B6. THE PRESSURE DERIVATIVES
OF ELASTIC CONSTANTS:
MICROSCOPIC GRÜNEISEN PARAMETERS

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Abstract—The values of the elastic constants are of fundamental importance in any study of the lattice vibrational excitations in crystals. They determine the dispersion relations in the non-dispersive region of the spectrum and from these, the low temperature limit of the Debye temperature.

In a similar manner, the pressure dependencies of the elastic constants provide non-thermally determined data on the shift of these lattice vibrational energies with lattice compression, the so called microscopic Grüneisen parameters defined by the relation $\gamma_j \equiv -\dfrac{d \ln \omega_j}{d \ln V}$ in which ω_j is one of the vibrational normal mode frequencies and V is the crystal volume. In the non dispersive region of the spectrum, simple considerations yield $\gamma_m = \dfrac{1}{2} B_T \dfrac{d \ln C_m}{dP} - \dfrac{1}{6}$, in which B_T is the bulk modulus and P the pressure. The subscript m refers to a particular mode type, and C_m is the elastic constant associated with that mode of propagation.

The quasi-harmonic oscillator model gives the result that the experimental Grüneisen constant defined by $\gamma_G \equiv \dfrac{\alpha B_T V}{C_v}$, where α is the volume coefficient of thermal expansion and the other terms have their usual meanings, is given by $\gamma_G = \dfrac{\Sigma_j \gamma_j C_{vj}}{\Sigma_j C_{vj}}$. γ_j is the value of $-\dfrac{d \ln \omega}{d \ln V}$ of the j'th mode, and C_{vj} is the Einstein heat capacity of that mode at the temperature of observation.

At the present time, the pressure dependencies of the elastic constants provide the *only direct measurements* of the γ_j. Somewhat surprisingly their values, used with an elastic continuum approximation account quite well for γ_G and its temperature dependence in many cases. The results of this approximation are discussed, and evidence is presented concerning the magnitude of the *temperature dependence* of the mode gammas, and the effects of a strong temperature dependence on the conclusions of the Quasi-Harmonic Model.

INTRODUCTION

THE microscopic theory of the temperature dependent equation of state of solids, introduces anharmonicity parameters of the form $\gamma_j = -\dfrac{d \ln \omega_j}{d \ln V}$ where ω_j is a lattice vibrational mode frequency and V is the crystal volume.[1,2] These "mode gammas" bear the following relation to Grüneisen's gamma:

$$\gamma_G(T) = \frac{\sum\limits_{j=1}^{3N} \gamma_j C_{vj}}{\sum\limits_{j=1}^{3N} C_{vj}},$$

in which C_{vj} is the Einstein heat capacity of the j'th mode at the temperature of observation. The

Grüneisen parameter is defined by: $\gamma_G = \dfrac{\alpha B_T V}{C_v}$ in which α is the volume coefficient of thermal expansion, B_T is the bulk modulus, C_v/V the heat capacity per unit volume of the crystal. In this quasi-harmonic oscillator model, the temperature dependence of Grüneisen's gamma arises in existence of different values of γ_j for different modes, coupled with changes in their relative weights by the temperature dependent mode heat capacities. In the case that all gammas were equal, one would expect on this model that Grüneisen's gamma would be rigorously temperature independent. In the most general spectral case, one would expect constancy of γ_G in the limit of classically high temperatures at which $C_{vj} = k$ for all modes, and the expression for γ_G reduces to the simple average of the γ_j:

$$\gamma_G = \frac{\sum\limits_{j=1}^{3N} \gamma_j}{3N} = \bar{\gamma}_j$$

and in the low temperature limit where only continuum lattice vibrational states are excited, and there is no change in the *relative* weighting factors of various mode gammas. In this true T^3 region γ_G reduces to $\gamma_G = -\dfrac{\mathrm{d} \ln \Theta_0}{\mathrm{d} \ln V}$ where Θ_0 is the low temperature limit of the Debye temperature.

Validity of the original assumption of constancy of Grüneisen's gamma seemed well verified experimentally until recent years when improved techniques of thermal expansion measurement revealed large changes in γ_G which appear at low temperatures.

SLATER'S GAMMA

Historically, there has been a distinct lack of availability of values of individual mode gammas, necessitating various approximations. The Slater gamma represents an attempt to obtain directly, i.e. from the definition $\gamma_j = -\dfrac{\mathrm{d} \ln \omega_j}{\mathrm{d} \ln V}$, a non-thermally determined gamma with which

Table 1. High temperature values of Grüneisen's Gamma and Slater's Gamma

Material	Slater's Gamma	Grüneisen's Gamma
Si	2·5	0·44
Ge	2·1	0·72
Cu	2·6	2·0
Ag	2·8	2·4
Au	2·9	3·0
Na	1·5	1·14
Al	2·3	2·34
NaCl	2·7	1·55
KCl	2·2	1·47
RbI	2·6	1·50

one could compare the value of the Grüneisen constant. The only experimental data available at that time was the extensive set of measurements of volume vs. pressure by Bridgman from which one could obtain in the bulk modulus and its pressure derivative.

Referring to Fig. 1, we see that the frequency of any particular normal mode j in the non-dispersive region of the spectrum is given by $\omega_j = k_j v$ where k_j is the mode wave vector and v the slope of the linear part of the dispersion curve equal to the velocity of a sound wave of the same mode type. The assumption was made that the solid could be treated as an isotropic elastic medium whence it was possible to obtain expressions for the velocity of longitudinal and transverse waves in terms of the bulk modulus, the density, and Poisson's ratio as follows:[1]

$$v_L = \sqrt{\left[\frac{3(1 - \sigma)B_s}{\varrho(1 + \sigma)} \right]}$$

$$v_T = \sqrt{\left[\frac{3(1 - 2\sigma)B_s}{2\varrho(1 + \sigma)} \right]},$$

where σ is Poisson's ratio, and ϱ the density of the material. If Poisson's ratio is assumed independent of volume, the result appears:

$$\gamma_L = \gamma_T = -\frac{1}{2} \frac{\mathrm{d} \ln B_s}{\mathrm{d} \ln V} - \frac{1}{6}$$