

The Origin of Uniaxial Negative Thermal Expansion in Layered Perovskites

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13 ABSTRACT

14 Why is it that ABO_3 perovskites generally do not exhibit negative thermal expansion
15 (NTE) over a wide temperature range, whereas layered perovskites of the same chemical
16 family often do? It is generally accepted that there are two key ingredients that determine
17 the extent of NTE: the presence of soft phonon modes that drive contraction (have negative
18 Grüneisen parameters); and anisotropic elastic compliance that predisposes the material
19 to the deformations required for NTE along a specific axis. This difference in thermal
20 expansion properties is surprising since both ABO_3 and layered perovskites often possess
21 these ingredients in equal measure in their high-symmetry phases. Using first principles
22 calculations and symmetry analysis, we show that in layered perovskites there is a significant
23 enhancement of elastic anisotropy due to symmetry breaking that results from the combined
24 effect of layering and condensed rotations of oxygen octahedra. This feature, unique to
25 layered perovskites of certain symmetry, is what allows uniaxial NTE to persist over a large
26 temperature range. This fundamental insight means that symmetry and the elastic tensor
27 can be used as descriptors in high-throughput screening and to direct materials design.

28 INTRODUCTION

29 Due to their unusual lattice couplings and dynamics, there has been renewed recent inter-
30 est in tuning the properties of layered materials based on the perovskite structure, including
31 proper [1, 2] and improper [3–5] ferroelectricity, the electrocaloric effect [6], and colossal
32 magnetoresistance [7]. Unprecedented control of ferroelectricity in layered perovskites has
33 been achieved, for example, by engineering non-polar lattice instabilities that can combine
34 in the ground state to produce a net polarisation. This approach to designing improper
35 ferroelectrics has been particularly successful when the property in question arises solely
36 from the ground state structure, rather than any lattice or spin dynamics, and the relevant
37 lattice couplings can be elucidated from symmetry analysis and static first principles calcu-
38 lations [3, 4]. However, many of the physical properties listed above rely on excitations of
39 the ground state structure and are mediated by phonon interactions and electron-phonon
40 couplings. We seek here to understand one of the most obvious consequences of phonon
41 couplings, namely thermal expansion, and how it may be tuned in layered perovskites to

42 achieve zero or even negative thermal expansion (NTE).

43 While elastically soft organometallic framework materials exhibiting NTE are becoming
44 increasingly common, the number of elastically hard ionic solids exhibiting this property
45 remains few. The prototypical NTE ceramic is zirconium tungstate (ZrW_2O_8) which displays
46 a large, isotropic NTE of -9ppm/K over a wide temperature range of $0.3 - 1050\text{ K}$ [8]. Since
47 the discovery of NTE in ZrW_2O_8 , a small number of NTE materials have been identified,
48 such as LiAlSiO_4 [9], $(\text{Zn,Cd})(\text{CN})_2$ [10–12] and $\text{Mn}_3(\text{Co}(\text{CN})_6)_2$ [13], which all possess
49 flexible network structures [14]. In many of these materials, NTE has been explained using
50 the theory of rigid unit modes (RUMs) [15] whereby the contraction of the material is driven
51 by soft vibrations of approximately rigid polyhedral units. With increasing temperature, the
52 amplitudes of these vibrations increase and all units are drawn closer together through an
53 effect known as the tension mechanism [16]. Active modes that drive NTE have negative
54 Grüneisen parameters γ , which quantify how mode frequencies change with cell volume and,
55 thereby, the contribution of each mode to the overall thermal expansion or contraction.

56 Surprisingly, although bulk ABO_3 perovskites are often proposed as a textbook example
57 of a material containing a large number of RUMs, NTE over a significant temperature
58 range in these systems where octahedral rotations are the dominant mechanism is extremely
59 rare. Conversely, we have recently highlighted the occurrence of uniaxial NTE in layered
60 perovskite Ruddlesden–Popper (RP) oxides, $\text{A}_{n+1}\text{B}_n\text{X}_{3n+1}$. NTE in the $n=2$ (RP2) system,
61 for example, appears to be linked to not just a particular space group symmetry ($Acaa$),
62 but also proximity to a thermodynamically competing phase of specific symmetry [17]. This
63 understanding allowed us to tune the chemistry of the RP2 solid solution $\text{Ca}_{3-3x}\text{Sr}_{3x}\text{Mn}_2\text{O}_7$
64 in the phase diagram space to precisely control its NTE [18]. Very recently NTE has also been
65 reported in the $n=1$ (RP1) compound Sr_2RhO_4 [19]. Examination of the literature reveals
66 that Ca_2MnO_4 [20], Sr_2RhO_4 [21] and Sr_2IrO_4 [22], which all crystallize in an equivalent
67 $I4_1/acd$ phase and exhibit evidence of uniaxial NTE (although the significance of this is not
68 commented on). While NTE in Sr_2RhO_4 and Ca_2MnO_4 has been ascribed to static changes in
69 octahedral rotation angle [19] our explanation for NTE in the RP2 phase directly implicates
70 specific soft phonon modes of RUM like character with negative Grüneisen parameters. This
71 understanding from prior publications leaves us with the question: (i) *If NTE originates from*
72 *octahedral rotations of RUM character, why is similar NTE not observed in equivalent bulk*
73 *ABO_3 perovskite phases?* Further to this, if phonons are soft and active in child NTE RP

74 phases and given that the symmetry-breaking structural distortions are so small, it is not
 75 obvious why these same phonons should not be soft and drive NTE in the parent phase, and
 76 yet NTE has only been previously reported in RP phases with condensed rotations. This
 77 leads to a second question: (ii) *Why can small changes in symmetry have a large effect upon*
 78 *the sign and magnitude of thermal expansion?*

79 To answer these questions, we begin by studying the RP oxide $A_{n+1}B_nO_{3n+1}$ with $n=1$
 80 (Figure 1a), which is the most structurally distinct phase from the perovskite (i.e. $n=\infty$).
 81 We find that while phonon modes with negative Grüneisen parameters associated with a
 82 phase competition between an NTE and PTE phase are important, crucially, it is the large
 83 off-diagonal elastic constant elements particular to the NTE phase that enhances NTE.
 84 These off-diagonal elements have the effect of cross-coupling PTE in the biaxial direction to
 85 NTE in the uniaxial direction, and only by considering these off-diagonal elements can the
 86 NTE observed experimentally be reproduced by first principles calculations over the whole
 87 temperature range. We show that the switching on and off of large off-diagonal elements
 88 in the elastic constant tensor at a symmetry changing phase transition not only explains
 89 the pronounced NTE in phases of these RP materials with frozen octahedral rotations,
 90 but is a general feature of a large number of other related layered perovskites. We show
 91 through symmetry arguments that the combined symmetry-breaking from the layering and
 92 condensed octahedral distortions gives rise to the strong strain coupling responsible for the
 93 large elastic anisotropy. As elastic tensors are more readily calculated than phonons and
 94 Grüneisen parameters, we suggest that this is a productive route for computational screening
 95 and data mining of NTE materials.

96 RESULTS

97 Our calculations (Figure 1b) performed within the quasi-harmonic approximation (QHA)
 98 on Ca_2GeO_4 show uniaxial NTE over the full simulated temperature range with close agree-
 99 ment of the c lattice strain to neutron diffraction measurements of Ca_2MnO_4 , especially at
 100 low temperatures. We simulated Ge in place of Mn for computational ease because Ge^{4+} and
 101 Mn^{4+} are known to have equal ionic radii [23] and spin-polarised calculations on Mn-based
 102 systems were extremely expensive; making lattice dynamics calculations over the full Brill-
 103 ouin zone for multiple structures unfeasible. Figure 1c shows that the elastic compliances

104 and lowest-frequency Γ -point phonons have very close agreement between equivalent phases
 105 of Ca_2MnO_4 and Ca_2GeO_4 . We also point out that the softest phonon modes retain the
 106 same eigenvector character between the different structures since this was used as a criterion
 107 to match them. The Ca_2GeO_4 phase was simulated with a 4.3 GPa biaxial pressure to fix
 108 the in-plane lattice parameter to that of relaxed Ca_2MnO_4 - see Methods for details.

109 Simulations predict a maximum negative coefficient of linear thermal expansion (CLTE)
 110 along the c axis, α_3 , of -4.7 ppm/K compared to -6 ppm/K in experiment. There is close
 111 agreement between predicted and observed changes in a and the frozen octahedral rotation
 112 angle θ , which was extracted from Rietveld refinements performed against neutron powder
 113 diffraction data. The small disparity between simulation and experiment, which becomes
 114 greater at higher temperatures, is likely the result of higher-order anharmonic interactions
 115 that are not included in the QHA.

116 In a tetragonal material, a useful measure for thermal expansion is the anisotropic mode
 117 Grüneisen parameter, γ_q^i , describing the change in frequency, ω^i , of phonon i with changing
 118 cell axis q with all other axes fixed:

$$\gamma_q^i = -\frac{q}{\omega^i} \left(\frac{\partial \omega^i}{\partial q} \right) = -\frac{\partial \ln(\omega^i)}{\partial \ln(q)}, \quad (1)$$

119 the subscript, $q=(1,2,3)$, corresponds to the directions of the (a,b,c) unit cell vectors
 120 respectively.

121 Analysis of the PDOS (Figure 2) of an example structure on the QHA grid (close to the
 122 minimum of the enthalpy landscape), shows a number of low frequency Γ -point phonons
 123 with negative Grüneisen parameters, γ_3 , corresponding to irreducible representations (*ir-*
 124 *reps*) with octahedral tilt character. When projected onto an $I4/mmm$ basis (Wyckoff
 125 Positions: Ge:(0,0,0), Ca:(0,0,0.64554), O:(0,0.5,0), O:(0,0,0.16268)), these modes overlap
 126 strongly with X_3^+ and P_5 irreps, which lie on the same phonon branches. In the unstressed
 127 Ca_2GeO_4 , the softest mode (X_3^+) is unstable and allowing the structure to fully relax with
 128 this mode condensed leads to a lower symmetry $Pbca$ child structure with $\Delta c = -0.47$ Å,
 129 thereby indicating in static calculations that the X_3^+ tilt reduces c . This phase competition
 130 is reminiscent of that which we identify as driving the NTE in the RP2 phase where the mag-
 131 nitude of NTE measured experimentally in $\text{Ca}_{3-x}\text{Sr}_x\text{Mn}_2\text{O}_7$ correlated with the computed
 132 imaginary frequency of an unstable octahedral tilt mode [18].

133 Unlike in isotropic materials, in tetragonal structures the CLTE is dependent upon the

134 effects of phonon modes upon both independent cell axes. Considering the tetragonal cell
 135 to retain shape (assuming no shearing) the CLTEs along the a and c axes are [24]:

$$\alpha_1(T) = \sum_i C_v^i(T) \left[(s_{11} + s_{12}) \gamma_1^i + s_{13} \gamma_3^i \right] \quad (2a)$$

$$\alpha_3(T) = \sum_i C_v^i(T) \left[2s_{13} \gamma_1^i + s_{33} \gamma_3^i \right] \quad (2b)$$

136 In Equations 2a-2b, $C_v^i(T)$ is the contribution of mode i to the specific heat capacity
 137 at temperature T . s_{pq} is a component of a 3×3 matrix $\mathbf{s}$ and represents the normal elastic
 138 compliance of axis p in response to the normal strain of axis q . $\mathbf{s}$ is, in principle, temperature
 139 dependent (although ignored in this work). We must stress that the compliance matrix $\mathbf{s}$
 140 is not the same as the elastic compliance tensor, which is rank-4 since it relates stress and
 141 strain, both rank-2 quantities. Use of the 3×3 matrix $\mathbf{s}$ relies on all shear stresses and
 142 strains being equal to 0 (enforcing at least orthorhombic symmetry) and therefore using
 143 3-dimensional vectors within Voigt notation.

144 For clarity of discussion we generalise Equations 2a and 2b to the orthorhombic case (still
 145 ignoring shear strains):

$$\alpha_p(T) = \sum_q s_{pq} \left\{ \sum_i C_v^i(T) \gamma_q^i \right\} = \sum_q s_{pq} \Phi_q(T), \quad (3)$$

146 where $\alpha_p(T)$ and $\Phi_q(T)$ are respectively components of $\boldsymbol{\alpha}(T)$, the thermal expansion
 147 vector and $\boldsymbol{\Phi}(T)$, a vector representing the dynamic driving force for thermal expansion
 148 from all modes. Equation 3 shows that $\boldsymbol{\alpha}(T)$ is given by the action of the matrix of elastic
 149 compliances $\mathbf{s}$ on the vector $\boldsymbol{\Phi}(T)$. The direction of $\boldsymbol{\alpha}(T)$ is thus dependent upon both
 150 the anisotropic thermodynamic driving force for thermal expansion and the elastic coupling
 151 between axes. In a material with largely decoupled axes (small off-diagonal s_{pq} components)
 152 the direction of $\boldsymbol{\alpha}(T)$ would track $\boldsymbol{\Phi}(T)$. However, in an anisotropic material where off-
 153 diagonal components s_{pq} are large, $\boldsymbol{\alpha}(T)$ may be rotated by the compliance tensor in the
 154 plane of a and c normal lattice strains towards a region corresponding to enhanced NTE (as
 155 illustrated in Figure 3a).

156 Figures 3b-3c display the $\alpha_1(T)$ and $\alpha_3(T)$ CLTEs, computed by numerical derivative
 157 with respect to T , for the Ca_2GeO_4 QHA data and fitted Ca_2MnO_4 neutron data shown

Figure 1b. The dynamic contribution to thermal expansion, $\Phi_{I4_1/acd}(T)$ is extracted from $\alpha(T)$ for the Ca_2GeO_4 QHA calculation by transforming $\alpha(T)$ by $\mathbf{s}_{I4_1/acd}^{-1}$ (that is to say by inverting Equation 3).

To highlight the importance of the elastic compliance matrix to thermal expansion, we may perform a computational thought experiment whereby we predict the $\alpha(T)$ that would arise if the same phonons were present in different related structures. $\alpha(T)$ for other structures is predicted by transforming $\Phi_{I4_1/acd}(T)$ by $\mathbf{s}$ of that phase; thereby assuming that these structures have the same dynamic phonons as $I4_1/acd$ Ca_2GeO_4 and that only the elastic constants have changed. Although qualitatively we may expect related structures to have similar lattice dynamics, it would be naïve to assume that $\Phi(T)$ could be transferred directly between materials to quantitatively predict thermal expansion. Instead this experiment allows us to isolate the effects of different $\mathbf{s}$ matrices on $\alpha(T)$.

We first imagine a fictitious isotropic structure with no coupling between different lattice directions (i.e. $s_{13}=s_{12}=0$). We then fix $s_{11}=s_{33}=\beta$, the bulk compressibility (the reciprocal of the Reuss bulk modulus) of $I4_1/acd$ Ca_2GeO_4 , and transform $\Phi(T)$ as in Equation 3. NTE is predicted along c only up to 20 K, above which there is PTE. Figure 2 showed that at frequencies, $\omega^i > 150 \text{ cm}^{-1}$, modes which form a large weight of the overall PDOS have small $\gamma_3^i > 0$. As these modes populate with increasing T , they outweigh the contribution from the few soft $\gamma_3^i < 0$ tilts. Whereas along c slight NTE and later moderate PTE are predicted, large PTE along a is predicted at all but the lowest temperatures. This gives an idea of the thermal expansion which would be predicted if there was no effect from $I4_1/acd$ Ca_2GeO_4 's elastic constants.

Applying now to $\Phi(T)$ the matrices, $\mathbf{s}$, computed from DFT of various $\text{Ca}_{n+1}\text{Ge}_n\text{O}_{3n+1}$ structures, Figure 3c predicts NTE over a larger temperature range using every $\mathbf{s}$. This shows that the large Φ component along the a axis is transformed to give NTE along c via the s_{13} off-diagonal terms. As expected, the $\mathbf{s}$ of $I4_1/acd$ Ca_2GeO_4 predicts the most negative α_3 . On the other hand, taking the $\mathbf{s}$ of bulk perovskite CaGeO_3 produces NTE of almost an order of magnitude less and only at much lower T . Perhaps more surprisingly, the $I4/mmm$ Ca_2GeO_4 compliance matrix too predicts NTE over a much narrower temperature range and with a reduced magnitude, despite having a similar structure to $I4_1/acd$ with only a slight difference in the phase symmetry.

To understand how small changes in symmetry can lead to a large change in thermal

expansion behaviour, the compliance matrices $\mathbf{s}$ are plotted in Figures 4a-4d as quadratic forms projected on the 2-dimensional plane of tetragonal deformations. The principal directions (eigenvectors) associated with the highest, s_H , and lowest, s_L , principal components of $\mathbf{s}$ are also plotted and labelled by the corresponding principal values. $I4_1/acd$ Ca_2GeO_4 (Figure 4d) has a strongly anisotropic $\mathbf{s}$ with the eigenvector corresponding to s_H lying in a strain direction that corresponds to cooperative expansion of a and contraction of c . Although other structures have their most compliant eigenvector in a similar direction, it is clear from the eigenvalue s_H that this direction is particularly compliant in $I4_1/acd$ Ca_2GeO_4 , despite s_L and the bulk compressibility, β , being similar to $I4/mmm$ Ca_2GeO_4 . Values of s_H and β are presented alongside experimental CLTE measurements for NTE phases for all structures discussed in Table I.

The link between compliant cooperative deformations and uniaxial NTE may be extended to other layered perovskite systems. Within the RP family, the $Acaa$ phase in the $n=2$ series also shows NTE experimentally [17, 18], and interestingly consists of an analogous frozen octahedral rotation as in the $n=1$ $I4_1/acd$. It should be noted that the unrelated ferroelectric $Cmc2_1$ phase of $\text{Ca}_3\text{Ti}_2\text{O}_7$ has also been predicted to show NTE when under sufficient pressure [25], but is beyond the scope of the current study. We find that $\text{Ca}_3\text{Ge}_2\text{O}_7$ possesses a similarly compliant eigenvector to Ca_2GeO_4 when compared to its parent $I4/mmm$ structure. Considering two more layered perovskite families with related uniaxial NTE: the tetragonal $I4/m$ phase of the double perovskite Sr_2MgWO_6 (NTE along the c axis between 15 – 300 K [26]) and the orthorhombic $Cmc2_1$ phase of LaTaO_4 , belonging to the $n=2$ member of the $\text{A}_n\text{B}_n\text{O}_{3n+2}$ family, (NTE along the b axis normal to the layering 373 – 573 K [27]), we again find more compliant eigenvectors as compared to higher symmetry parent phases of the same structure: $Fm\bar{3}m$ Sr_2MgWO_6 and $Cmcm$ LaTaO_4 respectively. Structural data of all relaxed structures may be found in Table S1 and the full elastic compliance matrices and eigenvectors in Table S2.

DISCUSSION

Uniaxial NTE predicted in $I4_1/acd$ Ca_2GeO_4 arises due to soft phonon modes with octahedral tilt character that have $\gamma_1 > 0$ and $\gamma_3 < 0$ which drive the contraction of the c axis with increasing T thanks to the large s_{13} components in the elastic compliance matrix.

Equations 2a-2b imply that a thermodynamic driving force is essential for NTE, and the Grüneisen parameters computed for Γ -point phonons in Figure 2 suggest that the softest modes provide this. The importance of anisotropic elasticity becomes evident in Figure 3c where we see that if the same lattice dynamics coexisted with an elastic compliance matrix other than that for $I4_1/acd$ Ca_2GeO_4 , then uniaxial NTE would not be predicted over such a wide temperature range. The range and magnitude of NTE is highly-dependent upon the level of coupling between the a and c axes. That our results show good quantitative agreement with experimental measurements of analogous Ca_2MnO_4 suggests that at low temperatures, the QHA captures most of the physics required to understand NTE in these materials.

The result that an anisotropic elastic compliance matrix is important for uniaxial NTE echoes theories first suggested many decades ago but with little microstructural analysis. Equations 2a-2b, as originally formulated by Grüneisen and Goens [28] utilise off-diagonal components to $\mathbf{s}$ and Munn [29] used these equations to compare the thermodynamic and elastic driving force for anisotropic thermal expansion in elemental materials based upon experimental observation. More recently, anisotropic NTE has been reported in metal-organic framework structures (MOFs)[30, 31]. In these materials with large open pores, which are typified by $\text{Ag}_3[\text{Co}(\text{CN})_6]$ cyanide “wine-rack structures”, large off-diagonal elements in the elastic compliance matrix seem to be responsible both for the observed NTE and the observed negative linear compressibility under hydrostatic pressure [32]. DFT calculations [33] of $\text{Ag}_3[\text{Co}(\text{CN})_6]$ uncover atomic vibrations with highly anisotropic Grüneisen parameters and a large value of s_{13} leading to a massive compliance eigenvalue, s_H , of 79 TPa^{-1} in a uniaxial NTE direction. Although anisotropy has been linked to NTE in these MOF materials and a microstructural explanation for the elastic anisotropy has been found, these MOFs are structurally very different to the ionic compounds of the present investigation.

As well as discovering the origin of uniaxial NTE in Ca_2MnO_4 , this study set out to answer two more fundamental questions: (i) *If NTE originates from octahedral rotations of RUM character, why is similar NTE not observed in equivalent bulk ABO_3 perovskite phases?* and also (ii) *Why can small changes in symmetry have a large effect upon the sign and magnitude of thermal expansion?*

It appears that the answer to both of these questions is: “because the layered NTE phase is more elastically anisotropic”. Considering the $\text{Ca}_{n+1}\text{Ge}_n\text{O}_{3n+1}$ and Sr_2MgWO_6

systems in Table I, we see that the bulk compressibility, β , between all high- and low-symmetry structures are very similar. Furthermore the anisotropy ratio, κ , of the compliance matrix remains approximately constant across these high-symmetry phases. The effect of the phase transition in all systems therefore is to enhance the value of κ and in fact the measure of anisotropy in the NTE phase correlates with the magnitude of NTE measured experimentally. The low-symmetry RP phases (that experimentally exhibit NTE) similarly have increased values of κ compared to the equivalent CaGeO_3 phase. Although structurally a very different system, an enhancement in κ is also simulated in LaTaO_4 across the transition between high- and low-symmetry structures and this system has both the largest calculated elastic anisotropy and the largest reported uniaxial NTE. That such a drastic change in elastic anisotropy accompanies phase transitions between a high-symmetry parent and a uniaxial NTE child phase has not been discussed previously to the best of our knowledge.

This correlation between uniaxial NTE in certain low-symmetry layered perovskite phases and anisotropic compliance is supported by the the computational experiment performed in Figures 3b-3c on the Ca_2GeO_4 system. *Even if* the same octahedral tilts were active in the parent $I4/mmm$ phase as in $I4_1/acd$ Ca_2GeO_4 , or in the analogous $I4/mcm$ CaGeO_3 phase (characterised like $I4_1/acd$ Ca_2GeO_4 by a frozen anti-phase rotation about c), in both phases NTE is predicted over a more narrow temperature range than if the $I4_1/acd$ Ca_2GeO_4 compliance matrix were used.

For an explanation of why certain layered perovskite systems have greater elastic anisotropy, we need to consider the atomic structure at the layer interface. All of the NTE structures investigated have at least two internal degrees of atomic structural freedom: one from the atoms involved in the layering along the axis perpendicular to the layers (the NTE axis) and another from symmetry breaking due to a frozen octahedral rotation — which allows movement along at least one other axis (a PTE axis). Therefore if these degrees of freedom, which are necessarily of the Γ_1^+ irrep, can couple to each other and to the strain of the axis along which they exist, then they facilitate a *strain*– Γ_1^+ –*strain* coupling.

This effect is illustrated for an $I4_1/acd$ A_2BO_4 phase in Figure 5a. As a result of the inherent symmetry-breaking caused by the inclusion of the AO layer, A and apical O ions have a degree of freedom along the c axis. This leads to the *rumpling* observed in the AO layer of RP phases. Furthermore, due to the frozen octahedral rotation, there is a degree of freedom in the a – b plane, represented by the rotation angle θ . Based upon the calculations of

284 bond stiffness in $I4_1/acd$ Ca_2GeO_4 , chemical bonds are labelled as rods or springs depending
 285 on their relative stiffness. Assuming rods remain perfectly stiff and only bonds represented
 286 as springs may change length, one can picture how a compressive strain Δa could induce
 287 a tensile strain Δc : The compression Δa necessarily leads to an increase in rotation angle
 288 $\Delta\theta$ which in turn pushes the A cation upwards along c and extends the c -axis by Δc . Since
 289 none of these changes are required by symmetry to deform *stiff* metal–oxygen bonds, these
 290 cooperative a and c deformations are low in energy.

291 This coupling leads to a correlation between a , θ and c reported in prior studies on $I4_1/acd$
 292 A_2BO_4 rotation phases [19–21] which we also observe in both simulation and experiment
 293 (inset Figure 1b). That the system is compliant to coupled changes in a , θ and c explains
 294 why θ and c temperature behaviour is correlated but does not imply, as has been previously
 295 asserted, that it is a change in θ which *causes* uniaxial NTE.

296 In contrast to $I4_1/acd$ A_2BO_4 , $I4/mcm$ ABO_3 (Figure 5b) does not allow the same strong
 297 a – Γ_1^+ – c coupling. Although the frozen anti-phase octahedral rotation does create an in-plane
 298 degree of freedom in the rotation angle, there is no internal atomic freedom along c for this
 299 to couple to. This is because without the symmetry breaking caused by the rock salt layer,
 300 A cations are fixed to c coordinates half way between neighbouring octahedra. There is
 301 also no way to strain c without stretching *stiff* B–O bonds. One might therefore speculate
 302 whether an ABO_3 phase with frozen in-plane rotations *and* tilts along c could exhibit strong
 303 a – c coupling and hence anisotropic thermal expansion. The problem would then be that
 304 with frozen tilts along the c axis, active tilts become unfavourable and there would be little
 305 thermodynamic driving force for NTE. The layering in RP structures thus breaks structural
 306 symmetry and creates internal degrees of freedom along the perpendicular axis before any
 307 octahedral distortions have condensed.

308 We do not conclude that uniaxial NTE along c could not occur in an $I4/mcm$ ABO_3
 309 phase; soft octahedral tilts may provide a thermodynamic driving force and an increase in
 310 anisotropic elasticity is seen in the transition between $Pm\bar{3}m$ and $I4/mcm$ CaGeO_3 (Figures
 311 4a-4b). It merely seems that without the strong a – Γ_1^+ – c coupling of many layered structures,
 312 anisotropic compliance is not as great in $I4/mcm$ ABO_3 as in equivalent layered phases.

313 Considering now the NTE structures studied from other systems we can find similar
 314 symmetry arguments for compliance. Since the RP1 mechanism is specific to the AO/ BO_3
 315 interface of an A_2BO_4 structure with a frozen octahedral rotation, it may be easily gen-

316 eralised to $A_{n+1}B_nO_{3n+1}$ phases with a frozen rotation of higher n . $I4/m$ $A_2BB'O_6$ has
 317 a degree of structural freedom in the a - b plane from the frozen octahedral rotation, but,
 318 unlike $I4/mcm$ ABO_3 , also has a degree of freedom in the apical O positions along the c
 319 axis between dissimilar BO_6 and $B'O_6$ octahedra. Finally, the NTE $Cmc2_1$ $LaTaO_4$ phase
 320 has a frozen octahedral rotation about a . Further Γ_1^+ structural freedom in the b - c plane is
 321 achieved as the BO_6 octahedra themselves are distorted to give four different O-B-O angles
 322 and A cations are also not constrained to high-symmetry positions along any direction in the
 323 b - c plane. This means that combined changes in external and internal octahedral rotation
 324 angles allow b to respond to changes in c , or visa versa, without extending any *stiff* B-O or
 325 A-O bonds. Annotated structures illustrating these symmetry arguments may be found in
 326 Figures S1-S3.

327 Our ceramic systems differ significantly from the MOFs discussed previously [30–33]
 328 since they are not elastically soft, having bulk moduli that are orders of magnitude harder.
 329 Consequently the kind of connectivity required for a wine-rack type mechanism cannot be
 330 achieved in these systems. However, we demonstrate here that similar enhancements of off-
 331 diagonal elements in the elastic constants may be achieved through the systematic lowering
 332 of the symmetry of various layered perovskite structures by the condensation of octahedral
 333 rotations. Moreover, despite the reduced connectivity, internal coupling between different
 334 degrees of structural freedom creates intricate atomic mechanisms, reminiscent of MOF
 335 wine-rack structures, to facilitate high compliance to specific cooperative deformations.

336 We have explained how the combination of structural distortions, such as layering, and
 337 more subtle symmetry breaking distortions, such as the condensation of octahedral rotation
 338 modes, can control the elastic compliance matrix in perovskite-like structures. Although
 339 major structural distortions are necessarily a feature of material systems, control of sub-
 340 tle symmetry-breaking can have large influences on elasticity and hence on the thermal
 341 expansion properties. Figure 3a illustrates schematically how altering $\mathbf{s}$ could transform
 342 phonon-driven PTE, Φ , into uniaxial NTE, which corresponds to the case studied here at
 343 intermediate T. One can imagine alternative interesting scenarios, such as the transformation
 344 of phonon-driven bulk PTE into anisotropic volume NTE.

345 Anisotropic thermal expansion is controlled in a large part by the elastic compliance ma-
 346 trix which we have shown can be engineered to make NTE more favourable. This thus poses
 347 the possibility to screen for potential uniaxial NTE materials using the elastic compliance

348 matrix and space group symmetry as descriptors. Elastic constant tensors are straightfor-
349 ward to calculate using many first principles methods and avoids the need for more taxing
350 lattice dynamics computations.

351 We conclude that robust uniaxial NTE in layered perovskites is due to the combination
352 of soft RUMs and highly anisotropic compliance. Through symmetry analysis we have
353 found that this anisotropic compliance arises from coupling between internal degrees of
354 structural freedom and lattice axes. This coupling requires the combination of symmetry
355 breaking distortions both perpendicular and parallel to the axis of NTE and thus phases of
356 layered perovskites with condensed octahedral rotations are predisposed to uniaxial NTE.
357 Our results hence explain that while bulk ABO_3 perovskites often show soft phonon modes
358 with negative Grüneisen parameters, they tend not to exhibit pronounced NTE due to their
359 symmetry restricting a more isotropic compliance. Moreover, this observation may prove
360 useful to screen for potential NTE materials since one may initially compute only elastic
361 constant tensors.

362 METHODS

363 The thermal expansion of tetragonal $I4_1/acd$ Ca_2MnO_4 was determined from neutron
364 diffraction at ambient pressure and compared with density functional theory (DFT) cal-
365 culations within the quasi-harmonic approximation (QHA). To reduce computational cost,
366 most of the DFT calculations were in practice performed on Ca_2GeO_4 , justified by the fact
367 that Ge^{4+} and Mn^{4+} have equal ionic radii [23], and the observation that structural changes
368 across the magnetic transition are negligible, indicating that magnetism has little effect on
369 the thermal expansion. We note that magnetoelastic super-exchange interactions do, how-
370 ever, alter slightly the tetragonality of the cell, which we capture by applying a compressive
371 biaxial pressure of 4.3 GPa to Ca_2GeO_4 , chosen to match the a lattice parameter of relaxed
372 Ca_2MnO_4 with experimental spin ordering [34]. DFT calculations show the elastic compli-
373 ance and the lowest frequency phonon modes to have close quantitative agreement between
374 $I4_1/acd$ phases of relaxed Ca_2MnO_4 and Ca_2GeO_4 with this corrective biaxial pressure ap-
375 plied (these results can be found in Tables S2 and S4 respectively).

Experimental Details

Ca₂MnO₄ was prepared by grinding the starting materials (MnO₂, 99.99% and CaCO₃, 99.95%) together in the desired stoichiometry and calcining at 900 °C for 8 hours. The sample was then fired at 1200 °C for 4 × 24 hours with intermediate regrindings. The resulting phase pure polycrystalline sample was studied at the high resolution powder diffractometer (HRPD) at the ISIS neutron spallation source in the temperature range 4.75 – 400 K. The diffraction data from the high resolution back-scattering bank was fit in *TOPAS* using the Rietveld method to extract both the lattice parameters and the amplitude of the MnO₆ octahedral rotation as a function of temperature. The structure was found to crystallise in the space group *I*4₁/*acd* (basis {(-1 -1 0), (1 1 0), (0 0 2)} + (1/4 3/4 3/4) with respect to the *I*4/*mmm* parent setting described in the paper) and retain this symmetry down to the lowest temperature studied.

Fitting Procedure for Neutron Diffraction Data

Lattice parameters, $a(T)$ and $c(T)$, and the frozen octahedral rotation angle, $\theta(T)$, as measured from neutron diffraction data were fitted to the forms as a function of temperature, T :

$$a(T) = a_0 + \frac{k_1}{\exp\left(\frac{k_2}{T}\right) - 1}, \quad (4)$$

$$c(T) = c_0 - \frac{k_1^n}{\exp\left(\frac{k_2^n}{T}\right) - 1} + \frac{k_1^p}{\exp\left(\frac{k_2^p}{T}\right) - 1}, \quad (5)$$

$$\theta(T) = \left[\theta_0^2 - \frac{k_1^2}{\exp\left(\frac{k_2}{T}\right) - 1} \right]^{1/2}. \quad (6)$$

In the above, a_0 , c_0 , θ_0 and all k s are fitting parameters optimised to the dataset. Equations 4 and 5 are derived from Equation 3 and use Bose–Einstein distributions to represent, within the Einstein approximation, the population of a single $\gamma_1 > 0$ phonon or one $\gamma_3 < 0$ and another $\gamma_3 > 0$ phonon, respectively. Equation 6 is adapted from the derivation by Dove [35] using the Einstein approximation to assume population of phonons with a single frequency.

398 CASTEP version 7.03 [36], a plane-wave [37] DFT code, is used for all DFT and DFPT
 399 calculations. The PBEsol [38] exchange-correlation functional has been used since this func-
 400 tional has been developed specifically for ionic solids and has been shown in similar studies to
 401 accurately reproduce structural parameters [39]. In all $\text{Ca}_{n+1}\text{Ge}_n\text{O}_{3n+1}$ systems, a 1400 eV
 402 energy cutoff for the plane-wave basis is used with a $3\times$ denser ‘fine grid’ to represent
 403 norm-conserving pseudopotentials [40] (generated on-the-fly within CASTEP version 16.0).
 404 A $7\times 7\times 2$ Monkhorst–Pack [41] grid of k-points shifted away from the Γ -point is employed
 405 for calculations of Ca_2GeO_4 $I4/mmm$ symmetry structures and an appropriately scaled grid
 406 is used for other cells. All energies are converged within 1 meV/atom. In all structural
 407 relaxation calculations, forces have been relaxed to within 10^{-4} eV/Å and stresses within
 408 10 MPa. DFPT phonons were computed on a $4\times 4\times 1$ q-point grid for a $(\sqrt{2}\times\sqrt{2}\times 2)$ equiv-
 409 alent $I4/mmm$ supercell and this dynamical matrix was interpolated onto a $32\times 32\times 4$ grid
 410 to generate each PDOS. Calculation parameters for other chemistries may vary and have
 411 been tabulated, alongside all pseudopotential strings used, in Tables S5 and S6.

412 **The Quasi-Harmonic Approximation**

413 In the QHA, relaxed structures are found for a range of volumes and the harmonic phonon
 414 frequencies computed for each structure. Since $I4_1/acd$ Ca_2GeO_4 is tetragonal, the a and
 415 c lattice parameters were varied independently to create 40 relaxed structures (see Figure
 416 S4). For each structure, the phonon density of states (PDOS) was computed for harmonic
 417 phonons and using this PDOS, $g(\omega)$, the vibrational free energy, F_{vib} , was calculated by:

$$F_{\text{vib}}(T) = \int g(\omega) \left[\frac{1}{2}\hbar + k_{\text{B}}T \ln \left(1 - e^{\frac{-\hbar\omega}{k_{\text{B}}T}} \right) \right] d\omega. \quad (7)$$

418 Hence the full Gibbs free energy, G , of a structure could be calculated at a given tem-
 419 perature, T :

$$G = E_{\text{DFT}} + PV_0 + V_0 \text{Tr}(\boldsymbol{\sigma}_{\text{ext}}\boldsymbol{\epsilon}) + F_{\text{vib}}(T), \quad (8)$$

420 where E_{DFT} is the cell energy calculated using DFT, $\boldsymbol{\sigma}_{\text{ext}}$ is the external stress tensor
 421 (corresponding to the applied biaxial stress of 4.3 GPa), P is the effective hydrostatic pres-

sure ($P=1/3 \text{Tr}(\boldsymbol{\sigma}_{\text{ext}})$), and $\boldsymbol{\epsilon}$ the strain tensor with respect to the fully relaxed structure with no external stress [42]. The equilibrium lattice parameters were found at each T as those which minimised G : For each a , a Murnaghan equation [43] was fitted to the isothermal energy surface to find the equilibrium volume, $V_{e|a}$, and hence lattice parameter $c_{e|a}$. These minimum $c_{e|a}$'s thus formed a valley in $a - c$ space (described by a fourth order polynomial, $p(a)$) and a second Murnaghan equation could be fitted to the volumes along this valley to give the global minimum volume, V_e . Thus the equilibrium lattice parameters, a_e and c_e , were found by solving $p(a)$ with the constraint $V_e = a_e^2 c_e$.

Equilibrium lattice parameters were found every 0.25 K over the range 0 – 250 K. Above this temperature, the equilibrium structure predicted had a softest phonon mode with a frequency so close to zero that its contribution to the free energy began to diverge causing it to dominate the overall lattice dynamics. Hence the temperature range was truncated to avoid unphysical behaviour due to the QHA. $\alpha(T)$ was computed numerically at each temperature by linear interpolation of all equilibrium lattice parameters vs T in a ± 5 K range. $\theta_e(T)$ data was found by inputting $(a_e(T), c_e(T))$ into a cubic spline of $\theta(a, c)$ fitted to the grid of relaxed structures.

DFT Force Constants

Force constants were computed by applying small displacements to O ions along each bond axis and recording the change in force on the adjoined ion. Simulations were performed in a relaxed $2\sqrt{2} \times 2\sqrt{2} \times 1$ supercell (to separate periodic displacements) of a Ca_2GeO_4 phase with (and without in Table S3) a single frozen in-phase rotation or a $2\sqrt{2} \times 2\sqrt{2} \times 2$ supercell of $I4/mcm$ CaGeO_3 .

Subsequent bond extension calculations were performed on single unit cells of rotation phases in which the rotation angle, θ , was altered and all epitaxial O ions constrained but all other ions and cell lengths free to relax in response.

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458 **COMPETING INTERESTS**

459 The authors declare no conflict of interest.

460 **AUTHOR CONTRIBUTIONS**

461 C.A. conducted all calculations. M.S.S., A.A.M. and N.C.B. advised on calculations.
462 S.C. synthesised experimental compounds, S.C. and M.S.S. performed neutron diffraction
463 experiments and S.C., M.S.S. and C.A. analysed the data resulting from these experiments.
464 M.S.S., A.A.M. and N.C.B. designed and organised the study. All authors discussed the
465 results and participated in writing the paper.

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469 **DATA AVAILABILITY**

470 Data underlying this article can be accessed on figshare at DOI:10.6084/m9.figshare.4491521,
471 and used under the Creative Commons Attribution licence.

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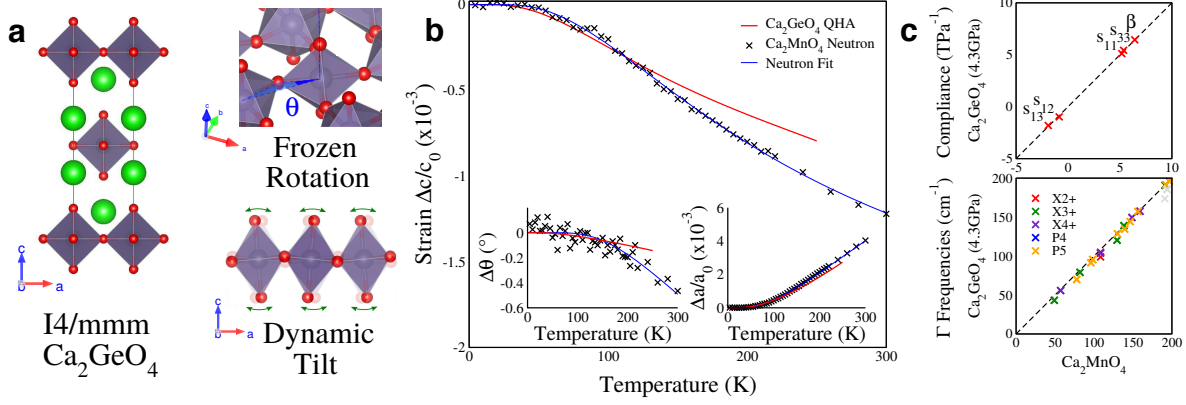


FIG. 1: (a) The octahedral rotation and tilting of the $n=1$ Ruddlesden–Popper (RP1) Ca_2GeO_4 structure (Ca = green, Ge = grey, O = red). (b) $\Delta c/c_0$ against temperature for: calculated equilibrium Ca_2GeO_4 structures (under 4.3 GPa biaxial stress) within the quasi-harmonic approximation (QHA) and neutron diffraction data for Ca_2MnO_4 . QHA and experimental $\Delta\theta$ and $\Delta a/a_0$ against temperature (inset). (c) Elements of the elastic compliance matrix, s_{pq} , bulk compressibility, β , and lowest-frequency Γ -point phonons compared between the fully relaxed Ca_2MnO_4 $I4_1/acd$ phase and $I4_1/acd$ Ca_2GeO_4 under 4.3 GPa biaxial stress. Ca_2MnO_4 phonons are paired with the Ca_2GeO_4 mode to which their eigenvectors have the greatest overlap. Γ -point $I4_1/acd$ modes are labelled if they are non-orthogonal to an irrep in the $I4/mmm$ basis corresponding to an unstable $I4/mmm$ mode, or else coloured grey.

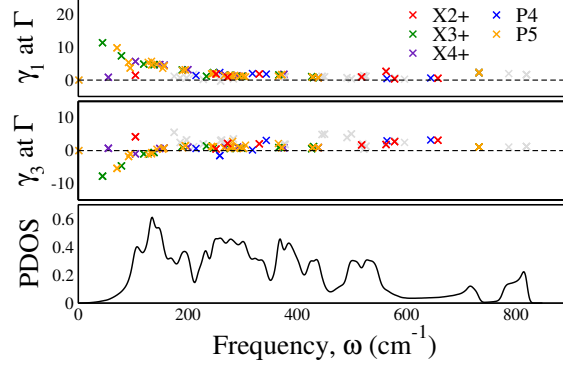


FIG. 2: Grüneisen parameters along a , $\gamma_1(\omega)$; and c , $\gamma_3(\omega)$, computed for Γ -point phonons; and full PDOS, $g(\omega)$. Γ -point $I4_1/acd$ modes are labelled if they are non-orthogonal to an irrep in the $I4/mmm$ basis corresponding to an unstable $I4/mmm$ phonon. Calculated about an $I4_1/acd$ Ca_2GeO_4 structure with $a = 5.129 \text{ \AA}$ and $c = 24.321 \text{ \AA}$.

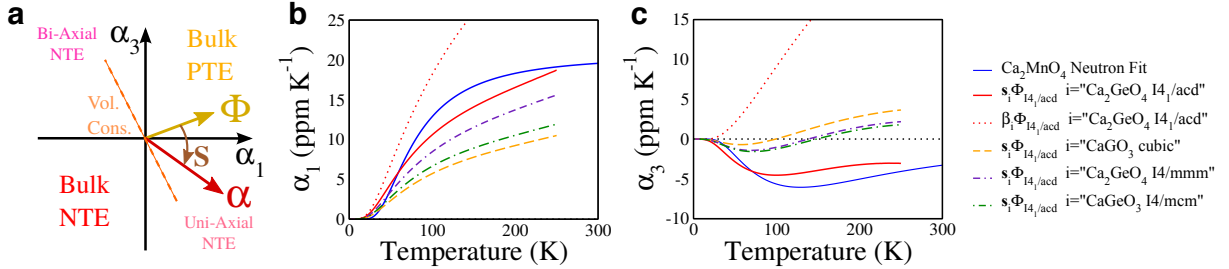


FIG. 3: (a) Illustration of how a vector (in the space of a and c strains) representing the dynamic driving force, Φ , is transformed by a matrix of compliances, $\mathbf{s}$, for a tetragonal material to give the thermal expansion α . (b) $\alpha_1(T)$ and (c) $\alpha_3(T)$ for Ca_2MnO_4 fitted neutron data (blue) and Ca_2GeO_4 QHA simulations (solid red). As a computational thought experiment, $\alpha_{struc}(T)$ for other structures predicted in coloured dashed lines (see legend) by transforming the $\Phi_{I4_1/acd}(T)$, from the Ca_2GeO_4 QHA calculation by $\mathbf{s}$ for each structure.

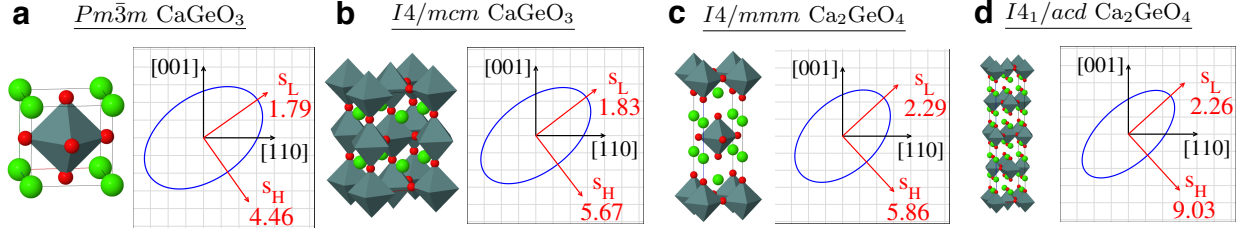


FIG. 4: Matrix, $\mathbf{s}$, displayed in quadratic form in the $(1\bar{1}0)$ plane of tetragonal deformations for CaGeO_3 and Ca_2GeO_4 structures, with eigenvectors labeled with corresponding eigenvalues (TPa^{-1}).

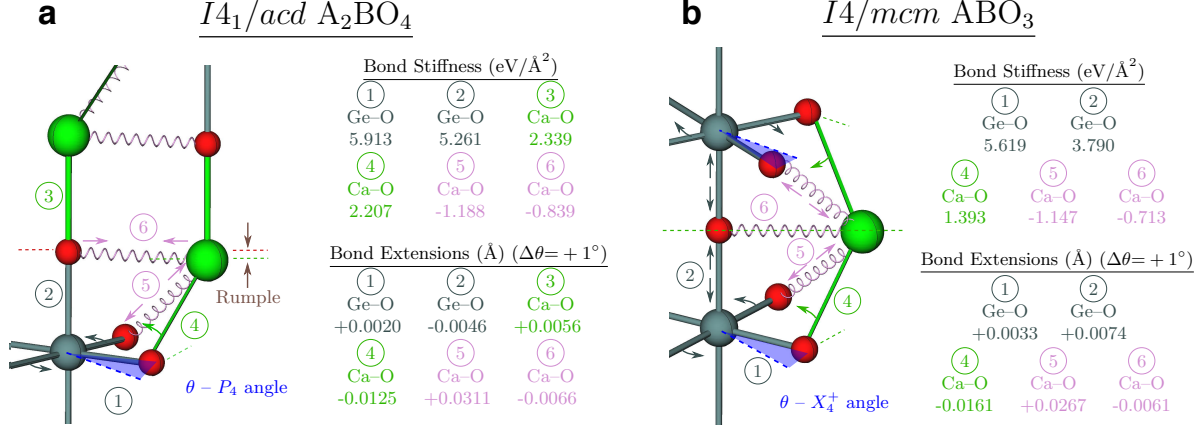


FIG. 5: The structure of (a) the ABO_3/AO interface in the $I4_1/acd$ phase of an A_2BO_4 RP oxide and (b) the $I4/mcm$ phase of an ABO_3 perovskite. Ions shown as spheres and bonds as rods or springs depending on bond strength. Bond strengths based on data calculated on $Ca_{n+1}Ge_nO_{3n+1}$ systems as shown. Bond extension data for both relaxed systems in response to a $\Delta\theta = +1^\circ$ change in fixed frozen rotation angle is also given and agrees with the computed stiffnesses. Arrows in figures illustrate which bonds *would have* to deform by symmetry to accommodate a decrease in a and subsequent increase in θ and c . In the high-symmetry $I4/mmm$ Ca_2GeO_4 phase bonds 4 and 5 are of equal stiffness since there is no frozen rotation (for the full table for stiffnesses see Table S3).

	CaGeO ₃		Ca ₂ GeO ₄		Ca ₃ Ge ₂ O ₇		Sr ₂ MgWO ₆		LaTaO ₄	
	<i>Pm</i> $\bar{3}m$	<i>I4/mcm</i>	<i>I4/mmm</i>	<i>I4₁/acd</i>	<i>I4/mmm</i>	<i>Acaa</i>	<i>Fm</i> $\bar{3}m$	<i>I4/m</i>	<i>Cmcm</i>	<i>Cmc2₁</i>
s_H	4.46	5.67	5.86	9.03	5.41	7.28	5.62	6.70	8.08	11.25
β	5.33	5.51	6.69	7.11	6.28	6.38	7.05	7.13	8.65	7.88
κ	2.49	3.10	2.56	4.00	2.59	3.52	2.39	2.84	4.28	4.77
α	-		-3.8*		-3.6* [17]		-2.7 [26]		-40 [27]	
			(5-400)		(250-300)		(15-300)		(375-575)	

TABLE I: Bulk compressibility, β , and most compliant eigenvalue, s_H , tabulated for all phases alongside κ , the anisotropy ratio ($\kappa = s_H/s_L$) and experimental α of NTE phase, with measurement temperature ranges in K given in brackets. All compliances given in units of TPa⁻¹ and α in units of ppm/K. *Ca_{*n*+1}Mn_{*n*}O_{3*n*+1} measured experimentally.