Ritz and Benedek Reply: The preceding Comment [1] raises some criticisms of our work along three general lines:

(1) *Physics.*—The authors make the obvious claim that the thermodynamic Grüneisen parameter, Eq. (2) of the Comment, which we denote $\gamma^G_{s,\mathbf{k}}$ in this Reply, must be negative in order for a material to exhibit negative thermal expansion (NTE); this trivially follows from Eq. (3) of the Comment. They then propose that this invalidates our Letter. Our response is that it is not clear to us how the authors arrived at such a conclusion. In fact, the entire point of our Letter was to show how the underlying physics of NTE, which is hidden in $\gamma^G_{s,\mathbf{k}}$, can be made clear by decomposing $\gamma^G_{s,\mathbf{k}}$ into physically distinct components via the generalized tensor definition of the Grüneisen parameter used in our work [2,3]:

$$\gamma^G_{s,\mathbf{k}} = B\sum_{i=1}^{3}\sum_{j=1}^{6} S_{ij}\gamma^j_{s,\mathbf{k}}, \tag{1}$$

where again $\gamma^G_{s,\mathbf{k}}$ is the thermodynamic mode Grüneisen parameter [3–5] for phonon mode s at wave vector $\mathbf{k}$, B is the bulk modulus, S_{ij} is an element of the compliance tensor, and $\gamma^j_{s,\mathbf{k}}$ is the generalized mode Grüneisen parameter. This decomposition clearly demonstrates that $\gamma^G_{s,\mathbf{k}}$ may be negative because either S_{ij} is negative *or* $\gamma^j_{s,\mathbf{k}}$ is negative. Hence, Eq. (3) of the Comment averages away the directional dependence between the vibrational properties and anisotropic elasticity, and it therefore hides the physics required to understand how the interplay between these two factors drives thermal expansion in noncubic materials. Our Letter clarifies this hidden physics. Incidentally, the generalized tensor definition of the Grüneisen parameter used in our Letter can be found in many standard thermodynamics textbooks and foundational theory going back to at least the 1960s [3,5–9] and is far from "unusual," as the authors of the Comment imply.

(2) *Numerics.*—The authors use the values of the bulk Grüneisen parameters (calculated for a structure with lattice constants at 300 K) and compliance tensor elements (calculated at 0 K) reported in our Letter to calculate the coefficient of volumetric thermal expansion, α_v [Eq. (7) of our Letter], and show that, instead of being negative (which would indicate NTE), α_v is positive. Furthermore, they calculate α_v again using compliance tensor elements calculated for a structure with lattice parameters predicted at 300 K (which we provided only in the Supplemental Material), and they again found α_v to be positive. Our response is that, as to the first point, the physical relevance of plugging two sets of data into a model that were calculated under different physical conditions is highly questionable, at best, and does not require further comment. As to the second point, this is not surprising. The finite temperature **S** in the Supplemental Material was calculated using the second derivative of the 0 K total energy from density-functional theory calculations with respect to strains about the predicted 300 K lattice parameters. These data neglect the vibrational contribution to the free energy, which is why we did not use Eq. (7) to calculate α_v. Instead, for quantitative calculations of α_v we used a robust theoretical approach (calculation of the full free energy surface) that explicitly accounts for the vibrational contributions to the free energy. We emphasize that we included the finite temperature **S** in the Supplemental Material primarily to justify our use of the 0 K elastic constants in Table I of the Letter, that is, to show that, as is known from experiments, the *signs* and *orders of magnitude* of the elastic constants most critical to our study do not change significantly with temperature. This was all the information we needed to be confident that our model had captured the essential physics of the problem. In addition, the elastic constants in the Supplemental Material, calculated using finite temperature lattice parameters, are not derived from the same data as the 0 K compliance tensor elements reported in Table I, and they should not be equivalent when inverted.

(3) *Experiments.*—Finally, Mittal *et al.* point out in the Comment that Raman scattering data presented in Ref. [10] indicate that some phonon modes of $PbTiO_3$ exhibit negative thermodynamic mode Grüneisen parameters ($\gamma^G_{s,\mathbf{k}}$). Our response is that our Letter concerns the generalized mode Grüneisen parameters, which are not the same as those being measured in Ref. [10]. In general, however, it is often the case for a material with positive (negative) *bulk* Grüneisen parameters to have phonons with negative (positive) *mode* Grüneisen parameters, as Fig. 2 of our Letter shows.

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[1] R. Mittal, M. K. Gupta, B. Singh, and S. L. Chaplot, preceding Comment, Phys. Rev. Lett. **123**, 179601 (2019).
[2] K. Brugger, Phys. Rev. **137**, A1826 (1965).
[3] T. Barron and R. Munn, Philos. Mag. **15**, 85 (1967).
[4] G. Grimvall, *Thermophysical Properties of Materials* (Elsevier, New York, 1999).
[5] D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).
[6] G. Leibfried and W. Ludwig, *Solid State Physics*, Vol. 12 (Academic Press, New York, 1961), p. 276.
[7] R. Munn, Phys. Rev. B **12**, 3491 (1975).

[8] J. Collins and G. White, in *Progress in Low Temperature Physics*, Vol. 4, edited by C. J. Gorter (Elsevier, New York, 1964), pp. 450–479.

[9] G. K. Horton and A. A. Maradudin, *Dynamical Properties of Solids*, Vol. 1 (Elsevier, New York, 1974).

[10] P.-E. Janolin, P. Bouvier, J. Kreisel, P. Thomas, I. Kornev, L. Bellaïche, W. Crichton, M. Hanfland, and B. Dkhil, Phys. Rev. Lett. **101**, 237601 (2008).