

$\frac{d \ln C_{ij}}{d \ln V} = -B_T \frac{d \ln C_{ij}}{d \rho}$  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  $10^{-18}$  (cm/sec)<sup>-3</sup>.

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.	$\gamma_0$		Exp.	$\gamma_{00}$		Theor. including optic modes
		Theoretical	Theoretical		Theoretical	Theoretical	
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,i</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>j,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>j</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,j,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> 1.60 <sup>f</sup>	2.16 <sup>g</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> 1.57 <sup>f</sup>	1.53 <sup>g</sup>
RbI	—	0.14 <sup>e</sup>	0.19 <sup>g</sup>	1.50 <sup>e</sup>	1.25 <sup>e</sup>		—

a. DANIELS W. B., *Phys. Rev. Letters* 8, 3 (1962).

b. COLLINS J. G., *Phil. Mag.* 8, 323 (1963).

c. G. K. WHITE has measurements down to 0.02  $\theta_0$  which have not yet levelled off to the "true  $T^3$ " limit. *Phys. Rev. Letters* 10, 234 (1963).

d. WHITE G. K., *Proceedings VII International Conference Low Temperature Physics*, Toronto: p. 685. University Press (1960); *Phil. Mag.* 6, 1425 (1961), *Proceedings VIII International Conference Low Temperature Physics*, Butterworths, London (1962).

e. SCHUELE D. E. and SMITH Charles S., private communication. Differences between the results of Schuele and Smith, of Collins and of Sheard in NaCl and KCl are probably due to differences in selection of raw data from the paper by Lazarus. We have quoted Smith's selection in Table 2.

f. SHEARD F. W., *Phil. Mag.* 3, 1381 (1958).

g. DANIELS W. B., Princeton University, unpublished.

h. GIBBONS D. F., *Phys. Rev.* 112, 36 (1958).

j. CORRUCINI R. J. and GNIEWEH J. J., *Thermal Expansion of Technical Solids at Low Temperatures*, National Bureau of Standards, Washington, Monograph 29.

k. FRASER D. B. and HOLLIS-HALLETT A. C., *Proceedings VII International Conference on Low Temperature Physics*, Toronto University Press (1960).

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