

Planar negative thermal expansion in the layered hybrid network material $\text{ZnB}_2(\text{CN})_8$ Junbiao Guo¹,¹ Guanqun Cai¹,¹ Kaiyue Zhao²,² Ben Durham³,³ Keith Refson⁴,⁴ and Martin T Dove^{5,1,6,*}¹*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, Sichuan 610065, China*²*Key Laboratory of Materials Physics of Ministry of Education, and School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450052, China*³*School of Physics, Engineering and Technology, University of York, Heslington, York YO10 5DD, United Kingdom*⁴*ISIS Facility, Science and Technology Facilities Council, Harwell Campus, Chilton, Didcot, Oxon OX11, United Kingdom*⁵*School of Mechanical Engineering, Guizhou University of Engineering Science, Bijie, Guizhou 551700, China*⁶*School of Physical and Chemical Sciences, Queen Mary University of London, Mile End Road, London, E1 4NS, United Kingdom*

(Received 30 August 2025; revised 4 November 2025; accepted 19 November 2025; published 11 February 2026)

We report a computational study of thermal expansion in the hybrid layer structure $\text{ZnB}_2(\text{CN})_8$ using density functional theory (DFT) methods. The crystal structure has a trigonal lattice, with a larger positive thermal expansion in the axial direction (c axis) and a very small negative thermal expansion within the layer normal to the axial axis (the a - b plane). The results of the DFT calculations for the structure, lattice dynamics and thermal expansion are consistent with experimental data, and, together with a flexibility analysis, it is possible to explain the large difference between axial and area thermal expansivities. We argue from some general features that the difference between the two expansivities is an inevitable consequence of a combination of the elasticity being stiffer within the layers than between the layers, and of the existence of a tension effect operating within the layers, which lowers the values of the area-strain Grüneisen parameters relative to the axial ones. These two factors combine in a way to enhance the axial expansivity but cancel in the calculation of the area expansivity. This is likely to be a general case for any layer structure in which the layers can be described as a partly flexible network.

DOI: [10.1103/gc3b-h3c2](https://doi.org/10.1103/gc3b-h3c2)

I. INTRODUCTION

The study of negative thermal expansion (NTE) in materials has expanded continuously over the past three decades [1], following the rediscovery of this phenomenon in the cubic material ZrW_2O_8 [2]. In truth, previous findings of NTE in materials [3–6] had been subsequently neglected [7] or even dismissed [8]. Yet in recent years, many materials have been discovered showing NTE in some or all directions [1], establishing the field of the study of NTE within a vibrant multidisciplinary community.

Much of the work on NTE has been carried out on isotropic materials, to the point where we can say that we probably understand the principles in this case fairly well [9]. Typically isotropic NTE materials can be described as three-dimensional networks of corner-sharing structural polyhedra, such as SiO_4 tetrahedra in silica or ScF_6 octahedra in ScF_3 . They can show NTE if the following holds:

(1) The network has stiff bonds between cations and anions, with near-linear connectivities of pairs of bonds. An

example is the linear Sc–F–Sc connections between two ScF_6 octahedra in ScF_3 [10]. These stiff bonds will typically show a small positive thermal expansion [11,12].

(2) The near-linear connection can flex by bending of the angle subtended at the central atom with low energy cost, forming part of the thermal vibrations, and this flexing will bring the two terminal atoms closer together on average. This is the crux of the *tension effect* [9,13–15], which is the typical mechanism proposed for NTE in network materials [2].

(3) These motions can occur cooperatively as part of a normal mode of relatively low frequency, which can have a significantly negative value of the mode Grüneisen parameter. In some cases, this is when the atomic motions are described as a rigid unit modes (RUMs) [16,17], as in ScF_3 [12,18,19]. In other cases, it is achieved when some of the polyhedra have a high degree of internal flexibility, as in ZrW_2O_8 [20].

(4) The normal modes giving the tension effect are spread over a sufficiently large volume of reciprocal space to give significant thermodynamic weighting. If the normal modes giving a tension effect are confined to only a few wave vectors, they will not have sufficient thermodynamic weighting to be important. This point has been articulated in our work on ScF_3 [12,19].

The tension effect can also occur in anisotropic materials, but in anisotropic materials there are additional elastic effects as we discuss in this paper. One class of anisotropic materials is the axial crystals (materials with a unique axis and isotropic properties in the plane normal to the axis, namely, crystals

*Contact author: martin.dove@icloud.com

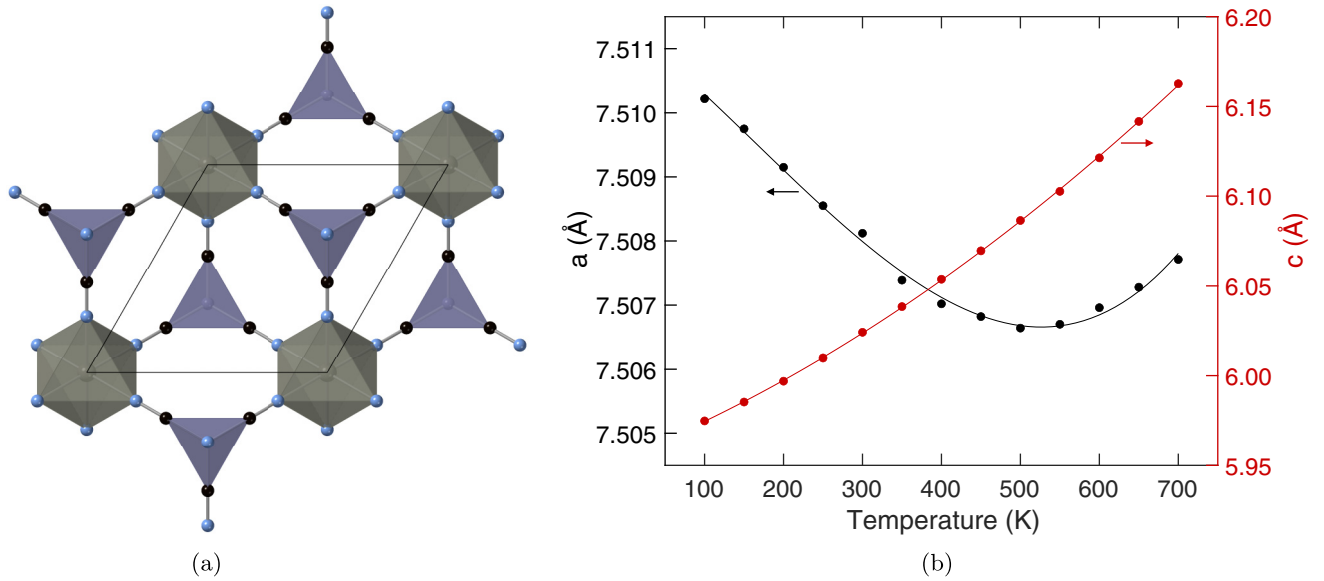


FIG. 1. (a) Crystal structure of $\text{ZnB}_2(\text{CN})_8$ (trigonal space group $P\bar{3}m1$) viewed down [001] [30]. The ZnN_6 octahedra are shown in gray, the BC_4 tetrahedra are shown in dark blue, carbon atoms are shown as black spheres, and nitrogen atoms are shown as light-blue spheres. It is useful to note that this is also the view of an individual layer in the crystal structure. (b) Variation of the two lattice parameters of $\text{ZnB}_2(\text{CN})_8$ with temperature [31], black (left axis) represents lattice parameter a , and red (right axis) represents lattice parameter c .

whose point group contains a single threefold, fourfold or sixfold rotation axis), and some observations and discussions for a few simple cases date back many years [21]. In this paper, we are interested in the crystal of $\text{ZnB}_2(\text{CN})_8$, which is an axial crystal having space group $P\bar{3}m1$, and having a crystal structure with layers that can individually support the operation of a tension effect. In fact, many axial materials have layered structures, but many show positive thermal expansion (PTE) in all three directions. Examples are the melilite group of sorosilicates, including gehlenite [22], VSe_2 [23], and classical layer silicates such as muscovite [24]. On the other hand, some layer structures such as $\text{Ni}(\text{CN})_2$ [25] and perovskite derivatives such as Ca_2GeO_4 [26,27] can show area or uniaxial NTE. It has long been known that graphite also shows area NTE [28,29,32], although graphite is a special case, given that its layers have a thickness of only one atom. Other examples of NTE in layer materials are given by Liang *et al.* [33].

$\text{ZnB}_2(\text{CN})_8$ is particularly interesting since its crystal structure [30] can be described as a hybrid cation-molecule structure with network layers, as shown in Fig. 1(a). Our view of hybrid network structures follows that presented in earlier reviews of Cheetham and Rao [34,35]. They describe crystal structures in which metal cations form coordination polyhedra with atoms in molecular anions, and these in turn act as bridges to other metal cations that form similar coordination polyhedra. In the case of $\text{ZnB}_2(\text{CN})_8$, the structure has layers that form as two-dimensional infinite networks in which ZnN_6 octahedra connect with BC_4 tetrahedra via shared CN molecular anions. The unit cell contains one formula unit, so the layers repeat in the [001] direction without staggering [Fig. 1(a)].

Furthermore, we specifically identify hybrid layer structures as having weak connections between layers, held together by dispersion interactions and residual electrostatic

interactions. Two examples cited above are $\text{Ni}(\text{CN})_2$ [25,36] and graphite, but we also noted that the structural networks within the layers of these two materials are more trivial than that of $\text{ZnB}_2(\text{CN})_8$. Other examples are given in Refs. [34] and [35]. Muscovite [24] is an example of an inorganic material with a two-dimensional network layer structure and weak interlayer interactions. On the other hand, layer structures such as Ca_2GeO_4 [26,27], which show uniaxial NTE, have perovskite-like network structures within the layers, but the layers are connected via stronger ionic bonds. We discuss the contrast with $\text{ZnB}_2(\text{CN})_8$ in Sec. V D.

The lattice parameters of $\text{ZnB}_2(\text{CN})_8$ and some key interatomic distances and angles are given in Table I. The octahedral and tetrahedral angles differ from their ideal values by less than 1.6° and 0.5° , respectively. In fact we see that it is most appropriate to think of the $\text{B}(\text{CN})_4$ tetrahedron as a near-rigid unit for low-frequency vibrations. The B–C–N angle departs from linearity by less than the experimental uncertainty. Three of the C–N bonds at the vertices of the BC_4 tetrahedra are connected to ZnN_6 octahedra, and the fourth vertex B–C–N bond is aligned vertically and not bonded. This bond actually penetrates the neighboring layer. The vertical width of a layer, defined as the distance between the two most extreme heights of N atoms, is 9.72 Å, and the extent of penetration is as large as 3.71 Å as measured from the heights of the extreme N atoms. This interlayer penetration brings the N atoms toward the horizontal face of a BC_4 tetrahedra, with three N...C distances of 3.13 Å and vertical N...B distances of 3.29 Å.

The variations of the lattice parameters of $\text{ZnB}_2(\text{CN})_8$ with temperature obtained from recent x-ray diffraction measurements [31] are shown in Fig. 1(b). There is significant PTE of the c lattice parameter, but near-zero expansivity for a . For c the thermal expansivity increases in value from 36 MK^{-1} at 50 K to 69 MK^{-1} at 700 K. The thermal expansion of a is

TABLE I. Some details of the crystal structure of $\text{ZnB}_2(\text{CN})_8$, comparing results (lattice parameters, some bond lengths and bond angles) from experimental data at 300 K [30] with DFT calculations presented in this paper. Uncertainties in the last digits of the values from experimental data are given in brackets. The two values of the B–C bond length are given for the bridging (upper values) and nonbridging (lower values) bonds.

	a (Å)	c (Å)	C–N (Å)	Zn–N (Å)	B–C (Å)	Zn–N–C (°)
Expt.	7.5092(9)	6.0159(6)	1.132(5)	2.136(2)	1.589(5) 1.595(2)	166.3(2)
Calc.	7.5148	5.9616	1.1569	2.1320	1.5792 1.5838	165.43

initially negative, with a value of linear expansivity of nearly -12 MK^{-1} for temperatures around 200 K, but turns positive at a temperature of around 525 K, reaching a value of $+14 \text{ MK}^{-1}$ at 700 K.

While $\text{ZnB}_2(\text{CN})_8$ may be the second-known hybrid layer structure to show area NTE, after $\text{Ni}(\text{CN})_2$ [25], it is significantly different from $\text{Ni}(\text{CN})_2$ because the layers in $\text{ZnB}_2(\text{CN})_8$ contain structural polyhedra connected in a way that is similar to the connectivities found within a three-dimensional network. On the other hand, the layers in $\text{Ni}(\text{CN})_2$ are one-atom thick, with square coordinations of nickel atoms to the cyanide anions forming linear metal–cyanide–metal linkages. These are similar to the metal–cyanide linkages in the one-dimensional chain cyanides such as CuCN [37], which show NTE along the direction of the chain, and of three-dimensional analogs of Prussian Blue, which show a simple cubic (or rocksalt) arrangement of cations connected linearly by the CN molecular anions, and $\text{Zn}(\text{CN})_2$ which shows the same for a diamond-like network, both of which show isotropic NTE [38,39]. The NTE in all these simple linear cyanide networks arises from the rigid unit mode flexibility of the networks [40], with the acoustic RUMs playing a particular important role [41,42]. However, because the layers in $\text{ZnB}_2(\text{CN})_8$ are more three-dimensional, their dynamics are likely to give the prospect for a more complex operation of the tension effect than in $\text{Ni}(\text{CN})_2$. Furthermore, in addition to considering the tension effect in $\text{ZnB}_2(\text{CN})_8$ enabled by some degree of flexibility of the layer networks, we also need to consider the role of elastic anisotropy [21]. In fact, we find here that this is the significant issue in understanding the low NTE in the basal plane of $\text{ZnB}_2(\text{CN})_8$.

Here we analyze the thermal expansion of $\text{ZnB}_2(\text{CN})_8$ from calculations of phonon frequencies using density functional theory (DFT) methods, interpreted with the help of an analysis of the layer network flexibility using concepts from the RUM model [16,17,43,44]. The important point that emerges from this study actually transcends the specific case of $\text{ZnB}_2(\text{CN})_8$. We believe that the thermal expansion of $\text{ZnB}_2(\text{CN})_8$, with large PTE seen along the unique axis and low thermal expansion in the perpendicular plane, will probably be found in any network layer material, because of the way that larger and weaker intrinsic expansivities, as quantified by the strain Grüneisen parameters, couple to the larger and weaker components of the elasticity. This point will be discussed in more detail in the final section of this paper.

II. METHODS

A. Density functional theory calculations

DFT calculations were performed using the CASTEP package [45], within the Perdew, Burke, and Ernzerhof (PBE) version of the generalized gradient approximation [46]. The calculations were mostly performed using version 21, but elastic constants were calculated using a newly implemented density functional perturbation theory (DFPT) method in a development version of CASTEP. CASTEP uses plane waves as the electron basis set, with pseudopotentials used to avoid the cost of accounting explicitly for the core electrons as part of the basis set. We used the NCP19 library pseudopotentials supplied within the CASTEP package with a cutoff energy of 1400 eV for the plane waves, determined by convergence tests. A Monkhorst–Pack grid of size $5 \times 5 \times 5$ was used for the integrations over Bloch waves. The Grimme D3 semi-empirical dispersion correction (SED3) with Becke–Johnson damping [47] was used to include the effects of dispersion interactions, which was found to be necessary to avoid large errors otherwise seen in the calculated value of the c lattice parameter. For energy minimization, the following tolerances were used: for energy a value of 10^{-6} eV, for forces a value of 0.002 eV/Å, for stresses a value of 0.01 GPa, and for displacements a value of 0.0001 Å.

The elastic constants were calculated using the DFPT method of Hamann *et al.* [48–50], building on earlier work of Baroni *et al.* [51,52], and checked using calculations performed using finite-strain methods.

Lattice dynamics were calculated using the finite-displacement method implemented within CASTEP [45] which uses the nondiagonal supercell technique of Lloyd-Williams and Monserrat [53]. Atomic displacements were 1% of the Bohr radius; we see below, Table V, that we achieved excellent agreement with the frequencies of Raman-active modes [31], with a root-mean-squared difference between calculation and experiment of only 1.7%. The dynamical matrices were evaluated for phonon wave vectors belonging to a $5 \times 5 \times 5$ Monkhorst–Pack grid, and subsequently Fourier interpolated to a finer set of wave vectors, either to construct a path through the Brillouin zone for plotting of dispersion curves (as in Fig. 2), or to obtain frequencies for the calculation of thermodynamics properties, including heat capacity and thermal expansion. Formally, these functions are defined as an integral over all wave vectors in the first Brillouin zone, weighted by the phonon occupation number. We approximated this integral

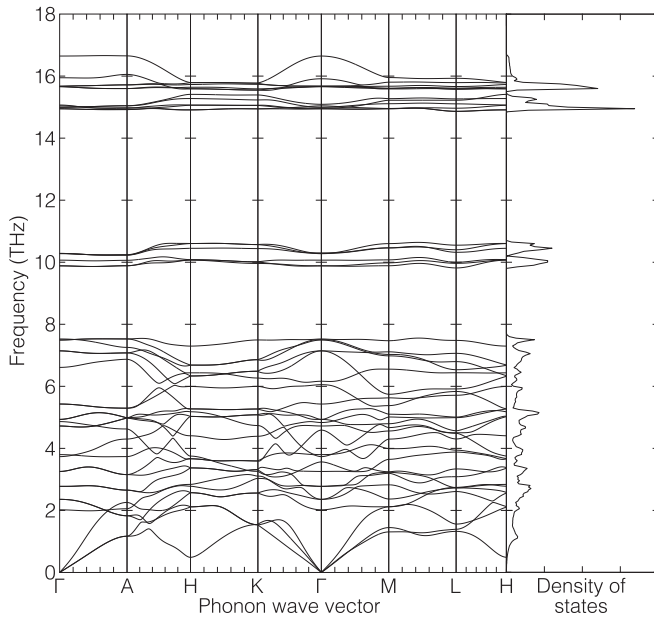


FIG. 2. Left side shows the calculated phonon dispersion relations up to around 17 THz. Wave-vector labels denote $\Gamma = [0, 0, 0]$, $A = (0, 0, \frac{1}{2})$, $H = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$, $K = (\frac{1}{3}, \frac{1}{3}, 0)$, $M = (\frac{1}{2}, 0, 0)$, $L = (\frac{1}{2}, 0, \frac{1}{2})$. On the right we show the calculated phonon density of states, evaluated from frequencies of 20 000 random wave vectors distributed throughout the Brillouin zone.

by performing calculations for 20 000 random wave vectors in the Brillouin zone to give a uniform sampling of the whole of reciprocal space.

Mode strain Grüneisen parameters—discussed later—were calculated from phonon frequencies after applying separately small strains in the axial direction and small area strains in the perpendicular direction. Several different values of strains were tested. The results shown in this paper were for area strain and uniaxial strains of 2% each. Significantly smaller or larger strains led to clear numerical errors. Results from this analysis were evaluated using our own software, including software described previously, and developed for anisotropic systems [54].

B. Flexibility calculations

In previous works, we analyzed the flexibility of network structures using simple force-field models that acted to enforce rigidity of specific polyhedral groups of atoms, but which allowed complete flexibility at the joints of connected polyhedra [20,54]. Here, this was carried out using the GULP lattice simulation code [55,56], which can compute elastic properties and lattice dynamics.

We used simple model forces. For the bonds we used simple harmonic forces as functions of the interatomic separation r ,

$$E(r) = \frac{1}{2}k(r - r_0)^2, \quad (1)$$

where r_0 is the experimental bond length, with separate values given for the C–N, B–C, and Zr–N bonds. For the bending terms within the two polyhedra, we used a simple harmonic

function of the bond angle θ ,

$$E(\theta) = \frac{1}{2}K(\theta - \theta_0)^2, \quad (2)$$

where $\theta_0 = 90^\circ$ or 109.47° for octahedra and tetrahedra, respectively. One other term was used to preserve the linear B–C–N connection, modeled as a function of the corresponding bond angle ϕ as

$$E(\phi) = A(1 + \cos \phi). \quad (3)$$

This last term reflects the fact that the basic rigid unit for low frequencies is the $B(CN)_4$ tetrahedron, with preserved linearity of the B–C–N linkage, rather than the BC_4 tetrahedron alone.

This model is the minimally complete model to allow a description of the flexibility of the structure. The values of the parameters k , K , and A were simply set to be large numbers because the key results are for the modes that have zero frequencies. The zero frequencies indicate which modes are RUMs [17], and the zero-frequency solutions to the dynamical matrix are unaffected by the exact values of the parameters k , K , and A .

III. FLEXIBILITY ANALYSIS

It is useful to preface the discussion of the DFT results with our analysis of the flexibility of the layers in ZrW_2O_8 using the standard Maxwell analysis of degrees of freedom and constraints [57]. Let us start with the simplest approach of considering the layer network of connected ZnN_6 octahedra and BC_4 tetrahedra, with the cyanide anion providing a rigid constraint between the two connected corners. In the model, this is achieved by setting $A = 0$ in Eq. (3). Each polyhedron has six degrees of freedom, giving a total number of degrees of freedom per unit cell of $F = 3 \times 6 = 18$. Each cyanide rod provides a distance constraint between two attached vertices, meaning that there is a total of $C = 6$ constraints per unit cell. This gives the possibility of $F - C = 12$ RUMs per wave vector, which is a very high degree of flexibility that we consider to be too high.

The DFT results for the lattice dynamics suggest that there is a relatively strong angular force that acts to preserve the linearity of the B–C–N linkage [large value of A in Eq. (3)]. This linearity is seen in the crystal structure, whereas the Zn–N–C linkage is bent (noted below). Furthermore, we find in the lattice dynamics that the Zn–N–C linkage can bend relatively easily. This means that we should think of the $B(CN)_4$ unit as a single rigid unit. In this case, the constraints are the three equations that connect the terminal N atom at the same three-dimensional position as the vertex atom of the ZnN_6 octahedra. This will give $C = 6 \times 3 = 18$ constraints per unit cell, and so we have the marginal case $F = C$. This is the same as in a three-dimensional silica network [44] and as in ZrW_2O_8 [58], although in fact the latter case gains most of its overall flexibility that enables the tension effect from the bending flexibility of the ZrO_6 octahedra rather than from the RUMs [20].

We stress that the term RUM does not imply infinite stiffness of the polyhedra but indicates that, in the normal mode, the polyhedra move without distortion as if they are rigid entities. This point has been discussed extensively [16,17].

TABLE II. Number of RUMs for a set of special wave vectors within the basal plane.

Wave vector	Number	Wave vector	Number
0,0,0	6	$\zeta, 0, 0$	2
$\frac{1}{2}, 0, 0$	2	$\zeta, \zeta, 0$	1
$\frac{1}{2}, \frac{1}{2}, 0$	2	$\zeta, \xi, 0$	1

Typically, as in silicate networks, the movement of polyhedra as effectively rigid entities is enabled by the fact that the bending forces within the polyhedra are typically larger than those operating at the shared vertices.

Note that three-dimensional fully connected networks containing structural octahedra—cubic perovskites being the one exception—do not support RUMs [59], because they are over-constrained (the exception of perovskite has been explained elsewhere [17]). In the case of ZrW_2O_8 [58] the single non-bridging bond on each WO_4 tetrahedron removes enough of the constraints to allow $F = C$. In the case of $\text{ZnB}_2(\text{CN})_8$ the existence of layers means that atomic bonds terminate at the surfaces, so that one out of the four B–C–N bonds within the tetrahedron is nonbridging.

It is commonly found in silica networks that symmetry allows some of the constraints to be degenerate, so that RUMs can be found to exist with wave vectors along special lines or planes in reciprocal space. We have performed an analysis of the flexibility of the network using the methods described in Sec. II B. The number of RUMs found for different wave vectors in the basal plane—that is, for $\mathbf{q} = [q_x, q_y, 0]$ —are given in Table II. Note that we only need to consider wave vectors for $q_z = 0$; because the layers are not connected, $q_z \neq 0$ is irrelevant in this analysis since the solution of the dynamical matrix for wave vector $[q_x, q_y, q_z]$ is equivalent to that for $[q_x, q_y, 0]$. What this means is that all RUMs found for $q_z = 0$ will be replicated for wave vectors for $q_z \neq 0$.

It is striking that the analysis gives one RUM for each wave vector of the form $[q_x, q_y, 0]$, and hence, by extension, for each wave vector in the crystal. The six RUMs at $\mathbf{q} = 0$ are the three acoustic modes, an optic mode which we identify as having symmetry A_{2g} and which involves rotations of the polyhedra about axes parallel to $[0,0,1]$, and a double-degenerate mode of symmetry E_g which involves rotations about axes in the $(0,0,1)$ plane. We see in the DFT calculations that the A_{2g} RUM has a negative value of its mode Grüneisen parameter for area (a - b) strain, whereas the E_g mode has a positive mode Grüneisen parameter for both area and uniaxial strains.

The flexibility model predicts large values for the elastic constants C_{11} , C_{12} , and C_{66} and, as expected, zero for all other values. Solving the Cristofell equation [60,61] shows that for all wave vectors with wave vectors of the form $[q_x, 0, 0]$ and $[q_x, q_x, 0]$ there is one transverse-acoustic mode that is a RUM (zero-frequency solution to the Cristofell dynamical matrix).

IV. RESULTS FROM LATTICE SIMULATIONS

A. Crystal structure, elasticity, and dynamics

1. Crystal structure

Some aspects of the crystal structure relaxed in the DFT calculations—lattice parameters and some bond lengths and

angles—are compared with the corresponding values for the experimental crystal structure [30] in Table I. Calculated atomic fractional coordinates are compared with experimental values [30] in Table III. There is reasonable agreement in all cases. The agreement for a is better than 0.1%, and is better than 1% accuracy for c . If we take account of thermal expansion the accuracy is better than 0.2%, but given that c is most affected by the SEDC, this level of accuracy may be mostly fortuitous. With the functional used, it is commonly found that DFT slightly overestimates lattice parameters.

The calculated and experimental values of the C–N bond lengths are in agreement to within 2%. The calculated and experimental values of the Zn–N bond length agree to within 0.2%, but the difference is actually similar to the size of the experimental uncertainty. The calculated and experimental values of the B–C bond length agree to better than 1%, but again the experimental uncertainties on the data are comparable to the differences. Note that we predict a difference between two B–C bond lengths (bridging and nonbridging) of 0.005 Å, which the experimental data give as 0.006(5) Å.

The DFT calculations give a near-linear B–C–N angle, with deviation from linearity calculated to be less than 0.6° . This is the same as seen in the experimental crystal structure, except that the experimental uncertainty is similar to this difference. The DFT calculations also give the Zn–N–C angle departing from linearity by 14° , with agreement with experimental data that is better than 1° , and which is not significantly above the experimental uncertainty.

2. Elasticity

The values of the elastic constants C_{ij} calculated by DFT are given in Table IV. The values for the pure tensile components, $i, j = 1, 2, 3$ are close to those of an independent calculation using a different DFT software package [31]. The in-layer elasticity is stiffer than between layers. C_{11} and C_{66} are both around 75% larger than C_{33} and C_{44} , respectively. C_{12} is around three times larger than C_{13} . However, note that the penetration of the nonbridging B–C–N bonds into adjacent layers adds more horizontal stiffness than would be found in systems with smoother layer surfaces—there are more points of atomic contacts between layers to stiffen the longitudinal interlayer forces, and the interpenetration stiffens the lateral interlayer forces.

3. Phonon frequencies

The phonon dispersion curves calculated by DFT are shown in Fig. 2 for frequencies up to 17 THz. The corresponding density of states is also shown in Fig. 2. Note that the density of states here has been formed by sampling across the whole of the Brillouin zone, as described above, rather than having been derived only from the frequencies shown in the dispersion curves, as is often presented in modern studies.

For zero wave vector, the mode decomposition in terms of irreducible representations gives $A_{2u} + E_u$ for the acoustic modes, and $7A_{1g} + 2A_{1u} + 2A_{2g} + 7A_{2u} + 9E_g + 9E_u$ for the optic modes [62]. The calculated frequencies of these modes are given in Table V. The calculated frequencies of the Raman-active modes, those of irreducible representations A_{1g} and E_g are compared with the results of recent measurements

TABLE III. Experimental (300 K) [30] and calculated atomic fractional coordinates. The positions are the atoms in the atomic basis have the form Zn (0 0 $\frac{1}{2}$), B, C2, and N2 ($\frac{2}{3}$ $\frac{1}{3}$ z), C1, and N1 ($2x x z$).

	B z	C1 $2x$	C1 z	C2 z	N1 $2x$	N1 z	N2 z
Exp.	0.1444(5)	0.4361(3)	0.2347(3)	−0.1198(6)	0.2719(3)	0.3009(3)	−0.3080(6)
Calc.	0.1422	0.4379	0.2328	−0.1227	0.2706	0.2984	−0.2984

by Raman spectroscopy [31], and agreement in all cases is excellent.

The frequencies of the C–N stretch modes are in the range 2243–2282 cm^{−1} (67.2–68.4 THz) at zero wave vector, consistent with known values. These are not shown in the dispersion curves presented in Fig. 2. Also not shown in the dispersion curves are branches for frequencies in the range 946–960 cm^{−1} (28.4–28.8 THz). These modes involve significant bending of the C–B–C angles.

The lowest optic branch with frequency 2.02 THz (67.4 cm^{−1}) and symmetry A_{2g} is one of the three optic RUMs, and involves rigid body rotations of the ZnN₆ and B(CN)₄ polyhedra about [001]. A double-generate mode of symmetry E_g and frequency 2.36 THz (78.6 cm^{−1}) is the second RUM, showing rotations of ZnN₆ about [110] with coupled translations of the B(CN)₄ tetrahedra. However, there is a second double-generate mode that is also of symmetry E_g at 2.78 THz (92.6 cm^{−1}). This also appears to have a significant RUM-like character, with rotations of the B(CN)₄ tetrahedra around the [1 $\bar{1}$ 0] direction and accompanying rotations of the ZnN₆ octahedra, leading to a wagging of the nonbridging B–C–N bond away from the vertical direction. We note that, because these two doublets have very close frequencies, they are allowed by symmetry to mix eigenvectors. Higher-frequency modes increasingly involve distortions of the polyhedra. For example, the twisting of the ZnN₆ octahedra occurs at frequencies above 3.7 THz.

B. Mode Grüneisen parameters and thermal expansion

We can define an overall strain Grüneisen tensor as

$$\bar{\gamma}_j = \frac{1}{C_V} \sum_{\lambda=1}^{3n} c_{\lambda} \gamma_{j,\lambda}, \quad (4)$$

where λ represents a normal mode of the crystal, and $C_V = \sum_{\lambda} c_{\lambda}$ is the constant-volume heat capacity. The mode strain Grüneisen parameters are defined as

$$\gamma_{i,\lambda} = -\frac{1}{\omega_{\lambda}} \frac{\partial \omega_{\lambda}}{\partial \epsilon_i} = -\frac{1}{2\omega_{\lambda}^2} \frac{\partial \omega_{\lambda}^2}{\partial \epsilon_i}, \quad (5)$$

where ϵ_i are the relevant components of the strain tensor; that is, for $i = \{1, \dots, 3\}$ in Voigt notation. The mode weighting parameters are defined as

$$c_{\lambda} = \frac{\partial E_{\lambda}}{\partial T} = \hbar \omega_{\lambda} \frac{\partial n(\omega_{\lambda}, T)}{\partial T}, \quad (6)$$

TABLE IV. Calculated values of the elastic constants, units GPa.

C ₁₁	C ₃₃	C ₁₂	C ₁₃	C ₄₄	C ₆₆	C ₁₄
41.34	23.30	21.54	7.06	5.54	9.90	2.71

where $n(\omega_{\lambda}, T)$ is the standard Bose-Einstein phonon occupation number, and the energy of each normal mode is $E_{\lambda} = \hbar \omega_{\lambda} [n(\omega_{\lambda}, T) + 1/2]$. While the values of mode Grüneisen parameters are independent of temperature, the weighting parameters c_{λ}/C_V are dependent on temperature. In particular, they give higher weighting to modes of lower frequency at lower temperatures.

The anisotropic thermal expansivity is given in general form [63–65] as

$$\alpha_i = \frac{C_V}{V_0} \sum_j S_{ij} \bar{\gamma}_j, \quad (7)$$

where V_0 is the corresponding volume, and S_{ij} are the components of the elastic compliance tensor.

For axial crystals it is convenient to work in terms of an axial strain, $\epsilon_c = \epsilon_3$, and an area strain $\epsilon_{ab} = 2\epsilon_1$, where we constrain $\epsilon_2 = \epsilon_1$ [66]. The primary advantage is in terms of both presentational and computational convenience, since ϵ_{ab} preserves the crystal symmetry. In this case, the equations for thermal expansion can be written in terms of the elastic constant tensor as

$$\alpha_1 = \alpha_{ab}/2 = \frac{C_V}{dV_0} (C_{33} \bar{\gamma}_{ab} - 2C_{13} \bar{\gamma}_c)/4, \quad (8)$$

$$\alpha_3 = \frac{C_V}{dV_0} [(C_{11} + C_{12}) \bar{\gamma}_c - C_{13} \bar{\gamma}_{ab}], \quad (9)$$

TABLE V. Calculated values of the phonon frequencies of ZnB₂(CN)₈ at zero wave vector, units cm^{−1}. For the modes of symmetry A_{1g} and E_g—the only Raman-active modes—we compare our results with measurements by Raman spectroscopy [31], with calculation and experiment being presented before (normal text) and after (italic text) the slash, respectively. The horizontal lines separate distinct groups of modes as seen in the dispersion curves and density of states (Fig. 2).

A _{1g} (calc/expt)	A _{2g}	E _g (calc/expt)	A _{1u}	A _{2u}	E _u
124.6/124.0	67.4	78.6/80.5	126.7		108.6
		92.6/91.3			157.5
		164.6/172.0		162.2	181.1
251.1/253.5		238.3/242.2		220.5	250.0
	335.8	329.7	342.8		343.1
501.7/504.1		498.6		502.6	500.2
555.3/558.7		522.4/523.8		531.9	522.8
951.6/950.6		946.1/942.3		960.1	948.8
2242.9		2275.7		2243.0	2276.8
2282.5				2281.0	

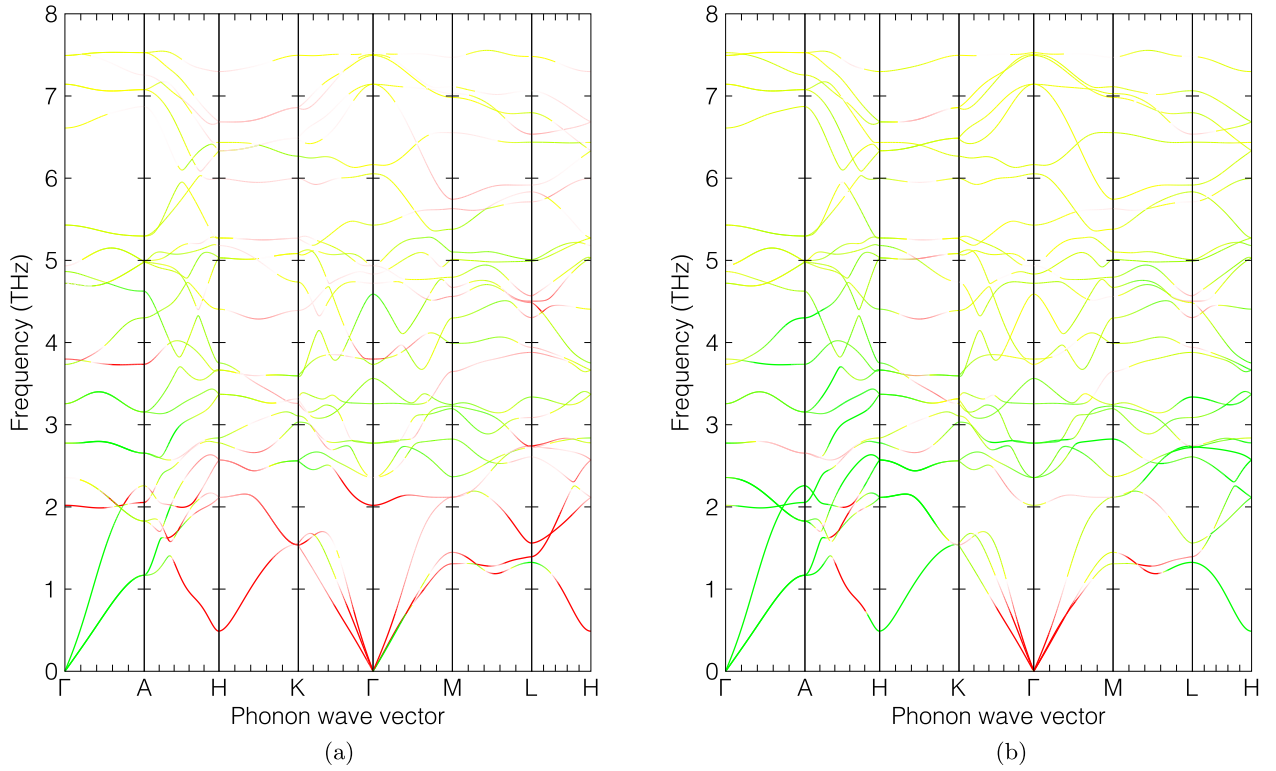


FIG. 3. Lower-frequency part of the dispersion curves of $\text{ZnB}_2(\text{CN})_8$ colored by the values of the mode Grüneisen parameters, (a) with area strain in the (001) plane, and (b) with axial strain in the [001] direction. Modes with negative values of the mode Grüneisen parameters are shown as red, and those with positive values are shown as green, zero values being shown as yellow, with the strength of color reflecting the size of the mode Grüneisen parameters, and with red and green saturating at values of -3 and $+3$, respectively.

where $d = (C_{11} + C_{12})C_{33} - 2C_{13}^2$. Note that these equations can also be written in terms of the components of the elastic compliance tensor [21,67].

One way to represent part of the relationship between the mode strain Grüneisen parameters and actual phonon modes is to color the phonon dispersion curves of Fig. 2 according to the values, positive or negative, of the mode strain Grüneisen parameters. The results for both area and axial strain mode Grüneisen parameters are shown in Fig. 3.

The most immediate impression from the results shown in Fig. 3 is that most branches of the dispersion curves have positive values of the two mode strain Grüneisen parameters. However, there are several branches at low frequencies showing negative values of the mode strain Grüneisen parameters, particularly for the area strain. These include the acoustic modes, stretching across the zone boundaries. Examples are the directions along the edges of the Brillouin zone A–H–K for the area strain, typically for frequencies below 1.5 THz. The RUM of symmetry A_{2g} and frequency around 2 THz, which involves rotations of the polyhedra about [0,0,1], shows a strong negative value of the mode strain Grüneisen parameters for the area strain, but positive values for the axial strain. This branch remains uniform in frequency and area strain Grüneisen parameter from Γ to A (along the c^* direction, which reflects a lack of correlation of this motion between layers). Along the direction Γ –M (the a^* direction), this mode also remains flat in frequency, but in the direction Γ –K (the [1,1,0] direction), the frequency increases with a correspond-

ing shift of the values of area strain Grüneisen parameter from negative to positive.

The A_{1u} mode at 3.8 THz (126.7 cm^{-1}) also shows a negative value of the area strain Grüneisen parameter, which extends as such from Γ to A, but not in other directions. This involves a twist distortion of the ZnN_6 octahedra about the [0,0,1] direction with coupled rotations of the BC_4 tetrahedra.

This analysis characterizes the contributions of the various modes to give a possible negative value of the overall area-strain Grüneisen parameter, but more important is the distribution across the whole of reciprocal space. The relationships between the two sets of mode strain Grüneisen parameters and corresponding frequencies across reciprocal space are shown as density maps in Fig. 4. The differences between the effects of the two types of strain on the phonon frequencies, as had been indicated in the dispersion curves, Fig. 3, are clearly seen in this image. The axial strain gives a much larger distribution of the Grüneisen parameters at positive values than for the area strain. It is also seen in the data for the area strain that much of the distribution of negative values is weighted toward lower frequencies.

Focussing on the area-strain Grüneisen parameter–frequency density map in Fig. 4(a), we see two main distributions with negative values of the Grüneisen parameters. One is around 1 THz, which is from the acoustic modes as can be seen in the dispersion curves shown in Figs. 2 and 3. The second is around 2 THz, which is the set of modes

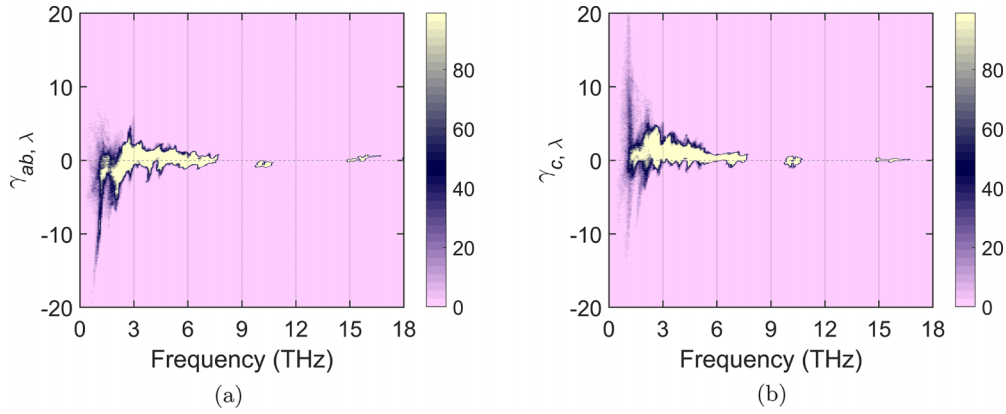


FIG. 4. Colored density maps showing the relationship between Grüneisen parameters and frequencies for the normal modes of $\text{ZnB}_2(\text{CN})_8$, (a) with area strain in the (001) plane, and (b) with axial strain in the [001] direction.

associated with the A_{2g} RUM spreading throughout reciprocal space.

We can look at these data in a different way, by plotting how the mean mode Grüneisen parameters within a range of frequencies vary with frequency, as shown in Fig. 5. Here we now incorporate the thermodynamic weighting parameter c_λ [Eq. (6)] ranging from near-zero to effectively infinite temperatures, coloring from blue to red, respectively. The contrast between the plots for the two strains is striking. The mean mode Grüneisen parameters for axial strains are very large and positive below 1.5 THz, falling to values of around +1 after 3 THz. Some small negative mean values are found at around 10 THz. On the other hand, the mean mode Grüneisen parameters for the area strain show more variation. It is seen that, at very low frequencies, there is a region of positive mean values up to around 0.5 THz, but from there to around 3 THz the mean values are all negative, with the most negative values at around -5 coming at around 1 THz. The RUM at 2 THz shows as a slight dip in the distribution with mean values of the area-strain Grüneisen parameters of around -2 .

Another way to assess the importance of individual groups of mode strain Grüneisen parameters is to assess their progressive contribution to the overall strain Grüneisen parameters stepping up in frequency. We define the accumulated

Grüneisen parameters as

$$\bar{\gamma}_{\text{acc}}(\omega) = \int_0^\omega c(\omega', T) g(\omega') \gamma(\omega') d\omega'. \quad (10)$$

This function allows us to see how contributions at lower frequency are augmented or canceled by contributions from higher frequencies. The two accumulated Grüneisen parameters are shown as functions of maximum frequency in Fig. 6, where again we present data with weightings by c_λ [Eq. (6)]. The results in Fig. 6 show that for the axial strain, higher frequency contributions damped downward the initial higher value from the low-frequency modes. For the area strain, we see that the largest negative contributions are coming from the modes around 1 THz, and that on increasing frequency, there is a similar damping. The effect of the RUMs at around 2 THz (A_{2g} at Γ) is indicated in the accumulation function for area strain, but clearly it is not as significant as the modes around 1 THz.

Now we are at the point where we can combine the results to give the two overall strain Grüneisen parameters, Fig. 7(a). From all that we have said, we anticipate that the overall axial-strain Grüneisen parameter shows a normal positive value, and we see in Fig. 7(a) that this is indeed the case. At the lowest temperature it has a relatively high value, but it falls to

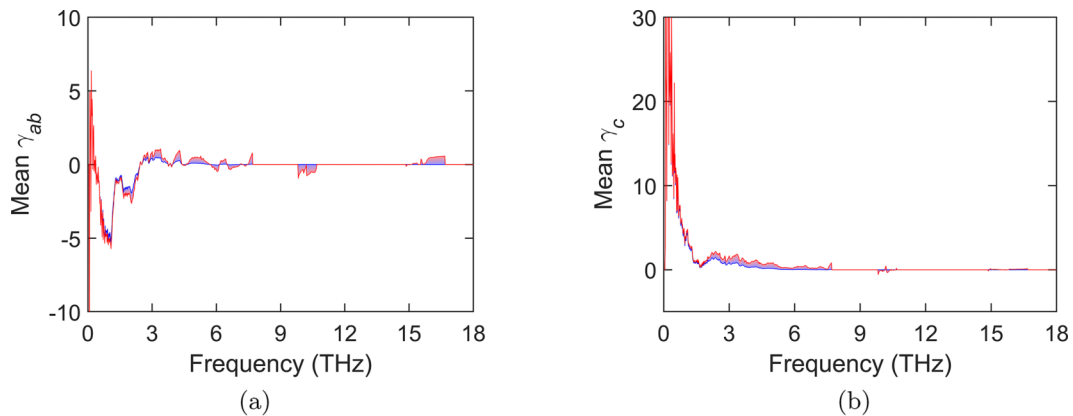


FIG. 5. Mean values of the mode Grüneisen parameters of $\text{ZnB}_2(\text{CN})_8$ for different frequencies of the normal modes of $\text{ZnB}_2(\text{CN})_8$, (a) with area strain in the (001) plane, and (b) with axial strain in the [001] direction. The data are shown weighting by the factor c_λ as defined by Eq. (6) for a range of temperatures from very low (blue) to very high (red).

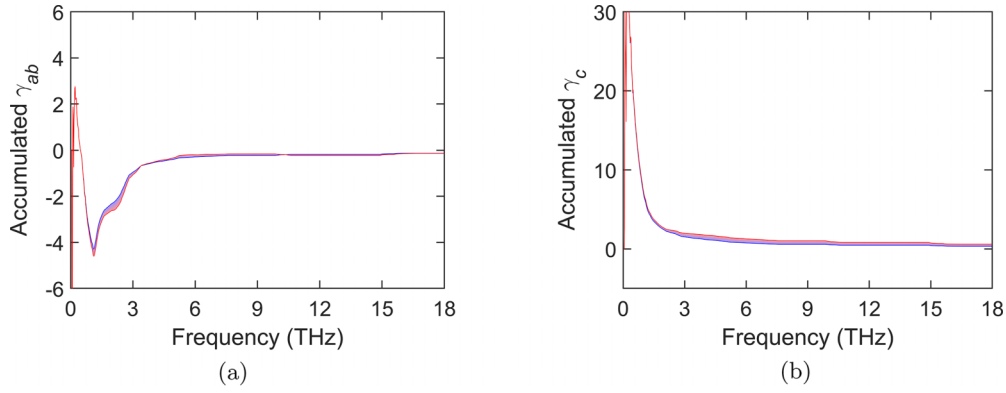


FIG. 6. Accumulated values of the mode strain Grüneisen parameters, Eq. (10), of $\text{ZnB}_2(\text{CN})_8$ for different frequencies of the normal modes of $\text{ZnB}_2(\text{CN})_8$, (a) with area strain in the (001) plane, and (b) with axial strain in the [001] direction.

a value of around 1 by 50 K. On the other hand, the area-strain overall Grüneisen parameter shows very small negative values for all temperatures above 50 K, and larger negative values for temperatures below 50 K. It is useful to note that an independent calculation [31] reproduced the behavior of the axial-strain overall Grüneisen parameter, but gave a slightly positive value for the area-strain overall Grüneisen parameter in contrast with our negative value. In practice, as we next see, this makes very little difference to the calculation of the two linear expansivities, which is the point we now arrive at.

The linear expansivities were calculated from Eqs. (8) and (9), using the values of the elastic constants given in Table IV. The results are shown as functions of temperature in Fig. 7(b). The key results are that α_3 has a large positive value, reaching a value of nearly $+60 \text{ MK}^{-1}$ at high temperatures, whereas α_1 is small and negative, across the range of temperatures, with a value of around -4 MK^{-1} . The experimental data [31] shown in Fig. 1(b) give a value of α_3 that is slightly larger than in our calculation at high temperature, but, nevertheless, the agreement between the large experimental and calculated values is good. Although we do not reproduce the transition of α_1 from NTE to PTE, the small calculated value reflects the small experimental negative value at lower temperatures. The small value of α_1 arises from the subtraction of two much larger numbers in Eq. (8), so the value of this function is very

sensitive to small variations in either the overall Grüneisen parameters or the elastic constants.

The point about the sensitivity of the area thermal expansion to the exact values of the elastic constants is particularly important. The elastic constants will vary with temperature and this will affect the balance in Eq. (8), and hence also the size and sign of area thermal expansion. Thus, it is quite possible that the transition from NTE to PTE of α_1 seen in Fig. 1(b) arises from the effects of temperature on the values of the elastic constants, something that cannot be incorporated into the calculations presented in this study.

V. DISCUSSION AND CONCLUSIONS

A. Thermal expansivity of $\text{ZnB}_2(\text{CN})_8$

Let us move from the graphs for thermal expansivities shown in Fig. 7(b) to think about the impact of the underlying equations (8) and (9). We substitute some numbers for $\text{ZnB}_2(\text{CN})_8$ from Table IV to give

$$\alpha_1 = \beta(23.30\bar{\gamma}_{ab} - 14.12\bar{\gamma}_c)/4$$

$$\alpha_3 = \beta(62.88\bar{\gamma}_c - 7.06\bar{\gamma}_{ab})$$

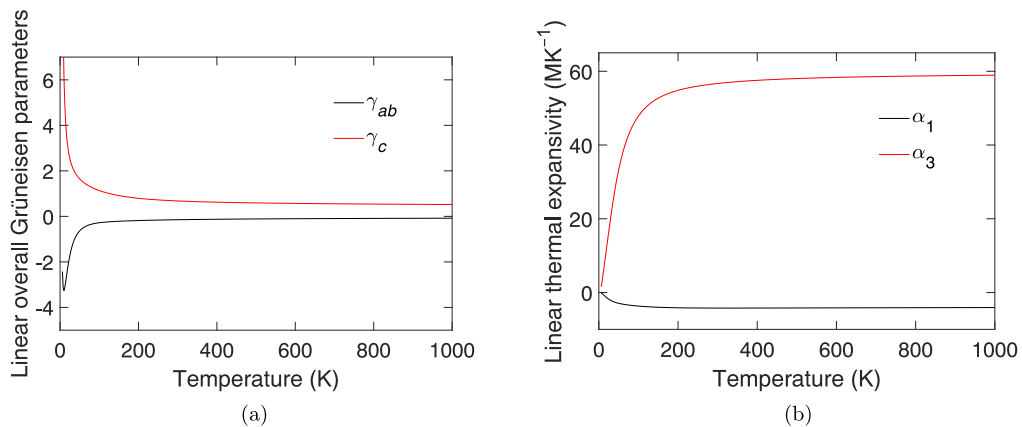


FIG. 7. (a) Calculated temperature-dependence of the two overall strain Grüneisen parameters. (b) Calculated temperature dependence of the two linear thermal expansivities.

where $\beta = C_V/dV_0$ is the constant coefficient, and we now discuss the linear strain $\alpha_1 = \alpha_2 = \alpha_{ab}/2$. A number of numerical points are obvious from the outset.

The *first point* is that in the equation for α_3 , the coefficient for the contribution from $\bar{\gamma}_c$ is the largest of all, and the negative coefficient for the contribution from $\bar{\gamma}_{ab}$ to α_3 is much smaller. In the event that $\bar{\gamma}_c > |\bar{\gamma}_{ab}|$, α_3 will automatically have a positive value.

The *second point* is that there is a much closer balance between the two components in the equation for α_1 , and that the coefficient for the contribution from $\bar{\gamma}_{ab}$ to α_1 is much smaller than the coefficient for the corresponding contribution from $\bar{\gamma}_c$ to α_3 .

The *third point* is that there is a division by a factor of 4 in the equation for α_1 that is not present in the equation for α_3 .

These immediately have a number of consequences for the anisotropic thermal expansivity of $\text{ZnB}_2(\text{CN})_8$. Most striking is that, if $\bar{\gamma}_c > 0$, which it is, its contribution to giving a positive value for α_3 far exceeds the contribution from $\bar{\gamma}_{ab}$. Furthermore, if $\bar{\gamma}_{ab} < 0$ —which appears to be the case in our calculations—its negative coefficient will ensure that it too will contribute positively to α_3 . Thus, we see why the overall expansivity of $\text{ZnB}_2(\text{CN})_8$ is dominated by α_3 . Even setting $\bar{\gamma}_{ab} = 0$ it follows that $\alpha_3/|\alpha_1| = 18$, so regardless of the sign of α_1 we see that for $\text{ZnB}_2(\text{CN})_8$ α_3 will be *much* larger than $|\alpha_1|$.

On the other hand, given that $\bar{\gamma}_c > 0$, its negative coefficient in the equation for α_1 ensures that it has a large negative contribution to α_1 . If we take the high-temperature value of $\bar{\gamma}_c = +0.5$, we see that, for all $\bar{\gamma}_{ab} < +0.3$, the basal plane will show NTE, even if $\bar{\gamma}_{ab}$ has a positive value. The tension effect operating within the layers of $\text{ZnB}_2(\text{CN})_8$ need not be significant for the crystal to show area NTE; the tension effect causes the value of $\bar{\gamma}_{ab}$ to be low enough—and by “low enough” we mean lower than 60% of the value of $\bar{\gamma}_c$ —to allow the balance of elasticity to create area NTE.

These factors explain why in $\text{ZnB}_2(\text{CN})_8$ we find $\alpha_3 \gg |\alpha_1|$. However, next we explain why this result is not specific to $\text{ZnB}_2(\text{CN})_8$, and that instead it will probably be found as a general feature of the anisotropic thermal expansion of all hybrid layer structures in which the layer network has some degree of flexibility.

B. General principles

It will help to phrase the generalization of our analysis with the help of a cartoon representation, as presented in Fig. 8. This shows two layers, and labels the strong and weak elasticity, and the large and small values of strain Grüneisen parameters.

Equations (8) and (9) have two contributing factors: the two strain Grüneisen parameters, and the elasticity. Regarding the strain Grüneisen parameters we automatically expect that $\bar{\gamma}_c > \bar{\gamma}_{ab}$ for two simple reasons: *First* is that there is no tension effect operating in the axial direction, but there will be one operating within the layers, meaning that the absolute value of $\bar{\gamma}_{ab}$ will be lowered. *Second* is that the forces operating in the axial direction are softer than within the layers, and softer forces usually lead to larger values of the mode

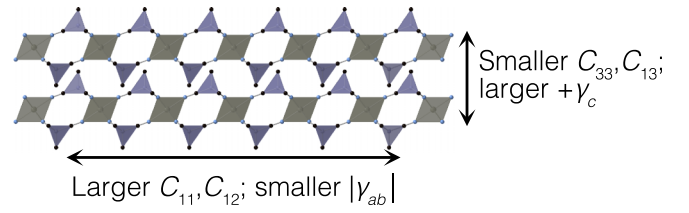


FIG. 8. Cartoon representation to illustrate our understanding of why a hybrid-network layer crystal structure is expected to show $\alpha_3 \gg |\alpha_1|$. The image shows two layers of $\text{ZnB}_2(\text{CN})_8$ viewed along the [110] direction. Each layer has high elasticity (C_{11} and C_{12}), and between layers is weaker elasticity (C_{33} and C_{13}). On the other hand, there is a large positive value of $\bar{\gamma}_c$ because the potential-energy function between layers is softer than within layers and because there is no opportunity for a tension effect, whereas within the layers $|\bar{\gamma}_{ab}|$ is smaller because a tension effect balances negative and positive values of mode Grüneisen parameters.

Grüneisen parameters (which can be understood from their definition).

Regarding the elasticity, because the forces operating in the axial direction are softer than within the layers, we automatically expect to have higher values of the in-plane elastic constants C_{11} and C_{12} —and hence of the combination $C_{11} + C_{12}$ in Eq. (9)—than for the axial elastic constants C_{33} and C_{13} . In Eq. (8) for α_1 and Eq. (9) for α_3 we respectively have products of smaller numbers, $C_{33}\bar{\gamma}_{ab}$ and $C_{13}\bar{\gamma}_c$, and of larger numbers, particularly $(C_{11} + C_{12})\bar{\gamma}_c$. On top of this is the factor of 1/4 in Eq. (8) for α_1 . Hence, two things follow automatically, namely, that α_3 is positive and much larger in value than $|\alpha_1|$, and that the crystal can show area NTE even if the overall area-strain Grüneisen parameter $\bar{\gamma}_{ab}$ is positive. This general result transcends the specific details of $\text{ZnB}_2(\text{CN})_8$ and leads to the general prediction that any hybrid layer structure will most likely show large positive axial thermal expansion and negative area thermal expansion, at least over some range of temperatures.

As an aside, we should note in this argument the importance of the flexibility of the network within the layers, because the same arguments do not apply exactly to layer silicates such as muscovite and clays. These layers contain edge-sharing octahedra, which stiffen the layers considerable and act against the operation of a tension effect. Mostly hybrid layers will show only corner-sharing polyhedra.

It is also worth making a brief comparison with thermal expansion of graphite, which for a long time [28,29,32] has been known to show NTE within the graphitic sheets, with a larger positive thermal expansion in the direction normal to these sheets [68,69]. The most recent calculations and assessment of the elasticity of graphite [70] suggest a very small value of C_{13} . From Eq. (8), this means that, unlike in $\text{ZnB}_2(\text{CN})_8$, the area NTE in graphite probably arises wholly from negative values of $\bar{\gamma}_{ab}$ [71], as in graphene [72,73].

We have identified the point that the anisotropic expansivity tensor of $\text{ZnB}_2(\text{CN})_8$ behaves as it does because of general rather than specific conditions, but it is nevertheless useful to identify what aspects of the phonon spectrum contribute toward the tension effect within its layers. We stress again that we should never identify the origin of NTE as coming

from single modes of vibrations, because, as argued elsewhere [12,19], the statistical contribution of a single mode is vanishingly small in a three-dimensional crystal. Thus, for example, we should not identify the A_{2g} RUM with its negative area-strain mode Grüneisen parameter as dominant in determining the size of the overall parameter $\bar{\gamma}_{ab}$. What we have learned from Figs. 3(a), 4(a), 5(a), and 6(a) is that although the group of modes distributed across reciprocal space but related to the A_{2g} RUM contribute to the tension effect seen within the layers of $\text{ZnB}_2(\text{CN})_8$, the greater effect comes from the modes of lower frequency, which are the acoustic modes spread across all wave vectors. This is also found to be the case in a number of three-dimensional network crystals, including $\text{Zn}(\text{CN})_2$ [41,74–76].

C. Sensitivity of the thermal expansion to the sign of the overall area Grüneisen parameter

Our results, Fig. 7(a), show that the overall area-strain Grüneisen parameters are negative for all temperatures (of value -0.0805 at our highest temperature). We have argued above that we expect to find area NTE even for positive values of $\bar{\gamma}_{ab} < +0.3$. However, this is for the high-temperature limit of the equations, so we have explored the effect of adding a small positive quantity to γ_{ab} to set $\bar{\gamma}_{ab}$ equal to zero at high temperature, and equal to our calculated high-temperature value of $-\bar{\gamma}_{ab}$. The effect is to progressively, but not significantly, reduce the size of α_1 , and to a greater extent at high temperatures. In fact, if we set the value of $\bar{\gamma}_{ab} > +0.3$, even up to $+0.8$ in our calculations, we find that α_1 remains zero at lower temperatures but becomes positive at high temperatures. A value of $\bar{\gamma}_{ab} = +0.39$ will lead to the area NTE extending across the range of temperatures of 0–500 K, with PTE for higher temperatures, as seen experimentally, Fig. 1(b). However, this analysis neglects the fact that our calculations will also be susceptible to variations of the elasticity with temperature, and so the required changes to the value of $\bar{\gamma}_{ab}$ should not be taken as indications of absolute errors in our calculation of $\bar{\gamma}_{ab}$. Increasing the value of $\bar{\gamma}_{ab}$ from negative to positive also has a small effect of reducing the value of α_3 , as expected from the numerics given at the start of Sec. V A.

In a similar vein, we also looked at the effect of changing the value of $\bar{\gamma}_c$ with a fixed negative value of $\bar{\gamma}_{ab}$. We found that this has a much larger effect on α_3 and an almost negligible effect on α_1 , which is consistent with the numerics presented at the start of Sec. V A.

D. Comparison with layered two-dimensional perovskite structures

In the introduction we mentioned that the perovskite-like layer structures show uniaxial NTE, with area PTE [26,27]. This is exactly the opposite of what is observed in $\text{ZnB}_2(\text{CN})_8$, and so is worthy of comment, particularly since the layers in these structures can be described as two-dimensional perovskite networks, albeit not as hybrid networks.

First, we note that the bonding between the layers is much stronger in the case of the uniaxial perovskite-like layer structures than in $\text{ZnB}_2(\text{CN})_8$, mediated by ionic bonds with

intermediate cations. The result of this is that the elastic constant C_{33} is much closer in value to C_{11} in the perovskite-like layer structures [26] than the factor of 2 difference seen in $\text{ZnB}_2(\text{CN})_8$, Table IV. Similarly, in the perovskite-like layer structures $C_{13} > C_{12}$ [26], whereas in $\text{ZnB}_2(\text{CN})_8$ $C_{13} \ll C_{12}$. The result is that with a change in the imbalance between the values of $\bar{\gamma}_{ab}$ and $\bar{\gamma}_c$ (note that Ref. [26] uses $\bar{\gamma}_1$ and $\bar{\gamma}_3$ for our $\bar{\gamma}_{ab}$ and $\bar{\gamma}_c$, respectively), the elasticity tensors allow for a switch between area or uniaxial NTE, even when both $\bar{\gamma}_{ab}$ and $\bar{\gamma}_c$ have positive values. On the other hand, with $\bar{\gamma}_{ab} \simeq \bar{\gamma}_c > 0$, the elasticity itself does not give NTE.

Second, although the authors of Ref. [26] do not report detailed results for their calculations of mode or overall strain Grüneisen parameters, it appears from their Fig. 2 for phonons at the Γ point that the tendency is for $\bar{\gamma}_{ab}$ to be positive and for $\bar{\gamma}_c$ to be negative, the opposite of what we find here for $\text{ZnB}_2(\text{CN})_8$, Fig. 7(a). Thus, in the case of the perovskite-like layer structures, it is likely that $\bar{\gamma}_c \sim -\bar{\gamma}_{ab} < 0$, whereas in $\text{ZnB}_2(\text{CN})_8$ we find that $\bar{\gamma}_c \gg |\bar{\gamma}_{ab}| > 0$. From our comments above regarding the contribution of the elasticity to giving NTE in the perovskite-like layer structures, uniaxial NTE can be achieved with positive values of $\bar{\gamma}_c \sim \bar{\gamma}_{ab}/2$.

We have highlighted the differences between elasticity and the relative signs of the overall strain Grüneisen parameters, but now we consider the reasons for the differences in signs. Recall that we noted that in $\text{ZnB}_2(\text{CN})_8$ we expect a tension effect to operate within the layers but not between the layers, which ensure positive values of $\bar{\gamma}_c$ and smaller or negative values of $\bar{\gamma}_{ab}$. On the other hand, in the perovskite-like layer structures, there is the possibility for a tension effect to operate within and between the layers. Certainly this then allows for a negative value of $\bar{\gamma}_c$ as observed. So what about the operation of a tension effect within the perovskite-like layers?

The perovskites are the archetypal network systems displaying RUMs [16,17,43], in part because the RUM eigenvectors are easier to both visualize and rationalize than in other network systems, such as the phases of silica [44]. However, this can give a misleading impression of the flexibility of perovskites, leading to the very pertinent question posed by the authors of Ref. [26], “Why is it that ABO_3 perovskites generally do not exhibit NTE over a wide temperature range?”

We have asked this question ourselves regarding the comparison with ScF_3 , which does have a perovskite-like crystal structure and does show NTE [12,19]. The answer appears to be that the RUMs in perovskite-like structures are constrained to have wave vectors along lines in reciprocal space. As a result, any dominant contribution of RUM-like motions to a negative tension effect, and hence to NTE, must arise from the ability of the structure to allow a RUM-like tension effect to spread into reciprocal space from the RUM lines. This is only possible if the octahedra have some degree of bond-bending flexibility, and it appears that there is insufficient flexibility in oxide octahedra but sufficient flexibility in ScF_3 . There is, in fact, more flexibility within the layers of perovskite-like structures, because the terminal oxygen atoms at the tops and bottoms of the layers have lost their constraints, corresponding to the arguments made in Sec. III. This allows for one RUM per wave vector in the case of layers that are one-octahedron thick, which is the transverse acoustic mode for out-of-layer displacements. In many systems the acoustic

modes are able to give a tension effect, as we have found in $\text{ZnB}_2(\text{CN})_8$ (Fig. 3), but we suspect that, in the case of the perovskite-like layer structures, the effect is muted by the interactions between the octahedra and the interlayer cations.

Put together, these arguments allow us to understand why in the perovskite-like layer structures we might have a tension effect operating in the direction perpendicular to the perovskite-like layers, giving uniaxial NTE, but with area PTE, the opposite to what is seen in $\text{ZnB}_2(\text{CN})_8$ and which we have argued will be seen also in other hybrid layer structures. Both hybrid layer structures and the perovskite-like layer structures show the form of the elasticity tensors to allow NTE to arise even if the overall Grüneisen parameters are positive, but there is greater anisotropy in hybrid layer structures such as $\text{ZnB}_2(\text{CN})_8$. The critical differences between the perovskite-like layer structures and hybrid layer structures essentially arise because the tension effects operate in different directions. In fact, in both cases we can see NTE even if both $\bar{\gamma}_{ab}$ and $\bar{\gamma}_c$ are positive, but whether we have area or uniaxial NTE depends on which is larger, which in turn depends on the direction that sees the greater tension effect.

E. Conclusion

In conclusion, we note that our DFT calculations reproduce the two linear thermal expansivities of the hybrid layer structure $\text{ZnB}_2(\text{CN})_8$, particularly the relatively large expansivity in the axial direction, and the near-zero and slightly negative value in the plane of the layers of the crystal structure. However, from our arguments immediately above we contest that this good agreement follows from the general principles we have identified in this study, namely, that in a hybrid layer structure the existence of partly flexible yet elastically stiff layers with weaker interlayer forces means that the combination of stronger and weaker intralayer and interlayer elasticity respectively, with a tension effect that operates only within the layers, inevitably leads to larger axial thermal expansivity and the possibility of area NTE. $\text{ZnB}_2(\text{CN})_8$ has thus served as a nice vehicle from which we have been able to derive these general principles. It will certainly be interesting to find other examples of similar hybrid layer materials to confirm the general points established here.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China, Grant No. 12350710177 (M.T.D.). We thank Branton Campbell of Brigham Young University for checking our flexibility calculations with his isotilt tool [77–79].

AUTHOR'S NOTE

This work was initially carried out in collaboration with the research group of Professor Gao of Zhengzhou University, who had identified the potential interest of $\text{ZnB}_2(\text{CN})_8$. They performed parallel calculations using the vasp software, complementing those we report here, which were performed using castop (Secs. II A and IV). We and the group of Professor Gao obtained similar results, as represented in Figs. 2 and 7, but we arrived at different conclusions regarding the origin of the thermal expansion, particularly in respect to the interpretation of the roles of the lower-frequency A_{2g} and E_g optic modes at zero wave vector, and of the relative importance (or otherwise) of the nonbridging B–C–N bonds. Their interpretation is being published elsewhere [31].

We stress that all the research reported here has been carried out independently of the group in Zhengzhou University, particularly in regards to the determination of network flexibility (Sec. III), DFT calculations (Sec. IV), all software used in the analysis of our data (Sec. IV; the software tools were written by the corresponding author, M.T.D., and shared with the group of Professor Gao for use in their analysis of phonon data [31]), all interpretations of the underlying theoretical concepts, and all interpretations of the results of calculations. The conclusions reached in Sec. V were also obtained independently.

In this paper we have reproduced experimental data from the group of Zhengzhou University [31] for the lattice parameters [Fig. 1(b)] and frequencies of the Raman-active modes (Table V), giving credit at the appropriate point in the paper.

We are grateful to Professor Gao for having invited us to participate in this collaboration, and for regular and free discussions and exchange of data with his group members.

Ben Durham: Software

Guanqun Cai: Investigation, writing, review, and editing

Junbiao Guo: Formal analysis, investigation, visualization, writing, review, and editing

Kaiyue Zhao: Investigation, writing, review, and editing

Keith Refson: Formal analysis, investigation, software, writing, review, and editing

Martin T. Dove: Conceptualization, formal analysis, funding acquisition, investigation, methodology, project administration, resources, supervision, software, visualization, writing original draft, writing, review, and editing

DATA AVAILABILITY

The data that support the findings of this article are not publicly available because they are owned by a third party [31] and the terms of use prevent public distribution. The data generated in this study are available from the authors upon reasonable request.

- [1] N. Shi, Y. Song, X. Xing, and J. Chen, Negative thermal expansion in framework structure materials, *Coord. Chem. Rev.* **449**, 214204 (2021).
- [2] T. A. Mary, J. S. O. Evans, T. Vogt, and A. W. Sleight, Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW_2O_8 , *Science* **272**, 90 (1996).

- [3] C. Martinek and F. A. Hummel, Linear thermal expansion of three tungstates, *J. Am. Ceram. Soc.* **51**, 227 (1968).
- [4] J. Alamo and R. Roy, Ultralow-expansion ceramics in the system $\text{Na}_2\text{O-ZrO}_2\text{P}_2\text{O}_5\text{-SiO}_2$, *J. Am. Ceram. Soc.* **67**, c78 (1984).

- [5] R. Roy, D. K. Agrawal, and H. A. McKinstry, Very low thermal expansion coefficient materials, *Annu. Rev. Mater. Sci.* **19**, 59 (1989).
- [6] J. W. Couves, R. H. Jones, S. C. Parker, P. Tschaufeser, and C. R. A. Catlow, Experimental verification of a predicted negative thermal expansivity of crystalline zeolites, *J. Phys.: Condens. Matter* **5**, L329 (1993).
- [7] R. Roy and D. Agrawal, Thermal-expansion materials not so new, *Nature (London)* **388**, 433 (1997).
- [8] C. N. Chu, N. Saka, and N. P. Suh, Negative thermal expansion ceramics: A review, *Mater. Sci. Eng.* **95**, 303 (1987).
- [9] M. T. Dove and H. Fang, Negative thermal expansion and associated anomalous physical properties: Review of the lattice dynamics theoretical foundation, *Rep. Prog. Phys.* **79**, 066503 (2016).
- [10] B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman, and A. P. Wilkinson, Pronounced negative thermal expansion from a simple structure: Cubic ScF_3 , *J. Am. Chem. Soc.* **132**, 15496 (2010).
- [11] M. G. Tucker, M. T. Dove, and D. A. Keen, Direct measurement of the thermal expansion of the Si–O bond by neutron total scattering, *J. Phys.: Condens. Matter* **12**, L425 (2000).
- [12] M. T. Dove, J. Du, Z. Wei, D. A. Keen, M. G. Tucker, and A. E. Phillips, Quantitative understanding of negative thermal expansion in scandium trifluoride from neutron total scattering measurements, *Phys. Rev. B* **102**, 094105 (2020).
- [13] T. H. K. Barron, On the thermal expansion of solids at low temperatures, *Philos. Mag.* **46**, 720 (1955).
- [14] T. H. K. Barron, Grüneisen parameters for the equation of state of solids, *Ann. Phys. (NY)*, **1**, 77 (1957).
- [15] G. D. Barrera, J. A. O. Bruno, T. H. K. Barron, and N. L. Allan, Negative thermal expansion, *J. Phys.: Condens. Matter* **17**, R217 (2005).
- [16] M. T. Dove, Flexibility of network materials and the rigid unit mode model: A personal perspective, *Philos. Trans. R. Soc. A* **377**, 20180222 (2019).
- [17] L. Tan, V. Heine, G. Li, and M. T. Dove, The rigid unit mode model: Review of ideas and applications, *Rep. Prog. Phys.* **87**, 126501 (2024).
- [18] S. U. Handunkanda, E. B. Curry, V. Voronov, A. H. Said, G. G. Guzmán-Verri, R. T. Brierley, P. B. Littlewood, and J. N. Hancock, Large isotropic negative thermal expansion above a structural quantum phase transition, *Phys. Rev. B* **92**, 134101 (2015).
- [19] M. T. Dove, Z. Wei, A. E. Phillips, D. A. Keen, and K. Refson, Which phonons contribute most to negative thermal expansion in ScF_3 ? *APL Mater.* **11**, 041130 (2023).
- [20] L. H. N. Rimmer, M. T. Dove, and K. Refson, Phonon mechanism for the negative thermal expansion of zirconium tungstate, ZrW_2O_8 , *Phys. Chem. Chem. Phys.* **25**, 16753 (2023).
- [21] R. W. Munn, Role of the elastic constants in negative thermal expansion of axial solids, *J. Phys. C: Solid State Phys.* **5**, 535 (1972).
- [22] L. Peters, K. Knorr, M. Knapp, and W. Depmeier, Thermal expansion of gehlenite, $\text{Ca}_2\text{Al}[\text{AlSiO}_7]$, and the related aluminates $\text{LnCaAl}[\text{Al}_2\text{O}_7]$ with $\text{Ln} = \text{Tb}, \text{Sm}$, *Phys. Chem. Miner.* **32**, 460 (2005).
- [23] G. A. Wiegers, The characterisation of VSe_2 : A study of the thermal expansion, *J. Phys. C: Solid State Phys.* **14**, 4225 (1981).
- [24] M. Catti, G. Ferraris, and G. Ivaldi, Thermal strain analysis in the crystal structure of muscovite at 700 °C, *Eur. J. Mineral.* **1**, 625 (1989).
- [25] S. J. Hibble, A. M. Chippindale, A. H. Pohl, and A. C. Hannon, Surprises from a simple material—the structure and properties of nickel cyanide, *Angew. Chem. Int. Ed.* **46**, 7116 (2007).
- [26] C. Ablitt, S. Craddock, M. S. Senn, A. A. Mosto, and N. C. Bristowe, The origin of uniaxial negative thermal expansion in layered perovskites, *npj Comput. Mater.* **3**, 44 (2017).
- [27] W.-T. Chen, C. Ablitt, N. C. Bristowe, A. A. Mostofi, T. Saito, Y. Shimakawa, and M. S. Senn, Negative thermal expansion in high pressure layered perovskite Ca_2GeO_4 , *Chem. Commun.* **55**, 2984 (2019).
- [28] J. B. Nelson and D. P. Riley, The thermal expansion of graphite from 15 °C. to 800 °C.: part I. Experimental, *Proc. Phys. Soc.* **57**, 477 (1945).
- [29] D. P. Riley, The thermal expansion of graphite: Part II. Theoretical, *Proc. Phys. Soc.* **57**, 486 (1945).
- [30] M. Neukirch, S. Tragl, H.-J. Meyer, T. Küppers, and H. Willner, $\text{M}[\text{B}(\text{CN})_4]_2$: Zwei neue Tetracyanoborate mit zweiwertigen Kationen ($\text{M} = \text{Zn}, \text{Cu}$), *Z. Anorg. Allg. Chem.* **632**, 939 (2006).
- [31] Q. Gao, S. Zhao, S. Lorenzen, K. Zhao, Q. Sun, M. Finze, G. Cai, S. Kawaguchi, E. Liang, and J. Chen, preceding paper, Biaxial zero thermal expansion in zinc tetracyanoborate, *Phys. Rev. B* **113**, 064107 (2026).
- [32] E. Kellett and B. Richards, The thermal expansion of graphite within the layer planes, *J. Nucl. Mater.* **12**, 184 (1964).
- [33] E. Liang, Q. Sun, H. Yuan, J. Wang, G. Zeng, and Q. Gao, Negative thermal expansion: Mechanisms and materials, *Front. Phys.* **16**, 53302 (2021).
- [34] A. K. Cheetham, C. N. R. Rao, and R. K. Feller, Structural diversity and chemical trends in hybrid inorganic–organic framework materials, *Chem. Commun.* 4780 (2006).
- [35] C. N. R. Rao, A. K. Cheetham, and A. Thirumurugan, Hybrid inorganic–organic materials: A new family in condensed matter physics, *J. Phys.: Condens. Matter* **20**, 083202 (2008).
- [36] A. L. Goodwin, M. T. Dove, A. M. Chippindale, S. J. Hibble, A. H. Pohl, and A. C. Hannon, Aperiodicity, structure, and dynamics in $\text{Ni}(\text{CN})_2$, *Phys. Rev. B* **80**, 054101 (2009).
- [37] S. J. Hibble, G. B. Wood, E. J. Bilbe, A. H. Pohl, M. G. Tucker, A. C. Hannon, and A. M. Chippindale, Structures and negative thermal expansion properties of the one-dimensional cyanides, CuCN , AgCN and AuCN , *Z. Kristallogr. - Cryst. Mater.* **225**, 457 (2010).
- [38] K. W. Chapman, P. J. Chupas, and C. J. Kepert, Compositional dependence of negative thermal expansion in the Prussian blue analogues $\text{M}^{\text{II}}\text{Pt}^{\text{IV}}(\text{CN})_6$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$), *J. Am. Chem. Soc.* **128**, 7009 (2006).
- [39] A. L. Goodwin and C. Kepert, Negative thermal expansion and low-frequency modes in cyanide-bridged framework materials, *Phys. Rev. B* **71**, 140301(R) (2005).
- [40] A. L. Goodwin, Rigid unit modes and intrinsic flexibility in linearly bridged framework structures, *Phys. Rev. B* **74**, 134302 (2006).
- [41] H. Fang, M. T. Dove, L. H. N. Rimmer, and A. J. Misquitta, Simulation study of pressure and temperature dependence of the negative thermal expansion in $\text{Zn}(\text{CN})_2$, *Phys. Rev. B* **88**, 104306 (2013).

- [42] J. Guo, K. Refson, and M. T. Dove, Negative thermal expansion in cyanide salts with linear connectivities (unpublished).
- [43] A. P. Giddy, M. T. Dove, G. S. Pawley, and V. Heine, The determination of rigid-unit modes as potential soft modes for displacive phase transitions in framework crystal structures, *Acta Crystallogr. Sect. A: Found. Crystallogr.* **49**, 697 (1993).
- [44] K. D. Hammonds, M. T. Dove, A. P. Giddy, V. Heine, and B. Winkler, Rigid-unit phonon modes and structural phase transitions in framework silicates, *Am. Mineral.* **81**, 1057 (1996).
- [45] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, First principles methods using CASTEP, *Z. Krist.-Cryst. Mater.* **220**, 567 (2005).
- [46] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [47] S. Grimme, S. Ehrlich, and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.* **32**, 1456 (2011).
- [48] D. R. Hamann, X. Wu, K. M. Rabe, and D. Vanderbilt, Metric tensor formulation of strain in density-functional perturbation theory, *Phys. Rev. B* **71**, 035117 (2005).
- [49] D. R. Hamann, K. M. Rabe, and D. Vanderbilt, Generalized-gradient-functional treatment of strain in density-functional perturbation theory, *Phys. Rev. B* **72**, 033102 (2005).
- [50] X. Wu, D. Vanderbilt, and D. R. Hamann, Systematic treatment of displacements, strains, and electric fields in density-functional perturbation theory, *Phys. Rev. B* **72**, 035105 (2005).
- [51] S. Baroni, P. Giannozzi, and A. Testa, Elastic constants of crystals from linear-response theory, *Phys. Rev. Lett.* **59**, 2662 (1987).
- [52] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, *Rev. Mod. Phys.* **73**, 515 (2001).
- [53] J. H. Lloyd-Williams and B. Monserrat, Lattice dynamics and electron-phonon coupling calculations using nondiagonal supercells, *Phys. Rev. B* **92**, 184301 (2015).
- [54] L. H. N. Rimmer and M. T. Dove, Simulation study of negative thermal expansion in yttrium tungstate $\text{Y}_2\text{W}_3\text{O}_{12}$, *J. Phys.: Condens. Matter* **27**, 185401 (2015).
- [55] J. D. Gale, GULP: A computer program for the symmetry-adapted simulation of solids, *J. Chem. Soc. Faraday Trans.* **93**, 629 (1997).
- [56] J. D. Gale and A. L. Rohl, The general utility lattice program (GULP), *Mol. Simul.* **29**, 291 (2003).
- [57] J. C. Maxwell, On the calculation of the equilibrium and stiffness of frames, *Philos. Mag.* **27**, 294 (1864).
- [58] A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, and M. C. Warren, Origin of the negative thermal expansion in ZrW_2O_8 and ZrV_2O_7 , *J. Phys.: Condens. Matter* **8**, 10973 (1996).
- [59] K. D. Hammonds, A. Bosenick, M. T. Dove, and V. Heine, Rigid unit modes in crystal structures with octahedrally coordinated atoms, *Am. Mineral.* **83**, 476 (1998).
- [60] E. B. Christoffel, Ueber die Fortpflanzung von Stößen durch elastische feste Körper, *Ann. Mat. Pura Appl.* **8**, 193 (1877).
- [61] F. I. Fedorov, *Theory of Elastic Waves in Crystals* (Springer, New York, 1968).
- [62] E. Kroumova, M. I. Aroyo, J. M. Perez-Mato, A. Kirov, C. Capillas, S. Ivantchev, and H. Wondratschek, Bilbao crystallographic server: Useful databases and tools for phase-transition studies, *Phase Transitions* **76**, 155 (2003).
- [63] T. H. K. Barron and R. W. Munn, Analysis of the thermal expansion of anisotropic solids: Application to zinc, *Philos. Mag.* **15**, 85 (1967).
- [64] T. H. K. Barron, Vibrational effects in the thermal expansion of noncubic solids, *J. Appl. Phys.* **41**, 5044 (1970).
- [65] T. Barron, J. Collins, and G. White, Thermal expansion of solids at low temperatures, *Adv. Phys.* **29**, 609 (1980).
- [66] P. R. L. Welche, V. Heine, and M. T. Dove, Negative thermal expansion in beta-quartz, *Phys. Chem. Miner.* **26**, 63 (1998).
- [67] H. Fang, M. T. Dove, and K. Refson, Ag–Ag dispersive interaction and physical properties of $\text{Ag}_3\text{Co}(\text{CN})_6$, *Phys. Rev. B* **90**, 054302 (2014).
- [68] P. L. Walker, H. A. McKinsty, and C. C. Wright, X-ray diffraction studies of a graphitized carbon - changes in interlayer spacing and binding energy with temperature, *Ind. Eng. Chem.* **45**, 1711 (1953).
- [69] E. Kellett and B. Richards, The *c*-axis thermal expansion of carbons and graphites, *J. Appl. Crystallogr.* **4**, 1 (1971).
- [70] K. H. Michel and B. Verberck, Theory of the elastic constants of graphite and graphene, *Phys. Status Solidi B* **245**, 2177 (2008).
- [71] R. Mittal, M. K. Gupta, B. Singh, S. Mishra, and S. L. Chaplot, Anharmonic phonons and anomalous thermal expansion of graphite, *Solid State Commun.* **332**, 114324 (2021).
- [72] D. Yoon, Y.-W. Son, and H. Cheong, Negative thermal expansion coefficient of graphene measured by Raman spectroscopy, *Nano Lett.* **11**, 3227 (2011).
- [73] S. Mann, R. Kumar, and V. K. Jindal, Negative thermal expansion of pure and doped graphene, *RSC Adv.* **7**, 22378 (2017).
- [74] J. W. Zwanziger, Phonon dispersion and Grüneisen parameters of zinc dicyanide and cadmium dicyanide from first principles: Origin of negative thermal expansion, *Phys. Rev. B* **76**, 052102 (2007).
- [75] L. H. N. Rimmer, M. T. Dove, B. Winkler, D. J. Wilson, K. Refson, and A. L. Goodwin, Framework flexibility and the negative thermal expansion mechanism of copper(I) oxide Cu_2O , *Phys. Rev. B* **89**, 214115 (2014).
- [76] L. H. N. Rimmer, M. T. Dove, A. L. Goodwin, and D. C. Palmer, Acoustic phonons and negative thermal expansion in MOF-5, *Phys. Chem. Chem. Phys.* **16**, 21144 (2014).
- [77] B. Campbell, C. J. Howard, T. B. Averett, T. A. Whittle, S. Schmid, S. Machlus, C. Yost, and H. T. Stokes, An algebraic approach to cooperative rotations in networks of interconnected rigid units, *Acta Crystallogr. Sect. A: Found. Adv.* **74**, 408 (2018).
- [78] B. J. Campbell, H. T. Stokes, T. B. Averett, S. Machlus, and C. J. Yost, The ISOTILT software for discovering cooperative rigid-unit rotations in networks of interconnected rigid units, *J. Appl. Crystallogr.* **54**, 1847 (2021).
- [79] B. J. Campbell, H. T. Stokes, and C. J. Yost, ISOTILT, <https://iso.byu.edu/isotilt.php>.