Gruneisen's gamma in Ge and Si over the temperature range considered. However, note that the large values of mode gammas are associated with stiff modes and the small gammas (one negative in Si) are associated with soft modes. This combination would on a continuum model lead to expectation of a monatonic increase of γ_{Gr} from γ_0 to γ_∞ as the

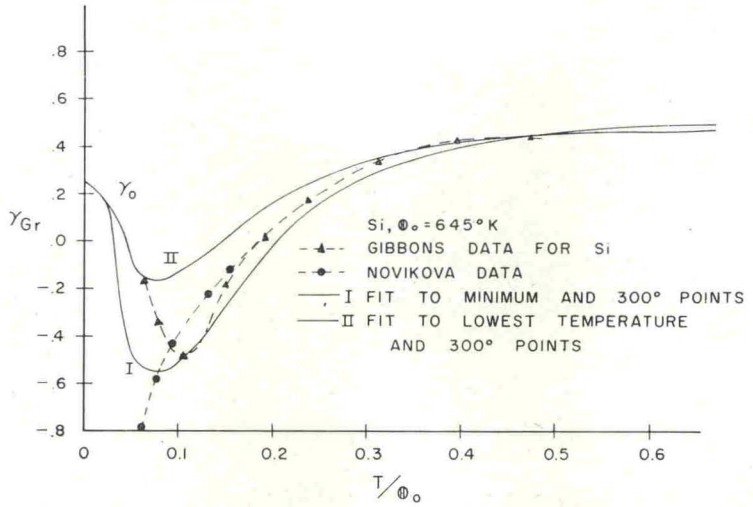

Figure 1. γ_{Gr} plotted against T in Si, showing experimentally determined values and synthetic values.

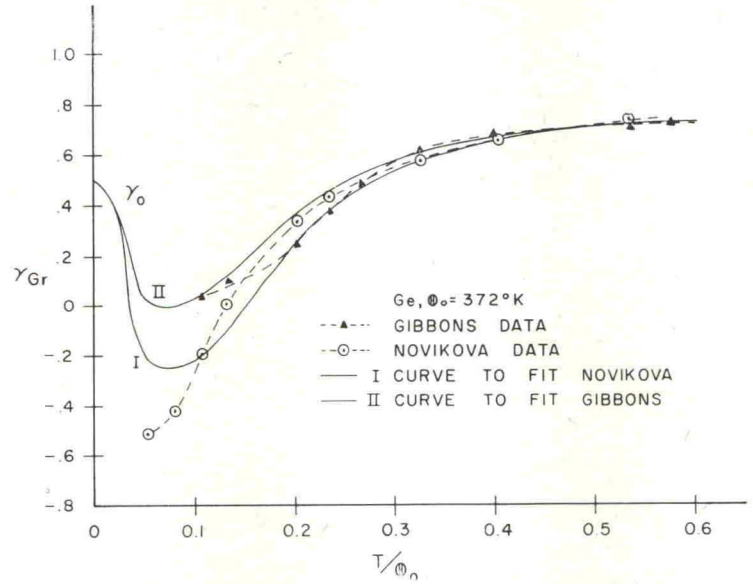

Figure 2. γ_{Gr} plotted against T in Ge showing experimentally determined values and synthetic values.

temperature is increased. In any case it is clear that no means of averaging a set of all positive mode gammas weighed by their positive heat capacities as in equation (1) will give a net negative gamma in some temperature range as is observed in Ge, or give a minimum value of $\gamma_{Gr} \simeq -0{\cdot}5$ in Si when the lowest mode $\gamma \simeq -0{\cdot}1$.

It must be then that some of the modes in the dispersive region have important negative γ's, since such negative values of γ_j do not occur strongly enough in the non-dispersive region. We can conclude that the agreement of γ_∞ with the high temperature average on the continuum model is fortuitous.

3. Gammas for dispersive modes

There are to date no direct measurements of the γ_j of modes in the dispersive region of the spectrum. As has been mentioned, experiments using slow neutron spectroscopy at high pressures would be ideally direct but difficult. One is forced to examine effects which will provide indirectly a measure of the volume dependences sought.

Two possibly useful effects are the temperature shift of the fine structure in the absorption edge spectrum of Ge measured by MacFarlane *et al.* (1957), and the infra-red lattice absorption bands studied in Ge, Si and diamond by Collins and Fan (1953) if one assumes the temperature dependence of the frequency shifts to be due entirely to their volume dependence through the thermal expansion of the lattice. Quantitatively however the effect is too small to be useful.

The work of Braunstein (private communication) on infra-red lattice absorption bands in Ge–Si alloys, however, is a more promising source of information. If one makes the assumption that the effect of dilute alloying is purely one of compression or expansion of the principal constituent, the following may be written:

$$\frac{1}{\nu}\left(\frac{d\nu}{dx}\right)_{P,T} = \frac{1}{\nu}\left(\frac{d\nu}{d(\ln V)}\right)\left(\frac{d(\ln V)}{dx}\right)_{P,T}$$

where x is the concentration of the alloying element, and $d\nu/dx$ is the alloy shift of a particular band.

We have computed $dx/d(\ln V)$ from Johnson and Christian's (1954) data of lattice parameter plotted against composition of Ge–Si alloys, assuming the deviations from Vegard's law to occur between 0 and 10% Si and 90 and 100% Si. This leads to the following values of gamma from Braunstein's data:

	Ge	Si
γ_{TA}	−21	−7·2
γ_{LALO}	+8·1	+1·7
γ_{TO}	+9·4	+2·7.

The results confirm our belief that negative gammas occur in the TA dispersion peaks. The values seem unreasonably large in magnitude in Ge, but this may merely be due to the failure of the approximation.

4. Fit of (γ_{Gr}, T) curve

Finally, we can attempt to use the expressions (1) together with the measured values of a and attempt to estimate the average gammas associated with the peaks of the spectrum corresponding to specific mode types. We have broken the Phillips (1958) spectrum up into two parabolic continuum contributions associated with transverse and longitudinal acoustic modes with small wave vector, and three delta functions associated with the TA, LA + LO and TO peaks of the actual distribution. Characteristics of these approximate