spectra for Ge and Si are given in table 2 in terms of their characteristic temperatures. Numbers in parenthesis following the temperature give the fractions of $3N$ states associated with each spectral detail. The effective (Θ_D, T) data computed from this spectrum agree very well with the data of Flubacher, Leadbetter and Morrison (1959), our computed values of Θ_D lying higher than the experimental values in the temperature region below the minimum, as would be expected considering the gap our approximations introduce in the spectrum below the TA delta function. Thus the minimum of our curve is displaced to slightly higher temperatures in both Ge and Si. Note that although the small continuum

Table 2

	Ge	Si
Transverse continuum Θ_D	72 ($6{\cdot}48 \times 10^{-3}$)	125 ($6{\cdot}48 \times 10^{-3}$)
Longitudinal continuum Θ_D	288 ($4{\cdot}95 \times 10^{-2}$)	499 ($4{\cdot}95 \times 10^{-2}$)
TA Θ_E	120 (0·3267)	217 (0·3267)
LALO Θ_E	327 (0·2838)	567 (0·2838)
TO Θ_E	396 (0·3333)	687 (0·3333)

regions included do not profoundly affect the shape of the (Θ_D, T) curve except at *very* low temperatures (their removal in Ge raises Θ_D (20°K) from 262 to 276°K), their effect *must* be included even to approximate the (γ_{Gr}, T) curves of Gibbons in Si.

Figures 1 and 2 show the curves of γ_{Gr} in germanium and silicon as measured by Gibbons, and curves of γ_{Gr} constructed from Novikova's thermal expansion measurements. The low temperature limits were calculated from data of the pressure dependence of the elastic constants. Two curves are fitted to measurements in each of Ge and Si. The values of the γ_j associated with each element of spectral structure were found as follows. The γ_T and γ_L of the transverse and longitudinal continua were computed from the data on pressure dependence of the elastic constants of Ge and Si. The gammas associated with the LALO and TO peaks were taken to be equal since the data and method did not suggest sufficient precision to warrant an attempt to distinguish the two values independently. Thus the LALO, TO γ must not be considered as more than an approximate average over the two mode types. That average, and the average γ of the TA peaks, were found by fitting to two points on the experimental (γ_{Gr}, T) curve. Values of the gammas obtained are as follows:

Ge curve I fitted to Novikova's curve at 40°K and 160°K

$$\gamma_T = 0{\cdot}398 \qquad \gamma_L = 1{\cdot}28 \qquad \gamma_{TA} = -0{\cdot}36 \qquad \gamma_{LALOTO} = 1{\cdot}42$$

Curve II fitted to Gibbons's curve at 40°K and 200°K

$$\gamma_T = 0{\cdot}398 \qquad \gamma_L = 1{\cdot}28 \qquad \gamma_{TA} = -0{\cdot}09 \qquad \gamma_{LALOTO} = 1{\cdot}21$$

Si curve I fitted to Gibbons's curve at 70°K and 300°K

$$\gamma_T = 0{\cdot}120 \qquad \gamma_L = 1{\cdot}34 \qquad \gamma_{TA} = -0{\cdot}69 \qquad \gamma_{LALOTO} = 1{\cdot}17$$

Curve II fitted to Gibbons's curve at 40°K and 300°K

$$\gamma_T = 0{\cdot}120 \qquad \gamma_L = 1{\cdot}34 \qquad \gamma_{TA} = -0{\cdot}26 \qquad \gamma_{LALOTO} = 0{\cdot}86$$

5. **Discussion of results**

It is clear that at best this type of analysis can yield only values of γ's averaged over all the modes lumped into a particular peak. Examination of table 1 indicates that in the

low frequency region the gammas of the transverse modes vary over wide limits. Presumably the same behaviour should occur in the dispersive region hence the individual mode gammas probably have a wide spread of values. More precise measurements of the thermal expansion to remove the discrepancies between the data of Novikova and Gibbons are highly desirable to permit further mode anharmonicity analysis.

6. **Thermal conductivities of Ge and Si**

The diamond structure elements C, Ge and Si are often quoted as examples of the failure of a simple formula for thermal conductivity in the high temperature region which may be put in the form $K_T \propto \gamma^{-2} T^{-1}$ where γ is taken to be γ_{Gr}, and T is the absolute temperature (Leibfried and Schlomann 1954). The relation above holds reasonably well for many materials, but fails very badly in C, Si, and Ge, i.e. the value of γ required to account for the thermal resistance is much higher than the Gruneisen gamma. Barron (1956) points out that this failure may be expected in part because of the nature of the averaging process leading to γ_{Gr}, i.e. modes with negative or positive gammas will make a positive contribution to the thermal resistance, but will cancel one another in the averaging process leading to γ_{Gr}. On this basis a better average might be made over γ_j^2. Performing this average over the γ's found in curves I of figures 1 and 2 leads to

$$(\overline{\gamma_j^2})^{1/2} = \begin{matrix} 1{\cdot}17 \text{ in Ge} \\ 1{\cdot}05 \text{ in Si} \end{matrix}$$

to be compared with the high temperature limiting value of γ_{Gr}, $\gamma_\infty = 0{\cdot}74$ in Ge, $0{\cdot}45$ in Si. Clearly these results are much closer to the thermal conductivity result $\gamma_k \simeq 2$ in both Ge and Si, agreeing within a factor of two, a particularly large improvement over the factor of 4 discrepancy with γ_∞ in Si.

This result is unsatisfactory, however, when one considers that in germanium all gammas are positive for small $|\mathbf{k}|$ yet some modes in the dispersive region have negative gammas. Assuming the dispersion curves to be continuous this implies the existence of modes with vanishingly small values of γ_j, i.e. modes having very little interaction with a longitudinal stress field. Further, these modes must be associated with a TA branch and will be populated at temperatures below 120°K. Because of the weakness of their interaction with the longitudinal stress field, the scattering mechanism for these modes must be by interaction with other *transverse* modes. This casts a shadow on any attempt to relate the thermal resistance to thermal expansion or to 'mode gammas' in these materials.

7. **Measurements to be made**

The fairly recent discovery of phonon-assisted tunnelling in Ge and Si (Hall 1961) provides a means of directly determining frequencies of certain modes in the dispersive region of the spectrum. It is possible in principle at least to study the pressure shift of the phonon kinks on the I–V characteristics. Then the γ of the mode in question is found using the relation $B_T(1/E)(dE/dP) = \gamma$, in which E is the voltage at which the kink appeared, and B_T is the isothermal bulk modulus. Unfortunately the experiments must be performed at liquid helium temperatures. Experiments combining very low temperatures with high pressures $\sim$5 kilobars are experimentally very difficult. We have been working on the