated Ga-Ga intralayer thickness values for α and β -GaGeTe are almost coincident in all the pressure range, thus the corresponding lines are graphically superposed.

Table S4. Theoretical bond lengths at 0 GPa for the different Ga (upper part of the Table) and Ge (lower part of the Table) tetrahedra in α -GaGeTe and in β -GaGeTe. For each polytype, the three Ga-Te bonds of the Ga tetrahedra are identical, as are the Ge-Ge bonds of the Ge tetrahedra. For comparison, experimental values (in italics) are shown as well, below each theoretical value.

	Ga1-Ge1 (Å)	(3×) Ga1-Te1 (Å)	Ga2-Ge2 (Å)	(3×) Ga2-Te2 (Å)
α (Ga)	2.42791	2.65906	-	-
	<i>2.34(3)</i>	<i>2.701(13)</i>	-	-
β (Ga1, Ga2)	2.42902	2.65686	2.42810	2.65895
	<i>2.34(3)</i>	<i>2.624(13)</i>	<i>2.34(3)</i>	<i>2.626(14)</i>
	Ge1-Ga1 (Å)	(3×) Ge1-Ge1 (Å)	(3×) Ge2-Ge2 (Å)	Ge2-Ga2 (Å)
α (Ge)	2.42791	2.46831	-	-
	<i>2.34(3)</i>	<i>2.457(11)</i>	-	-
β (Ge1)	2.42902	2.46787	-	-
	<i>2.34(3)</i>	<i>2.454(9)</i>	-	-
β (Ge2)	-	-	2.46787	2.42810
	-	-	<i>2.454(9)</i>	<i>2.34(3)</i>

Table S5. Theoretical bulk modulus B_0 of the different Ga and Ge tetrahedra in α -GaGeTe and β -GaGeTe, as calculated from data of Figure S6b using a 2nd order Birch-Murnaghan equation of state (B_0' fixed to 4).

	V_0 (Å ³)	B_0 (GPa)	B_0'
α (Ga)	8.728(4)	68.7(4)	4
α (Ge)	7.606(5)	60.6(3)	4
β (Ga1)	8.712(4)	69.2(3)	4
β (Ga2)	8.723(2)	73.11(17)	4
β (Ge1)	7.611(2)	62.75(18)	4
β (Ge2)	7.609(2)	62.81(18)	4

2.- Vibrational data

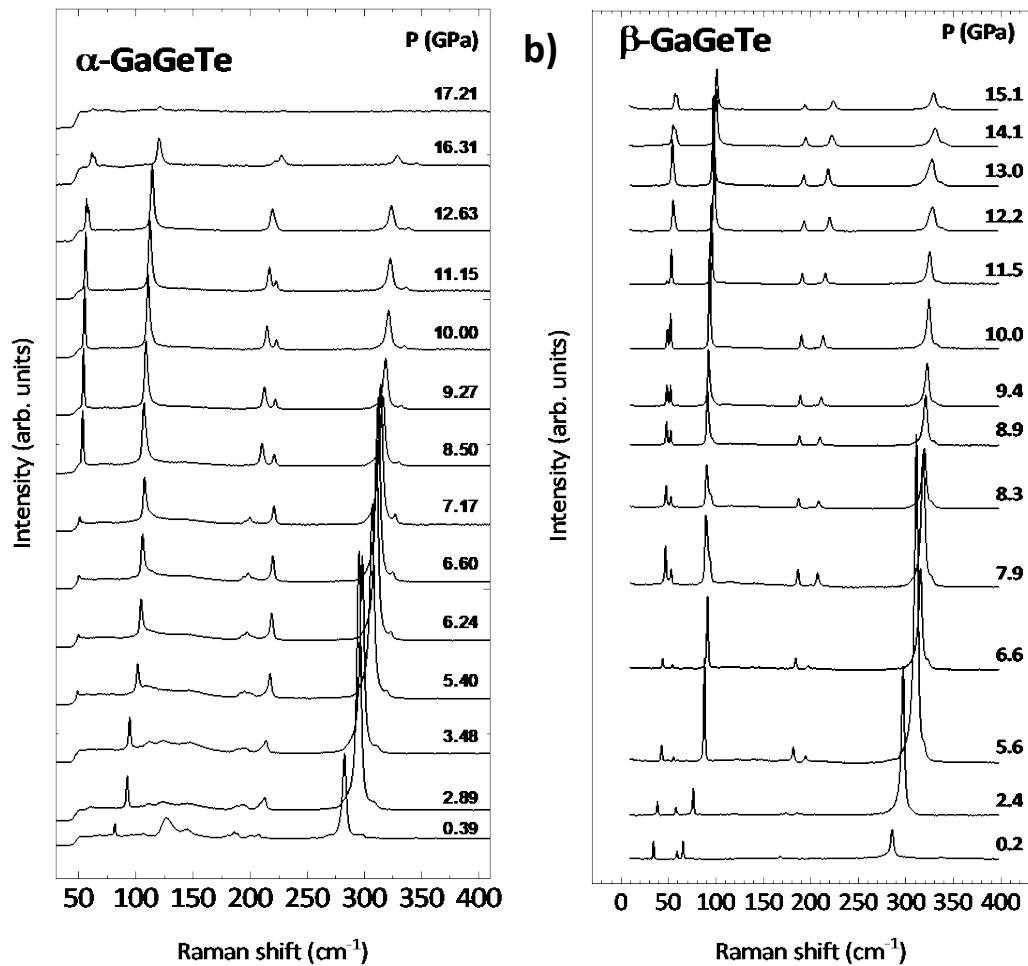


Figure S8. Raman spectra for a) $\alpha\text{-GaGeTe}$ and, b) $\beta\text{-GaGeTe}$ at selected pressure (P), as obtained using a red laser ($\lambda=632.8 \text{ nm}$). Pressure is indicated in GPa for each spectrum.

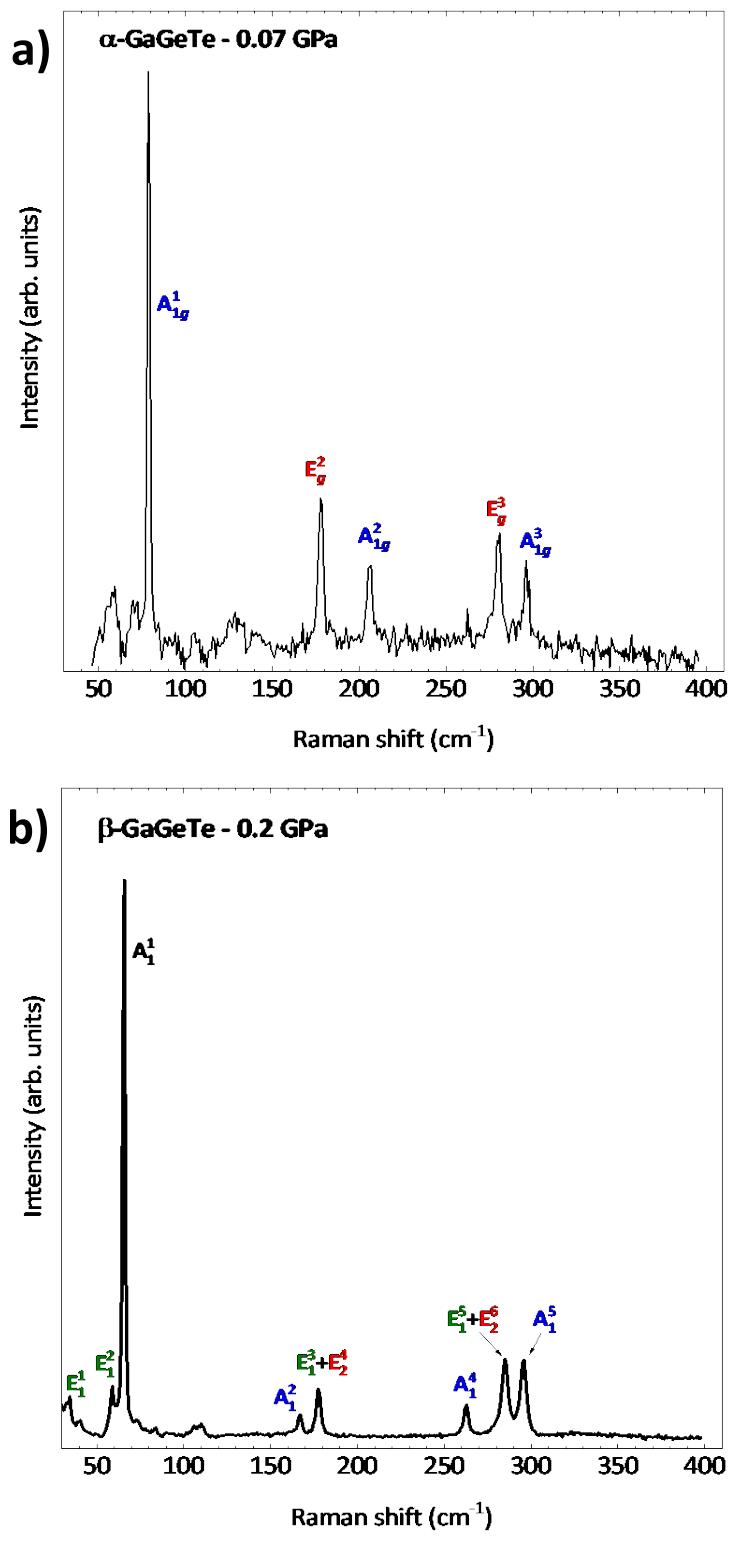


Figure S9: Raman spectra at nearly-room pressure for a) $\alpha\text{-GaGeTe}$ and, b) $\beta\text{-GaGeTe}$ as measured with a green laser ($\lambda=532$ nm). The peaks corresponding to the Raman modes detected experimentally have been identified by their symmetry (according to Ref. [1]).

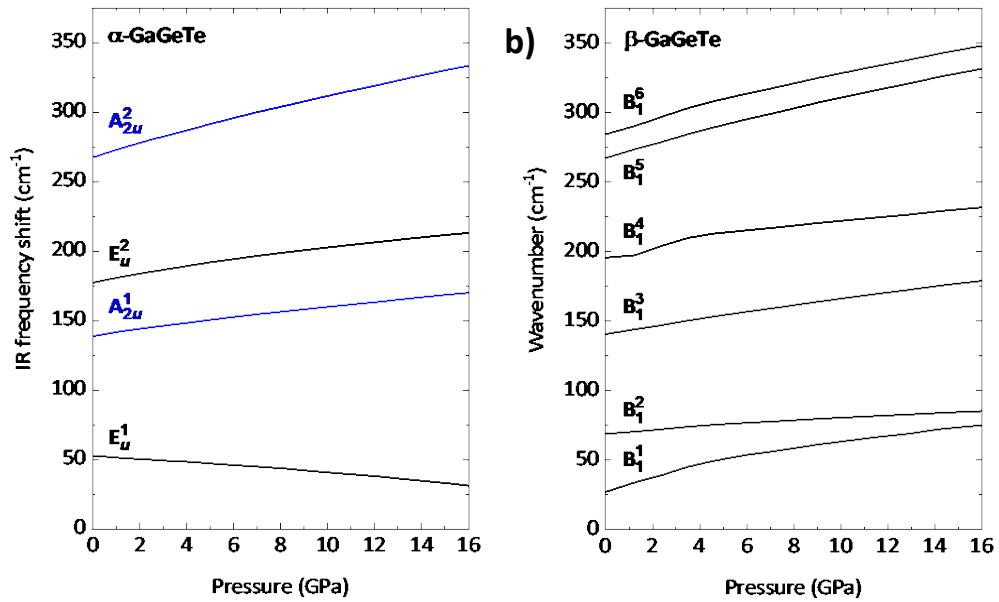


Figure S10. Theoretical (PBEsol) pressure dependence of the wavenumbers of IR-active modes in α -GaGeTe (a) and silent modes in β -GaGeTe (b). E and A modes in α -GaGeTe are plotted in black and blue respectively.

Table S6. Theoretical zero-pressure frequencies, pressure coefficients, and Grüneisen parameters, γ , obtained from a second-order polynomial fit, $\omega=\omega_0+aP+bP^2$, for the IR-active modes in α -GaGeTe. For the calculation of the theoretical Grüneisen parameters, a bulk modulus of 41.6 GPa has been used, respectively (see main manuscript).

Mode	ω_0 (cm ⁻¹)	a (cm ⁻¹ /GPa)	b (cm ⁻¹ /GPa ²)	γ
E_u^1	52.3	-0.9	-0.03	-0.72
A_{2u}^1	139.1	2.4	-0.03	0.72
E_u^2	177.6	3.1	-0.05	0.73
A_{2u}^2	267.8	4.9	-0.05	0.76

Table S7. Theoretical zero-pressure frequencies, pressure coefficients, and Grüneisen parameters, γ , obtained from a second-order polynomial fit, $\omega = \omega_0 + aP + bP^2$, for the silent modes in β -GaGeTe. For the calculation of the theoretical Grüneisen parameters, a bulk modulus of 48.5 GPa has been used (see main manuscript).

Mode	ω_0 (cm ⁻¹)	a (cm ⁻¹ /GPa)	b (cm ⁻¹ /GPa ²)	γ
B_1^1	28.2	4.9	-0.13	8.43
B_1^2	68.9	1.5	-0.03	1.06
B_1^3	140.5	2.8	-0.03	0.97
B_1^4	195.1	3.7	-0.10	0.92
B_1^5	267.5	4.9	-0.06	0.89
B_1^6	284.7	5.2	-0.08	0.89

Table S8. Theoretical frequencies and pressure coefficients obtained from a second-order polynomial fit, $\omega=\omega_0+aP+bP^2$, for the Raman and IR-active modes in α' -GaGeTe at 8 GPa.

Mode	ω_0 (cm ⁻¹)	a (cm ⁻¹ /GPa)	b (cm ⁻¹ /GPa ²)
E_g^1	61.8	2.3	-0.03
E_u^1	84.2	2.1	-0.03
A_{1g}^1	116.1	3.2	-0.03
A_{2u}^1	129.9	2.0	-0.01
E_g^2	136.5	1.2	-
E_u^2	151.5	3.3	-0.03
A_{1g}^2	169.4	0.8	-
E_g^3	175.8	3.3	-0.02
A_{2u}^2	178.7	3.9	-0.04
A_{1g}^3	189.9	2.4	-

Table S9. Theoretical frequencies and pressure coefficients obtained from a second-order polynomial fit, $\omega=\omega_0+aP+bP^2$, for the Raman, IR, and silent modes in β' -GaGeTe at 8 GPa.

Mode	ω_0 (cm ⁻¹)	a (cm ⁻¹ /GPa)	b (cm ⁻¹ /GPa ²)
E_2^1	31.6	3.1	-0.08
E_2^2	38.0	3.7	-0.11
E_1^1	56.1	6.3	-0.18
B_1^1	58.5	1.4	-0.01
B_1^2	69.2	2.7	-0.05
E_1^2	82.9	3.6	-0.08
E_2^3	88.6	4.5	-0.11
A_1^1	108.2	2.4	-0.01
A_1^2	129.4	2.2	-0.02
B_1^3	137.5	8.5	-0.21
E_1^3	137.7	0.9	-0.01
E_2^4	138.3	-2.5	0.15
E_1^4	150.0	4.0	-0.05
E_2^5	150.1	3.5	-0.04
B_1^4	160.0	5.5	-0.12
A_1^3	161.8	7.8	-0.21
B_1^5	167.0	5.0	-0.05
E_1^5	167.7	4.9	-0.05
E_2^6	169.9	5.1	-0.07
A_1^4	176.3	4.0	-0.04
A_1^5	183.8	5.9	-0.12
B_1^6	185.6	3.7	-0.01

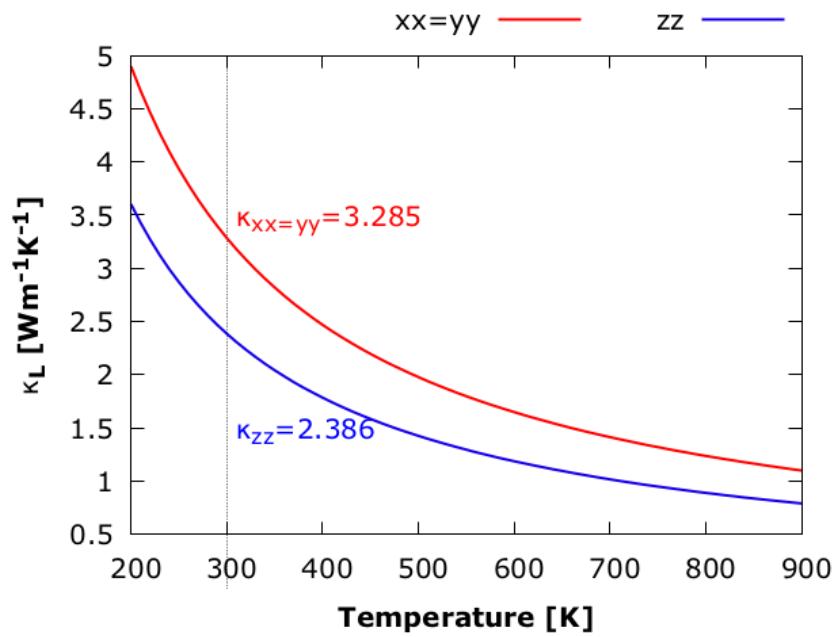


Figure S11. Lattice thermal conductivity (κ_L) for bulk α -GaGeTe at 5 GPa along the main directions of the hexagonal unit cell: layer plane (xx = yy) and c axis (zz).

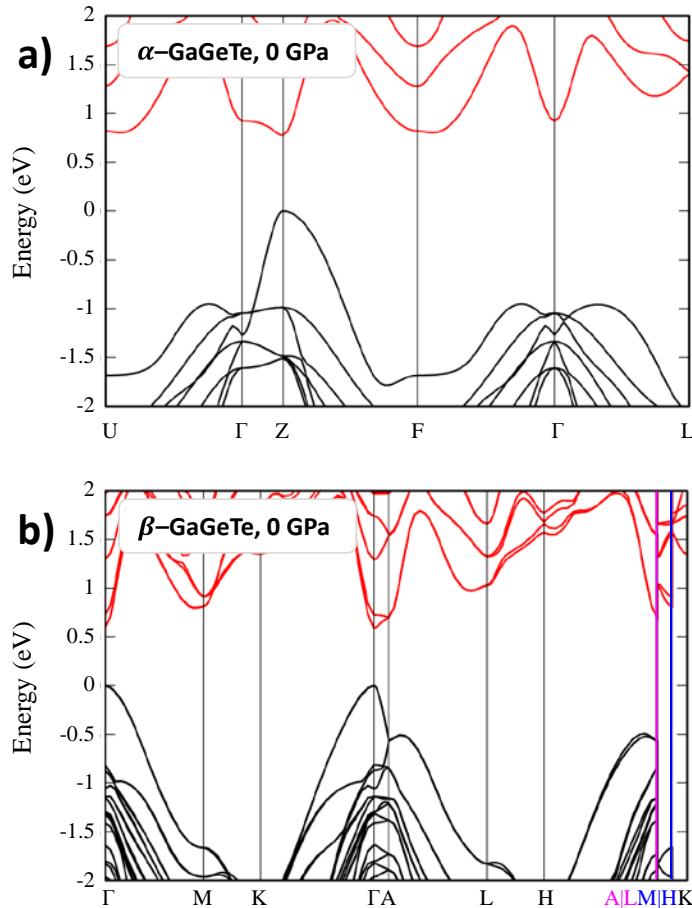


Figure S12. Theoretical (*meta*-GGA (MBJ)) electronic band structure at 0 GPa of a) α -GaGeTe along the U- Γ -Z-F- Γ -L directions, and b) β -GaGeTe, along the the Γ -M-K- Γ -A-L-H-A-L-M-H-K directions. Given the short distance between the A, L and M, H points of the BZ of β -GaGeTe, these have been indicated as A|L (in violet) and M|H (in blue), for better readability. On the plots, the patterns corresponding to A|L and M|H are indicated in violet and in blue, respectively. The meta-GGA (MBJ) were performed with the modified Becke-Johnson (MBJ) potential [2,3] that provides band gaps similar to hybrid functionals.

References

- [1] S. Gallego-Parra, E. Bandiello, A. Liang, E. Lora da Silva, P. Rodríguez-Hernández, A. Muñoz, S. Radescu, A.H. Romero, C. Drasar, D. Errandonea, F.J. Manjón, Layered topological semimetal GaGeTe: New polytype with non-centrosymmetric structure, Mater. Today Adv. 16 (2022) 100309. <https://doi.org/10.1016/j.mtadv.2022.100309>.
- [2] A.D. Becke, E.R. Johnson, A simple effective potential for exchange, J. Chem. Phys. 124 (2006) 221101. <https://doi.org/10.1063/1.2213970>.
- [3] F. Tran, P. Blaha, Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential, Phys. Rev. Lett. 102 (2009) 226401. <https://doi.org/10.1103/PhysRevLett.102.226401>.