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Generalized Grüneisen Parameters in the Anisotropic Debye Model

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The description of anharmonic effects in solids involves generalized Grüneisen parameters which measure the strain dependence of the lattice vibrational frequencies. These parameters are here expressed in the Debye approximation in terms of second- and third-order elastic coefficients for arbitrary crystal symmetry. The general relations are also specialized to cubic point groups with a fourfold axis.

THE calculation of anharmonic effects in solids such as thermal expansion or the interaction of acoustic and thermal phonons involves generalized Grüneisen parameters, which describe the volume or strain dependence of the lattice vibrational frequencies. In the Debye model, these vibrations are replaced by standing wave modes of a dispersionless elastic continuum. The generalized Grüneisen parameters are then no longer frequency-dependent, and they can be expressed in terms of second- and third-order elastic coefficients. These relations are here derived for arbitrary crystal symmetry and specialized to the cubic point groups with a fourfold axis.

A generalized Grüneisen parameter specifying the isothermal strain dependence of a lattice frequency $\omega_p(\mathbf{q})$ is defined by

$$ {}_{jk}\gamma_p{}^T(\mathbf{q}) = -\left\{\frac{1}{\omega_p(\mathbf{q})}\left[\frac{\partial\omega_p(\mathbf{q})}{\partial\eta_{jk}}\right]_T\right\}_{\eta=0}, \tag{1}$$

where $p=1, 2, 3$ is the polarization index, $\mathbf{q}$ the wave vector, and η is the Lagrangian strain tensor. According to the standing wave condition of the Debye model, the frequencies are related for any state of strain to the wave speed S and the dimension L of the crystal by

$$\omega_p(\mathbf{q}) \propto S_p(\mathbf{N})/L = W_p(\mathbf{N})/L_0. \tag{2}$$

The equality in (2) defines W as the wave speed referred to the natural or unstrained dimension L_0. Since dispersion is neglected, S_p and W_p do not depend on the magnitude of $\mathbf{q}$, but only on its direction specified by the unit vector $\mathbf{N}$. Hence, Eq. (1) can now be written as

$$ {}_{jk}\gamma_p{}^T(\mathbf{N}) = -\frac{1}{2w_p(\mathbf{N})}\left[\frac{\partial\rho_0 W_p{}^2(\mathbf{N})}{\partial\eta_{jk}}\right]_{T,\eta=0}, \tag{3}$$

with $w=[\rho_0 W^2]_{\eta=0}$, and where ρ_0 is the density of the unstrained crystal. $\rho_0 W^2$ in a homogeneously deformed medium is given by[1]

$$\rho_0 W_p{}^2(\mathbf{N})U_u = w_{uv}U_v, \tag{4}$$

with

$$w_{uv} = [\delta_{uv}\bar{t}_{mn} + (\delta_{vw} + 2\bar{\eta}_{vw})\bar{c}_{munw}{}^S]N_m N_n, \tag{5}$$

where summation over repeated indices is implied. t represents the thermodynamic tension, and the c's are elastic stiffnesses. The bar over a symbol indicates that the quantity is to be evaluated in the deformed state. $\mathbf{N}$ gives the direction of propagation in the unstrained state, and $\mathbf{U}$ is the unit vector along the material line, which upon deformation, lies along the direction of polarization appropriate to p. With the strain derivative of Eq. (4) evaluated at zero strain, the Grüneisen parameter becomes

$$ {}_{jk}\gamma_p{}^T(\mathbf{N}) = -\frac{1}{2w_p(\mathbf{N})}[2w_p(\mathbf{N})U_j U_k + (c_{jkmn}{}^T + C_{jkmunv}U_u U_v)N_m N_n]. \tag{6}$$

with

$$w_p(\mathbf{N}) = c_{munv}{}^S N_m N_n U_u U_v. \tag{7}$$

The third-order stiffnesses in the last term of Eq. (6) are those determined by ultrasonic experiments, namely isothermal strain derivatives of isentropic second-order stiffnesses.

The isothermal Grüneisen parameters γ^T defined above are suitable for the evaluation of the equation of state for general homogeneous strains. On the other hand, the calculation of the attenuation of elastic waves by phonon-phonon interaction[2] involves isentropic parameters γ^S, in which $\rho_0 W^2$ has to be considered as a function of an adiabatically applied strain. Equation (6) is left unchanged, except that in the second and third terms isentropic stiffnesses will appear.

As the equation of state of solids is usually considered for volume changes produced by a hydrostatic stress P, another type of generalized Grüneisen parameter is introduced[3]:

$$ {}_H\gamma_p{}^T(\mathbf{q}) = -\left\{\frac{V}{\omega_p(\mathbf{q})}\left[\frac{\partial\omega_p(\mathbf{q})}{\partial V}\right]_T\right\}_{P=0}. \tag{8}$$

To relate it to the coefficients defined above the volume derivative is written as

$$\left(\frac{\partial}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial \tau_{ab}}{\partial P}\right)_T \left(\frac{\partial t_{gh}}{\partial \tau_{ab}}\right)_T \left(\frac{\partial \eta_{jk}}{\partial t_{gh}}\right) \left(\frac{\partial}{\partial \eta_{jk}}\right)_T. \tag{9}$$

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[1] R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).

[2] W. P. Mason and T. B. Bateman, J. Acoust. Soc. Am. **36**, 644 (1964).

[3] The Grüneisen parameter γ is the average of the generalized parameters of Eq. (8) weighted by the specific heat associated with each mode. See, for example, J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939).

For hydrostatic pressure P, the stresses τ are

$$\tau_{ab}=-\delta_{ab}P\,, \qquad (10$$

and Eq. (9) becomes in the limit of zero pressure

$$V\left(\frac{\partial}{\partial V}\right)_{T,P=0}=\frac{1}{\kappa_T}s_{aajk}{}^T\left(\frac{\partial}{\partial\eta_{jk}}\right)_{T,\eta=0}, \qquad (11)$$

with κ_T the isothermal compressibility which can also be written as $\kappa_T=s_{aabb}{}^T$. Hence

$$\begin{aligned}{}_H\gamma_p{}^T(\mathbf{N})=&-[2\kappa_T w_p(\mathbf{N})]^{-1}[1+s_{aajk}{}^T\\&\times\{2w_p(\mathbf{N})U_jU_k+C_{jkmunv}N_mN_nU_uU_v\}]. \qquad (12)\end{aligned}$$

Similarly for a uniaxial compressive stress of magnitude P along a direction $\mathbf{M}$

$$\tau_{ab}=-M_aM_bP\,, \qquad (13)$$

$$V\left(\frac{\partial}{\partial V}\right)_{T,P=0}=\frac{1}{\kappa_T}M_aM_bs_{abjk}{}^T\left(\frac{\partial}{\partial\eta_{jk}}\right)_{T,\eta=0}, \qquad (14)$$

and

$$\begin{aligned}{}_M\gamma_p{}^T(\mathbf{N})=&-[2\kappa_T w_p(\mathbf{N})]^{-1}[(\mathbf{N}\cdot\mathbf{M})^2\\&+M_aM_bs_{abjk}{}^T\{2w_p(\mathbf{N})U_jU_k+C_{jkmunv}N_mN_nU_uU_v\}].\end{aligned}$$

For cubic crystals with point groups 432, 43m, or $(4/m)\bar{3}(2/m)$, Eq. (6) becomes

$$\begin{aligned}&{}_{11}\gamma_p{}^T(\mathbf{N})\\&=-(1/2w)\{2wU_1^2+c_{11}{}^TN_1^2\\&\quad+c_{12}{}^T(N_2^2+N_3^2)+C_{111}N_1^2U_1^2\\&\quad+C_{112}[N_2^2U_2^2+N_3^2U_3^2+2N_1U_1(N_2U_2+N_3U_3)]\\&\quad+2C_{123}N_2N_3U_2U_3+C_{144}(N_2U_3+N_3U_2)^2\\&\quad+C_{155}[(N_1U_2+N_2U_1)^2+(N_1U_3+N_3U_1)^2]\}, \qquad (6a)\end{aligned}$$

$$\begin{aligned}&{}_{23}\gamma_p{}^T(\mathbf{N})\\&=-(1/w)\{wU_2U_3+c_{44}{}^TN_2N_3\\&\quad+C_{144}N_1U_1(N_2U_3+N_3U_2)\\&\quad+C_{155}[N_2N_3(U_2^2+U_3^2)+(N_2^2+N_3^2)U_2U_3]\\&\quad+C_{456}[N_2N_3U_1^2+N_1^2U_2U_3\\&\qquad\qquad+N_1U_1(N_2U_3+N_3U_2)]\}, \qquad (6b)\end{aligned}$$

from which the other elements follow readily by cyclic permutation of the indices. ${}_H\gamma$ can be obtained either directly from Eq. (12) or from Eq. (6a), using Eq. (11), which gives for cubic crystals

$${}_H\gamma_{\text{cubic}}=1/3\;{}_{jj}\gamma_{\text{cubic}}. \qquad (11a)$$

One obtains

$$\begin{aligned}&{}_H\gamma_p{}^T(\mathbf{N})\\&=-(1/6w)\{2w+c_{11}{}^T+2c_{12}{}^T\\&\quad+(C_{111}+2C_{112})(N_1^2U_1^2+N_2^2U_2^2+N_3^2U_3^2)\\&\quad+(C_{144}+2C_{155})[(N_2U_3+N_3U_2)^2\\&\quad+(N_3U_1+N_1U_3)^2+(N_1U_2+N_2U_1)^2]\\&\quad+2(C_{123}+2C_{112})(N_2N_3U_2U_3\\&\qquad\qquad+N_3N_1U_3U_1+N_1N_2U_1U_2)\}. \qquad (12a)\end{aligned}$$

In the equations for these cubic crystals w is given by

$$\begin{aligned}w=&\,c_{11}{}^S(N_1^2U_1^2+N_2^2U_2^2+N_3^2U_3^2)\\&+c_{44}{}^S[(N_2U_3+N_3U_2)^2+(N_3U_1+N_1U_3)^2\\&+(N_1U_2+N_2U_1)^2]+2c_{12}{}^S(N_2N_3U_2U_3\\&\qquad\qquad+N_3N_1U_3U_1+N_1N_2U_1U_2). \qquad (7a)\end{aligned}$$