

Supporting Information for “The Origin of Uniaxial Negative Thermal Expansion in Layered Perovskites”

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Compound	Phase	a (Å)	b (Å)	c (Å)	ΔE (meV/at)
Ca ₂ GeO ₄	<i>I4/mmm</i>	3.749	3.749	11.646	0.0
Ca ₂ GeO ₄	<i>I4₁/acd</i>	5.234	5.234	23.889	-9.1
Ca ₂ GeO ₄	<i>Pbca</i>	5.318	5.297	23.421	-11.9
CaGeO ₃	<i>Pm$\bar{3}m$</i>	3.748	3.748	3.748	0.0
CaGeO ₃	<i>I4/mcm</i>	5.221	5.221	7.672	-49.2
Ca ₃ Ge ₂ O ₇	<i>I4/mmm</i>	3.754	3.754	19.074	0.0
Ca ₃ Ge ₂ O ₇	<i>Acaa</i>	5.229	5.230	19.612	-22.0
Ca ₂ MnO ₄	<i>I4/mmm</i>	5.181	5.181	23.564	0.0
Ca ₂ MnO ₄	<i>I4₁/acd</i>	5.127	5.127	24.081	-7.6
LaTaO ₄	<i>Cmcm</i>	3.983	15.303	5.621	0.0
LaTaO ₄	<i>Cmc2₁</i>	3.947	14.505	5.690	-35.0
Sr ₂ MgWO ₆	<i>Fm$\bar{3}m$</i>	5.573	5.573	7.881	0.0
Sr ₂ MgWO ₆	<i>I4/m</i>	5.541	5.541	7.952	-9.3

Table S1. Table of all relaxed cell parameters from DFT calculations with no external pressure applied. Energies are given compared to the parent phase.

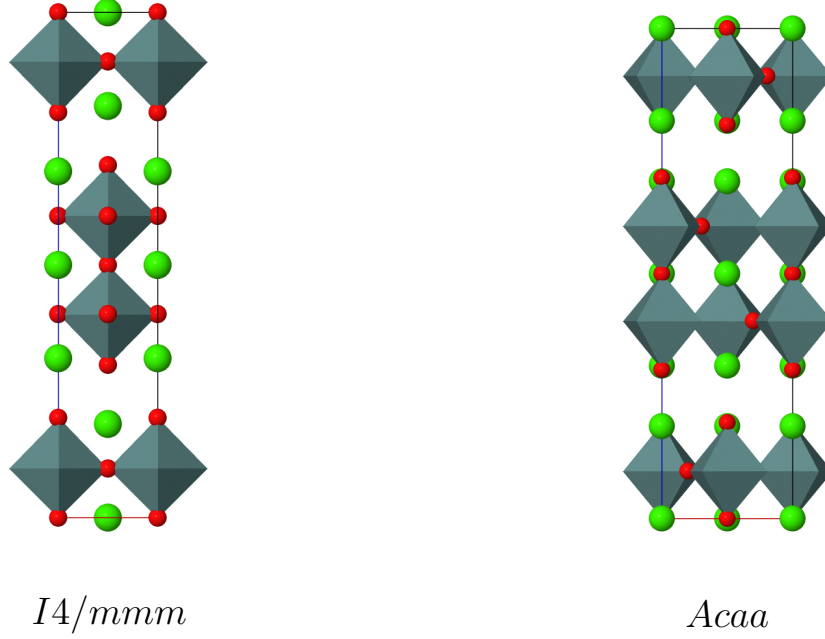


Figure S1. Fully relaxed high symmetry *I4/mmm* and low symmetry (NTE) *Acaa* Ca₃Ge₂O₇ structures. Since the strain coupling mechanism illustrated in Figure 5 of the main paper is specific to the ABO₃/AO interface of RP materials with frozen rotations about the *c* axis, this mechanism may also be generalised to explain strain coupling in the NTE *Acaa* phase of Ca₃Mn₂O₇ (modelled as Ca₃Ge₂O₇ in DFT calculations).

Chemistry	Phase	β	$\mathbf{s}$	s_L	$\hat{s}_L$	s_M	$\hat{s}_M$	s_H	$\hat{s}_H$
CaGeO ₃	$Pm\bar{3}m$	5.33	$\begin{bmatrix} 3.57 & -0.89 & -0.89 \\ -0.89 & 3.57 & -0.89 \\ -0.89 & -0.89 & 3.57 \end{bmatrix}$	1.79	$\begin{pmatrix} 0.58 \\ 0.58 \\ 0.58 \end{pmatrix}$	4.46	$\begin{pmatrix} 0.58 \\ 0.58 \\ 0.58 \end{pmatrix}$	4.46	$\begin{pmatrix} 0.58 \\ 0.58 \\ 0.58 \end{pmatrix}$
	$I4/mcm$	5.51	$\begin{bmatrix} 4.07 & -0.82 & -1.31 \\ -0.82 & 4.07 & -1.31 \\ -1.31 & -1.31 & 4.25 \end{bmatrix}$	1.83	$\begin{pmatrix} 0.56 \\ 0.56 \\ 0.61 \end{pmatrix}$	4.90	$\begin{pmatrix} 0.71 \\ -0.71 \\ 0.00 \end{pmatrix}$	5.67	$\begin{pmatrix} -0.43 \\ -0.43 \\ 0.79 \end{pmatrix}$
Ca ₂ GeO ₄	$I4/mmm$	6.69	$\begin{bmatrix} 4.58 & -0.64 & -1.26 \\ -0.64 & 4.58 & -1.26 \\ -1.26 & -1.26 & 4.21 \end{bmatrix}$	2.29	$\begin{pmatrix} 0.52 \\ 0.52 \\ 0.68 \end{pmatrix}$	5.22	$\begin{pmatrix} 0.71 \\ -0.71 \\ 0.00 \end{pmatrix}$	5.86	$\begin{pmatrix} -0.48 \\ -0.48 \\ 0.73 \end{pmatrix}$
	$I4_1/acd$	7.11	$\begin{bmatrix} 5.93 & -0.60 & -2.38 \\ -0.60 & 5.93 & -2.38 \\ -2.38 & -2.38 & 5.96 \end{bmatrix}$	2.26	$\begin{pmatrix} 0.52 \\ 0.52 \\ 0.67 \end{pmatrix}$	6.53	$\begin{pmatrix} 0.71 \\ -0.71 \\ 0.00 \end{pmatrix}$	9.03	$\begin{pmatrix} -0.48 \\ -0.48 \\ 0.74 \end{pmatrix}$
Ca ₃ Ge ₂ O ₇	$I4/mmm$	6.28	$\begin{bmatrix} 4.21 & -0.79 & -1.15 \\ -0.79 & 4.21 & -1.15 \\ -1.15 & -1.15 & 4.09 \end{bmatrix}$	2.09	$\begin{pmatrix} 0.55 \\ 0.55 \\ 0.63 \end{pmatrix}$	5.00	$\begin{pmatrix} 0.71 \\ -0.71 \\ 0.00 \end{pmatrix}$	5.42	$\begin{pmatrix} -0.45 \\ -0.45 \\ 0.78 \end{pmatrix}$
	$Acaa$	6.38	$\begin{bmatrix} 5.00 & -0.70 & -1.82 \\ -0.70 & 5.00 & -1.82 \\ -1.82 & -1.82 & 5.05 \end{bmatrix}$	2.07	$\begin{pmatrix} 0.53 \\ 0.53 \\ 0.65 \end{pmatrix}$	5.70	$\begin{pmatrix} 0.71 \\ -0.71 \\ -0.00 \end{pmatrix}$	7.28	$\begin{pmatrix} -0.46 \\ -0.46 \\ 0.76 \end{pmatrix}$
LaTaO ₄	$Cmcm$	8.65	$\begin{bmatrix} 3.02 & -1.22 & -1.44 \\ -1.22 & 7.66 & -0.91 \\ -1.44 & -0.91 & 5.10 \end{bmatrix}$	1.89	$\begin{pmatrix} -0.85 \\ -0.25 \\ -0.46 \end{pmatrix}$	5.81	$\begin{pmatrix} -0.49 \\ 0.10 \\ 0.87 \end{pmatrix}$	8.08	$\begin{pmatrix} 0.17 \\ -0.96 \\ 0.21 \end{pmatrix}$
	$Cm2_1$	7.88	$\begin{bmatrix} 3.29 & -0.07 & -2.18 \\ -0.07 & 8.23 & -3.22 \\ -2.18 & -3.22 & 7.26 \end{bmatrix}$	1.95	$\begin{pmatrix} -0.83 \\ -0.26 \\ -0.50 \end{pmatrix}$	5.58	$\begin{pmatrix} -0.54 \\ 0.65 \\ 0.54 \end{pmatrix}$	11.25	$\begin{pmatrix} -0.18 \\ -0.72 \\ 0.67 \end{pmatrix}$
Sr ₂ MgWO ₆	$Fm\bar{3}m$	7.05	$\begin{bmatrix} 4.66 & -1.24 & -1.09 \\ -1.24 & 4.66 & -1.09 \\ -1.09 & -1.09 & 4.54 \end{bmatrix}$	2.35	$\begin{pmatrix} 0.58 \\ 0.58 \\ 0.57 \end{pmatrix}$	5.90	$\begin{pmatrix} 0.71 \\ -0.71 \\ 0.00 \end{pmatrix}$	5.62	$\begin{pmatrix} -0.41 \\ -0.41 \\ 0.82 \end{pmatrix}$
	$I4/m$	7.13	$\begin{bmatrix} 4.95 & -0.88 & -1.50 \\ -0.88 & 4.95 & -1.50 \\ -1.50 & -1.50 & 4.99 \end{bmatrix}$	2.36	$\begin{pmatrix} 0.55 \\ 0.55 \\ 0.63 \end{pmatrix}$	5.83	$\begin{pmatrix} 0.71 \\ -0.71 \\ -0.00 \end{pmatrix}$	6.70	$\begin{pmatrix} -0.44 \\ -0.44 \\ 0.78 \end{pmatrix}$
Ca ₂ MnO ₄ *	$I4_1/acd$	6.44	$\begin{bmatrix} 5.11 & -0.98 & -1.81 \\ -0.98 & 5.11 & -1.81 \\ -1.81 & -1.81 & 5.43 \end{bmatrix}$	2.14	$\begin{pmatrix} 0.56 \\ 0.56 \\ 0.61 \end{pmatrix}$	6.09	$\begin{pmatrix} 0.71 \\ -0.71 \\ 0.00 \end{pmatrix}$	7.43	$\begin{pmatrix} -0.43 \\ -0.43 \\ 0.79 \end{pmatrix}$
Ca ₂ GeO ₄ *	$I4_1/acd$	6.42	$\begin{bmatrix} 5.18 & -0.85 & -1.90 \\ -0.85 & 5.18 & -1.90 \\ -1.90 & -1.90 & 5.35 \end{bmatrix}$	2.11	$\begin{pmatrix} 0.54 \\ 0.54 \\ 0.64 \end{pmatrix}$	6.02	$\begin{pmatrix} 0.71 \\ -0.71 \\ -0.00 \end{pmatrix}$	7.58	$\begin{pmatrix} -0.45 \\ -0.45 \\ 0.77 \end{pmatrix}$

Table S2. Bulk compressibility, β , elastic compliance matrix, $\mathbf{s}$ and eigenvalues, $s_L/s_M/s_H$, and corresponding normalised eigenvectors, $\hat{s}_L/\hat{s}_M/\hat{s}_H$, of $\mathbf{s}$ computed by DFT for all structures. All values given with units of TPa⁻¹. *These structures had a fixed to match that of relaxed $I4_1/acd$ Ca₂MnO₄ but with c and the internal coordinates free to relax.

Bond Stiffness (eV/Å ²)		
①	②	③
Ge-O	Ge-O	Ca-O
1.07	1.09	0.67
	⑤	⑥
	Ca-O	Ca-O
	-0.14	0.07

Bond Extensions (Å) ($\Delta\theta = +1^\circ$)		
①	②	③
Ge-O	Ge-O	Ca-O
+0.0000	+0.0003	+0.0003
④	⑤	⑥
Ca-O	Ca-O	Ca-O
-0.0237	+0.0248	-0.0004

Table S3. Bond stiffness data for bonds equivalent to those labelled in Figure 5a but for relaxed $I4/mmm$ Ca_2GeO_4 . No bond 4 stiffness is shown since in $I4/mmm$ 4 and 5 are equivalent by symmetry. Bond extension data shows the effect on bonds of introducing a 1° fixed frozen rotation angle into the $I4/mmm$ structure, and hence transforming to a child $I4_1/acd$ phase. Bond extensions are in some cases an order of magnitude smaller than in fully relaxed $I4_1/acd$ since the shorter Ca-epitaxial O bond is not stiff enough to mediate the strain coupling mechanism. The effect of the phase transition upon elastic anisotropy is thus continuous in this case with the order parameter (the frozen rotation angle) but will seem drastic if these small distortions are not realised over a significant temperature range.

Ca_2MnO_4			Ca_2GeO_4		
freq (cm ⁻¹) $I4/mmm$ irrep			freq (cm ⁻¹) $I4/mmm$ irrep		
1	-0.032515	GM3- P2	1	-0.028411	GM5- P5
2	-0.02288	GM5- P5	2	-0.028411	GM5- P5
3	-0.02288	GM5- P5	3	0.098514	GM3- P2
4	49.081805	X3+ LD5 X3-	4	43.164015	X3+ LD5 X3-
5	49.081805	X3+ LD5 X3-	5	43.164015	X3+ LD5 X3-
6	57.180099	X4+ LD5	6	55.736129	X4+ LD5
7	57.180099	X4+ LD5	7	55.736129	X4+ LD5
8	77.82673	M5+ GM5- P5	8	69.982469	M5+ GM5- P5
9	77.82673	M5+ GM5- P5	9	69.982469	M5+ GM5- P5
10	81.99501	X3+ LD5 X3-	10	79.099242	X3+ LD5 X3-
11	81.99501	X3+ LD5 X3-	11	79.099242	X3+ LD5 X3-
12	95.96236	M5- GM5+ P5	12	91.36391	M5- GM5+ P5
13	95.96236	M5- GM5+ P5	13	91.36391	M5- GM5+ P5
14	98.317913	M5- P5	14	95.472284	M5- P5
15	98.317913	M5- P5	15	95.472284	M5- P5

Table S4. Phonon frequencies of the softest modes in $I4_1/acd$ phases of Ca_2MnO_4 and Ca_2GeO_4 with a fixed to match that of relaxed $I4_1/acd$ Ca_2MnO_4 and c free to relax (and therefore equivalent to the biaxial pressure correction applied to Ca_2GeO_4 in the calculations using the QHA). Phonons were computed in both structures using the finite differences method in a single unit cell (and therefore taken at the Γ -point of the phonon Brillouin zone). Labels indicate irreps in the $I4/mmm$ parent structure with which modes have a non-zero overlap when the phonon eigenvectors are projected onto these irreps.

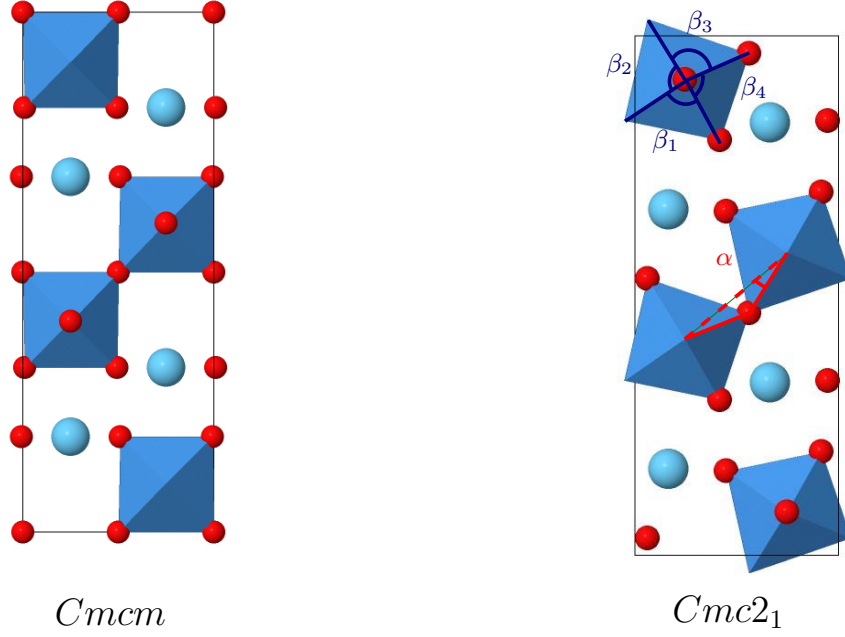


Figure S2. Fully relaxed high symmetry $Cmc m$ and low symmetry (NTE) $Cmc2_1$ $LaTaO_4$ structures. The ABX_4 class of layered perovskites involve layering of BX_6 octahedra along the perovskite $[110]$ direction. The aristotype $Cmc m$ ABX_4 structure does have a degree of frozen structural freedom which could couple b (the experimentally observed NTE direction in daughter phase $Cmc2_1$) to c because the tetragonal cell means that octahedra are not required by symmetry to have all 90° angles in the $b-c$ plane, and in fact DFT calculations find two different near- 90° Ta-O angles in $LaTaO_4$. In the daughter $Cmc2_1$ phase, an octahedral rotation about a (by an angle we will call α) leads to a greater degree of Γ_1^+ structural freedom in the $b-c$ plane but the BO_6 octahedra themselves are further distorted to give four different O-B-O angles lying in the $b-c$ plane in each octahedra (we will label these angles β_1 through β_4). A cations are also not constrained to high-symmetry positions along any direction in the $b-c$ plane. This means that combined changes in the rotation angles α and β_{1-4} (under the condition of course that $\sum \beta_i = 360^\circ$) allow b to respond to changes in c , or visa versa, without extending any *stiff* B-O or A-O bonds and without introducing any additional symmetry breaking distortions.

System	Ca_2MnO_4	$LaTaO_4$	Sr_2MgWO_6
Plane-wave cut-off energy (eV)	1400	800	800
Monkhorst-Pack k-point grid	$7 \times 7 \times 2$	$12 \times 3 \times 8$	$8 \times 8 \times 8$
Reference Phase	$I4/mmm$	$Cmc m$	$Fm\bar{3}m$
MP grid includes Γ -point?	X	X	X
Relaxation Criteria			
$ \Delta E _{max}$ (meV/atom)	1.0	1.0	1.0
$ F _{max}$ (meV/Å)	0.1	1.0	1.0
$ S _{max}$ (MPa)	10	10	10
pseudopotentials	NC	US	US

Table S5. Calculation parameters used for different chemistries. For the lattice parameters of the reference phase for each k-point grid, see Table S1. Generally, spin polarisation was not considered, however, spin polarised calculations on $I4/mmm$ and $I4_1/acd$ Ca_2MnO_4 used a density mixing scheme with no fixed occupancy for SCF minimisation with mix charge amplitude of 0.2, a mix spin amplitude of 0.4 and with 60% additional electronic bands. Each Mn ion was given an initial spin state of ± 2.0 [34] which was not constrained during the SCF and geometry optimisation procedures. Calculations were performed on phases with an initial checkerboard arrangement of spins in-plane with antiferromagnetic alignment between equivalent layers to match the experimental spin ordering measured by Cox [34].

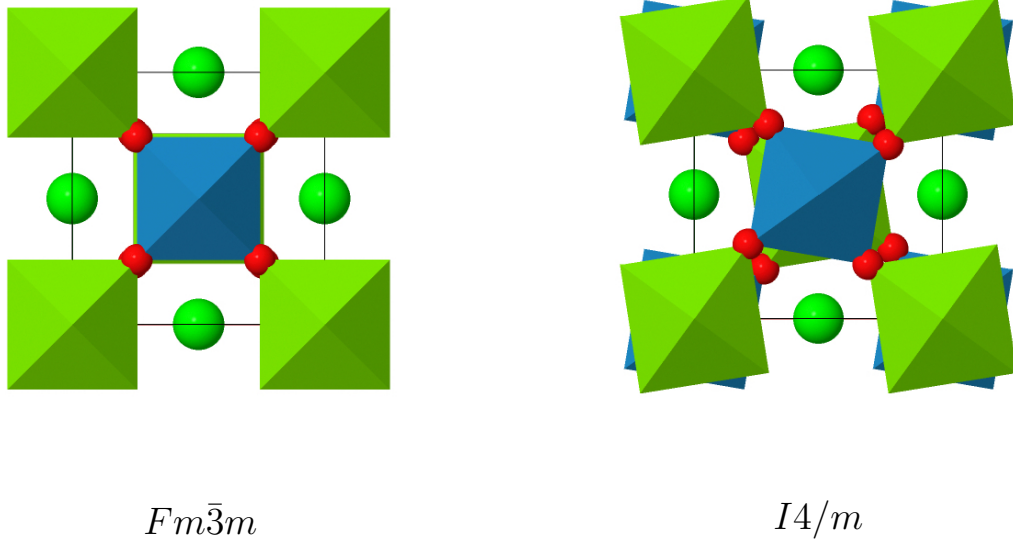


Figure S3. Fully relaxed high symmetry $Fm\bar{3}m$ and low symmetry (NTE) $I4/m$ Sr_2MgWO_6 structures. Double perovskites, of general formula $\text{A}_2\text{BB}'\text{O}_6$ consist of a three-dimensional checkerboard lattice of BO_6 and $\text{B}'\text{O}_6$ octahedra, with A cations filling the interstitial sites. In $Fm\bar{3}m$ Sr_2MgWO_6 , there is a degree of freedom in the Wyckoff position of bridging O ions which corner-link the MgO_6 and WO_6 octahedra not present in $Pm\bar{3}m$ ABO_3 perovskites. With the freezing in of anti-phase octahedral rotations, the introduction of a symmetry breaking distortion to transform the material to the $I4/m$ phase, the position of O ions along the c direction (apical O ions) becomes decoupled from the position of O ions in the plane of rotation (equatorial O ions). There are therefore independent degrees of structural freedom in the a - b plane (the positions of equatorial Os the octahedral rotation angle) and along the c -direction, the positions of apical O ions. Both of these independent degrees of structural freedom appear in the Γ_1^+ irrep and thus may couple a to c .

Ca	NC	3 2.0 9 10 12 30N:40N:31N:32N(qc=6)
Ge	NC	3 1.8 28 32 38 40N:41N:32N1.5(qc=5,q2=10)
O	NC	1 1.2 23 26 31 20N:21L(qc=9)
Mn	NC	3 1.3 32 37 43 30N:40N:31N:32NN(qc=10.5)
Sr	US	3 2.0 2.0 1.2 6 8 9 40U:50U:41:42
Mg	US	2 1.6 2 1.4 6 7 8 30NH:21U:31UU:32LGG(qc=4.5)
W	US	3 2.1 2.1 2.1 8 9 10 50U:60U:51:52
O	US	2 1.0 1.3 0.7 13 16 18 20:21(qc=7)
La	US	2 2.3 2.3 1.4 4 5 6 50U:60U:51:52(qc=4.5)
Ta	US	3 2.1 2.1 2.1 8 9 10 50U:60U:51:52

Table S6. Pseudopotential strings used in all DFT calculations, generated on-the-fly within CASTEP version 16.0, with the pseudopotential type: norm-conserving (NC) vs ultra-soft (US), indicated.

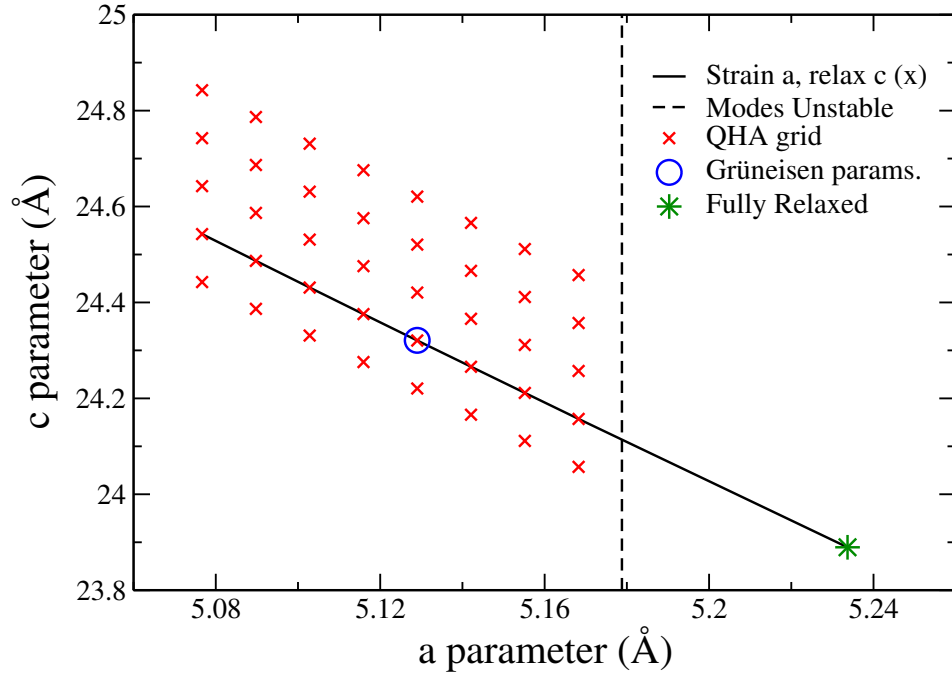


Figure S4. Relaxed Ca_2GeO_4 $I4_1/acd$ structures used for QHA calculations. Lattice parameters of fully relaxed $I4_1/acd$ Ca_2GeO_4 are shown, as are lattice parameters of the structure about which γ_1^i and γ_3^i Grüneisen Parameters were computed in Figure 2 of the main paper. The line showing how *c* relaxes in response to different fixed *a* is shown and labeled *x*. A dashed line is sketched to give an indication of the value of *a* (with *c* free to relax) at which the frequency of the softest optical phonon becomes imaginary. All structures shown to the left of this line have all real phonon frequencies.