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Grüneisen Parameter for Born–von Kármán Lattices

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The Grüneisen parameter is derived in closed form in terms of the elements of the secular determinant. The method is applied to face- and body-centered structures with nearest- and next-nearest-neighbor central forces. Results are presented for seven elements, and comparisons are made with some commonly used approximate methods.

INTRODUCTION

IN an earlier demonstration, based on the Debye theory, it was pointed out that the contribution of the shear modes to the calculation of the Grüneisen parameter is significantly more important than that of the compressional modes.[1] We show by a demonstration based on the Born–von Kármán theory that a similar result is obtained in this case as well. The Grüneisen parameter in this case will be shown to be most heavily dependent on the shear modulus c_{44} and its pressure derivative.

PREVIOUS DETERMINATIONS OF γ

Slater[2] has proposed that the Grüneisen parameter γ be calculated from the Debye theory of solids with the additional assumption that Poisson's ratio be constant. Birch[3] has written the correction to be applied if Poisson's ratio is not constant. However, this expression, written with a term in the pressure derivative of the bulk modulus as apparently the most dominant, hides the fact that the shear term is, in fact, the dominant one.

The Dugdale-MacDonald relation[4,5] is derived on the assumption that the individual terms

$$-\gamma_j = \frac{\partial \ln\omega_j}{\partial \ln v}\bigg|_T ,$$

the rate of change of the eigenfrequencies with volume, are equal to one another. This assumption is not valid. Below we amend the calculation of γ to take into account the dependence of ω_j upon v.

The frequencies of a Bravais lattice can be found as the roots of a cubic equation:

$$(\omega^2-\omega_1^2)(\omega^2-\omega_2^2)(\omega^2-\omega_3^2)=0 .$$

If we differentiate this expression implicitly and solve for γ,

$$(\omega^2-\omega_1^2)(\omega^2-\omega_2^2)+(\omega^2-\omega_1^2)(\omega^2-\omega_3^2) + (\omega^2-\omega_2^2)(\omega^2-\omega_3^2)$$

appears as a denominator where the ω_j's are the roots. As long as the roots are distinct, evaluation of the resulting expression at $\omega^2=\omega_j^2$ gives a nonzero denominator. In the case when a double root exists, such as happens along the cube diagonal in θ space[6] for a face-centered lattice, the denominator approaches zero and the resulting γ becomes infinite.[7] Thus any derivation which relies on the equality of the individual Grüneisen parameters is certainly open to question.

GRÜNEISEN PARAMETER FOR BORN–VON KÁRMÁN LATTICES

The Grüneisen parameter is defined as[8]

$$\gamma=\sum_{j,\mathbf{k}} \gamma_j(\mathbf{k}) E\left(\frac{\hbar\omega_j(\mathbf{k})}{k_B T}\right) \Bigg/ \sum_{j,\mathbf{k}} E\left(\frac{\hbar\omega_j(\mathbf{k})}{k_B T}\right), \qquad (1)$$

where

$$\gamma_j(\mathbf{k}) = -\frac{\partial \ln\omega_j(\mathbf{k})}{\partial \ln v}\bigg|_T , \qquad (2)$$

and

$$E(x)=x/(e^x-1) ,$$

the Einstein specific-heat function. Here $\mathbf{k}$ is the propagation vector and j is the branch index. At sufficiently high temperatures, all modes are fully excited and Eq. (1) reduces to

$$\gamma=\left\langle \sum_{j=1}^{3} \frac{\gamma_j(\mathbf{k})}{3} \right\rangle, \qquad (3)$$

where angular brackets denote averages over all directions of propagation.

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[1] L. Knopoff and J. N. Shapiro, J. Geophys. Res. **74**, 1439 (1969).

[2] J. C. Slater, Phys. Rev. **57**, 744 (1940).

[3] F. Birch, J. Geophys. Res. **57**, 227 (1952).

[4] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **89**, 832 (1953).

[5] M. H. Rice, R. G. McQueen, and J. M. Walsh, Solid State Phys. **6**, 1 (1958).

[6] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Solid State Phys. Suppl. **3**, 26 (1963).

[7] In the case of a double root, there is always a compensating effect between the γ's of common frequencies. In the limit a finite nonzero sum is obtained. This difficulty is surmounted by the method to be presented, as individual γ's are never calculated.

[8] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

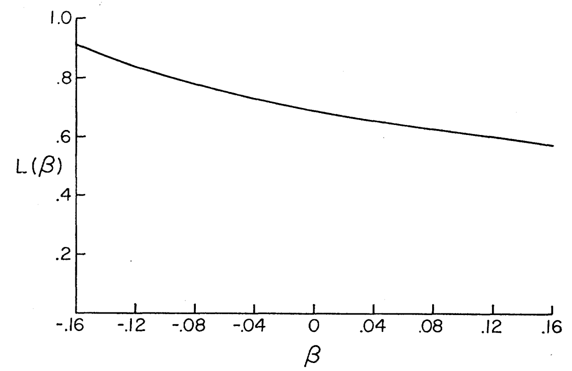

FIG. 1. $L(\beta)$ versus β for face-centered lattices.

In the preceding paper[9] we have discussed the conditions under which the use of Born–von Kármán dynamics, including only first- and second-neighbor central forces, is justified. Throughout the remainder of this paper we assume that the dynamics of the lattice can be described by a three-by-three symmetric matrix. The cubic equation which results from expanding the determinant can be written symbolically in the standard form

$$y^3+py^2+qy+r=0\,, \tag{4}$$

where y is the eigenvalue

$$y=\omega^2/\omega_0^2\,, \tag{5}$$

and p, q, and r are homogeneous functions of order one, two, and three, respectively, in the matrix elements, and ω_0 is a function of the lattice parameter and the force constants. In a previous paper[9] we have shown, by summing over the branches first, how to compute the moments of the frequency distribution for each value of $\mathbf{k}$ in terms of the coefficients p, q, and r. In the case of the moment calculation, the summation over $\mathbf{k}$ can be done simply to yield the positive even moments exactly.

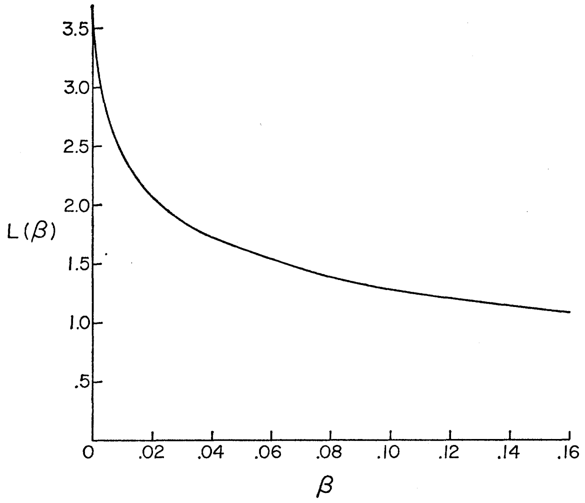

FIG. 2. $L(\beta)$ versus β for body-centered lattices.

Here we proceed similarly by noting that

$$r=-y_1y_2y_3\,, \tag{6}$$

the product of three roots of Eq. (4). Differentiating Eq. (6) we find

$$\frac{1}{2}\frac{\partial\ln r}{\partial\ln v}\bigg|_T=\sum_{j=1}^{3}\frac{\partial\ln\omega_j(\mathbf{k})}{\partial\ln v}\bigg|_T-3\frac{\partial\ln\omega_0}{\partial\ln v}\bigg|_T\,. \tag{7}$$

Averaging over all directions of the wave number $\mathbf{k}$, comparison with Eqs. (2) and (3) yields

$$\gamma=K_T\frac{\partial\ln\omega_0}{\partial P}\bigg|_T+\frac{K_T}{2}\left\langle\frac{1}{3}\frac{\partial\ln r}{\partial P}\bigg|_T\right\rangle \tag{8}$$

at sufficiently high temperatures. K_T is the usual isothermal bulk modulus.

Substituting for r and ω_0 the appropriate quantities[10] and using Fuchs's relations to express the force constants in terms of the elastic constants for face- and body-centered systems, we find the general expression

$$\gamma=-\tfrac{1}{6}+\tfrac{1}{2}\frac{K_T}{c_{44}}\frac{\partial c_{44}}{\partial P}\bigg|_T+\tfrac{1}{2}K_T\frac{\partial\beta}{\partial P}\bigg|_T L(\beta) \tag{9}$$

with

$$L(\beta)=\frac{C}{3(2\pi)^3}\int_{-\pi}^{\pi}d\theta_1\int_{-\pi}^{\pi}d\theta_2\int_{-\pi}^{\pi}d\theta_3\left[\frac{-s_1^2a_{22}a_{33}-s_2^2a_{11}a_{33}-s_3^2a_{11}a_{22}+s_1^2a_{23}^2+s_2^2a_{13}^2+s_3^2a_{12}^2}{-a_{11}a_{22}a_{33}+a_{11}a_{23}^2+a_{22}a_{13}^2+a_{33}a_{12}^2-2a_{12}a_{23}a_{13}}\right],$$

$$\beta=\frac{\alpha_2}{\alpha_1}=\left\{\frac{c_{11}-c_{12}}{3c_{44}}\right\}\text{bcc} \tag{10}$$

$$=\left\{\frac{c_{11}-c_{12}-c_{44}}{4c_{44}}\right\}\text{fcc}$$

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[9] J. N. Shapiro, preceding paper, Phys. Rev. B 1, 3982 (1970).

[10] J. deLaunay, Solid State Phys. 2, 219 (1956).

TABLE I. Comparison of thermal and theoretical Grüneisen parameters for body-centered lattices.[a]

Element	u_L	γ_{SI}	γ_{DM}	$\Delta\gamma$	γ Eq. (9)	γ_{th}
Sodium	0.51	1.64	1.31	−0.00	1.04	1.15
Potassium	0.29	1.80	1.47	−0.02	1.13	1.13

[a] All data from G. R. Barsch and Z. P. Chang, Phys. Status Solidi **19**, 139 (1967).

where $s_i = \sin\theta_i$, $C = 2$ for fcc's and $\frac{3}{2}$ for bcc's, and the a_{ij}'s are given by deLaunay[10] and are reproduced in the Appendix. The presence of the denominator in Eq. (10) precludes the possibility of performing the integral (or sum) analytically as in the moment calculation. Instead we have chosen to perform the integration numerically using some 816 points in the irreducible 1/48th of the Brillouin zone. The results are presented in Figs. 1 and 2. The last term in Eq. (9) is always small; for this reason the curves of Figs. 1 and 2 are sufficient for accurate calculations of γ.

RESULTS

In Tables I and II we compare Grüneisen's parameter obtained from Eq. (9) with the values computed from the Slater and Dugdale-MacDonald models. Available acoustic data on second- and third-order elastic constants have been used. γ_{th} is the thermodynamic γ

$$\gamma_{\mathrm{th}} = K_S \alpha V / C_P \tag{11}$$

and should be equal to the average value of the result of Eq. (3) at high temperatures. The quantity $u_L = \hbar\omega_L / k_B T$ with ω_L the maximum frequency and $T = 300$°K. The last term in Eq. (9) is called $\Delta\gamma$ and is listed separately.

For the seven elements tabulated, Eq. (9) yields significantly better values than those obtained from the Slater method and slightly better than those of Dugdale and MacDonald. There is a strong correlation between u_L and the values of Eq. (9) and γ_{th}: Potassium and lead have the smallest values of u_L and the best values of γ from Eq. (9), while the worst determination is for aluminum which, together with copper, has the largest value of u_L. Thus the accuracy of Eq. (3), and hence of Eq. (9), depends on the complete excitation of all modes, since it is only in this case that the high-temperature approximation of Eq. (3) can be made.

TABLE II. Comparison of thermal and theoretical Grüneisen parameters for face-centered lattices.[a]

Element	u_L	γ_{SI}	γ_{DM}	$\Delta\gamma$	γ Eq. (9)	γ_{th}
Copper	1.15	2.64	2.31	−0.05	1.87	1.99
Silver	0.74	2.97	2.64	−0.05	2.35	2.35
Gold	0.52	3.05	2.72	−0.14	3.22	2.96
Aluminum	1.15	2.45	2.12	−0.10	2.72	2.13
Lead[b]	0.33	2.60	2.27	−0.12	2.59	2.69

[a] Data source same as Table I except for Pb.

[b] Data on Pb from R. A. Miller and D. E. Schuele, J. Phys. Chem. Solids **30**, 589 (1969); C_P used to reduce K_S to K_T taken from *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio, 1959), 40th ed.

When u_L is not small the Grüneisen parameter defined by Eq. (1) becomes temperature dependent via the weighting factors, and the equality of γ_{th} from Eq. (11) with the theoretical value no longer holds.

With the exception of aluminum, for which u_L is not small, we conclude that the determination of the Grüneisen parameter by means of Eq. (9) is superior to that by either the Slater or Dugdale-MacDonald relations.

ACKNOWLEDGMENT

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APPENDIX: MATRIX ELEMENTS FOR FACE- AND BODY-CENTERED LATTICES

bcc:

$$a_{ii} = 1 - c_1 c_2 c_3 + 3\alpha_2 s_i^2 / 2\alpha_1 ,$$

$$a_{ij} = s_i s_j c_k , \quad i \neq j ;$$

fcc:

$$a_{ii} = 2 - c_i (c_j + c_k) + 2\alpha_2 s_i^2 / \alpha_1 ,$$

$$a_{ij} = s_i s_j , \quad i \neq j ;$$

where

$$s_i = \sin\theta_i ,$$

$$c_i = \cos\theta_i .$$