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# 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  $\gamma_j \equiv -\frac{d \ln \omega_j}{d \ln V}$  in which  $\omega_j$  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  $\gamma_m = \frac{1}{2} B_T \frac{d \ln C_m}{dP} - \frac{1}{6}$ , 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  $\gamma_G \equiv \frac{\alpha B_T V}{C_v}$ , where  $\alpha$  is the volume coefficient of thermal expansion and the other terms have their usual meanings, is given by  $\gamma_G = \frac{\sum_j \gamma_j C_{vj}}{\sum_j C_{vj}}$ .  $\gamma_j$  is the value of  $-\frac{d \ln \omega}{d \ln V}$  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  $\gamma_j$ . Somewhat surprisingly their values, used with an elastic continuum approximation account quite well for  $\gamma_G$  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  $\gamma_j = -\frac{d \ln \omega_j}{d \ln V}$  where  $\omega_j$  is a lattice vibrational mode frequency and  $V$  is the crystal volume.<sup>(1,2)</sup> These "mode gammas" bear the following re-

lation to Grüneisen's gamma:

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

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:  $\gamma_G = \frac{\alpha B_T V}{C_v}$

in which  $\alpha$  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  $\gamma_j$  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  $\gamma_G$  in the limit of classically high temperatures at which  $C_{vj} = k$  for all modes, and the expression for  $\gamma_G$  reduces to the simple average of the  $\gamma_j$ :

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

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  $\gamma_G$  reduces to  $\gamma_G = -\frac{d \ln \Theta_0}{d \ln V}$  where  $\Theta_0$  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  $\gamma_G$  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  $\gamma_j = -\frac{d \ln \omega_j}{d \ln V}$ , 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:<sup>(1)</sup>

$$v_L = \sqrt{\frac{3(1 - \sigma)B_s}{\rho(1 + \sigma)}}$$

$$v_T = \sqrt{\frac{3(1 - 2\sigma)B_s}{2\rho(1 + \sigma)}}$$

where  $\sigma$  is Poisson's ratio, and  $\rho$  the density of the material. If Poisson's ratio is assumed independent of volume, the result appears:

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

in which the fact that  $d \ln k_j / d \ln V = -\frac{1}{3}$ ,  $d \ln \rho / d \ln V = -1$  has been used. The Slater gamma gives reasonably good agreement with Gruneisen's gamma at high temperatures, having in general a value larger than  $\gamma_G$  as shown in Table 1. Notable exceptions are silicon, germanium and the zinc blende structure materials where  $\gamma_s \gg \gamma_G$ .

#### GENERAL ACOUSTIC CONTINUUM GAMMAS

Recent acoustic measurements of all of the elastic constants of crystals as a function of pressure<sup>(3)</sup> permits one to relax several of the assumptions made above, namely the assumption of elastic isotropy and that of pressure independence of Poisson ratios. That is, referring again to Fig. 1, the slope of any dispersion curve in the continuum region which is the velocity of

sound for waves of that mode type, is given by  $v = \sqrt{\frac{C}{\rho}}$  where  $C$  is the adiabatic elastic constant associated with the type of deformation involved in propagation of the wave. For example, the velocity of a longitudinal wave propagation along [100] of a cubic crystal is given by  $(C_{11}/\rho)^{\frac{1}{2}}$ , that of a similarly propagating transverse wave is given by  $(C_{44}/\rho)^{\frac{1}{2}}$  and the mode gammas appropriate to each of these modes become:

$$\gamma_L [100] = -\frac{1}{2} \frac{d \ln C_{11}}{d \ln V} - \frac{1}{6},$$

$$\gamma_T [100] = -\frac{1}{2} \frac{d \ln C_{44}}{d \ln V} - \frac{1}{6}.$$

(The relation to the pressure derivatives is

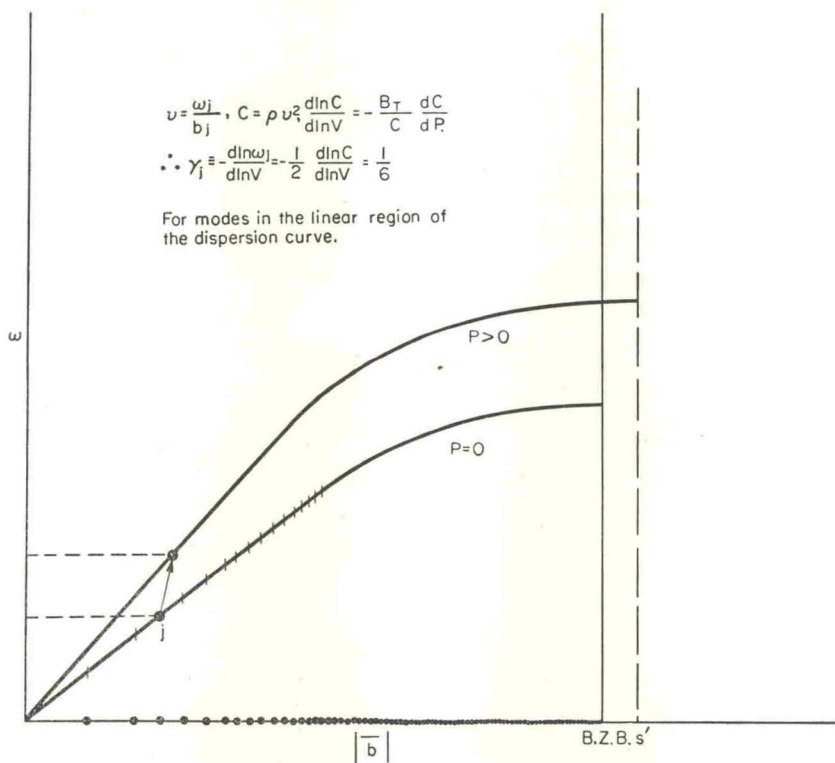


FIG. 1. Dispersion curve indicating the effect of pressure on a normal mode frequency.

Table 2. Values of mode gammas in symmetry directions of cubic crystals, together with their weighting factors  $v^{-3}$  for low temperatures.  $v^{-3}$  in units  $10^{-18}$  (cm/sec) $^{-3}$

Direction of propagation		$\gamma_L$	$v_L^{-3}$	$\gamma_{\tau 1}$	$v_{\tau 1}^{-3}$	$\gamma_{\tau 2}$	$v_{\tau 2}^{-3}$
Si <sup>a</sup>	[100]	1.37	(1.64)	0.33	(5.01)	0.33	(5.01)
	[110]	1.33	(1.30)	0.33	(5.01)	-0.12	(9.76)
	[111]	1.32	(1.21)	0.08	(7.47)	0.08	(7.47)
Ge <sup>b</sup>	[100]	1.29	(8.39)	0.584	(22.4)	0.584	(22.4)
	[110]	1.28	(6.33)	0.584	(22.4)	0.170	(48.1)
	[111]	1.27	(5.78)	0.360	(35.9)	0.36	(35.9)
Na <sup>c</sup>	[100]	1.51	(47.7)	1.06	(111)	1.06	(111)
	[110]	1.36	(26.2)	1.06	(111)	1.06	(2138)
	[111]	1.34	(22.5)	1.06	(400)	1.06	(400)
Cu <sup>d</sup>	[100]	2.48	(13.4)	1.92	(41.4)	1.92	(41.4)
	[110]	2.30	(8.8)	1.92	(41.4)	1.49	(243)
	[111]	2.19	(7.8)	1.76	(105)	1.76	(105)
Ag <sup>d</sup>	[100]	2.71	(25)	2.38	(108)	2.38	(108)
	[110]	2.69	(17.7)	2.38	(108)	1.96	(569)
	[111]	2.68	(16.0)	2.21	(263)	2.21	(263)
Au <sup>d</sup>	[100]	2.86	(31.9)	3.38	(312)	3.38	(312)
	[110]	3.00	(26.1)	3.38	(312)	2.31	(1500)
	[111]	3.03	(24.6)	2.94	(731)	2.94	(731)
Al <sup>e</sup>	[100]	2.28	(3.97)	2.80	(29.3)	2.80	(29.3)
	[110]	2.43	(8.61)	2.80	(29.3)	2.36	(39.5)
	[111]	2.43	(3.63)	2.53	(35.6)	2.53	(35.6)
NaCl <sup>f</sup>	[100]	2.64	(9.81)	0.14	(72.2)	0.14	(72.2)
	[110]	1.87	(11.55)	0.14	(72.2)	2.72	(43.8)
	[111]	1.57	(12.26)	2.04	(50.9)	2.04	(50.9)
	optic	1.20		3.61		3.61	
KCl <sup>f</sup>	[100]	2.18	(11.33)	-0.74	(184)	-0.74	(184)
	[110]	1.42	(17.9)	-0.74	(184)	2.42	(41.9)
	[111]	1.04	(21.6)	1.92	(59.5)	1.92	(59.5)
	optic	0.74		2.61		2.61	
RbI <sup>g</sup>	[100]	2.53	(54.3)	-1.06	(1447)	-1.06	(1447)
	[110]	1.91	(98.4)	-1.06	(1447)	2.56	(186)
	[111]	1.54	(128)	2.15	(273)	2.15	(273)

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$\frac{d \ln C_{ij}}{d \ln V} = -B_T \frac{d \ln C_{ij}}{d \rho}$  where  $B_T$  is the isothermal bulk modulus). Thus from these data one can obtain directly a non-thermal measure of the individual mode gammas for all modes in the continuum region of the lattice vibrational spectrum.

Table 2 contains values of  $\gamma_j$  of modes in certain branches of the acoustic spectrum of several cubic crystals. The number in parentheses following each entry is the reciprocal of the cube of the velocity of sound which is the low temperature weighting factor of the mode gamma of that branch in units  $10^{-18} (\text{cm/sec})^{-3}$ .

The results in Table 2 demonstrate that in any given crystal the values of mode gammas may be even more anisotropic than the velocity of sound e.g. in rubidium iodide the mode gammas range from a value +2.56 for longitudinal waves propagating along [100] down to -1.06 for shear waves propagating along [100]. It is also noteworthy that although the average gamma does not vary strongly from material to material, the range of values of mode gammas does. Thus any attempt to find an "average anharmonicity parameter" to relate to a macroscopic anharmonic effect such as thermal conductivity must concern itself not only with the values of the parameters, but also with the nature of the averaging process used. Also, with a few exceptions, it may be seen that the gammas of the transverse modes are algebraically smaller than those of longitudinal modes.

SHEARD,<sup>(4)</sup> COLLINS,<sup>(5)</sup> SCHUELE *et al.*<sup>(6)</sup> have calculated limiting low and high temperature values of Gruneisen's gamma from various of these data on an anisotropic continuum model. Collins has in addition used this model to calculate an approximate temperature dependence of Gruneisen's gamma. DANIELS<sup>(7)</sup> has calculated the low temperature limit of  $\gamma_G$  in Si and Ge using the relation  $\gamma_0 = -\frac{d \ln \Theta_0}{d \ln V}$  where  $\Theta_0$  is the low temperature limiting value of the Debye temperature. It was possible in this case to interpolate in the tables of DE LAUNAY<sup>(8)</sup> to re-

place the integrations used by the other authors. Table 3 gives a summary of the results of these calculations, compared with limiting low and high temperature values of Gruneisen's gamma calculated by WHITE from thermal expansion measurements made with an extremely sensitive three terminal capacitance method.<sup>(9)</sup> In all the cases where comparisons are possible, the agreement of the experimental and calculated values of  $\gamma_0$  is impressive. However, we shall return to this point of agreement later. Agreement of the high temperature limiting values is good in Si, Ge, Na and the monovalent noble metals. Analysis of the entire curve of  $\gamma_G$  vs.  $T$  in Si and Ge<sup>(10)</sup> reveals this agreement to be fortuitous. In the alkali halides one would not expect an averaging over acoustic modes alone to be representative of the behavior of the optical modes as well so that the agreement in the case of NaCl is more surprising than the disagreement in KCl. We have attempted to estimate the values of optic mode gammas in NaCl and KCl, using the Szigeti Relations with MAYBURG'S<sup>(11)</sup> data on the pressure dependence of the low frequency dielectric constant, and data by BURSTEIN and SMITH<sup>(12)</sup> on strain dependence of the index of refraction, together with the pressure dependences of the elastic constants. The effect of this modification is to improve the agreement in KCl, and worsen the agreement in NaCl.

## DISCUSSION

It appears from Table 3 that the low temperature limit of the Gruneisen constant is quite well accounted for by the values of the pressure dependencies of the elastic constants of those crystals, using values of the constants and their pressure derivatives measured at 300°K. The question arises concerning the temperature dependencies of the quantities  $dC/dP$ , here assumed to be negligible. The only data bearing on the subject are the classical measurements by BRIDGMAN of pressure-volume relations in solids.<sup>(13)</sup> Many of these measurements were made at two temperatures, 30 and 75°C. We have studied these results in detail for the alkali hal-

Table 3. Comparison of experimental high and low temperature limiting values of Grüneisen's gamma compared with theoretical values calculated from pressure dependencies of the elastic constants and of the dielectric constant and index of refraction in NaCl and KCl

Material	Exp.	$\gamma_0$		$\gamma_{\infty}$			Theor. including optic modes
		Theoretical	Exp.	Theoretical	Exp.	Exp.	
Si	—	0.25 <sup>a</sup>	0.25 <sup>b</sup>	0.44 <sup>h</sup>	0.54 <sup>b</sup>	—	—
Ge	— <sup>c</sup>	0.49 <sup>a</sup>	0.48 <sup>b</sup>	0.72 <sup>h</sup>	0.71 <sup>b</sup>	—	—
Cu	1.69 <sup>d</sup>	1.79 <sup>e</sup>	1.77 <sup>b</sup>	2.00 <sup>d</sup>	2.01 <sup>e</sup>	1.98 <sup>b</sup>	1.97 <sup>f</sup>
Ag	2.2 <sup>d</sup>	2.22 <sup>e</sup>	2.22 <sup>b</sup>	2.4 <sup>d,j</sup>	2.40 <sup>e</sup>	2.40 <sup>b</sup>	2.40 <sup>f</sup>
Au	—	2.91 <sup>e</sup>	2.92 <sup>b</sup>	3.0 <sup>d,k</sup>	3.03 <sup>e</sup>	3.04 <sup>b</sup>	3.02 <sup>f</sup>
Na	—	—	1.06 <sup>b</sup>	1.14 <sup>l</sup>	—	1.14 <sup>b</sup>	—
Al	2.65 <sup>d</sup>	2.61 <sup>e</sup>	2.62 <sup>b</sup>	2.34 <sup>d,i,k</sup>	2.55 <sup>e</sup>	2.58 <sup>b</sup>	—
NaCl	0.93 <sup>d</sup>	1.09 <sup>e</sup>	1.22 <sup>b</sup>	1.23 <sup>f</sup>	1.55 <sup>d</sup>	1.51 <sup>e</sup>	1.61 <sup>b</sup>
KCl	0.32 <sup>d</sup>	0.31 <sup>e</sup>	0.43 <sup>b</sup>	0.52	1.47 <sup>d</sup>	1.06 <sup>e</sup>	1.25 <sup>b</sup>
RbI	—	0.14 <sup>e</sup>	0.19 <sup>g</sup>	1.50 <sup>e</sup>	1.25 <sup>e</sup>	—	—

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ides with surprising results. These are shown in Table 4 giving the fractional change in volume, bulk modulus and  $\frac{dB}{dP}$  for a 300° temperature change. Note that  $\frac{dB}{dP}$  does exhibit even a stronger temperature dependence than either of the volume or the bulk modulus proper. If the other mode gammas had temperature dependencies of this order, it is possible that the calculated values of  $\gamma_0$  would be considerably different, probably larger than those quoted in Table 3. This

implies, in turn, that the experimentally determined values of Grüneisen's Gamma have not in fact been carried down to the "true  $T^3$ " region in which only the elastic continuum states are excited, and that  $\gamma_G$  would exhibit a rise at the lowest temperatures, the entire curve of  $\gamma_G$  vs.  $T$  resembling qualitatively then a typical curve of "Formula Debye Temperature" vs. temperature with a very narrow true  $T^3$  region, a dip to a minimum, then a rise to a high temperature limit. Recent measurements by SWENSON *et al.*<sup>(14)</sup> on the thermal expansion of RbI in the range 2 to

Table 4. Linearly extrapolated fractional changes over the temperature range 300–0°K of the bulk modulus and its pressure derivative in the alkali halides, from data by Bridgman

Material	$\frac{V(300^\circ) - V(0^\circ)}{V(300^\circ)}, (\%)$	$\frac{B_T(0^\circ) - B_T(300^\circ)}{B_T(300^\circ)}, (\%)$	$\frac{\frac{dB_T}{dP}(0^\circ) - \frac{dB_T}{dP}(300^\circ)}{\frac{dB_T}{dP}(300^\circ)}, (\%)$
LiF	3	6	13
LiCl	3.7	20	49
LiBr	4.2	25	65
NaF	3.0	3	-10
NaCl	3.5	26	39
NaBr	3.6	23	60
KF	3.0	4	10
KCl	3.3	15	37
KBr	3.5	18	48
KI	3.7	18	48
RbBr	3.1	5	14
RbI	3.6	21	54

8°K do reveal the minimum in Grüneisen's gamma which we expect will be a feature appearing in general in the alkali halides. Since the values of  $dC/dP$  can easily be measured at several temperatures to check this point quantitatively such measurements should and will be made. We have also used the Born-Mayer model to attempt to estimate that part of the temperature dependence of mode gammas due simply to change in the crystal volume with temperature. These calculations indicate fractional changes in mode gammas of the same order as the fractional change in volume. Thus the large changes in  $dB/dP$  measured by Bridgman must, if real, be due largely to an *explicit* temperature dependence.

The occurrence of a strong decrease of the mode gammas with increasing temperature would also force a revision of our ideas about the constant high temperature limit of the Grüneisen's gamma observed, for example, to remain unchanged over the entire range 50–750°C<sup>(15)</sup> in KCl. The quasiharmonic oscillator model would predict a decrease in  $\gamma_G$  with increasing temperature if the mode gammas decrease. The observed constancy of  $\gamma_G$  could only come about if the *anharmonic contribution* to the entropy (e.g. from the "linear term" in  $C_v$ ) had a sufficiently

large-positive volume dependence to maintain a large value of the thermal expansion coefficient as the temperature was increased, or that a vacancy contribution to the expansion was present.

#### GAMMAS OF DISPERSIVE MODES

The critical test of the Quasi Harmonic Oscillator model of the thermal expansion of non metallic crystals requires a knowledge of the values of  $\gamma_j$  for dispersive as well as non-dispersive modes. We have attempted without success to date to obtain directly mode gammas of certain dispersive modes in silicon and germanium by examination of the effect of pressure on the energies of the "phonon kinks" in tunnel diode characteristics at liquid helium temperature. Neutron spectroscopy performed on crystals at high pressures will in principle provide all of the information desired. We are constructing a high pressure vessel for this purpose and it is to be hoped that such experiments prove feasible.

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