Negative Thermal Expansion and Some Elastic properties of a Class of Solids

Yan He, Vladimir Cvetkovic, C. M. Varma

Department of Physics, University of California, Riverside, CA
(Dated: April 16, 2010)

We consider the thermal expansion, change of sound velocity with pressure and temperature, and the Poisson ratio of lattices which have rigid units (polyhedra very large stiffness to change in bond-length and to bond-angle variations) connected to other such units through relatively compressible polyhedra. We show that in such a model, the potential energy for rotations of the rigid units can occur only as a function of the combination \( \Theta_i \equiv (\theta_i - (\nabla \times u_i)/2) \), where \( \theta_i \) are the orthogonal rotation angles of the rigid unit \( i \) and \( u_i \) is its displacement. Given such new invariants in the theory of elasticity and the hierarchy of force constants of the model, a negative thermal expansion coefficient as well as a decrease in the elastic constants of the solid with temperature and pressure is shown to follow. These are consistent with the observations.

PACS numbers: 65.40.De, 62.20.de, 62.20.dj

I. INTRODUCTION

Most solids expand on raising temperature. There has been a large interest recently in materials that do the opposite. A particular example is ZrW\(_2\)O\(_8\) in which the volume decreases linearly with temperature from about 10 K to about 1000 K. The thermal expansion coefficient \( \alpha = (1/V) \partial V/\partial T \approx -2.6 \times 10^{-5} K^{-1} \) and is isotropic over this range.\(^1\) Other examples are discussed by Tao and Sleight.\(^2\) These solids appear to share the feature that they contain "rigid units". By this is meant that the complicated lattice structure of such solids is composed of corner or edge sharing polyhedra which are very stiff towards internal bond-stretching or bond-bending compared to the stiffness for change of the relative angles of the polyhedra and to other elastic forces which determine the sound-velocities.

It was proposed very early\(^\text{2,3}\) that the dynamics of rigid units must be of primary importance in negative thermal expansion in such solids. One of the first models proposed was the one in which each polyhedra is connected to others by three or more polyhedra in ZrW\(_2\)O\(_8\). In this case, rotation of any polyhedra must be accompanied by the rotation of the whole solid. Rotation of individual polyhedra, which was the idea behind the negative thermal expansion is then not a thermodynamic variable. Perhaps, to circumvent this problem, a model was introduced\(^\text{4}\) in which the atoms connecting the polyhedra was split in to two with a spring in between them. The analysis of such a model was carried out by standard methods of evaluating the dynamical matrix with some assumed potential functions. This gave what were termed "rigid unit modes" throughout the Brillouin zone which appear not to agree with the spectra measured by neutron scattering\(^\text{2}\) or with the temperature dependence of the specific heat in ZrW\(_2\)O\(_8\),\(^\text{4}\) which appear anomalous only at low temperatures.

Figure 1: The unit cell in our problem. In the ground state at \( T = 0 \) the distance between the neighboring squares is \( a \) (lattice constant). The displacement of the center of each square \( i \) is \( u_i \), and its rotation from the equilibrium is expressed through angle \( \theta_i \). The rods \( l_s \) connect neighboring squares and they are very rigid. The other rigidity is due to the varying angle between rods and squares.

A variant of the model\(^\text{5}\), represented in two dimensions by Fig. 1 of Ref. \([9]\) for such crystals was proposed. The essential feature of this model is that the polyhedra are of two kinds, those that are three or more-fold connected and those that are only two fold connected. In such a model the two fold connected squares can be replaced by rigid rods. The generalization of this to three dimensions is also given in Ref. \([\text{5}]\) and has the same properties as the two-dimensional model. The polyhedra in ZrW\(_2\)O\(_8\), for example satisfy such properties. The two dimensional model is the same as that represented by Fig. \([\text{1}]\) here, with the springs between squares replaced by fixed rods.

In Fig.1 of Ref. \([9]\) the squares do not change their shape of size and the only degree of freedom in the unit-cell is the angle \( \theta \). The area (volume in 3d) occupied by the solid is the sum of the area (volume) occupied by the solid squares (polyhedra) and to the area (volume) between them. The latter are bounded by fixed perimeters (areas). Under this condition, the area (volume) is maximum when the perimeter (surface) is most symmetric. Any distortion from the condition of equilibrium leads to change in \( \theta \) with a change in area (volume) \( \propto (\delta \theta)^2 \). Since the thermal average \( \langle (\delta \theta)^2 \rangle \propto T \) for \( T \gtrsim \omega_0 \),
the bond-bending energy, a decrease in volume with temperature proportional to temperature is to be expected.

The model of Fig. 1 of Ref. [9], though adequate to describe the physics of thermal expansion, is however not a good representation of a solid. The only degree of freedom is the rotation angle \( \theta \). The non-linearity of the problem leads to an interesting mathematical problem but there there are no elastic modes in such models which all solids must have. A simple modification of the model removes this serious shortcoming and in fact makes the problem solvable much more easily.

The modification is to replace the rigid sticks or the rigid two-fold connected polyhedra with sticks or polyhedra with finite compressive stiffness to obtain the model represented in Fig. 1. It is important that this stiffness be large compared to the energy to change \( \theta \). As we will show, this hierarchy of stiffnesses — very large (so as to be taken to be infinity or rigidly constrained) for all internal co-ordinates of the four-fold connected squares compared to that of the spring which is in turn is large compared to the stiffness for changing \( \theta \) preserves the feature which gives negative \( \alpha \) in the earlier model. It has the virtue of having finite elastic constants required of a solid so that sound velocity as a function of volume or pressure or temperature can also be calculated and compared with experiments. Recent experiments show that solids with \( \alpha < 0 \) also have a decrease in elastic constants both with temperature and with pressure. [10]. We will also be able to explain this behavior. We will also show that these properties are consistent with the general relation between the Grüneisen parameter \( \gamma \) which gives the change in vibration frequencies with volume and \( \alpha \).

The two dimensional model is exhibited in Fig. 1. Just as in the previous paper [2], a three dimensional model with the same properties can be shown to have similar properties. Instead of just one rotational degree, they have three rotational degrees of freedom per unit-cell. But the primary feature, the new invariant in the energy, exhibited in Eq. (1) and its coupling to other degrees of freedom, has similar properties in the three-dimensional model. Our intent in this paper is only to exhibit the special features introduced by the hierarchy of the stiffnesses in solids with rigid units and not to calculate the elastic properties quantitatively.

We should add that the physical features of the model are similar to those in the model of previous investigators [2-3]. Our formulation of the problem reveals new general physical and mathematical features of the problem. Some numerical work has also been done on a model similar to that treated here [8].

II. EQUATIONS OF MOTION AND NORMAL MODES

Let us count the degrees of freedom per unit-cell in the model. There are 8 total degrees of freedom per unit-cell and five rigid constraints which fix the lengths and the internal angles of the squares. That leaves 3 dynamical degrees of freedom per unit-cell. (In the earlier model [2], the length of the rods was also fixed introducing two more constraints thus leaving only one degree of freedom, \( \theta \) per unit-cell.) The three degrees of freedom may be taken to be \( \{u_i, \theta_i\} \) where \( u_i = (R_i - R_i(0)) \equiv (u_i^x \hat{x} + u_i^y \hat{y}) \) is the displacement of the center of the mass of the square labelled \( (ij) \) from its equilibrium position at \( T = 0 \). The two extra degrees of freedom compared to the earlier model ensure elastic properties of the model, the \( \theta_i \) degree of freedom provides an optic mode which is crucial as before for the anomalous thermal properties for \( T \) comparable or larger than its energy.

Let us focus on a unit cell. The geometric position of the squares and springs are shown in the schematic figure Fig. 1. For convenience, we consider a single square at position \( i \), and find its free energy. The summation over the entire lattice is then assumed.

The two neighboring corners of squares \( i \) and \( i + \hat{x} \) are spaced apart by vector

\[ l_{i,\hat{x}} = a\hat{x} + u_{i+\hat{x}} - u_i - a\hat{\xi}(\hat{r}_i + \hat{r}_{i+\hat{x}}). \]  

(1)

Unit vectors \( \hat{r}_i = (\cos \theta_i, \sin \theta_i) \) and \( \hat{s}_i = (-\sin \theta_i, \cos \theta_i) \) point along diagonals of square \( i \), and \( \xi \) is the ratio of square diagonal to the square (i.e., lattice) spacing \( a \). The vector \( l_{i,\hat{x}} \) corresponds to the rod between squares \( i \) and \( i + \hat{x} \). Analogously, for the other three corners/rods we have

\[ l_{i,\hat{y}} = a\hat{y} + u_{i+\hat{y}} - u_i - a\hat{\xi}(\hat{r}_i + \hat{r}_{i+\hat{y}}), \]  

\[ l_{i,-\hat{x}} = -a\hat{x} + u_{i-\hat{x}} - u_i + a\hat{\xi}(\hat{r}_i - \hat{r}_{i-\hat{x}}), \]  

\[ l_{i,-\hat{y}} = -a\hat{y} + u_{i-\hat{y}} - u_i + a\hat{\xi}(\hat{s}_i - \hat{s}_{i-\hat{y}}). \]  

(2)

The nominal length of each of the rods at \( T = 0 \) is \( l(0) = a(1 - \xi) \).

In this model there are two contributions to the potential energy. There is a rotational stiffness due to bending between the rods and a square; this is parametrized by an angle \( \mu_{i,\alpha} \) defined through (\( \alpha = \pm \hat{x} \) or \( \pm \hat{y} \))

\[ \cos \mu_{i,\pm \hat{x}} = \pm \frac{\hat{r}_i \cdot l_{i,\pm \hat{x}}}{|l_{i,\pm \hat{x}}|}, \]  

\[ \cos \mu_{i,\pm \hat{y}} = \pm \frac{\hat{s}_i \cdot l_{i,\pm \hat{y}}}{|l_{i,\pm \hat{y}}|}. \]  

(3)

The other stiffness is due to the tendency of the rods to preserve their nominal length \( l(0) \) and it is proportional to the elastic constant of the rods \( g \) that is taken to be large compared to the rotational stiffness. The total potential energy is

\[ V = \sum_{i,\alpha} \left[ K(1 - \cos \mu_{i,\alpha}) + \frac{g}{2}(|l_{i,\alpha}| - l(0))^2 \right]. \]  

(4)

The potential energy Eq. (4) needs to be augmented with the kinetic term. Assuming each square has mass \( M \), the kinetic energy reads

\[ T = \frac{M}{2} \sum_i \left( \dot{u}_i^2 + a^2 \xi^2 J(\dot{\theta}_i)^2 \right). \]  

(5)

The second term, the rotational energy, is proportional to the moment of inertia \( M(a\xi)^2J \). The constant \( J \) is a dimensionless number depending on the mass distribution in each square. For example, the uniform mass distribution yields...
\( J = 1/3 \), while mass concentrated at the square corners results in \( J = 1 \).

In Appendix A, we calculate the potential energy for long wave-length vibrations up to the fourth order in the displacements \( u \) and rotations \( \theta \). The harmonic part of the potential energy, Eq. (4), at long wavelengths is

\[
V_h = a^2 g \left[ \kappa \Theta^2 + \frac{1}{2}(u_{xx}^2 + u_{yy}^2) + \kappa u_{xy}^2 \right]
\]

(6)

where \( \kappa = 2K/(a^2 g(1 - \xi^2)) \) is a dimensionless parameter. Also,

\[
\Theta = \left( \theta - \frac{1}{2} \nabla \times u \right).
\]

(7)

The second and the third terms in Eq. (6) are the familiar terms from the theory of elasticity, where we also introduced strain fields:

\[
u(x,y) \equiv \left( \frac{\partial u^i}{\partial x_j} + \frac{\partial u^j}{\partial x_i} + \frac{\partial u^k}{\partial x_i} \frac{\partial u^k}{\partial x_j} \right).
\]

(8)

The first term in Eq. (6) is unique to the model. A term in energy proportional to \( (\nabla \times u)^2 \) is forbidden because a global rotation of the solid should cost no energy. However, a term proportional to \( \Theta^2 \), as derived in the appendix, is obviously allowed. In fact the interaction expanded to any order in the displacement can depend on \( \Theta \) and \( \nabla \times u \) only in the combinations \( \Theta \), as explicitly shown in the appendix to cubic and quartic order. This is the basic new feature of the vibrations of solids with rigid units. All the interesting new results of this paper can be traced to this feature.

Arranging the degrees of freedom into a column \( \psi = (\theta, u^x, u^y) \) the equations of motion to harmonic order can be concisely written as

\[
M \text{ diag} [Ja^2 \xi^2, 1, 1] \theta_t^2 \psi + M_V \psi = 0.
\]

(9)

In the long wavelength limit, we have

\[
M_V = a^2 g \left( \begin{array}{ccc}
\frac{\kappa}{\sqrt{2}} & \frac{\kappa i q_y}{\sqrt{2}} & -\frac{\kappa i q_x}{\sqrt{2}} \\
\frac{\kappa i q_y}{\sqrt{2}} & -q_x^2 - q_y^2 & 0 \\
-\frac{\kappa i q_x}{\sqrt{2}} & 0 & -q_x^2 - q_y^2
\end{array} \right)
\]

(10)

It is easy to verify that

\[
M_V \left( \begin{array}{c}
-i q_y/2 \\
i q_x/2
\end{array} \right) \approx a^2 g \kappa \left( \begin{array}{c}
1 \\
i q_y/2
\end{array} \right)
\]

(11)

Then the above vector is an eigenvector and we can rewrite

\[
\left( \begin{array}{c}
-i q_y/2 \\
i q_x/2
\end{array} \right)^t \psi = \theta^t + i q_y u^x - i q_x u^y = \Theta
\]

(12)

The corresponding eigenvalue is \( \omega^2 = 2a^2 g \kappa / (Ma^2 \xi^2 J) = 2a^2 g \kappa / (2M a \xi^2 J) \). There are also two gapless elastic modes (linear combinations of \( u_x, u_y \)) required of a two dimensional lattice with eigenvalues \( \approx \frac{a^2 g}{2M} q_{x,y} \).

Setting \( q_x = q \cos \phi \) and \( q_y = q \sin \phi \), the dispersion up to \( q^2 \) can be written as

\[
(\omega_{1,2})^2 = \frac{a^2 g}{4M} \left[ 2 + \kappa \pm \right.
\]

\[
\sqrt{2 - 2(1 - \kappa) \cos 4\phi}
\]

(13)

\[
(\omega_3)^2 = \frac{2g \kappa}{JM \xi^2} \left[ 1 + \frac{\xi(\xi + 2 + 2 \xi)}{8} q^2 \right] = \frac{4K}{JM a^2 \xi^2 (1 - \xi^2)} \left[ 1 + \frac{\xi(\xi + 2 + 2 \xi)}{8} a^2 g^2 \right]
\]

(14)

In order to obtain the \( q^2 \) term in Eq. (14) we need to use the subleading long-wavelength expansion of the potential energy given in Appendix B. Up to this order, the dispersion of the optical mode, which is the mode of the \( \Theta \) degree of freedom Eq. (14) is isotropic and does not depend on the spring constant \( g \).

The elastic modes have a velocity anisotropy consistent with the underlying lattice symmetry, and correspond to a square lattice with leading order elastic constants

\[
C_{11}^0 = g, \quad C_{12}^0 = 0, \quad C_{44}^0 = g \kappa / 2 = \frac{K}{a^2(1 - \xi^2)}.
\]

(15)

It should be noted that we have constructed a very simple model to highlight the new features due to the dynamics of rigid units and kept only the bare minimum of rigidities relevant for the anomalous thermal properties. Because we chose only nearest neighbor central force constants \( C_{12}^0 = 0 \). We can therefore make comparison to experiments only for the elastic constants \( C_{11} \) and \( C_{44} \).

We will consider corrections to these elastic constants at finite temperature and with changing pressure in Sec. IV.

The Poisson ratio of the model follows from the effective elastic constants Eq. (15). For \( C_{12}^0 = 0 \) the Poisson ratio is

\[
\nu_{2D} = \frac{(C_{11}^0 - 2C_{14}^0)(1 + \cos 2\phi)}{(1 + \cos 2\phi) + 2C_{44}^0 \sin^2 2\phi} = \frac{1 - \kappa \sin^2 2\phi}{(1 + \cos 2\phi) + \kappa \sin^2 2\phi}.
\]

(16)

When \( \kappa < 1 \), as it is in our case, the Poisson ratio is strictly positive. Conversely, when \( \kappa > 1 \) it is always negative. So, it appears that not all solids with constraints have auxetic behavior (i.e., \( \nu < 0 \)).

We can compare this spectrum of this model with the rigid constraint model. If we assume the angle \( \theta \) is small and the difference of displacement is high order than angles \( (u_{i+\alpha} - u_i) = O(\theta^2) \) for \( \alpha = \pm \hat{x}, \pm \hat{y} \), we can approximately solve the constraint \( ||u_{i+\alpha}|| = o(1 - \xi) \). We find

\[
u_{\pm \hat{x}} - u_{\pm \hat{x}}^t = \frac{-a \xi}{8(1 - \xi)} \left[ (2 - \xi)(\theta_{i+\hat{x}}^2 + \theta_{i-\hat{x}}^2) + 2 \xi \theta_i \theta_{i+\hat{x}} \right]
\]

(17)

\[
u_{\pm \hat{y}} - u_{\pm \hat{y}}^t = \frac{-a \xi}{8(1 - \xi)} \left[ (2 - \xi)(\theta_{i+\hat{y}}^2 + \theta_{i-\hat{y}}^2) + 2 \xi \theta_i \theta_{i+\hat{y}} \right]
\]

(18)
Thus they are smaller by a factor of concentrate on the first term in Eq. (23). For the same reason
harmonic term to the Lagrangian the equations of motion (at
be omitted hereafter in all other calculations. Adding this
anharmonic term was omitted in Eq. (23) and will
The resulting dispersion is
\[ \omega^2 = \frac{K}{JM a^2 \xi^2} \left[ 1 + \frac{\xi(-2+\xi)}{8} (a \mathbf{q})^2 \right] \] (21)

We compare this result to the optical mode Eq. (14). The gaps
are the same, however, the long wavelength dispersion differs
slightly. We notice, however, that if we were to take first the
limit \( g \to \infty \), and \( \kappa \to 0 \) of the harmonic terms in a controlled
way such that their product \( K = \kappa g a^2 (1 - \xi)^2 / 2 \) remains
finite, the dispersions coincide.

III. CHANGE IN VOLUME WITH TEMPERATURE

So far we have only considered the harmonic approximation
for the new model. At this level, the thermal expansion
must be zero. The change of volume \( \delta V \) is proportional to the
divergence of the displacement field. In harmonic approximation:
\[ \delta V / V = \langle \nabla \cdot \mathbf{u} \rangle \approx \langle u_{ii} \rangle = 0. \] (22)

Here and after the summation over indices is assumed in term
\( u_{ii} = u_{xx} + u_{yy} \).

In order to get non-zero \( \delta V \), we must consider anharmonic
terms in our Hamiltonian which we find from the expansion
of Eq. (4) given in the Appendix. The cubic anharmonic term
is
\[ V^{(3)}_{pot} = \int \frac{g}{2(1-\xi)} \left\{ \xi(u_{ii}) \Theta^2 - 2 \xi \Theta (u_{xx} - u_{yy}) (u_{xy}) + \\
\xi (u_{xy})^2 (u_{ii}) - (1-\xi) [(u_{xx})^3 + (u_{yy})^3] \right\}. \] (23)

If we were to keep all the anharmonic terms the thermal
expansion would depend on the thermal averages \( \langle \Theta^2 \rangle_T \),
\( \langle (u_{ij}) \Theta \rangle_T \), and \( \langle (u_{ij} u_{ij}) \rangle_T \). We know, however, that in the
physical limit that we are interested in \( \kappa \ll 1 \), the first average
is of order \( O(\kappa)^{-1} \), while the others are of order \( O(\kappa)^0 \).
Thus they are smaller by a factor of \( \kappa \), which allows us to
concentrate on the first term in Eq. (23). For the same reason,
terms proportional to \( \kappa \) were omitted in Eq. (23) and will
be omitted hereafter in all other calculations. Adding this
anharmonic term to the Lagrangian the equations of motion (at
\( \omega = 0 \)) become
\[ g \partial_{\omega}^2 u^\alpha = - \frac{g \xi}{2(1-\xi)} \partial_\alpha (\Theta^2), \] (24)

Index \( \alpha \) my be either \( x \) or \( y \). Eq. (24) is equivalent to the Eqs.
(17-18) derived earlier from consideration of the constraints
alone.

Integrating Eq. (24) and taking its average we arrive to
\[ \langle \nabla \cdot \mathbf{u} \rangle (T) = - \frac{\xi}{1-\xi} \langle \Theta^2 \rangle (T). \] (25)

The thermal average of \( \Theta^2 \) is given below, and the classical
limit is
\[ \langle \Theta^2 \rangle (T) = \int \frac{d\mathbf{q}}{\beta} \sum_{\omega_n} \frac{1}{M a^2 \xi^2 J [(i \omega_n)^2 - (\omega_3 (\mathbf{q}))^2]}
= \int \frac{d\mathbf{q}}{\beta} \frac{1}{2Ma^2 \xi^2 J \omega_3 (\mathbf{q})} \coth \frac{\beta \omega_3 (\mathbf{q})}{2}
\approx \frac{k_B T}{2a^2 \kappa} + O(\kappa)^0. \] (26)

In the last step we assumed that the massive optical mode is
only weakly dispersive. The thermal expansion coefficient obtained
by combining Eqs. (25) and (26) is
\[ \alpha = - \frac{k_B \xi}{2a^2 g \kappa (1-\xi)} = - \frac{k_B \xi (1-\xi)}{4K}. \] (27)

The physics of the negative thermal expansion coefficient is
the same as in the earlier model and discussed in the Intro-
duction. The usual anharmonicity of the longitudinal and
the transverse acoustic modes cannot change this because in the
hierarchy of the assumed stiffnesses, such modes have low
occupation compared to the rotation modes of the rigid units
because their energy is higher than \( \omega_3 \), Eq. (14) over
most of the Brillouin zone. The thermal contraction (as well
as the change in sound velocity with temperature derived be-
low) comes from the first anharmonic term in Eq. (23) which
in turn can be traced to the fundamental constraint, Eq. (1)
which links the rotation freedom of the rigid units which costs
low energy to the motion of the degrees of freedom \( \mathbf{u} \), which
determine the volume of the lattice.

IV. CHANGE IN VELOCITY OF SOUND WITH TEMPERATURE, PRESSURE OR VOLUME

The change in the elastic constants with temperature at
fixed pressure of \( ZrW_2O_{\kappa} \) is similar to those of the normal
solids which expand on increasing temperature, i.e., they decrease
on increasing temperature. At a fixed temperature the elastic
constants also decrease with pressure. It is worth dis-
cussing in general that the two properties are mutually consis-
tent and consistent with the relation of the Grüneisen parameter
\( \gamma \) and the thermal expansion coefficient.

The relation
\[ \frac{\partial \omega}{\partial V} \bigg|_T = \frac{\langle \partial \omega / \partial P \rangle_T}{\langle \partial V / \partial P \rangle_T} \] (28)
gives that since \((\partial V/\partial P)_T < 0\) for stability, decrease in the vibration frequencies \(\omega\) with pressure must be accompanied by an increase in \(\omega\) with volume. \(\gamma_\omega \equiv (-\partial \omega/\partial V)_T\) is therefore negative. The thermal expansion coefficient is shown in general to be proportional to \(\gamma\) defined to be an average over all \(\omega\) of \(\gamma_\omega\), on thermodynamic grounds.\(^15\) It thus follows that the observed behavior of the change in volume with temperature, and the change in elastic constants with pressure are mutually consistent. However, we proceed to show this explicitly by calculating both the change in the elastic constants with temperature and with pressure.

Consider the cubic anharmonic terms in Eq. (23). As seen above, a change in temperature leads to a nonzero expectation value for strains at finite temperature

\[
\langle u_{ij}\rangle(T) = \frac{1}{2} \alpha T \delta_{ij}.
\]  

Therefore term such as \(u_{xx},\) and \(u_{yy}\) in Eq. (23) can be replaced by their expectation value. This leads to corrections to the harmonic part of the potential.\(^16\) This correction is linear in \(T\):

\[
V^{(3)}(T) \rightarrow \int d\mathbf{r} \frac{g}{2(1-\xi)} \left\{ \xi \Theta^2 + \xi(u_{xy})^2 - 3 \frac{1-\xi}{2} \left[ (u_{xx})^2 + (u_{yy})^2 \right] \right\} (\nabla \cdot \mathbf{u})(T).
\]  

Small correction due to \(\kappa\) are ignored in Eq. (30). The first term of Eq. (30) yields small corrections (proportional to \(T\)) to the mass of the optical mode and can therefore be neglected in our work. Only the second and the third term contribute to renormalization of the elastic constants Eq. (45).

In addition to Eq. (30), there is another term of the same order in temperature affecting the dispersion of elastic modes. It is derived from quartic anharmonic term and the fact that the average \(\langle \mathbf{g}^2 \rangle_T\) also depends on temperature. Expanding potential Eq. (4) up to the forth order and keeping only \(O(\kappa)^6\) terms, we find

\[
V^{(4)} = \int d\mathbf{r} \frac{ag\xi}{4(1-\xi)^2} \left\{ \Theta^4 + \Theta^2 \left[ 6 \xi (u_{xy})^2 - (1 + \xi) \left[ (u_{xx})^2 + (u_{yy})^2 \right] \right] + \ldots \right\}.
\]  

Here we have introduced a parameter \(a\) to fix the relative magnitude of the quartic to the cubic anharmonicity. In the simple model that we have introduced, this parameter is necessary to get the right variation of all the elastic constants with temperature as well as pressure. Terms of kind \(\Theta(\partial u)^3\) and \(\partial (u)^4\) lead to higher order corrections and have been dropped. Substituting the thermal average \(\langle \Theta^2 \rangle_T\) in Eq. (31) we obtain another correction to the harmonic potential

\[
V^{(4)}(T) \rightarrow \int d\mathbf{r} \frac{ag\xi\langle \Theta^2 \rangle_T}{4(1-\xi)^2} \left\{ 2 \Theta^2 + 6 \xi (u_{xy})^2 - (1 + \xi) \left[ (u_{xx})^2 + (u_{yy})^2 \right] \right\}.
\]  

Same as in Eq. (30), the first term only affects the optical mode mass and is therefore neglected.

Combining the two corrections Eqs. (30) and (32) to potential, the temperature dependence of effective elastic constants is found

\[
\left( \frac{\partial C_{11}}{\partial T} \right)_P = -g \frac{(3 - a - \xi (3 + a))}{2(1 - \xi)} \alpha, \tag{33}
\]

\[
\left( \frac{\partial C_{44}}{\partial T} \right)_P = g \frac{(1 - 3a)\xi}{1 - \xi} \alpha, \tag{34}
\]

where \(\alpha\) is the (negative) thermal expansion coefficient found in Eq. (27).

The pressure dependence of the elastic constants at a constant temperature is derived in an analogous fashion.

\[
\left( \frac{\partial C_{11}}{\partial P} \right)_T = g \frac{(3 - a) - (3 + a)\xi}{2(1 - \xi)} \kappa_T, \tag{35}
\]

\[
\left( \frac{\partial C_{44}}{\partial P} \right)_T = -g \frac{(1 - 3a)\xi}{1 - \xi} \kappa_T, \tag{36}
\]

where \(\kappa_T\) is the isothermal compressibility measuring change in volume proportional to applied pressure: \((\delta V)/V = -\kappa_T(\delta P)\). Within the present model

\[
\langle \nabla \cdot \mathbf{u} \rangle(P) = -\frac{2}{C_{11}^0 + C_{12}^0} P = -\frac{2}{g} P. \tag{37}
\]

The change of the elastic constants with pressure and temperature are consistent with the thermodynamic requirement discussed in Eq. (28).

V. COMPARISON WITH NORMAL SOLIDS WITH \(\alpha > 0\)

It is worthwhile discussing how the differences from solids with normal thermal expansion coefficient \(\alpha > 0\) come about. We may consider the following (schematic) long wavelength Hamiltonian for them.

\[
H = KE + (1/2)\partial \mathbf{u} \cdot \mathbf{C} \partial \mathbf{u} + g_3 \partial \mathbf{u} \cdot \partial \mathbf{u} \partial \mathbf{u}. \tag{38}
\]

KE is the kinetic energy, \(\kappa\) is the matrix of harmonic force constants and \(g_3\) the cubic-anharmonic tensor. An expectation value \((\partial \mathbf{u})\partial \mathbf{u}) = w^2(T)\) is finite at all temperatures so that we may decouple the last term and minimize to get that there is a change in volume which may be schematically represented by

\[
\langle \partial \mathbf{u} \rangle = -g_3 w^2(T)/\kappa. \tag{39}
\]

Solids usually have \(g_3 < 0\). This ensures that an increase(decrease) of interatomic distance decreases (increases) interatomic interaction energy relative to the harmonic case. This then leads to a positive thermal expansion. This is to be contrasted with the \(g\) derived above in the model with rigid units from the expansion of potential energy subject to the constraint Eq. (1). In this case \(g_3 > 0\), as also required by the general argument given in the Introduction.

Given a finite \(\langle \partial \mathbf{u} \rangle\), we may decouple the second term in Eq. (38) also in the alternative way to find an effective stiffness renormalization:

\[
\kappa_{eff} = \kappa_0 + 2g_3 \langle \partial \mathbf{u} \rangle = \kappa - 2g_3^2 w^2(T)/\kappa. \tag{40}
\]
We see that the correction to the effective stiffness does not depend on the sign of \( g_3 \); we always have a decrease in the elastic constants with temperature due to the cubic anharmonic term since the mean square displacement \( \omega^2(T) \) must always increase with temperature consistent with entropy always increasing with temperature. However the quartic term acts in an opposite direction in general and to get elastic softening their effect should be smaller than that of the cubic anharmonicity. As we see below to get this feature of the experiments we have to introduce the parameter \( a \ll 1 \).

VI. COMPARISON WITH THE EXPERIMENTS

Zirconium tungstate is about the most studied materials with negative expansion coefficient. We now check whether our calculations of the thermal expansion coefficient Eq. (22), and the temperature (Eqs. (33) and (34)) and pressure (Eqs. (35) and (36)) corrections to the elastic constants are in qualitative accord with the experiments.

In our model a negative thermal expansion coefficient \( \alpha \), linear in temperature occurs for temperatures above the energy of the rotation optic mode. In experiments, \( \alpha \propto -T \) above about 10 K. We can estimate the parameter \( K \approx 100 \text{K} \) using an effective mass of \( O(500) \) atomic units, to get \( \omega_3 \approx 10 \text{K} \).

The thermal expansion coefficient \( \alpha = -2.6 \times 10^{-5} \text{K}^{-1} \). Our result yields this order of magnitude with \( K \approx 10^2 \text{K} \) for \( \xi \approx 0.9 \).

The relative decrease of the elastic constant \( (1/C_{11}^0)\partial C_{11}(T)/\partial T \) is \( O(10^{-3}) \) and of \( (1/C_{44}^0)\partial C_{44}(T)/\partial T \) is an order of magnitude smaller.

Similarly the decrease of \( C_{44} \) with pressure is an order of magnitude smaller than that of \( C_{11} \). To get the ratio between these quantities, we need to use \( a \approx 1/4 \) in Eqs. (34) and (35).

With these values, we calculate \( (1/C_{11}^0)\partial C_{11}(T)/\partial T \) of the right sign but about 5 times larger in magnitude. This indicates the perils of trying to get the experimental numbers through a model which is too simple in terms of details despite our introduction of the phenomenological parameter \( a \). Part of the difficulty stems from our ignoring normal anharmonic terms to concentrate on the new physics due to the rigid unit rotations. The usual anharmonic terms are always used as adjustable parameters anyway.

VII. CONCLUSIONS

We have constructed a model of a solid with negative thermal expansion coefficient. The solid consists of rigid units interconnected by elastic units where the elastic stiffness is much higher than the next relevant stiffness related to the bond bending. The model has sensible elastic properties even though the optical mode is identical to that found earlier in fully constrained models, which did not have that virtue. A novel feature is the uncovering of a new invariant in the theory of elasticity in this class of models. This may be of relevance also in other contexts.

We do obtain the correct qualitative features for the thermal expansion coefficient and the ratio of the change in the temperature and pressure dependence of the two elastic constants we have calculated. The quantitative agreement cannot be aspired for, although we obtain the thermal expansion coefficient, which depends on the details less than the elastic constants, quite well quantitatively with reasonable parameters. We have had to introduce an ad-hoc parameter \( a \), the ratio of the cubic to the quartic anharmonic parameter, to estimate the change of elastic constants with temperature and pressure quantitatively. Despite that this simple model gives the quantitative value only to within a factor of about 5 although the relative change in the two elastic constants calculated is given much better.
fourth order potential terms are given as follows.

\[ V_3 = \frac{a^2 g}{2(1 - \xi)} \left[ \xi \theta^2 (\partial_x u^x + \partial_y u^y) + 2 \xi \theta (\partial_y u^x \partial_y u^y - \partial_x u^y \partial_x u^x) + \partial_x u^x (\partial_x u^x)^2 + \partial_y u^y (\partial_y u^y)^2 \right] \]

\[ V_4 = \frac{a^2 g}{4(1 - \xi)^2} \left( \xi \theta^4 + 2 \xi^2 \theta^3 (-\partial_x u^y + \partial_y u^x) + \xi \theta^2 \left[ (1 + 2 \xi) [(\partial_x u^y)^2 + (\partial_y u^x)^2] - 2 \xi [(\partial_x u^x)^2 + (\partial_y u^y)^2] \right] + \cdots \right) \]

Here \( \cdots \) in \( V_4 \) are \( \Theta(\partial u)^3 \) and \( (\partial u)^4 \) type of terms which lead to higher order corrections. Plug \( \theta = \Theta + \frac{1}{4}(\partial_x u^y - \partial_y u^x) \) into \( V_3 \), then rearrange terms, we find

\[ V_3 = \frac{a^2 g}{2(1 - \xi)} \left[ \xi \Theta^2 (\partial_x u^x + \partial_y u^y) - \xi \Theta (\partial_x u^y + \partial_y u^x) (\partial_x u^x - \partial_y u^y) \right. \]

\[ + \left. \frac{\xi}{4} \left( \partial_x u^y + \partial_y u^x \right)^2 (\partial_x u^x + \partial_y u^y) \right] + \frac{a^2 g}{2} \left( \partial_x u^x (\partial_x u^x)^2 + \partial_y u^y (\partial_y u^y)^2 \right) \]

(A3)

Now we want to write this in terms of strains. But we have to remember there are cubic order contributions from \( V_2 \). We find

\[ V_2 = \frac{a^2 g}{2} \left[ (u_{xx})^2 + (u_{yy})^2 \right] - \frac{a^2 g}{2} \left[ (\partial_x u^x)^3 + (\partial_x u^x)(\partial_x u^y)^2 + (\partial_y u^y)^3 + (\partial_y u^y)(\partial_y u^x)^2 + O^4(\partial u) \right] \]

(A4)

In Eq. (A4), \( O^4(\partial u) \) denote the 4th or higher order terms of \( \partial u \). The second term of Eq. (A4) should be combined with \( V_3 \).

\[ V_3 = -\frac{a^2 g \xi}{4(1 - \xi)} \left[ \frac{\xi}{\Theta^2} u_{ii} - 2 \frac{\xi}{\Theta} (u_{xx} - u_{yy}) u_{xy} + \xi u_{xy} u_{ii} \right] - \frac{a^2 g}{2} \left[ u_{xx}^3 + u_{yy}^3 \right] + O^4(\partial u, \Theta) \]

(A5)

Here \( O^4(\partial u, \Theta) \) are 4th or higher order terms in \( \partial u \) and \( \Theta \) which we ignored in \( V_3 \) and \( u_{ii} = u_{xx} + u_{yy} \).

We can go on to rewrite \( V_4 \) in terms of \( \Theta \) and strains. We should include the 4th order contribution from \( V_2 \) and \( V_3 \). But for \( V_4 \), we only need terms proportional to \( \Theta^4 \), \( \Theta^3 \) and \( \Theta^2 \), thus the only correction terms we need is the following

\[ -\frac{a^2 g \xi}{4(1 - \xi)} \left[ \Theta^2 (\partial_x u^x)^2 + (\partial_y u^y)^2 (\partial_x u^y)^2 + (\partial_y u^y)^2 \right] \]

which is coming from \( \xi \Theta (\partial_x u^x + \partial_y u^y) \) term in Eq. (A3). Then after some algebraic calculation, we find

\[ V_4 = \frac{a^2 g \xi}{4(1 - \xi)^2} \left( \xi \Theta^4 + \Theta^2 \left[ 6 \xi u_{xy}^2 - (1 + \xi)(u_{xx}^2 + u_{yy}^2) \right] + \cdots \right) + O^3(\partial u, \Theta) \]

(A6)

These contributions are rewritten in Sec. III. However, to compare with experiments, it is found necessary in Sec. III to introduce a phenomenological parameter \( a \), which is the ratio of the quartic to the cubic anharmonic potentials.

**Appendix B: Subleading long wavelength expansion of the potential energy**

In this section we present the gradient expansion of potential energy Eq. (4) where the next order terms in lattice spacing \( a \) are not truncated. These terms are relevant for finding the weak dispersion of the optical mode in Eq. (14) and the comparison of our model to the fully constrained model at the end of Sec. II. For all other purposes, these terms can be truncated and the harmonic potential in Eq. (6) are sufficient.

Using earlier defined phase space vector \( \psi \), the potential energy is written as

\[ V_{pot} = \frac{a^2 g}{2} \left( \begin{array}{c} \theta u^x \\ u^y \end{array} \right) \left( \begin{array}{cc} 2 \kappa & -\frac{\kappa}{6} \\ -\frac{\kappa}{6} & 0 \end{array} \right) \left( \begin{array}{c} \frac{\theta^2 \partial^2}{2} \\ \frac{\theta^2 \partial^2}{2} + \frac{\kappa}{6} \end{array} \right) \left( \begin{array}{c} \theta u^x \\ u^y \end{array} \right) \]

(B1)

In the constrained model, the limiting procedure where \( \kappa \to 0 \) and \( g \to \infty \), in such way that their product (and therefore \( K \)) remains finite yields the dispersion of Eq. (21).
3 J. S. O. Evans, T. A. Mary, T. Vogt, M. Subramanian, A. W. Sleight, Chem. Mater. 8, 2809 (1996).
4 J. Z. Tao, A. W. Sleight, J. Solid State Chem. 173, 442 (2003).
5 A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, and M. C. Warren, J. Phys. Condens. Matter 8, 10973 (1996).
6 G. Ernst, C. Broholm, G. R. Kowach, and A. P. Ramirez, Nature (London) 396, 147 (1998).
7 Z. Schlesinger, J. A. Rosen, J. N. Hancock, A. P. Ramirez, Phys. Rev. Lett. 101, 015501 (2008).
8 J. N. Hancock, C. Turpen, Z. Schlesinger, G. R. Kowach, A. P. Ramirez, Phys. Rev. Lett. 93, 225501 (2004).
9 M. E. Simon, and C. M. Varma, Phys. Rev. Lett. 86, 1781 (2001).
10 C. Pantea, et al., Phys. Rev. B 73, 214118 (2006).
11 L. Landau, and E. Lifshitz, *Theory of Elasticity*, (Pergamon, New York, 1970).
12 J. Turley, and J. Sines, J. Phys. D 4, 264 (1971).
13 M. C. Rechtsman, F. H. Stillinger, and S. Torquato, Phys. Rev. Lett. 101, 085501 (2008).
14 A. Ahsan, J. Rudnick, R. Bruinsma, Phys. Rev. E 76, 061910 (2007).
15 See for example, N. W. Ashcroft, and N. D. Mermin, Chapter 25, *Solid State Physics*, Harcourt Brace College Publishers, New York (1976).
16 H. Kleinert *Gauge fields in Condensed Matter*, Vol. II: *Stresses and Defects, Differential Geometry, Crystal Defects* (World Scientific, Singapore, 1989)