

Thermal expansion and Grüneisen parameters for anisotropic solids

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An improved definition of Grüneisen parameters $\hat{\gamma}_\mu$ for anisotropic solids leads to a clearer relationship with the measured thermal expansivities α_μ . The corresponding definition of mode Grüneisen parameters $\hat{\gamma}_\mu^i$ expresses the contribution of mode i to α_μ , and these are related to the cubic coefficients in the potential-energy function. A phenomenological two-component model due to Grüneisen is then revived in a simplified form and is shown to yield insight into the temperature dependence of α_μ . The data on tellurium are analyzed as an example.

I. INTRODUCTION

Grüneisen parameters^{1,2} have always been useful phenomenological concepts for understanding thermal expansion. This paper discusses three issues concerning their generalization³⁻⁶ and application³⁻¹⁸ to anisotropic solids. (1) We show that a new and more natural definition of the bulk Grüneisen parameters (to be denoted as $\hat{\gamma}_\mu$ to distinguish them from the conventional γ_μ) simplifies the relation with the thermal expansivities α_μ , the index μ denoting different strain components. The new $\hat{\gamma}_\mu$ have attractive thermodynamic interpretations parallel to those of γ_μ . (2) It is shown that a corresponding new definition of mode Grüneisen parameters $\hat{\gamma}_\mu^i$ expresses the contribution of each normal mode i to α_μ , whereas the conventionally defined γ_μ^i cannot be interpreted this way. The relationship with the lattice Hamiltonian is also established. (3) Elastic anisotropy implies great differences between various classes of lattice modes, and therefore suggests that while $\hat{\gamma}_\mu^i$ may be nearly constant for i within a certain class (e.g., a phonon branch), the difference between various classes of modes cannot be ignored. This simple observation leads to a phenomenological two-component model, first discussed by Grüneisen himself.³ However, that early work, obscured by the conventional definition of γ_μ and γ_μ^i and by inappropriate identification of the polarization of vibration with direction of expansion, has been largely ignored in recent decades. We clarify this model, which is seen to provide considerable insight into the temperature dependence of $\alpha_\mu(T)$. The data on tellurium are analyzed as an example.

II. BULK GRÜNEISEN PARAMETERS

A. Conventional definition

The bulk Grüneisen parameter $\gamma(T)$ for isotropic materials^{1,2} is related to the volume expansivity β by

$$\beta = \frac{C_p}{V} \frac{1}{B^S} \gamma, \quad (1)$$

where B^S is the adiabatic bulk modulus, and $C_p(T)$ is the heat capacity at constant pressure p . It follows thermodynamically that

$$\gamma = \frac{1}{C_v} \left[V \frac{\partial S}{\partial V} \right]_T, \quad (2)$$

where S is the entropy.

For anisotropic materials, the strains η_μ ($\mu=1, \dots, 6$) define corresponding expansivities

$$\alpha_\mu = \left[\frac{\partial \eta_\mu}{\partial T} \right]_t, \quad (3)$$

the derivative being at constant stress components t_ν ($\nu=1, \dots, 6$). Equation (2) suggests the following generalization⁴⁻⁶ of bulk Grüneisen parameters:

$$\gamma_\mu = \frac{1}{C_\eta} \left[\frac{\partial S}{\partial \eta_\mu} \right]_{T, \eta'}, \quad (4a)$$

where C_η is the heat capacity at constant strain and η' indicates that other strain components are held fixed. γ_μ can also be written in terms of the Helmholtz free energy F as

$$\gamma_\mu = - \frac{1}{C_\eta} \frac{\partial^2 F}{\partial T \partial \eta_\mu}. \quad (4b)$$

It follows thermodynamically that

$$\alpha_\mu = \frac{C_t}{V} \sum_\nu S_{\mu\nu}^S \gamma_\nu = \frac{C_\eta}{V} \sum_\nu S_{\mu\nu}^T \gamma_\nu, \quad (5)$$

where C_t (C_η) is the heat capacity at constant stress (strain) and $S_{\mu\nu}^S$ ($S_{\mu\nu}^T$) are the adiabatic (isothermal) compliances

$$S_{\mu\nu}^S = \left[\frac{\partial \eta_\mu}{\partial t_\nu} \right]_{S, t'}, \quad (6)$$

$$S_{\mu\nu}^T = \left[\frac{\partial \eta_\mu}{\partial t_\nu} \right]_{T, t'},$$

in which other stress components t' are held fixed.

This definition of γ_μ , almost universally used in the literature, unfortunately mixes different strain components through the off-diagonal elements of $S_{\mu\nu}^S$. As a consequence, the three principal γ_μ 's do not average to the γ_v associated with volume expansion, defined in analogy

to (1) (Ref. 19):

$$\begin{aligned} \gamma_v &\equiv \beta V B^S / C_t \\ &\neq \frac{1}{3}(\gamma_1 + \gamma_2 + \gamma_3). \end{aligned} \quad (7)$$

Moreover, (5) is inconvenient. For example, γ_v are generally extracted from experimental values of α_μ by the inverse of (5):

$$\gamma_v = \frac{V}{C_t} \sum_{\mu} C_{\nu\mu}^S \alpha_\mu = \frac{V}{C_\eta} \sum_{\mu} C_{\nu\mu}^T \alpha_\mu, \quad (8)$$

where $C^{S,T} = (\underline{S}^{S,T})^{-1}$ are the adiabatic and isothermal stiffness tensors, respectively. Many anisotropic systems exhibit negative expansivity along one direction and positive expansivity along another (Refs. 3, 9, 10, 14, 17, and 20–26), so partial cancellations on the right-hand side of (8) magnify experimental uncertainties. More importantly, the positive and negative contributions may be due to diverse mechanisms,^{27–31} which are mixed and therefore obscured by the use of γ_μ . We now show that these difficulties are automatically avoided by a different generalization of Eq. (2).

B. New definition

The Grüneisen parameters γ in the isotropic case could just as well be written as

$$\gamma = \frac{1}{C_p} \left[-B^S \frac{\partial S}{\partial p} \right]_T, \quad (9)$$

where p is the hydrostatic pressure. Equation (9) suggests the alternative generalization

$$\hat{\gamma}_\mu = \frac{3}{C_t} B^S \left[\frac{\partial S}{\partial t_\mu} \right]_{T,t'}, \quad (10a)$$

Parallel to (4b), $\hat{\gamma}_\mu$ can also be written as

$$\hat{\gamma}_\mu = \frac{3B^S}{C_t} \frac{\partial^2 G}{\partial T \partial t_\mu}, \quad (10b)$$

where the Gibbs free energy

$$G = F - V \sum_{\mu} t_\mu \eta_\mu,$$

in which V is the volume of the crystal in the reference state, is the natural thermodynamic potential when stresses are taken as independent variables.

The factor of 3 accounts for the three nonzero stress components $t_1 = t_2 = t_3 = -p$ in the case of a hydrostatic pressure p , and the adiabatic bulk modulus B^S may be thought of as setting a natural scale for the incremental stresses dt_μ . Note that for anisotropic materials, B^S is still defined in terms of the volume change induced by a hydrostatic pressure and is given by

$$B^S = \left[\sum_{\mu,\nu=1}^3 S_{\mu\nu}^S \right]^{-1}. \quad (11)$$

Although (2) and (9) are equivalent, (4) and (10) define different quantities, related by

$$\hat{\gamma}_\mu = 3B^S \sum_{\nu} S_{\mu\nu}^S \gamma_\nu. \quad (12)$$

Of course, in the isotropic case $\hat{\gamma}_\mu = \gamma_\mu = \gamma$.

In discussing thermal expansivity, one treats the strains as functions of the independent variables, temperature, and stresses [see Eq. (3)]. Equation (9) conforms to this spirit while Eq. (2) does not; so (9) and its generalization (10) are more natural than (2) and its generalization (4). This point of view is vindicated since we find from (5) and (12) that

$$\alpha_\mu = \frac{C_t}{V} \frac{1}{3B^S} \hat{\gamma}_\mu, \quad (13)$$

showing that the new $\hat{\gamma}_\mu$ are related to the expansivities without mixing of components, with advantages that have already been noted. In particular, the γ_v defined in terms of volume expansion in (7) is related to $\hat{\gamma}_\mu$ by

$$\begin{aligned} \gamma_v &= \frac{1}{3}(\hat{\gamma}_1 + \hat{\gamma}_2 + \hat{\gamma}_3) \\ &= \frac{B^S}{C_t} \sum_{\mu=1}^3 \left[\frac{\partial S}{\partial t_\mu} \right]_{T,t'}. \end{aligned} \quad (14)$$

We may also note some thermodynamic relationships. The conventional Grüneisen parameters can be expressed as

$$\gamma_\mu = - \left[\frac{\partial \ln T}{\partial \eta_\mu} \right]_{S,\eta'} = -V \left[\frac{\partial t_\mu}{\partial E} \right]_\eta, \quad (15)$$

where E is the internal energy. It therefore has the well-known interpretation in terms of the thermal stress induced in a clamped solid upon increase of energy density. Analogously

$$\hat{\gamma}_\mu = -3B^S \left[\frac{\partial \ln T}{\partial t_\mu} \right]_{S,t'} = 3B^S V \left[\frac{\partial \eta_\mu}{\partial H} \right]_t, \quad (16)$$

where H is the enthalpy. It can therefore be interpreted in terms of the free expansion of a solid upon increase in enthalpy density—a process operationally related to the measurement of expansivity.

In fact, the new $\hat{\gamma}_\mu$'s (apart from a factor of 3) are essentially those considered by Brugger and Fritz,¹¹ who in effect took (13) as the definition but did not show how $\hat{\gamma}_\mu$ is naturally related to $\partial S / \partial t_\mu$ or $\partial \eta_\mu / \partial H$. Moreover they did not investigate (as we shall do in the next section) the role of the microscopic counterparts $\hat{\gamma}_\mu^i$.

As an example of the use of $\hat{\gamma}_\mu$, consider tellurium,^{23–25} for which $\alpha_{||}$ ($\equiv \alpha_3$) is negative, while α_{\perp} ($\equiv \alpha_1 = \alpha_2$) is positive (Fig. 1). The former has an interesting minimum around 30 K, which will be discussed in Sec. IV. We have extracted $\hat{\gamma}_\mu$ and γ_μ from the data (Fig. 2). In Sec. IV we shall see that the significant variation of $\hat{\gamma}_\mu$ with temperature reflects the contribution of two different classes of modes, whose relative importance changes with temperature. This tends to be obscured by the use of γ_μ .

III. MODE GRÜNEISEN PARAMETERS

Ultimately, the merit of any particular definition rests upon its ability to shed light on the microscopic mecha-

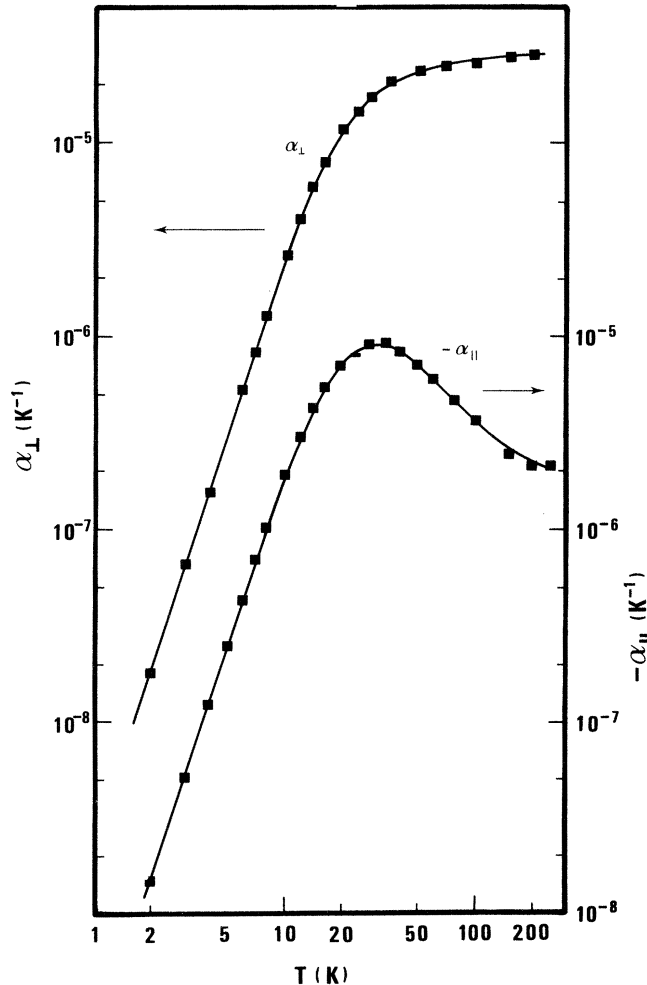


FIG. 1. (a) $-\alpha_{\parallel}$ and (b) α_{\perp} for tellurium up to 200 K. Data from Refs. 23–25. The line represents the best fit using the two-component model, with parameters given in Sec. IV.

nisms responsible for thermal expansion, and the crucial question is as follows: How much does each normal mode i contribute to α_{μ} ? To this end it is necessary to consider the mode Grüneisen parameters.^{2,4–6} The connection between macroscopic and microscopic quantities is most immediately established by noticing that (insofar as the modes are weakly coupled), S (and hence $\partial S/\partial \ln V$) is the sum of contributions from each mode i :

$$S = \sum_i S^i, \quad (17)$$

so that from (2)

$$\gamma(T)C_v(T) = \sum_i \gamma^i C^i(T), \quad (18)$$

where γ^i is the Grüneisen parameter for mode i . The linear superposition in (17) and (18) is valid only to lowest order in anharmonic effects, a limitation inevitable in all discussions on mode Grüneisen parameters. To be consistent, we shall henceforth neglect differences such as $C_t - C_{\eta}$ and $S_{\mu\nu}^T - S_{\mu\nu}^S$, both being $O(\alpha_{\mu}^2)$.

In (18), $C^i(T)$ is the heat capacity of mode i , which for

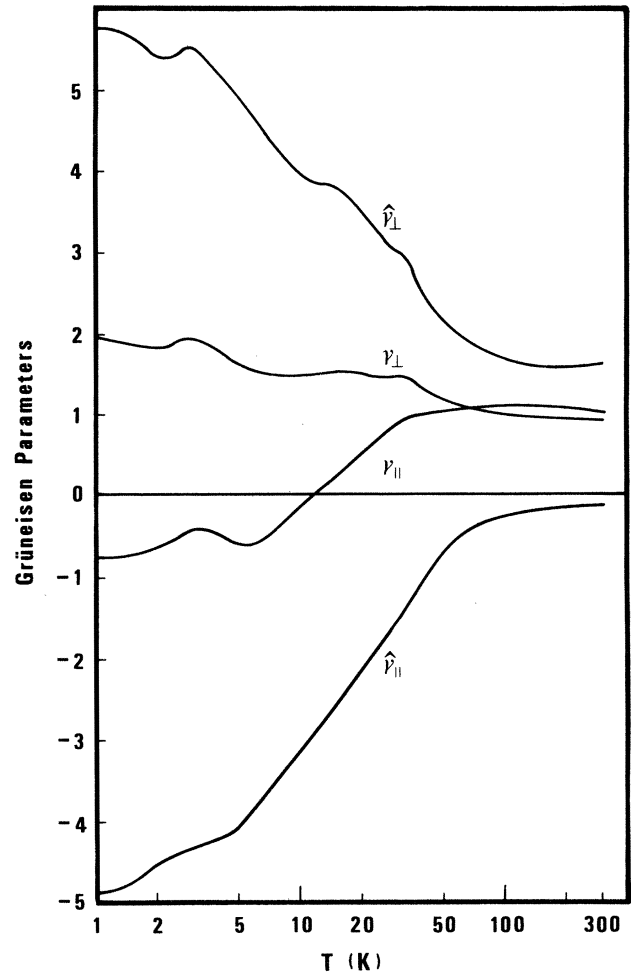


FIG. 2. $\hat{\gamma}_{\mu}$ and γ_{μ} for tellurium. C_p data are after Ref. 32 for $T < 20$ K and Ref. 33 for $T \geq 20$ K. (See also Refs. 34 and 35.) The expansivity data are after Ref. 25 for $T \leq 30$ K and Ref. 23 for $T > 30$ K. (See also Ref. 24.) The bulk modulus is extrapolated from Ref. 36 with the use of the method of Ref. 24.

a boson mode of frequency ω_i is given by

$$C^i(T) = C(\omega_i/T) = k(z_i/\sinh z_i)^2,$$

$$z_i = \frac{\hbar\omega_i}{2kT},$$

k being Boltzmann's constant. In analogy to (2) one has

$$\gamma^i = \frac{1}{C^i} \left[V \frac{\partial S^i}{\partial V} \right]_T.$$

This is readily evaluated for a boson mode, and turns out to be

$$\gamma^i = - \left[V \frac{\partial \ln \omega_i}{\partial V} \right]_T, \quad (19)$$

which is independent of temperature.³⁷ Equation (19) is often taken to be the definition of the mode Grüneisen parameters in the isotropic case.

A. Conventional generalization

The obvious generalization of (19) to anisotropic materials would seem to be⁴⁻⁶

$$\gamma_{\mu}^i = - \left[\frac{\partial \ln \omega_i}{\partial \eta_{\mu}} \right]_{T, \eta'} , \quad (20)$$

which is obviously related to γ_{μ} by

$$\gamma_{\mu}(T) C_{\eta}(T) = \sum_i \gamma_{\mu}^i C^i(T) . \quad (21)$$

B. New definition

Parallel to the discussion of the bulk Grüneisen parameters, and neglecting higher-order anharmonic effects, (19) could be written as

$$\gamma^i = B^S \left[\frac{\partial \ln \omega_i}{\partial p} \right]_T , \quad (22)$$

which suggests the following alternative generalization:

$$\hat{\gamma}_{\mu}^i = -3B^S \left[\frac{\partial \ln \omega_i}{\partial t_{\mu}} \right]_{T, t'} . \quad (23)$$

Of course, in analogy to (18) and (21),

$$\hat{\gamma}_{\mu}(T) C_t(T) = \sum_i \hat{\gamma}_{\mu}^i C^i(T) . \quad (24)$$

Moreover, the new and conventional Grüneisen parameters are related by

$$\hat{\gamma}_{\mu}^i = 3B^S \sum_{\nu} S_{\mu\nu}^T \gamma_{\nu}^i . \quad (25)$$

It follows immediately from the foregoing that

$$\alpha_{\mu}(T) = \frac{1}{3B^S V} \sum_i \hat{\gamma}_{\mu}^i C^i(T) . \quad (26)$$

The interpretation of this equation sheds light on the importance of $\hat{\gamma}_{\mu}$ and $\hat{\gamma}_{\mu}^i$: $\hat{\gamma}_{\mu}^i$ is a measure of how much a unit amount of excitation in mode i contributes to the strain component η_{μ} , while $C^i(T)$ describes how the actual amount of excitation varies with temperature, so their product is directly related to $\alpha_{\mu} = \partial \eta_{\mu} / \partial T$. An analogous but more complicated expression can be written in terms of γ_{μ}^i , but the above interpretation would be lost.

Equation (26) can also be written more explicitly as

$$\alpha_{\mu}(T) = - \frac{1}{V} \sum_i \left[\frac{\partial \ln \omega_i}{\partial t_{\mu}} \right]_{T, t'} C^i(T) , \quad (27)$$

which emphasizes that α_{μ} is related to the stress dependence of mode frequencies, the latter being experimentally measurable. Moreover, expansivity along one principal axis (α_{μ}) is related only to response to stress on the same axis (t_{μ}).

C. Relation to Hamiltonian

To fully understand the microscopic origin of expansivity in any particular system, one must also express γ_{μ}^i or $\hat{\gamma}_{\mu}^i$ in terms of the lattice Hamiltonian. Such calcula-

tions have been undertaken for various specific models^{15,16,27,28,38}; we now present the general result.

Let Q_i be the normal phonon coordinates, with conjugate momenta P_i . For calculating the thermal expansivities, one needs only keep up to cubic terms in Q_i , so the most general Hamiltonian is

$$H = \sum_i \frac{1}{2} \hbar \omega_i^0 (P_i^2 + Q_i^2) - \sum_{i,j,k} g_{ijk} Q_i Q_j Q_k , \quad (28)$$

where ω_i^0 is the frequency for small oscillations about $Q_i = 0$ and g_{ijk} is by definition symmetric. From (28), one has as Hamiltonian equations in the classical case or Heisenberg equations of motion for operators

$$\frac{dP_j}{dt} = - \frac{\partial H}{\partial Q_j} = - \hbar \omega_j^0 Q_j + 3 \sum_{i,k} g_{jik} Q_i Q_k . \quad (29)$$

Upon taking a time or ensemble average, denoted by $\langle \dots \rangle_{\text{en}}$, one has

$$\langle Q_j \rangle_{\text{en}} = \frac{3}{\hbar \omega_j^0} \sum_{i,k} g_{jik} \langle Q_i Q_k \rangle_{\text{en}} \quad (30)$$

To lowest order in the anharmonicity g_{jik} ,

$$\langle Q_i Q_k \rangle_{\text{en}} = \langle Q_i^2 \rangle_{\text{en}} \delta_{ik} = \frac{1}{\hbar \omega_i^0} U^i(T) \delta_{ik} , \quad (31)$$

where $U^i(T)$ is the energy in mode i at temperature T . Hence

$$\langle Q_j \rangle_{\text{en}} = 3 \sum_i \frac{g_{jii}}{(\hbar \omega_i^0)(\hbar \omega_j^0)} U^i(T) . \quad (32)$$

Once $\langle Q_j \rangle_{\text{en}}$ is known, the mean displacement of each atom is uniquely determined; then the strains η_{μ} are fixed by a purely kinetic relation with the atomic displacements. In general, the relation between η_{μ} and $\langle Q_j \rangle_{\text{en}}$ is linear:

$$\eta_{\mu} = \sum_j \lambda_{\mu}^j \langle Q_j \rangle_{\text{en}} . \quad (33)$$

So we have

$$\alpha_{\mu} = \frac{d\eta_{\mu}}{dT} = 3 \sum_{i,j} \frac{g_{ijj}}{(\hbar \omega_i^0)(\hbar \omega_j^0)} \lambda_{\mu}^j C^i(T) , \quad (34)$$

where $C^i(T) = dU^i/dT$. Note that $d\eta_{\mu}/dT$ in (34) is at zero stress, since the Hamiltonian (28) includes no external forces. Comparing (34) with (26) allows us to identify

$$\hat{\gamma}_{\mu}^i = 9B^S V \sum_j \frac{g_{ijj}}{(\hbar \omega_i^0)(\hbar \omega_j^0)} \lambda_{\mu}^j , \quad (35)$$

whereas γ_{μ}^i takes the more complicated form

$$\gamma_{\mu}^i = \sum_{\nu} C_{\mu\nu}^T 3V \sum_j \frac{g_{ijj}}{(\hbar \omega_i^0)(\hbar \omega_j^0)} \lambda_{\nu}^j . \quad (36)$$

Equation (35) has a ready interpretation.²⁹⁻³¹ The i th mode ("cause") has a mean-square excitation

$$\langle Q_i^2 \rangle_{\text{en}} \propto \frac{1}{\hbar \omega_i^0} .$$

This drives the j th mode ("effect") via the $g_{ijk} Q_i Q_j Q_k$ term, with a coupling g_{ij} . The resultant nonzero $\langle Q_j \rangle_{\text{en}}$

contributes to the strain η_μ with a coefficient $\lambda_\mu^i/\hbar\omega_j^0$. Thus as mentioned earlier, $\hat{\gamma}_\mu^i$ expresses the strength with which the i th mode couples to the thermal expansivity in the μ direction; there is no such interpretation for γ_μ^i .

In one point of view, the mode Grüneisen parameters may be regarded as stepping stones in the process of calculating expansivities from the Hamiltonian, as illustrated in Fig. 3. Whether we proceed by the top line or the bottom line in Fig. 3, the result for α_μ is, of course, the same. However, the bottom line, corresponding to the use of conventional Grüneisen parameters, involves a gratuitous mixing of the μ, ν indices by $C_{\mu\nu}^T$ in (36), which is undone in the end by the inverse matrix $S_{\mu\nu}^T$ in (5). The ultimate result (34) contains no such mixing at all, and the point of these two sections is to urge recognition of this simple fact by adopting the new Grüneisen parameters $\hat{\gamma}_\mu^i$ and $\hat{\gamma}_\mu$.

It will also be noticed that B^S does not appear in the end result (34). This amplifies our earlier remark that B^S serves only to provide a convenient scale for the incremental stresses dt_μ , thus making the Grüneisen parameters dimensionless. First of all, any other scale could do just as well, hence the absolute magnitude of Grüneisen parameters is of little intrinsic physical significance. Second, it may be convenient to use not the actual value of $B^S(T)$, but the value of B^S at a fixed reference temperature, say, 0 K. Then from (35), the mode Grüneisen parameters would be independent of temperature.³⁹ After all, the point of the mode analysis is to express the T dependence of $\hat{\gamma}_\mu(T)$ in terms of the i dependence of $\hat{\gamma}_\mu^i$ (or equivalently the dependence on mode frequency ω_i), in much the same way as one expresses the heat capacity $C(T)$ in terms of the density of states $\rho(\omega)$. For such an analysis to be profitable, it is necessary for the mode parameters [$\hat{\gamma}_\mu^i$ in the case of expansivity or $\rho(\omega)$ in the case of heat capacity] to be independent of temperature, with all T dependence attributed to the occupation of these modes through the Bose-Einstein factor $C(\omega_i/T)$. For this reason, we have used $B^S(0)$ for calculating the Grüneisen parameters $\hat{\gamma}_\mu$ and $\hat{\gamma}_\mu^i$.

IV. Two-component model

Recall that in Eq. (26) the index i refers to various modes which cause the expansivity. In many cases, one may approximate $\hat{\gamma}_\mu^i$ by its average value over i , denoted by $\langle \dots \rangle$:

$$\alpha_\mu(T) = \frac{1}{3B^S V} \langle \hat{\gamma}_\mu^i \rangle C_V(T). \quad (37)$$

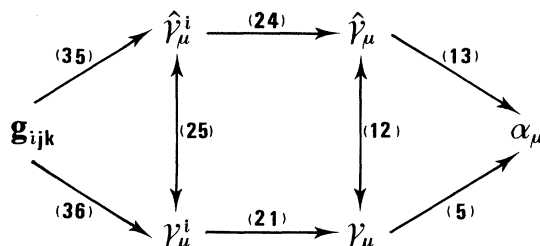


FIG. 3. Logical relation among variables.

So $\langle \hat{\gamma}_\mu^i \rangle$ is recognized as nothing more than the bulk Grüneisen parameter $\hat{\gamma}_\mu$, which is therefore, to this approximation, temperature independent. However, elastic anisotropy necessarily means a substantial difference *between* phonon branches. In various "one-dimensional" solids (e.g., polymer crystals, tellurium, and selenium), spectroscopic and heat-capacity data suggest that broadly speaking there are two classes of modes, one of which involves intrachain vibrations, while the other does not. The Tarasov model⁴⁰ for the heat capacity attempts to take account of these differences. Similarly large differences are found in "two-dimensional" solids such as graphite. Not only are the frequency spectra widely disparate, but the Grüneisen parameters for the different classes may have opposite signs, the negative contributions often arising from the so-called tensional effect.^{16,27,29}

To take account of the discrete difference *between* branches, divide all the lattice modes into various classes A, B, \dots (e.g., stretching, bending, optical, etc.), and assume that $\hat{\gamma}_\mu^i$ is constant within each class, e.g.,

$$\hat{\gamma}_\mu^i = \hat{\gamma}_\mu^A \text{ for all } i \in A.$$

Then (37) becomes

$$\alpha_\mu(T) = \frac{1}{3B^S V} [\hat{\gamma}_\mu^A C^A(T) + \hat{\gamma}_\mu^B C^B(T)], \quad (38)$$

where

$$C^A(T) = \sum_{i \in A} C^i(T), \quad (39)$$

etc., and we have for simplicity assumed only two classes of modes; generalization is, of course, trivial.

The behavior of $C^A(T)$ and $C^B(T)$ depends on the density of states within each class, which could be represented by three-dimensional Debye distributions, one-dimensional distributions in the manner of Tarasov,⁴⁰ Einstein modes, etc. However, the spirit of the model is to regard the details *within* each class of modes as secondary, so we first give a general discussion without reference to these details. The two classes of modes may be described by characteristic frequencies ω_A, ω_B , with corresponding temperatures T_A, T_B ; without loss of generality let $T_A < T_B$. Now suppose $\hat{\gamma}_\mu^A < 0$ and $\hat{\gamma}_\mu^B > 0$; then the qualitative behavior of α_μ would be as shown in Fig. 4. Thus the minimum in α_μ (which is quite common in chain-structure axial solids) is explained in terms of the interplay between the negative contribution of the softer modes (A) and the positive contribution of the harder modes (B), with the latter being excited only at higher temperatures. Generally α_μ for chain-structure axial solids is positive and has no minima or maxima; the interpretation would be that only one of the two classes of modes makes a significant contribution. The T dependence would indicate that only the soft modes contribute to α_μ . The value of the two-component model lies precisely in these insights, and the questions that they prompt: e.g., what are the natures of the soft and hard modes? Are they related to interchain and intrachain vibrations?

To give quantitative substance to the above remarks, we have used the two-component model (38) to fit the data on tellurium.²³⁻²⁵ For simplicity, we have assumed the

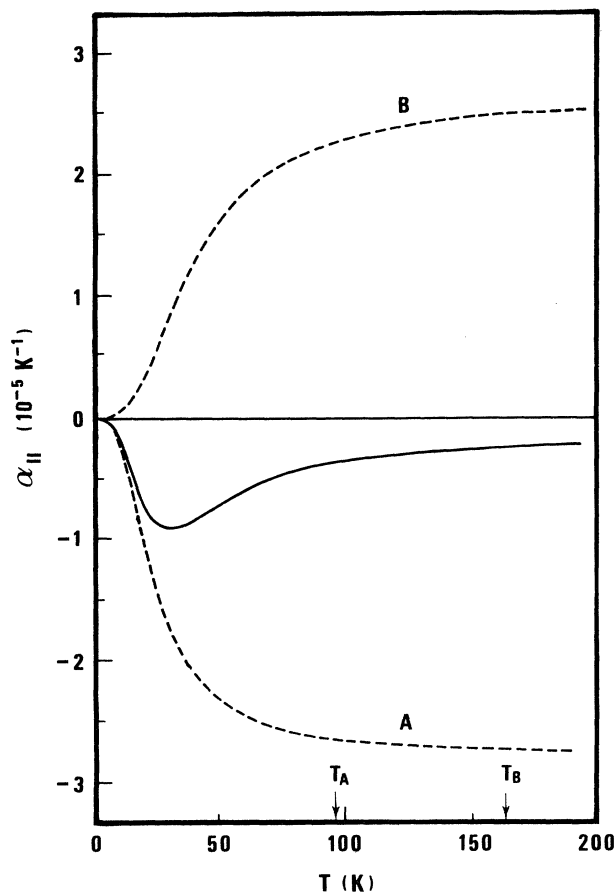


FIG. 4. Schematic diagram showing how a minimum in $\alpha_{||}$ (solid line) can arise from the interplay of two components (broken line) with opposite signs and different characteristic temperatures.

modes in each class follow the Debye distribution, so that

$$C^A(T) = n_A C(T_A/T), \quad C^B(T) = n_B C(T_B/T),$$

where n_A, n_B are the number of modes in each class and

$$C(\xi) = 24k\xi^{-3} \int_0^{2\xi} dz z^4 (\sinh z)^{-2} \quad (40)$$

is the Debye specific heat function. The values of the parameters chosen were (T_A and T_B in units of K) as follows:

$$\begin{aligned} T_A &= 97, \quad T_B = 163, \\ (n_A/n)\hat{\gamma}_{||}^A &= -1.51, \quad (n_B/n)\hat{\gamma}_{||}^B = 1.42, \\ (n_A/n)\hat{\gamma}_{\perp}^A &= 1.57, \quad (n_B/n)\hat{\gamma}_{\perp}^B = 0, \end{aligned} \quad (41)$$

and we have used the fact that the total number of modes $n = n_A + n_B$ is 3 per atomic volume: $n/V = 8.9 \times 10^{22} \text{ cm}^{-3}$. The fit is shown in Fig. 1. Data above 200 K has not been included, since the effect of phonon dispersion and of possible Einstein modes would certainly invalidate the quantitative results of the model at high temperatures. The excellent agreement with data should not be taken to mean that the modes necessarily follow the Debye distribution; rather the success demonstrates that the precise

distribution within each class may be modeled in the most naive way as long as the difference between the two classes has been taken into account.

The expansivities alone do not permit separation of the individual factors n_A/n , $\hat{\gamma}_{\mu}^A$, etc. If one takes fitting of the heat capacity³³ at face value, the soft modes *A* seem to comprise 40% of the total: $n_A/n \sim 0.4$, $n_B/n \sim 0.6$. Using these values, one finds $\hat{\gamma}_{||}^A \sim -3.8$, $\hat{\gamma}_{\perp}^A \sim 3.9$, $\hat{\gamma}_{||}^B \sim 2.4$, $\hat{\gamma}_{\perp}^B = 0$.

The fitted values should not be taken too literally; nevertheless, T_A and T_B are in fair agreement with values obtained in similar two-component analyses of heat capacity.³³ It may in fact be argued that the expansivities $\alpha_{\mu}(T)$ provide a better way of separating the two components than the corresponding analysis of heat capacity. Firstly, there are two (and in some systems three) expansivities $\alpha_{||}, \alpha_{\perp}$ to be simultaneously fitted. Much more importantly, the heat capacity is *sum* of two Debye terms, which would be difficult to resolve if T_A and T_B are not too far apart. However, as in the example of tellurium, the two components contribute to $\alpha_{||}$ with *opposite* signs, and are readily resolved.

Tellurium is by no means an isolated case. The expansivities of selenium¹⁷ can be explained by the same ideas. Polymer crystals such as polyethylene can also be accommodated, with one simplification. In this case, the hard modes, involving vibrations along the chain, are for all purposes not excited²⁹⁻³¹ [i.e., $C^B(T) \ll C^A(T)$] so most of the contribution comes from the soft modes only. Thus $\alpha_{||}(T)$ is negative and monotonic in T ; moreover, $\alpha_{||}$ and α_{\perp} both depend only on $C(T_A/T)$ and so have a similar temperature dependence (though with opposite signs).^{41,42}

In Sec. II it was argued that the significant temperature variation of $\hat{\gamma}_{\mu}$ (e.g., for tellurium) reveals important aspects of the underlying physics. We can now clarify this remark in the context of the two-component model. It is easy to see from (24) that⁴³

$$\hat{\gamma}_{\mu}(T) = \frac{C^A(T)}{C_V} \hat{\gamma}_{\mu}^A + \frac{C^B(T)}{C_V} \hat{\gamma}_{\mu}^B. \quad (42)$$

Thus variation of $\hat{\gamma}_{\mu}(T)$ reflects two important properties: (i) the difference between $\hat{\gamma}_{\mu}^A$ and $\hat{\gamma}_{\mu}^B$, and (ii) the difference between T_A and T_B , causing C^A/C_V and C^B/C_V to change with temperature. The conventional γ_{μ} , being linear combinations of $\hat{\gamma}_{\mu}$, masks these telling features.

Historically, the two-component model seems to have been first discussed by Grüneisen himself.³ There are, however, two differences with our present treatment. First of all, the conventional parameters γ_{μ}^i were used, resulting in formulas which were less meaningful. Second, it should be emphasized that mode Grüneisen parameters $\hat{\gamma}_{\mu}^i$ (or $\hat{\gamma}_{\mu}^A$) carry two indices: the *i* mode (or *A* modes) cause the expansion along direction μ . In the earlier works,^{3,7,8} these two indices were identified, so that (with two components) there were only two Grüneisen parameters (labeled as $\langle \gamma_x \rangle$, $\langle \gamma_z \rangle$) (Refs. 7 and 8) rather than our four ($\hat{\gamma}_{||}^A, \hat{\gamma}_{||}^B, \hat{\gamma}_{\perp}^A, \hat{\gamma}_{\perp}^B$). This is a conceptual error, corresponding to the ignoring of the tensional effect,^{16,27,29} which couples transverse vibrations to longitudinal thermal expansion. Probably for these reasons, these early

works have been largely ignored in recent decades. It is hoped that the present paper has clarified the model and demonstrated its utility in understanding experimental data.

Logically the two-component model has no relation to anisotropy; however, strong elastic anisotropy brings out the advantage of segregating the two components. The idea is not limited to lattice modes; similar considerations have been used to separate the lattice and electronic contributions to thermal expansivity.^{4,6,9-12,14,44}

V. CONCLUSION

At the purely phenomenological level, Grüneisen parameters γ_μ for the bulk sample are useful for summarizing data, and in addition have definite thermodynamic significance in terms of the entropy. The new $\hat{\gamma}_\mu$, while retaining the connection with entropy, yields a more direct relationship with the thermal expansivities, and average to the volumetric γ_v .

At a microscopic level, thermal expansion is to be understood as follows: Various modes i are thermally excited to mean-square values $\langle Q_i^2 \rangle_{en}$; these drive other modes into having mean displacements $\langle Q_j \rangle_{en}$, which then project onto the strains η_μ . The central question is therefore: How much does a unit amount of excitation in mode i affect η_μ ? The new mode Grüneisen parameters $\hat{\gamma}_\mu^i$ are exactly the answer to this question, whereas γ_μ^i are not.

The discussion on both the bulk and mode Grüneisen parameters in Secs. II and III is general and rigorous; however, these parameters may not be most convenient for data analysis, $\hat{\gamma}_\mu$ being overly simple and $\hat{\gamma}_\mu^i$ being possibly too detailed. The two-component model is a judicious compromise. By focusing on the difference between various classes of lattice modes, the model provides qualitative understanding of the T dependence of the thermal expansivities.

It must finally be emphasized that the new definitions of bulk and mode Grüneisen parameters are not meant to supplant the conventional ones, but to complement them.

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