journal

J. Am. Ceram. Soc., **82** [7] 1793–802 (1999)

Geometrical Origin and Theory of Negative Thermal Expansion in Framework Structures

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By framework structures are meant materials consisting of relatively stiff units such as octahedra or tetrahedra, joined by shared oxygen (or other) atoms at the corners. Examples are ZrW_2O_8 and many aluminosilicates. Rigid rotation of the units often gives a reduction of the volume or of some lattice constant as a purely geometrical effect. The theory of this effect is developed and shown to give a negative contribution to the thermal expansion coefficient. This is in addition to the usual positive contribution from anharmonicity of the interatomic forces. The negative effect varies through the phonon spectrum, being strongest for low frequencies, but the sign of the temperature coefficient may be reversed above a soft mode phase transition.

I. Introduction

The ability of a ceramic to withstand thermal shock depends (inter alia) on the coefficient of thermal expansion (COTE). A few have a negative COTE, of which ZrV_2O_7 and ZrW_2O_8 are currently arousing major interest because they have cubic symmetry.[1–4] Other materials have a small positive one or nearly zero such that one infers a negative contribution to the COTE in addition to the usual positive effect from anharmonicity in the interatomic forces.[5]

The present work is a theoretical study of how negative thermal expansion can arise as a geometrical effect in framework structures. Detailed computations for β-quartz and their analysis using the present theory are given elsewhere.[6]

By framework structures we mean crystal structures consisting of rather stiff atomic units such as AX_4 tetrahedra or/and AX_6 octahedra which are joined by shared X atoms (usually oxygen) at the corners.[7] Thus as well as in ZrV_2O_7 and ZrW_2O_8,[1,2] negative COTEs exist in cordierite $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$ in the *c* direction,[8] β-eucryptite $LiAlSiO_4$ also in the *c* direction,[9–11] β-quartz (i.e., above the α–β phase transition temperature),[6,12,13] some zeolites,[14] and dehydrated analcime.[15] The list becomes longer if we include cases where the COTE is approximately zero,[16,17] much less than would be expected from the normal anharmonicity of interatomic potentials, and implying the presence of some additional negative contribution.

We can easily see a qualitative picture of how a negative contribution to the COTE arises. It is a geometrical effect in framework structures, associated with the rotation of the rather stiff structural units,[18–22] or what is the same thing, the bond bending at the shared oxygen (or other) corner atoms. Figure 1 shows the framework structure which we shall refer to as 2D-perovskite. We can consider it either as a 2D (two-dimensional) framework of linked squares or as a (001) section through the octahedra of the cubic or tetragonal perovskite structure. Figure 1(a) shows the ideal structure (lattice constant a_0), and Fig. 1(b) the result of rotating alternate squares by an angle θ. Clearly in the latter the area $A(\theta)$ of the unit cell is reduced and we may write to lowest order

$$A(\theta) = a_0^2(1 - \eta_A\theta^2) \tag{1.1}$$

where η_A is a geometrically calculable constant (equal to unity in this case). The important point is that the area or lattice constant is reduced by the rotation as a straightforward geometrical effect. If we now think of fluctuating positive and negative rotations as being a manifestation of thermal agitation, then we have a negative COTE. We have

$$\langle A(\theta)\rangle_T = A_0(1 - \eta_A\langle\theta^2\rangle_T) \tag{1.2}$$

where $\langle\theta^2\rangle$ increases and $\langle A\rangle$ decreases with *T*.

We can develop this picture further. Most framework structures have maximum volume or maximum lattice constants when in an ideal symmetrical form. This is not true of some structures[23] which we shall exclude from our consideration. Analogous to Eq. (1.1) we can write for some lattice constant *a* of our structure

$$a = a_0(1 - \eta_a\theta^2) \tag{1.3}$$

where θ is again the rotation angle of the units and we expect η_a to be positive. Applying the principle of equipartition of

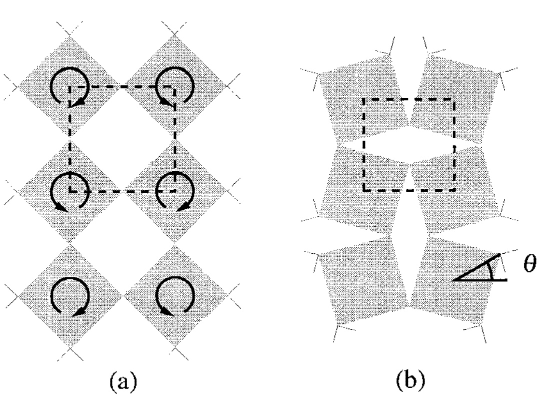


Fig. 1. Rotational motion in "2D-perovskite," showing the rotation of the units by an angle θ: (a) ideal structure before rotations, (b) after rotations. Note the reduction, due to the rotation, of the size of the square unit cell (dashed).

R. Raj—contributing editor

Manuscript No. 190904. Received June 23, 1997; approved October 27, 1997.
Supported by the Engineering and Physical Sciences Research Council and the Natural Environment Research Council of the United Kingdom, and by a research studentship for P. R. L. Welche.

energy to the potential energy of oscillation, we can write for the rotation due to thermal fluctuation

$$\frac{1}{2}I\omega_E^2\langle\theta^2\rangle_T = \frac{1}{2}k_BT \tag{1.4}$$

Here I is the moment of inertia of the units, ω_E is some average or Einstein frequency for the rotations, $\langle\theta^2\rangle_T$ is the equilibrium fluctuating value of θ^2 at temperature T, k_B is Boltzmann's constant, and we have made the high-temperature approximation for the thermal excitation. From Eqs. (1.3) and (1.4) we obtain the change Δa as

$$\frac{\Delta a}{a_0} = -\frac{\eta_a k_B T}{I\omega_E^2} \tag{1.5}$$

and the coefficient α_a of linear expansion of a as

$$\alpha_a = -\frac{\eta_a}{I}\frac{k_B}{\omega_E^2} \tag{1.6}$$

So far we have lumped the whole dynamics of the system into an effective Einstein frequency ω_E in Eqs. (1.4) to (1.6). A more detailed theory involves a summation over all phonon modes (band index j, and wavevector $\mathbf{k}$ in the Brillouin zone), each with its own geometrical constant $\eta_{a\mathbf{k}j}$ analogous to Eq. (1.3). The result is

$$\frac{\Delta a(T)}{a_0} = -\sum_{\mathbf{k}j}\frac{C_{\mathbf{k}j}k_BT\,\eta_{a\mathbf{k}j}}{\omega_{\mathbf{k}j}^2} \tag{1.7}$$

as will be shown in Section III, where k_BT and $\omega_{\mathbf{k}j}^2$ enter from the equipartition of energy as in Eq. (1.4) and where $C_{\mathbf{k}j}$ is some constant which may depend on the mode. A negative COTE results as before:

$$\alpha_a = -\sum_{\mathbf{k}j}\frac{C_{\mathbf{k}j}k_B\eta_{a\mathbf{k}j}}{\omega_{\mathbf{k}j}^2} \tag{1.8}$$

The above outline already shows all the main features of the theory, which we will enumerate as a guide through the algebra to follow. First, the negative contribution to the COTE is a geometrical effect inherent to many framework structures. The angular fluctuations of the units about an ideal structure cause a reduction in one or more lattice constants, because the structure in a sense folds up under rotation. The volume of the ideal structure by symmetry usually has to be a minimum or a maximum, the former being perhaps a dense metallic structure and the latter our more open framework structure. The measure of the effect is an η coefficient in the sense of Eqs. (1.3), (1.7), and (1.8).

Second, we note from Eqs. (1.6) and (1.8) that the negative contribution to the COTE is proportional to ω^{-2} and hence is largest for the low-frequency modes, which arises from the way the frequency apears in the potential energy on the left side of Eq. (1.4) and its generalization. Of course, one also has the normal positive COTE due to the anharmonic form of interatomic potentials, but this ends to be roughly constant through the phonon bands: it is the same for all phonons in a simple linear chain model. Thus adding the two effects together, one might expect a net negative effect from the lower frequency phonon bands and a net positive one from the higher bands. For example, in β-quartz it was found that the lowest 10 phonon bands (out of 27) with $\mathbf{k}$ in the a^* direction in the Brillouin zone gave net negative contributions to the COTE.

Third, we can expect difficulties from Eq. (1.6) from the soft mode (SM) in the case of a soft mode phase transition[16,24] where one ω_{SM} goes to zero as T tends to the phase transition temperature T_c from above, i.e., where at $T > T_c$

$$\omega_{SM}^2(T) \propto T - T_c \tag{1.9}$$

In differentiating Eq. (1.7) to obtain Eq. (1.8), we assumed that $\omega_{\mathbf{k}j}$ was effectively constant, but this cannot be a satisfactory approximation in the case of a soft mode with the temperature dependence of Eq. (1.9). It turns out that we still have a negative contribution to Δa as in Eq. (1.7) of the form

$$\text{contribution to } \frac{\Delta a(T)}{a_0} = -(\text{constant})\frac{T}{T - T_c} \tag{1.10}$$

where we have substituted Eq. (1.9) into Eq. (1.7). However, differentiating this with repect to T gives a positive COTE because the increase in the denominator in Eq. (1.10) is faster that that of the numerator:

$$\text{contribution to } \alpha_a = (\text{constant})\frac{T_c}{(T - T_c)^2} \tag{1.11}$$

which is positive. Such an anomalous positive expansion is seen in β-quartz just above its T_c (841 K).[13]

Fourth, we note that our geometrical ideas can be incorporated within the conventional theory of thermal expansion in the harmonic approximation. This is expressed in terms of the Grüneisen parameter

$$\gamma_s = -\frac{1}{2\omega^2}\frac{\partial\omega^2}{\partial s} \tag{1.12}$$

associated with a mode frequency ω and its behavior under some strain s, e.g., elongation of the a lattice parameter. The normal anharmonicity of interatomic potentials gives a positive γ_s. However, with a framework structure such as in Fig. 1, stretching the structure would make it more difficult to rotate the stiff units, i.e., would increase ω^2. Conversely squeezing the structure would tend to make the units rotate, thus decreasing ω^2. Either way, it leads to a negative Grüneisen parameter for the mode, and hence a negative contribution to the COTE from it.

In Section II we shall recapitulate the formal theory of thermal expansion in the conventional Grüneisen form of the quasiharmonic approximation. We shall express it in a form suitable for our purposes and formulate it for a hexagonal crystal (point group $P6_222$ to be precise) with only two independent lattice constants $a = b$ and c, with a view to later application to β-quartz.[6] This suffices to show how to treat more general cases than cubic crystals, without the full panoply of elastic tensors for triclinic crystals. In Section III we shall develop the geometrical theory outlined in Section I and connect it with the formal theory in Section IV.

We want to express our geometrical effect in terms of a negative Grüneisen parameter Eq. (1.12), because in practice that is what one might measure or compute and the objective of our theory would be to give a geometrical interpretation of it, as we shall for β-quartz elsewhere.[6] In Section IV we go more deeply into the geometrical effect from the point of view of the general Grüneisen theory. The theme of Section IV is continued in Section V for the acoustic modes, one of which turns out to give a surprisingly large contribution in β-quartz.[6] In Section VI we shall investigate how the negative geometrical effect combines with the normal positive expansion due to anharmonic forces. We shall do this by analyzing a simple generic one-dimensional model, namely one row of the structure of Fig. 1. It turns out that the two contributions simply add, but the geometrical effect is proportional to ω^{-2} while the anharmonic one is more or less constant. This gives a characteristic pattern for the variation of the Grüneisen parameter $\gamma_i(\mathbf{k}j)$ through the phonen spectrum, from large negative for the lowest frequency bands to positive for the high-frequency ones, as already mentioned.

II. The Grüneisen Theory

In this section we will recapitulate some of the conventional theory of the COTE in the specific form in which we will need it. With a view to subsequent application to β-quartz[6] we shall write the theory in the form appropriate to hexagonal symmetry. This differs sufficiently from the simplest cubic case so that extension to any other symmetry should be trivial, while avoiding the plethora of tensorial suffices needed for general triclinic crystals.

We consider N unit cells of volume Ω of a hexagonal crystalline material, and write for its Gibbs free energy

$$G = G_0 + G_{\mathrm{el}}(e_{ab}, e_c) + G_{\mathrm{vib}}(e_{ab}, e_c, T) \tag{2.1}$$

$$G_{\mathrm{el}} = N\Omega\left[(c_{11} + c_{12})e_{ab}^2 + 2c_{13}e_{ab}e_c + \frac{1}{2}c_{33}e_c^2\right] \tag{2.2}$$

$$G_{\mathrm{vib}} = k_{\mathrm{B}}T\sum_{\mathbf{k}j} \ln\left[2\sinh\left(\frac{\hbar\omega_{\mathbf{k}j}}{2k_{\mathrm{B}}T}\right)\right] \tag{2.3}$$

where G_{el} and G_{vib} are the elastic and thermally excited vibrational parts of G.[25] Since thermal expansion conserves the assumed hexagonal symmetry, we have only two strain components $e_3 \equiv e_c = \delta c/c$ and $e_1 = e_2 = e_{ab} = \delta a/a$, where throughout we shall use the subscript ab to denote an equal change in the a and b hexagonal axes. The c_{ij} are the usual elastic constants. The vibrational free energy is written in the harmonic approximation as the usual free energy of a simple harmonic oscillation, summed over all the phonon spectrum, i.e., over normal modes of frequency $\omega_{\mathbf{k}j}$ in band j at point $\mathbf{k}$ in the Brillouin zone. Each $\omega_{\mathbf{k}j}$ depends on e_{ab} and e_c, and may depend explicitly on T due to anharmonicity, e.g., around a soft mode phase transition.[24] Elastic equilibrium gives

$$\frac{\partial G}{\partial e_{ab}} = 0 = N\Omega[2(c_{11} + c_{12})e_{ab} + 2c_{13}e_c] - \sum_{\mathbf{k}j} E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}\gamma_{ab}^{\mathrm{red}}(\mathbf{k}j) \tag{2.4a}$$

$$\frac{\partial G}{\partial e_c} = 0 = N\Omega[2c_{13}e_{ab} + c_{33}e_c] - \sum_{\mathbf{k}j} E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}\gamma_c^{\mathrm{red}}(\mathbf{k}j) \tag{2.4b}$$

where

$$E_{\mathbf{k}j}(T) = \left(n_{\mathbf{k}j} + \frac{1}{2}\right)\hbar\omega_{\mathbf{k}j} \tag{2.5}$$

with

$$n_{\mathbf{k}j} = \left[\exp\left(\frac{\hbar\omega_{\mathbf{k}j}}{k_{\mathrm{B}}T}\right) - 1\right]^{-1}$$

is the energy in the mode $\mathbf{k}j$, which becomes

$$E_{\mathbf{k}j}(T) \approx k_{\mathrm{B}}T \tag{2.6}$$

for

$$T > \frac{\hbar\omega_{\mathbf{k}j}}{k_{\mathrm{B}}}$$

in the classical high-temperature approximation. The $\gamma_{ab}^{\mathrm{red}}$ and γ_c^{red} are what we shall term “reduced” Grüneisen constants

$$\gamma_s^{\mathrm{red}}(\mathbf{k}j) = -\frac{1}{2}\left(\frac{\partial\omega_{\mathbf{k}j}^2}{\partial e_s}\right)_{e_t,T} \tag{2.7}$$

for the mode $\mathbf{k}j$ defined for any strain e_s (i.e., e_{ab} and e_c in our case) and related to the conventional Grüneisen parameters

$$\gamma_s(\mathbf{k}j) = \omega_{\mathbf{k}j}^{-2}\gamma_s^{\mathrm{red}}(\mathbf{k}j) = -\left(\frac{\partial \ln \omega_{\mathbf{k}j}}{\partial e_s}\right)_{e_t,T} \tag{2.8}$$

Solving Eqs. (2.4) yields

$$e_{ab} \equiv \frac{\delta a}{a} = \frac{c_{33}\xi_{ab} - c_{13}\xi_c}{(c_{11} + c_{12})c_{33} - 2c_{13}^2} \tag{2.9a}$$

$$e_c \equiv \frac{\delta c}{c} = \frac{(c_{11} + c_{12})\xi_c - 2c_{13}\xi_{ab}}{(c_{11} + c_{12})c_{33} - 2c_{13}^2} \tag{2.9b}$$

where ξ_{ab} and ξ_c can be regarded as the thermally induced stresses in the a, b, and c directions

$$\xi_{ab} = (2N\Omega)^{-1}\sum_{\mathbf{k}j} E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}\gamma_{ab}^{\mathrm{red}}(\mathbf{k}j) \tag{2.10a}$$

$$\xi_c = (N\Omega)^{-1}\sum_{\mathbf{k}j} E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}\gamma_c^{\mathrm{red}}(\mathbf{k}j) \tag{2.10b}$$

The extra factor ½ appears in Eq. (2.10a) because $\gamma_{ab}^{\mathrm{red}}$ involves changing both the a and b axes.

We can check that Eq. (2.10) reduces to the standard textbook result for a cubic material

$$e_a = e_b = e_c = \frac{k_{\mathrm{B}}T\gamma_{\mathrm{V}}}{B\Omega_{\mathrm{at}}} \tag{2.11}$$

as follows, where Ω_{at} is the volume per atom and γ_{V} is the standard Grüneisen constant Eq. (2.8) for differentiation with respect to volume change. If we assume in Eq. (2.9) that the c axis is elastically the same as the a and b axes, i.e., $c_{33} = c_{11}$ and $c_{13} = c_{12}$, then the elastic symmetry is the same as in a cubic material, which also makes $\xi_{ab} = \xi_c$. Then Eq. (2.9) becomes

$$e_a = e_b = e_c = \frac{\xi_c}{3B} \tag{2.12}$$

where B is the bulk modulus

$$B = \frac{1}{3}(c_{11} + 2c_{12}) \tag{2.13}$$

Let us also assume that all modes have the same Grüneisen constant, as is true in the simplest model of a linear chain, or that γ_{V} is an appropriate average value. Note that in general γ_{V} is the average of γ_a, γ_b, and γ_c, not their sum. This is best seen by thinking of the differentiation in terms of small finite differences and noting that 1% strains $e_a = e_b = e_c$ give a 3% volume change e_{V}. The summation in Eq. (2.10) contributes a factor $3Nn$ where n is the number of atoms in the unit cell. We also use the classical limit Eq. (2.6), after which Eq. (2.12) then reduces to Eq. (2.11).

Finally, we note that the differentiation in Eqs. (2.7) and (2.8) is with respect to strain, so that the Grüneisen constants are in the nature of stresses, as is also evident in Eqs. (2.9) and (2.10).

III. Geometrical Effect

This section will develop more fully the geometrical effect, which gives a negative contribution to the COTE as outlined in Section I in an oversimplified form for pedagogic purposes. The major simplification there was to lump all the phonons together into one Einstein mode in Eq. (1.4), which we will now avoid.

We consider a phonon mode $\boldsymbol{kj}$ of frequency $\omega_{\mathbf{k}j}$ with energy $E_{\mathbf{k}j}(T)$, Eq. (2.5), in the mode at temperature T. As always in simple harmonic motion, the energy is equally divided between kinetic energy and potential energy, the latter having the form

$$\frac{1}{2}E_{\mathbf{k}j}(T) = \frac{1}{2}(\text{inertia term})\omega_{\mathbf{k}j}^2\langle\theta^2\rangle_{\mathbf{k}j} \tag{3.1}$$

There are only rotations in the mode depicted in Fig. 1 but in general there will also be some translations If we neglect the latter, we can substitute rNI for the inertia term in Eq. (3.1), where r is the number of rigid units (considered identical) each with moment of inertia I in each of the N unit cells. We obtain (for the rotational geometrical effect only!)

$$\langle\theta^2\rangle_{T,\mathbf{k}j} \approx \frac{E_{\mathbf{k}j}(T)}{NrI\omega_{\mathbf{k}j}^2} \tag{3.2}$$

for the contribution of the particular mode to $\langle\theta^2\rangle_T$. Of course, there are usually concomitant translations along with the rotations which can alter the arithmetic by a factor of 2, and in the case of quartz[6] we specifically point to this effect in connection with the differences in γ^{red} for the soft mode at $\mathbf{k} = 0$ and the Vallade mode along a^*. Because of the assumption about the inertia term, our theory is still approximate and intended only as an interpretation of detailed calculations with the Grüneisen theory, e.g., for quartz[6] and of the negative COTE phenomenon. In particular, Eq. (3.2) applies only to modes that are primarily rotational, and not to longitudinal acoustic modes, for example.

We will confine ourselves to the case of hexagonal symmetry for the same reasons as in Section II, and write for the *a* and *c* lattice parameters

$$a = a_0(1 - \eta_a\theta^2) \tag{3.3a}$$

$$c = c_0(1 - \eta_c\theta^2) \tag{3.3b}$$

Here we have introduced the crucial geometrical constants η_a and η_c describing the reduction in lattice parameters due to rotations. Substituting Eq. (3.2) into Eq. (3.3) and summing over all modes we obtain

$$e_{ab}(T) = \frac{\delta a}{a} \approx N^{-1}\sum_{\mathbf{k}j}(rI)^{-1}E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}[-\eta_a(\mathbf{k}j)] \tag{3.4a}$$

$$e_c(T) = \frac{\delta c}{c} \approx N^{-1}\sum_{\mathbf{k}j}(rI)^{-1}E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}[-\eta_c(\mathbf{k}j)] \tag{3.4b}$$

It is immediately apparent that Eqs. (3.4) are rather similar to the result in Eqs. (2.9) and (2.10) of the proper Grüneisen theory, with the factor $E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}$ occurring in each. The relationship becomes more evident if we rewrite Eqs. (3.4) and the theory of Eqs. (2.1) to (2.10) for arbitrary strains e_t and elastic constants c_{st} (s, $t = 1$ to 6) without special symmetry. Equations (2.9) and (2.10) become

$$\xi_s = c_{st}e_t(T) \tag{3.5a}$$

$$\xi_s = \frac{1}{N\Omega}\sum_{\mathbf{k}j}E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}\gamma_s^{\mathrm{red}}(\mathbf{k}j) \tag{3.5b}$$

and Eqs. (3.4) become

$$e_t(T) \approx -\frac{1}{NrI}\sum_{\mathbf{k}j}E_{\mathbf{k}j}\omega_{\mathbf{k}j}^{-2}\eta_t(\mathbf{k}j) \tag{3.5c}$$

which when substituted into Eq. (3.5a) gives

$$\gamma_s^{\mathrm{red}}(\mathbf{k}j) \approx -\frac{\Omega}{rI}c_{st}\eta_t(\mathbf{k}j) \tag{3.6}$$

where we have used the summation convention for the suffix *t*. The approximation in Eqs. (3.5c) and (3.6) relates to the inertia term *rI* because in general a phonon will involve translation of the units as well as rotation.

We note that Eq. (3.6) gives negative values of γ^{red} as expected, and that it allows us to interpret a computed (or measured) $\gamma_s^{\mathrm{red}}(\mathbf{k}j)$ (e.g., for quartz[6]) in terms of geometrical constants η_t. We also note from Eq. (3.6) that the geometrical effect makes a roughly constant contribution to the reduced Grüneisen constants $\gamma^{\mathrm{red}}(\mathbf{k}j)$, not to the usual $\gamma(\mathbf{k}j)$, for all rotational modes.

Table I. Reduced Grüneisen Parameters from Split Atom Model of β-Quartz at k = 0

j	$\frac{1}{2}\gamma_{ab}^{\mathrm{red}}/4\pi^2$ (THz^2)	$\gamma_c^{\mathrm{red}}/4\pi^2$ (THz^2)	$\gamma_V^{\mathrm{red}}/4\pi^2$ (THz^2)
4	−44	−74	−53
5	−32	−73	−45
6	−32	−73	−45
7	−86	0	−56
8	−86	0	−56
9	−13	−37	−20
10	0	0	0
11	0	0	0
12	−7	−19	−11
13	−7	−19	−11
14	−11	−18	−13
15	−19	−56	−31
16	−86	0	−56
17	−47	−91	−60
18	−47	−91	−60

Table I gives some calculated results on an idealized model of β-quartz, designed to pick up the geometrical effects. It consists of regular tetrahedra joined at the corners into the correct β-quartz structure, but there are no interunit forces. In an arbitrary phonon, the tetrahedra will need to distort in various ways, but in the present model all types of distortion are represented by a single average stiffness parameter as described in Section VI and elsewhere.[26] Moreover, the stiffness is described by a simple spring so that there are no anharmonic contributions. The value of the parameter has been fixed to fit the overall width of the phonon frequency band. Such a simple model is obviously a gross oversimplification, but in fact the phonon spectrum it gives is recognizably similar to that of the most sophisticated calculations. The phonon frequencies were calculated with this model at $\mathbf{k} = 0$ at two values of each of the *a* and *c* lattice constants, with the reduced Grüneisen constants Eq. (2.7) then calculated by differencing. The results in Table I show that our geometrical effect is zero for many phonons, and gives a negative reduced Grüneisen constant for phonons where it is nonzero, as expected, which would lead to a negative COTE. The first three bands have been omitted from Table I because they are rather meaningless at $\mathbf{k} = 0$, and the modes only go up to $j = 18$ in the model of stiff tetrahedra because the internal motion of the silicon atoms has been eliminated. We see from Table I that the geometrical effect is not limited to low-frequency phonons but extends throughout the bands. Moreover, it is the reduced Grüneisen parameters Eq. (2.7) that are roughly of constant order of magnitude, not the traditional Grüneisen parameters Eq. (2.8) themselves; note there is quite a sizeable difference between them since ω^2 varies by more than a factor of 100 through the phonon band. This is all in accordance with our expectations as expressed in Eq. (3.6).

We now turn to another issue. In Fig. 1 we have a phonon mode which we have described as purely rotational. It is a rigid unit mode (RUM) in the language of Refs. 18–21 involving no distortion of the units, and it is in fact the only such mode for the system of Fig. 1. It is easy to see that this RUM leads to negative expansion in the manner shown in Fig. 1 and discussed in Section I. But what of the other modes that involve the distortion of the units: Will they not give a severely smaller geometrical effect? We have glossed over this question in going from the RUM in Eqs. (1.1) to (1.3) to an average over modes in Eq. (1.4). The answer to our question is both "yes" and "no": yes to the extent that non-RUMs have higher frequencies and there is a weighting factor ω^{-2} in Eqs. (2.10), but not beyond that. The geometrical γ_A^{red} is roughly the same for all rotational phonons in the model of Fig. 1 which we can understand in the following way. Lattice contraction is a local effect. Consider one ring of four squares in Fig. 1 and rotate them by +θ, −θ, +θ, −θ counting around the ring. Clearly the area enclosed by the four squares will be reduced by the amount given by Eq. (1.1) (with $\eta_A = 1$ as mentioned there). We ignore the rotations of the other squares, assuming them to be some random amounts; this of course will necessarily involve distortions of the units and hence higher frequency of phonons. Returning to our ring of four squares, let us number them 1 to 4 and now suppose they are rotated by more general angles θ_1 to θ_4. We may expect the area of the enclosed square to be reduced by something of order

$$\delta A \approx -A_0 \eta_A \bar{\theta}^2 \tag{3.7}$$

where

$$\bar{\theta} = \frac{1}{4}(\theta_1 - \theta_2 + \theta_3 - \theta_4) \tag{3.8}$$

is an average amount of coherent rotation. We have

$$\bar{\theta}^2 = \frac{1}{16}(\theta_1^2 + \theta_2^2 + \theta_3^2 + \theta_4^2) + \frac{1}{8}(-\theta_1\theta_2 + \theta_1\theta_3 - \theta_1\theta_4 - \theta_2\theta_3 + \theta_2\theta_4 - \theta_3\theta_4) \tag{3.9}$$

Now very crudely we may write

$$-\theta_1\theta_2 \approx \frac{1}{2}(\theta_1^2 + \theta_2^2) \tag{3.10}$$

by noting that we expect θ_1 and θ_2 to be roughly correlated with $\theta_1 \approx -\theta_2$ because that requires minimum distortion of the stiff units. Substituting Eqs. (3.8) to (3.10) into Eq. (3.7) we have

$$\delta A \approx -A_0 \eta_A \frac{1}{4}(\theta_1^2 + \theta_2^2 + \theta_3^2 + \theta_4^2) \tag{3.11}$$

We now sum Eq. (3.11) over all 4-rings in our sample. Since each unit is a member of four 4-rings, we obtain for the average δA

$$\frac{\delta A}{A_0} = e_A \approx -\eta_A \frac{1}{N} \sum_n^N \theta_n^2 \tag{3.12}$$

where the summation extends over all N units and e_A is the areal strain.

We already see here that there is (very roughly, in view of all the approximations) just one geometrical η_A constant for all the rotational modes. We can carry the analysis one step further by expressing θ_n in terms of the normalized phonon amplitudes $\Theta_{\mathbf{k}}$ as

$$\theta_n = \sum_{\mathbf{k}} \Theta_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{l}_n) \tag{3.13}$$

where $\mathbf{l}_n$ is the positional lattice vector of the nth unit. Hence we have

$$\begin{aligned}\sum_n \theta_n^2 &= \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \Theta^*_{\mathbf{k}'} \Theta_{\mathbf{k}} \left(\sum_n \exp[i(\mathbf{k} - \mathbf{k}')]\cdot\mathbf{l}_n \right) \\ &= N \sum_{\mathbf{k}} |\Theta_{\mathbf{k}}|^2 \end{aligned} \tag{3.14}$$

in the usual way.[24] Combining Eq. (3.14) with Eq. (3.12) gives

$$e_A \approx -\eta_A \sum_{\mathbf{k}} |\Theta_{\mathbf{k}}|^2 \tag{3.15}$$

Thus we conclude that each phonon $\mathbf{k}$ has the same geometrical constant η_A, within the various approximations made en route. There is no radical difference between the η constants for modes which do and do not require substantial distortions of the stiff units of the framework structure.

IV. Relationship between the Two Approaches

When a new theory is developed, it is often desirable to look at it from different points of view, if only to check the result. In the present instance, we can derive Eq. (3.6) directly along a different route, and we shall discuss what is achieved thereby at the end.

Let us develop the model of a framework structure depicted very simply in Fig. 1. As in Section III we will take the units as having a large internal stiffness, with negligible bond bending force constant at the oxygen atoms joining the units, and we want to apply to this system the general methodology of Section II. We consider some phonon with rotation θ of the units. The rotations of the units will not be all the same in some general phonon but they all oscillate with a constant amplitude ratio between them so that we can characterize the amplitude of the whole mode by the angle θ of one particular unit. To calculate the phonon frequency we can use the general theory of oscillations which gives for the energies

$$\text{kinetic energy} = \frac{1}{2}(\text{inertia constant})\left(\frac{d\theta}{dt}\right)^2 \tag{4.1a}$$

$$\text{potential energy} = \frac{1}{2}\omega^2(\text{inertia constant})\theta^2 \tag{4.1b}$$

We will again take our inertia constant as NrI for N cells with r units per cell of moment of inertia I, ignoring any translational motion attendant on the rotations. The ω^2 is therefore

$$\omega^2 = \frac{2(\text{coefficient of } \theta^2 \text{ in potential energy})}{NrI} \tag{4.2}$$

We also note from Section II, in particular Eq. (2.7), that we need ω^2 at varying strain.

Thus we need to develop the energy of the system, as a function simultaneously of θ and strain e_t. The elastic energy per unit volume for $\theta = 0$ is

$$E = \frac{1}{2} c_{st} e_s e_t \tag{4.3}$$

(with the summation convention as before) where the c_{st} are the elastic constants of our system due to the stiffness of the units, evaluated in its equilibrium form with $\theta = 0$. Let us now start with the system in its ground state with no applied stresses, and rotate the units: this costs zero energy because there are no interunit forces by assumption and no stresses, but results in contractions

$$e_t^{\text{rot}} = -\eta_t \theta^2 \tag{4.4}$$

where the η_t are geometrical constants analogous to the η constants of Eq. (1.1), (1.3), and (3.3). If we now apply stresses, we first have to stretch the system to undo the contraction of Eq. (4.4) to reach a state of zero strain. Thus we have to substitute $e_t - e_t^{\text{rot}}$ for e_t in Eq. (4.3), giving an energy

$$E(e_t, \theta) = \frac{1}{2} N\Omega c_{st}(e_s + \eta_s\theta^2)(e_t + \eta_t\theta^2) \tag{4.5}$$

for N cells of volume Ω. We expand Eq. (4.5) to order θ^2:

$$E(e_t, \theta) = N\Omega\left(\frac{1}{2} c_{st} e_s e_t + c_{st} e_s \eta_t \theta^2\right) \tag{4.6}$$

From Eq. (4.2) the frequency is given by

$$\omega^2(e_s) = 2\left(\frac{\Omega}{rI}\right) c_{st} e_s \eta_t \tag{4.7}$$

whence from Eq. (2.7) we have for our particular mode

$$\gamma_s^{\text{red}} = -\left(\frac{\Omega}{rI}\right) c_{st} \eta_t \tag{4.8}$$

in agreement with Eq. (3.6) where rI is again an approximation to the inertia factor per cell.

We can test the result Eq. (4.8) on the soft mode giving the $\beta \rightarrow \alpha$ transition in β-quartz. We use the simple one-parameter model already described in Section III and used in Section VI, with a value $\lambda = 193.3\ \text{J}\cdot\text{m}^{-2}$ for the spring constant in Eq. (6.1). From the same model a calculation of the phonon spectrum gives the velocities of sound along a few of the main crystallographic axes, from which we have deduced the elastic constants for the model $c_{11} = 247.4$ GPa, $c_{33} = 213.1$ GPa,

$c_{12} = 13.5$ GPa, $c_{13} = 50.4$ GPa and $c_{44} = 0$. A rotation of the tetrahedra by an angle $\pm\theta$ in the manner of the soft mode gives

$$c(\theta) = c_0\left(1 - \frac{1}{2}\theta^2\right) \tag{4.9}$$

whence $\eta_c = 0.5$. From a similar geometrical calculation we obtain

$$\eta_a = \frac{\sqrt{3}}{2(1+\sqrt{3})} = 0.317 \tag{4.10}$$

To calculate the moment of inertia of each Si(½O)$_4$ tetrahedron we ascribe each oxygen atom half and half to the two tetrahedra which it joins, giving $I = 1.78 \times 10^{-45}$ kg·m^2. The cell volume $\Omega = 119$ Å^3 for $r = 3$ tetrahedra in the ideal structure then gives from Eq. (4.8) the result

$$\begin{aligned}\gamma_c^{\text{red}} &= -\left(\frac{\Omega}{rI}\right)(2c_{13}\eta_a + c_{33}\eta_c) \\ &= -78(4\pi^2)\ \text{THz}^2 \end{aligned}\tag{4.11}$$

Note that the η_t for $t = 4, 5, 6$ are zero by symmetry for the soft mode. This gives adequate agreement with $\gamma_c^{\text{red}}/4\pi^2 = -74$ THz^2 in Table I, which was computed numerically by stretching the cell in the c direction and calculating γ_c^{red} from the change in soft mode frequency with c as in Eq. (2.7).

Let us recapitulate what the above algebra and numerical test have achieved. The general Grüneisen theory of Section II is, of course, perfectly general, and rigorous within the harmonic approximation. It is applicable to all materials and as such has no predictive power. In contrast to that, our geometrical theory of Section III has predictive power in that the geometrical constants η_a and η_c of Eqs. (3.4) can be calculated analytically, or for complicated structures by some elementary computer modeling. The geometrical theory is only approximate and is written in different terms from the Grüneisen theory, but from a comparison of the two results one has the connection (3.6) which indicates roughly the values of the reduced Grüneisen parameters to be expected for particular modes in a particular framework material. What has been done in Eqs. (4.1) to (4.8) is to take our grossly simplified model of a framework structure in a form which can be treated by both methods. Giving the units some finite stiffness and carrying out the Grüneisen analysis for the system allows one to derive rigorously the connection Eqs. (3.6), (4.8) of the Grüneisen parameters for any given mode to its geometrical η constants. The mode system is grossly simplified in our model, but a recognizable representation of many real silicates, namely stiff units rather loosely jointed at the corners. Furthermore, our numerical test in Eq. (4.11) is a further check on the whole theory by choosing a situation where the γ^{red} can be calculated in two ways.

To have verified the complete equivalence of the two approaches therefore underpins the whole theory. It will also allow us to treat acoustic modes in the next section, and will open the door in Section VI to combining our geometrical effect with the usual positive contribution to the COTE from the anharmonic nature of the interatomic forces.

V. Geometrical Effect from Acoustic Modes

Calculating the geometrical contribution to the COTE from the acoustic phonon modes is a little more complicated. While the negative geometrical effect from optic modes such as in Fig. 1 is intuitively obvious, it was not so clear whether the acoustic modes would be very interesting from this point of view. However, it turned out that the acoustic TA$_z$ modes in β-quartz make the largest negative contribution.[6] Let us therefore develop the theory specifically for the TA$_z$ modes for a hexagonal system for **k** along the a^* direction at low k_x, i.e., in the acoustic region. We have

$$\omega^2(k_x) = v^2 k_x^2 \tag{5.1}$$

with the velocity v given by

$$v^2 = \frac{c_{55}}{\rho} \tag{5.2}$$

where ρ is the density. For thermal strains (expansions) e_s ($s = 1, 2, 3$) we will need $\partial\omega^2/\partial e_s$ from Eq. (1.12). From Eq. (5.1) we expect this to be proportional to k_x^2, i.e., to ω^2, so that it is more convenient to work in terms of the Grüneisen constant $\gamma_s(k_x)$, Eqs. (1.12) and (2.8), instead of the reduced $\gamma_s^{\text{red}}(k_x)$, Eq. (2.7).

From Eq. (5.2) we will clearly need the elastic constant c_{55} as a function of e_s, to which we now turn. It is convenient to work in terms of an orthorhombic unit cell with $b = \sqrt{3}a$. To calculate c_{55} we apply an xz shear (Fig. 2) by applying the displacement

$$\mathbf{u}(\mathbf{r}) = (0, 0, \theta x) \tag{5.3}$$

giving

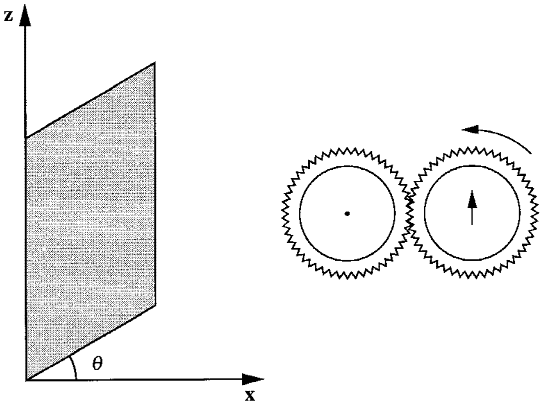
$$\begin{aligned} e_5 = 2e_{xz} &= \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \\ &= \theta \end{aligned}\tag{5.4}$$

We imagine a stress ξ_5 applied to hold the xz strain but that the system is otherwise allowed to relax, which will result in spontaneous strains

$$e_t^{\text{rot}} = -\eta_{t,5}\theta^2 \qquad (t = 1, 2, 3) \tag{5.5}$$

In fact in our very simple model applied to β-quartz, the e_5 shear can be achieved by the tetrahedra rolling over one another. The contractions of Eq. (5.5) are therefore completely analogous to those in Fig. 1, Eq. (1.3). The e_t^{rot} for $t = 4, 6$ are zero by symmetry, and e_5 is set externally as in Fig. 1. We now apply strains e_t ($t = 1$ to 4, 6) which we think of as infinitesimal, after applying the finite e_5 strain of Fig. 2. In applying these strains, we first have to overcome the e_t^{rot} of Eq. (5.5) as in Section IV, so that the work done is

$$\begin{aligned}\text{Elastic energy per unit volume} &= \frac{1}{2}c_{st}(e_s + |e_s^{\text{rot}}|)(e_t + |e_t^{\text{rot}}|) \\ &= \frac{1}{2}c_{st}(e_s + \eta_{s,5}e_5^2)(e_t + \eta_{t,5}e_5^2) \\ &= \frac{1}{2}c_{55}e_5^2 + \frac{1}{2}c_{st}e_se_t \\ &\quad + (c_{st}e_s\eta_{t,5})e_5^2 + \mathcal{O}(e_5^4) \end{aligned}\tag{5.6}$$



(a) (b)

Fig. 2. (a) xz shear of magnitude $e_5 = \theta$, pictured (b) by a cogwheel rolling over another.

where the second term is summed except for $s = t = 5$ and the third term except for $s = 5$. Thus c_{55} is given as a function of e_s by the general relation

$$c_{55}(e_s) = c_{55} + 2c_{st}e_s\eta_{t,5} \qquad (\text{not } t = 5) \tag{5.7}$$

where only the $\eta_{t,5}$ of Eq. (5.5) are nonzero for hexagonal β-quartz.

We have in Eq. (5.7) the c_{55} as a function of the e_s, but in order to calculate the Grüneisen constant of Eq. (1.12) we will also need to know how the rest of Eqs. (5.1) and (5.2) vary with e_s. Since we are focusing on the effect of the TA$_z$ modes at (k_x,0,0), we have to distinguish between expansion in a perpendicular *b* or *c* direction and expansion in the *a* direction. Of course by symmetry the total effect in the *a* and *b* directions will be the same after summing over all phonons but we are here focusing on the effect from the phonons along k_x only. Let us first consider expansion in the *c* direction. We have

$$\rho = \frac{M}{abc(1 + e_3)} \tag{5.8}$$

where *M* is the mass per unit cell and we have included the factor $1 + e_3$ to represent variation of the *c* lattice parameter with e_3. Thus we have from Eqs. (5.1), (5.2), and (5.7)

$$\omega^2(k_x,e_3) = c_{55}(e_3)(1 + e_3)\left(\frac{k_x^2}{\rho}\right)_{e_3=0} \tag{5.9}$$

and the Grüneisen constant

$$\begin{aligned}\gamma_c(k_x) &= -\frac{1}{2\omega^2}\frac{\partial\omega^2}{\partial e_3} \\ &= -\frac{1}{2c_{55}}\frac{\partial}{\partial e_3}[c_{55}(1 + e_3)] \\ &= -\frac{1}{2}\left[\frac{1}{c_{55}}\frac{\partial c_{55}}{\partial e_3} + 1\right]\end{aligned} \tag{5.10}$$

We have to take another aspect into account for the expansion in the *a* direction. In the differentiation $\partial\omega^2/\partial e_1$ we have to take the variation of a particular mode which in this case includes a change in k_x. Let us define our modes in terms of periodic boundary conditions on a rectangular block of $N = N_a \times N_b \times N_c$ cells. The values of k_x in the Brillouin zone are then

$$k_x = \frac{n_a}{N_a}\frac{2\pi}{a} \tag{5.11}$$

where n_a is an integer which defines the particular n_ath mode along the k_x axis. Thus as we apply strain e_1 in the *x* direction, it is the production ($k_x a$) that remains constant, not k_x itself. We therefore write analogously to Eqs. (5.7) and (5.8)

$$\begin{aligned}\omega^2(k_x,e_1) &= c_{55}(e_1)\frac{1}{\rho a^2}(k_x^2a^2) \\ &= c_{55}(e_1)(1 + e_1)^{-1}\left(\frac{k_x^2a^2}{\rho a^2}\right)_{e_1=0}\end{aligned} \tag{5.12}$$

which gives

$$\begin{aligned}\gamma_a(k_x) &= -\frac{1}{2\omega^2}\frac{\partial\omega^2}{\partial e_1} \\ &= -\frac{1}{2}\left[\frac{1}{c_{55}}\frac{\partial c_{55}}{\partial e_1} - 1\right]\end{aligned} \tag{5.13}$$

in contrast to Eq. (5.10).

Finally, we substitute Eq. (5.7) into Eqs. (5.9) and (5.12), remembering that for our hexagonal system the only nonzero $\eta_{t,5}$ are those in Eq. (5.5), to give the geometrical Grüneisen constants along the k_x axis for the TA$_z$ modes

$$\gamma_a(k_x) = -\left\{\frac{1}{c_{55}}(c_{11}\eta_{1,5} + c_{12}\eta_{2,5} + c_{13}\eta_{3,5}) - \frac{1}{2}\right\} \tag{5.14a}$$

$$\gamma_c(k_x) = -\left\{\frac{1}{c_{55}}[c_{13}(\eta_{1,5} + \eta_{2,5}) + c_{33}\eta_{3,5}] + \frac{1}{2}\right\} \tag{5.14b}$$

VI. Combined Anharmonic and Geometrical Effects

We now consider how the geometrical effect combines with the anharmonicity of interatomic forces, which is the usual source of thermal expansion. So far we have focused on the geometrical effect in isolation whereas of course one has both contributions in any real framework material. Do the two simply add?

Let us first sharpen our question. We have seen (Section III) that it is γ^{red}, Eq. (2.7), rather than γ, Eq. (2.8), that is a measure of the geometrical effect, i.e., without the factor $1/\omega^2$. This is a big difference, since ω^2 typically varies by a factor of 100 through the phonon band (excluding the acoustic modes where $\omega \rightarrow 0$). On the other hand, one has for acoustic phonons that γ (not γ^{red}) is roughly constant through the phonon band. This is exactly true for simple models having only one type of (anharmonic) interatomic force, e.g., a linear chain of alternating A and B atoms, and remains approximately true more generally. Clearly the geometrical and anharmonic effects appear to have somewhat different physical behavior, and their combination is not a trivial question.

We will investigate the interaction of the geometrical and anharmonic effects in the simplest possible model containing both, returning at the end to enquire whether complicating the model to make it more realistic will alter the qualitative conclusions. Our system is a single row of squares from the perovskite model to Fig. 1. We will consider them rotating about fixed centers a distance $a(1 + e)$ apart where *e* is the linear strain: remember we will need to calculate the variation of the frequencies with *e* to obtain γ or γ^{red}, as in Sections IV and V. Any pattern of rotations (phonon), except the simple alternation shown in Fig. 1, will require distortions of the squares. Now there are five geometrically distinct ways of distorting a square, with four different restoring force constants. We want to have a one-parameter model, as already used in Sections III and IV, in which all types of distortion are described in terms of a single average force constant. We will define below a measure *s* of the distortion and write for the energy the anharmonic form

$$V(s) = \frac{1}{2}\lambda s^2 - \mu s^3 \tag{6.1}$$

where the distortions are such that μs^3 remains small compared with $\frac{1}{2}\lambda s^2$ and we will make expansions in terms of the anharmonicity μ.

The geometry of the distortion is depicted in Fig. 3, with adjacent squares rotating by angles θ_1 and θ_2. Of course, in reality the squares are joined at the corners P_1 and P_2, but we will consider for a moment notional separate rotations of each square as completely rigid units which open up a gap *s* equal to the distance P_1P_2 in the figure between the corners. In reality the units will have to distort to keep the two units joined at the

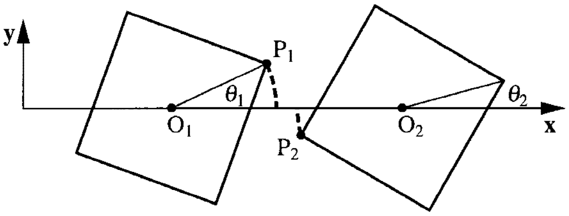


Fig. 3. Geometry of adjacent squares rotating by angles θ_1 and θ_2.

corners P_1, P_2, and we will take the distance $s = P_1P_2$ as our measure in Eq. (6.1) of how much they have to distort. To summarize: we consider notional rigid rotations of the units which would open a gap s between corners, and we therefore have to apply a distortion of magnitude s to join the corners together again. This is a convenient way to construct a one-parameter model, but there are others. We need to calculate

$$s^2 = s_x^2 + s_y^2 \tag{6.2}$$

where s_x and s_y are the components of the vector $\mathbf{s} = P_1P_2$ along the axes (Fig. 3). The semidiagonals O_1P_1 and O_2P_2 are of length $(1/2)a$, whence

$$s_y = \frac{1}{2}a \sin \theta_1 + \frac{1}{2}a \sin \theta_2 \tag{6.3}$$

Remembering that the distance O_1O_2 is $a(1 + e)$, we have

$$s_x = ae + \frac{1}{2}a(1 - \cos \theta_1) + \frac{1}{2}a(1 - \cos \theta_2) \tag{6.4}$$

The potential energy in our anharmonic "spring" is now given by substituting Eqs. (6.3) and (6.4) into Eq. (6.2). To lowest order in θ^2 we have

$$s^2 = a^2e^2 + \frac{1}{4}a^2(\theta_1 + \theta_2)^2 + \frac{1}{2}a^2e(\theta_1^2 + \theta_2^2) \tag{6.5}$$

In order to derive the equation of motion, we need to calculate the torque $G_{1,2}$ acting on unit 1 due to the anharmonic potential energy Eq. (6.1):

$$\begin{aligned} G_{1,2} &= -\frac{\partial V}{\partial \theta_1} \\ &= -\left[\frac{1}{2}\lambda - \frac{3}{2}\mu(s^2)^{1/2}\right]\frac{\partial(s^2)}{\partial \theta_1} \end{aligned} \tag{6.6}$$

where we have taken s^2 as the variable and written s^3 as $(s^2)^{3/2}$. We have from Eq. (6.5)

$$\frac{\partial s^2}{\partial \theta_1} = \frac{1}{2}a^2(\theta_1 + \theta_2) + a^2e\theta_1 \tag{6.7}$$

This expression is of order θ, and hence to obtain the phonon frequencies as simple harmonic motions we need to evaluate the square bracket in Eq. (6.6) only to zeroth order in θ to give the torque

$$G_{1,2} = -\frac{1}{4}a^2(\lambda - 3\mu ae)(\theta_1 + \theta_2 + 2e\theta_1) \tag{6.8}$$

We can now set up the equations of motion for the linear chain of squares. The nth square will experience torques from its coupling to the $(n + 1)$th and $(n - 1)$th squares, giving its equation of motion as

$$\begin{aligned} I\frac{d^2\theta_n}{dt^2} &= G_{n,n+1} + G_{n,n-1} \\ &= -\frac{1}{4}a^2(\lambda - 3\mu ae)(2\theta_n + \theta_{n-1} + \theta_{n+1} + 4e\theta_n) \end{aligned} \tag{6.9}$$

where I is the moment of inertia, and where $G_{n,n+1}$ is just given by Eq. (6.8) and $G_{n,n-1}$ can be derived similarly. We now take θ_n proportional to $\exp(ikna)$ and replace d^2/dt^2 by $-\omega^2$ as usual[24] to obtain the phonon spectrum

$$\omega^2(k,e) = \frac{a^2}{2I}(\lambda - 3\mu ae)(1 + 2e + \cos ka) \tag{6.10}$$

From Eq. (6.10) we have the reduced Grüneisen parameter

$$\begin{aligned} \gamma_a^{\mathrm{red}}(k) &= -\frac{1}{2}\left(\frac{\partial \omega^2}{\partial e}\right)_{e=0} \\ &= \left(\frac{3\mu a}{2\lambda}\right)\omega^2(k) - \left(\frac{a^2\lambda}{2I}\right) \end{aligned} \tag{6.11}$$

The second (negative) term is the geometrical effect corresponding exactly to Eq. (3.6). The length in the x direction varies as $\cos \theta$, giving $\eta_a = ½$. The "volume" Ω of the unit cell is a, and the elastic constant $c_{11} = \lambda a$. Thus Eq. (6.11) agrees with Eq. (3.6) for the pure rotational mode of Fig. 1, as it should.

We note that the geometrical contribution in Eq. (6.11) is not just constant to order of magnitude: it is constant throughout the band, even for the modes with k far from $k = \pi/a$ having large distortions of the units. This is completely in accordance with the expectation developed at the end of Section III. The positive first term of Eq. (6.11) comes from the anharmonicity, and is proportional to ω^2 so that it corresponds to a constant Grüneisen parameter through the band, not a reduced Grüneisen parameter. That is a well-known result for longitudinal modes of a linear chain of point masses, and it is interesting that it also applies here to the rotational modes.

We return now to the question of whether we can expect the form of Eq. (6.11) to apply qualitatively quite generally, i.e., that $\gamma^{\mathrm{red}}(\mathbf{k}j)$ consists of a positive anharmonic part roughly proportional to ω^2 and a negative geometrical part of roughly constant order of magnitude. The fact that the anharmonic part for the rotational modes has the same form as in ordinary displacive modes makes this very likely. We can enlarge our simple model to allow translation of the units along the x-axis as well as the rotations. The equations of motion will give a 2 × 2 dynamical determinant of which one diagonal element is the same as in our model and the other as for acoustic longitudinal modes, i.e., of the same form. The same will be true of the off-diagonal elements because they all arise from the potential Eqs. (6.1) and (6.5), i.e., from the same force: what differs is whether we take the rotational moment of the force as in Eq. (6.6) or take the force directly as producing linear acceleration. The anharmonic part scales with ω^2 because it is of higher order in s in Eq. (6.1): a small/large ω^2 implies a small/large restoring force in the simple harmonic motion, which implies a small/large s, which implies a small/large ratio of the anharmonic to harmonic part of Eq. (6.1). We conclude that the combination of anharmonic and geometrical effects is expected to show qualitatively the same form as in Eq. (6.11) quite generally.

Because of the ω^2 factor in the first term of Eq. (6.11), we may expect γ^{red} to be negative for low-frequency phonons in a framework structure, and positive near the top of the phonon band. That is exactly the situation found in the detailed atomistic calculations for β-quartz[6] using the interatomic forces of Tsuneyuki.[27] Table II shows the calculated results at the point $\mathbf{k} = (1/4)\mathbf{a}^*$, and we see the gradation from most negative γ^{red} at low ω to most positive for high ω. Note that the top six modes correspond to optic modes of the Si atoms vibrating inside the tetrahedra, which fall outside the present discussion. There should, of course, be nine such modes for three tetrahedra per unit cell, but three have gotten inextricably mixed with the translational and rotational modes of the tetrahedra.

VII. Discussion and Conclusions

In Section I we put forward a qualitative picture of how a negative coefficient of thermal expansion (COTE) can arise in the kind of framework structures which are common among aluminosilicates and other ceramics. We call it the geometrical effect because it can be visualized quite simply as a contraction of the network as its units rotate and fold together (Fig. 1). Indeed, it had already been suggested earlier by various authors[2,16,18,22] and in even more qualitative form as bond fluc-

Table II. Calculated Reduced Grüneisen Parameters of β-Quartz at $k = \frac{1}{4}a^*$

j	$\omega/2\pi$ (THz)	$\frac{1}{2}\gamma_{ab}^{\mathrm{red}}/4\pi^2$ (THz^2)	$\gamma_c^{\mathrm{red}}/4\pi^2$ (THz^2)	$\gamma_V^{\mathrm{red}}/4\pi^2$ (THz^2)	$\frac{1}{2}\gamma_{ab}$	γ_c	γ_V
1	0.4	−36	−39	−37	−65.12	−70.31	−66.35
2	1.6	−57	−67	−59	−23.17	−27.03	−24.13
3	4.1	−44	−53	−47	−2.68	−3.22	−2.81
4	4.1	−69	−78	−71	−4.14	−4.70	−4.29
5	4.7	−65	−60	−64	−3.05	−2.82	−2.99
6	5.5	−56	−59	−57	−1.90	−2.02	−1.94
7	8.0	−34	−67	−43	−0.55	−1.08	−0.69
8	8.2	−43	−73	−51	−0.65	−1.10	−0.77
9	10.0	9	−19	2	0.10	−0.20	0.02
10	13.5	−13	35	0	−0.07	0.19	0.00
11	13.9	−18	−56	−28	−0.09	−0.28	−0.14
12	14.6	67	216	106	0.31	0.99	0.48
13	15.2	33	8	27	0.14	0.04	0.12
14	15.4	166	212	178	0.68	0.87	0.73
15	16.3	72	226	112	0.27	0.83	0.41
16	17.1	23	−184	−30	0.08	−0.61	−0.10
17	18.9	220	190	212	0.59	0.51	0.57
18	19.1	181	269	204	0.47	0.70	0.53
19	20.3	325	239	303	0.75	0.55	0.70
20	21.8	261	223	251	0.53	0.45	0.51
21	23.4	248	416	291	0.48	0.81	0.57
22	29.0	1450	1636	1497	1.59	1.80	1.65
23	29.4	1448	1250	1396	1.55	1.34	1.50
24	29.5	1232	1396	1275	1.32	1.49	1.36
25	32.3	1284	1455	1328	1.22	1.38	1.26
26	33.2	1388	1497	1416	1.23	1.33	1.26
27	33.2	1433	1420	1430	1.26	1.25	1.26

tuation, e.g., by Mary *et al.*[1] in connection with ZrV_2O_7 and ZrW_2O_8.

The present paper has added flesh and blood around that qualitative skeleton. It had not been at all clear initially how this geometrical effect could be incorporated within the standard, more or less rigorous, general theory of thermal expansion which we refer to conveniently as the Grüneisen theory, since one thinks of the latter more in terms of anharmonic interatomic forces. However, the Grüneisen theory as a general formulation must be able to encompass the geometrical effect, and the present work shows how the geometrical theory can be developed and fitted into the standard Grüneisen framework. That adds confidence that the geometrical effect is indeed real!

The most important finding is that the geometrical negative contribution to the COTE extends throughout the whole phonon spectrum. It is due to rotation of the tetrahedral and octahedral units of the framework, and does not depend specifically on these being “floppy modes”[28] or “rigid unit modes”[18–21] of very low frequency ω. However, the geometrical negative contribution to the COTE is weighted by a factor ω^{-2}, so that the low-frequency phonons have a disproportionate effect. The theory also shows how the geometrical effect adds to that from the anharmonicity of the interatomic forces (Section VI).

All of these points will be demonstrated in more quantitative detail in a computational study of β-quartz[6] using the best available potentials. This material is sufficiently simple that one can calculate the geometrical constants η for some modes to check that the computed reduced Grüneisen constants work out more or less as the present theory expects. It is important to make such a check. An important point in quartz concerns the behavior of the COTE near a displacive, soft mode, phase transition. As mentioned in Section I, a negative Grüneisen parameter can give a positive COTE due to the temperature dependence of the ω^{-2} weighting factor.

The geometrical effect can be visualized most easily in terms of optic mode phonons, for example in Fig. 1. Indeed, originally the acoustic modes had not been expected to be very interesting. It therefore came as a surprise in the calculations of quartz[6] that the band giving the largest overall negative contribution to the COTE is an acoustic band. Section V therefore shows how the theory of the geometrical effect can be developed for acoustic modes.

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