

Grüneisen parameters for molecular crystals

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In molecular crystals and other crystals with internal degrees of freedom, the fundamental measures of anharmonicity are generalized mode Grüneisen parameters. These are derivatives of the frequency with respect to external or internal strain, with all other external and internal strains held constant. Zallen's vibrational scaling law corresponds to the special case of negligible off-diagonal anharmonicity.

A Grüneisen parameter is a dimensionless quantity defined as minus the strain derivative of the logarithm of some frequency. This definition can encompass a wide variety of quantities, and so one may ask which measures of strain give the most theoretically significant Grüneisen parameters for any particular frequency. Zallen¹ has recently argued that for modes of vibration in molecular crystals it is preferable to use bond length rather than volume to define the strain. Here we describe how there exists a hierarchy of successively more informative Grüneisen parameters, and show how Zallen's conclusion can be understood in terms of a generalized treatment of strain² which has been applied in detail to the lattice dynamics of tellurium.³ Within the quasiharmonic approximation, averages of Grüneisen parameters for lattice modes weighted by their heat capacity contributions give Grüneisen functions, which are useful in theoretical discussions of thermal expansion.⁴ Some of the present treatment extends results for the thermodynamic Grüneisen functions to the Grüneisen parameters for individual modes. Appropriate Grüneisen parameters are useful because they are constants depending only on the anharmonic part of the lattice potential, and it is these properties which permit quasiharmonic analysis and interpretation of thermal expansion.

For a mode ν of frequency $\omega^{(\nu)}$, the bulk Grüneisen parameter $\gamma^{(\nu)}$ is defined as

$$\gamma^{(\nu)} = - \frac{\partial \ln \omega^{(\nu)}}{\partial \ln V}. \quad (1)$$

In general, the properties of a solid depend not only on its volume but also on its shape: that is, on independent strain coordinates η_λ ($\lambda = 1, \dots, 6$).⁵ Only in cubic and isotropic solids is the shape unimportant, to first order. Equation (1) therefore does not define a unique quantity. In practice, the volume usually changes under the restrictions of isotropic stress and constant temperature, and this is what $\gamma^{(\nu)}$ normally implies. The alternative of constant entropy is discussed in Ref. 4, Appendix; see also below.

For solids of general symmetry, directional

Grüneisen parameters are defined as

$$\gamma_\lambda^{(\nu)} = - \left(\frac{\partial \ln \omega^{(\nu)}}{\partial \eta_\lambda} \right)_{\eta'}, \quad (2)$$

where η' denotes that strains other than η_λ are held constant. The $\gamma_\lambda^{(\nu)}$ can be related to $\gamma^{(\nu)}$ by considering the pressure derivative of $\omega^{(\nu)}$, when it is found that

$$\gamma^{(\nu)} \chi = \gamma_\lambda^{(\nu)} \chi_\lambda, \quad (3)$$

where λ is summed over. Here χ is the bulk compressibility $-\partial \ln V / \partial p$ and χ_λ is a linear compressibility

$$\chi_\lambda = - \frac{\partial \eta_\lambda}{\partial p} = s_{\lambda 1} + s_{\lambda 2} + s_{\lambda 3}, \quad (4)$$

the $s_{\lambda\mu}$ being elastic compliances. For cubic and isotropic solids,

$$\gamma_1^{(\nu)} = \gamma_2^{(\nu)} = \gamma_3^{(\nu)}, \quad \gamma_4^{(\nu)} = \gamma_5^{(\nu)} = \gamma_6^{(\nu)} = 0, \quad (5)$$

$$\chi_1 = \chi_2 = \chi_3 = \frac{1}{3} \chi, \quad \chi_4 = \chi_5 = \chi_6 = 0, \quad (6)$$

so that $\gamma^{(\nu)} = \gamma_1^{(\nu)}$, etc. For solids of lower than cubic symmetry, $\gamma^{(\nu)}$ is an average of the $\gamma_\lambda^{(\nu)}$ weighted by the compressibilities, and two consequences ensue. The first is that the compressibilities may be either adiabatic or isothermal, giving rise to more than one $\gamma^{(\nu)}$, as already noted. Since the difference between the adiabatic and isothermal compressibilities is an anharmonic effect, it happens that the difference between the two $\gamma^{(\nu)}$ is relatively small, especially at low temperatures (Ref. 4, Appendix). The second, more important, consequence is that *even if the $\gamma_\lambda^{(\nu)}$ depend only on the anharmonic part of the potential, $\gamma^{(\nu)}$ does not*: it depends also on the compressibilities, which are determined principally by the harmonic part of the potential. This means that, for example, quasiharmonic analyses of thermal expansion for non-cubic solids are not strictly valid if they use $\gamma^{(\nu)}$; in practice, the errors in such analyses may be small.

Now in solids containing more than one atom in the primitive unit cell, and hence in all molecular crystals, the lattice potential depends on the rela-

tive separations of all the atoms, and not merely on those fixed by the unit cell shape and size and hence by the external strains η_λ . The internal strains, describing the positions of atoms within the unit cell, are at equilibrium fixed so as to minimize the free energy for given external strains. However, in optical modes of lattice vibration it is these very internal strains which vary. The choice of internal strain variables is almost arbitrary,² but it is convenient to take them as the logarithm of the normal coordinates for the $\vec{q}=0$ optical modes. It is then clear that the frequencies of such modes should depend strongly on these internal strain variables as well as on the external strains.

Denote the internal strains by ϵ_k , and the complete set of strains by $\{\mathcal{E}_A\} \equiv \{\eta_\lambda, \epsilon_k\}$. Then generalized mode Grüneisen parameters are defined by³

$$\Gamma_A^{(r)} = - \left(\frac{\partial \ln \omega^{(r)}}{\partial \mathcal{E}_A} \right)_{\mathcal{E}'}, \quad (7)$$

where \mathcal{E}' means that strains other than \mathcal{E}_A are held constant. The equilibrium or macroscopic regime in which the ϵ_k adjust to minimize the free energy is a part of this generalized regime defined by the restriction that the internal stresses τ_k conjugate to the ϵ_k are held constant.² Thus, the directional Grüneisen parameter $\gamma_\lambda^{(r)}$ of Eq. (2) is evaluated at constant η' and τ , whereas its analog $\Gamma_\lambda^{(r)}$ [obtained from Eq. (7) when $\mathcal{E}_A = \eta_\lambda$] is evaluated at constant η' and ϵ . This identification enables us to relate the two quantities by

$$\gamma_\lambda^{(r)} = \Gamma_\lambda^{(r)} + \Gamma_k^{(r)} R_{k\lambda}, \quad (8)$$

where $R_{k\lambda}$ describes how the internal strain depends on the external strain under macroscopic conditions (constant τ)

$$R_{k\lambda} = \left(\frac{\partial \epsilon_k}{\partial \eta_\lambda} \right)_{\eta', \tau}, \quad (9)$$

and so is a generalization of Kleinman's internal strain parameter.⁶ The $R_{k\lambda}$'s are obtained from generalized elastic constants,² and hence depend on whether adiabatic or isothermal conditions prevail. So there are different versions of $\gamma_\lambda^{(r)}$, but these probably differ by as little as the corresponding versions of $\gamma^{(r)}$. Since we now allow all interatomic distances to change independently, the generalized mode Grüneisen parameters $\Gamma_A^{(r)}$ depend only on the anharmonic part of the potential, but the $\gamma_\lambda^{(r)}$ do not. As emphasized by Gibbons,³ the

second term on the right-hand side of Eq. (8) can be understood as the contribution to $\gamma_\lambda^{(r)}$ from relaxation of the internal strain, and this relaxation depends principally on the harmonic part of the potential.

Zallen suggests¹ that for any bond the force constant varies as $r^{-6\gamma}$, where γ is the same for all bonds. The equivalent in the present formalism is to set $\Gamma_A^{(r)}$ to zero unless the strain A is the coordinate for the mode r , so that off-diagonal anharmonicity is neglected; all nonzero $\Gamma_A^{(r)}$ are set equal to one another. Consider an internal mode labeled 0 and an external mode labeled 1, and corresponding strain coordinates labeled similarly. The generalized Grüneisen parameters are then

$$\Gamma_1^{(0)} = \Gamma_0^{(1)} = 0, \quad (10)$$

$$\Gamma_0^{(0)} = \Gamma_1^{(1)} = \Gamma, \quad (11)$$

leading to macroscopic ones

$$\gamma_1^{(0)} = \Gamma R_{01}, \quad (12)$$

$$\gamma_1^{(1)} = \Gamma. \quad (13)$$

Equations (12) and (13) correspond to Zallen's equations (10) giving his γ_0 and γ_1 , respectively. The quantity Γ is his 2γ , and R_{01} is his ratio of force constants, which is equivalent to the general expression for $R_{k\lambda}$ as a ratio of elastic constants. From the definition (9) we see directly that R_{01} describes the generally weak dependence of the internal strain upon external strain, so that $\gamma_1^{(0)}$ would be expected to be much less than $\gamma_1^{(1)}$. Zallen points out¹ that it is γ rather than γ_0 and γ_1 which describes anharmonicity, and this accords with the equivalence between γ and the generalized Γ . In general we expect that $\gamma_\lambda^{(r)}$ will be large only when r is an external mode; for internal modes, $\gamma_\lambda^{(r)}$ will be reduced by the coupling between internal and external strain. Similarly, it has recently been pointed out⁷ that rigid-molecule librational modes could have smaller Grüneisen parameters than translational modes, because of the difference between the librational coordinates and the external strain coordinates.

In summary, we have provided a general basis for the conclusions obtained by Zallen¹ from his analysis of a simple force model. For a proper description of anharmonicity in molecular crystals (and all others with internal degrees of freedom), it is necessary to treat internal strain explicitly and to use the generalized mode Grüneisen parameters which alone depend only on the anharmonic part of the crystal potential.

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