Comment on "Interplay between Phonons and Anisotropic Elasticity Drives Negative Thermal Expansion in $PbTiO_3$"

In a recent Letter [1], it is claimed that "negative Grüneisen parameters are neither sufficient nor necessary for a material to undergo negative thermal expansion (NTE)." Here we demonstrate that this is not correct for the kind of materials considered in Ref. [1]. Ritz and Benedek [1] use the example of tetragonal $PbTiO_3$ and claim that NTE in this material arises from positive Grüneisen parameters. We also point out that Raman scattering experiments [2] show a decrease of phonon frequencies of several modes with increasing pressure, which corresponds to negative Grüneisen parameters.

The mode Grüneisen parameter of a phonon mode of frequency ω_{qj} (of wave vector $\mathbf{q}$ and index j) is defined as [3]

$$\gamma_{q,j} = -\left(\frac{\partial \ln \omega_{q,j}}{\partial \ln V}\right)_T, \tag{1}$$

where V is the volume. This may be calculated and measured by the pressure dependence of the phonon frequency as

$$\gamma_{q,j} = -B\left(\frac{\partial \ln \omega_{q,j}}{\partial P}\right)_T, \tag{2}$$

where B is the bulk modulus. The calculation of the thermal expansion coefficient is performed under quasiharmonic approximation and is given by the following relation [3]:

$$\alpha_V(T) = \frac{1}{BV_0}\sum_{q,j} C_v(q,j,T)\gamma_{q,j}, \tag{3}$$

where $C_v(q,j,T)$ is the specific-heat contribution of the phonons of frequency ω_{qj}. We note that all of the quantities on the right-hand side of the Eq. (3) are always positive except for $\gamma_{q,j}$. Therefore, it is possible to achieve NTE—that is, negative $\alpha_V(T)$—only when $\gamma_{q,j}$ is negative.

Reference [1] does not report the calculation of the mode Grüneisen parameters as usually defined. Instead, Ritz and Benedek report the anisotropic Grüneisen parameters that involve anisotropic stresses. Such anisotropic Grüneisen parameters could be positive in the presence of negative anisotropic elasticity compliance parameters, even when the mode Grüneisen parameter is negative. In summary, while Ref. [1] claims that negative Grüneisen parameters are not necessary, we assert that negative Grüneisen parameters are necessary, but their anisotropic components may or may not be negative.

Further, we would like to point out some numerical inconsistencies in Ref. [1]. As an example, we find that the reported values of the elements of the compliance tensor (S) are not consistent with the reported elements of the elastic constant tensor (C), given that $S = C^{-1}$. The reported value of S and that derived from C^{-1} are given in Table I. Row 1 (0 K) is from Table I of Ref. [1]. Rows 2 (300 K) and 3 (500 K) are calculated by taking the inverse of the elastic constant matrix given in Tables S1 and S2, respectively, of the Supplemental Material of Ref. [1]. We note that the values of S_{13} and S_{33} show a large difference between 0 and 300 K, but not between 300 and 500 K. This may not be expected since the changes in lattice parameter on the increase of temperature from 0 to 300 K and 300 to 500 K are similar (see Fig. 1 of Ref. [1]).

TABLE I. Selected elements of compliance tensor and left-hand-side (lhs) of Eq. (4) (see text) in units of 10^{-3} GPa^{-1}.

T (K)	S_{11}	S_{12}	S_{13}	S_{33}	lhs of Eq. (4)
0	7.44	0.49	−11.94	55.69	1.34
300	6.26	−0.72	−6.21	28.95	4.71
500	6.08	−0.94	−5.20	24.15	5.33

It is noted in Ref. [1] that for NTE to occur, the following condition should be satisfied [see Eq. (7) of Ref. [1]]:

$$2(S_{11}+S_{12}+S_{13})\gamma_a^{\text{bulk}} + (S_{33}+2S_{13})\gamma_c^{\text{bulk}} < 0. \tag{4}$$

We calculate the left-hand side of the above equation using the compliance tensor values (Table I) and the anisotropic bulk Grüneisen parameters $\gamma_a^{\text{bulk}} = 1.42$ and $\gamma_c^{\text{bulk}} = 0.40$ at 300 K [from the Wu-Cohen (WC)-functional calculation in Ref. [1]], which are the only values provided in Ref. [1]. The result is shown in Table I [row 2 (300 K)], which does not satisfy the above requirement of NTE at 300 K in Eq. (4). This is also not consistent with NTE shown in Fig. S1 (from the WC-functional calculation in Ref. [1]). We also note that the lhs of Eq. (4) remains positive even when we use the compliance tensor values given in row 1 (0 K) or row 3 (500 K).

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