

# The anomalous thermal expansion of germanium, silicon and compounds crystallizing in the zinc blende structure

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**Abstract.** The thermal expansion coefficients of the diamond-like materials C (diamond), Si, Ge,  $\alpha$ -Sn, InSb, GaAs, ZnSe and CdTe for which data are available, are unusual in the following respects: (i) the magnitude of  $\alpha$  at high temperatures is low, (ii) the 'Slater gamma'  $\gamma_S = -\frac{1}{2} d(\ln B_T)/d(\ln V) - \frac{1}{6}$  is very much larger than Gruneisen's  $\gamma$ ,  $\gamma_{Gr} = \alpha B_T V / C_V$  in contrast with the behaviour of most materials, (iii) very large deviations from the Mie-Gruneisen equation of state appear in all the materials listed. The thermal expansion coefficient has a negative value over a range of low temperatures in each case. This behaviour is discussed in terms of the Slater model, a more general elastic continuum model, and a model in which details of the lattice vibrational spectrum are considered.

The large discrepancy between the 'anharmonicity' parameter found from thermal conductivity and that found from thermal expansion is considered.

## 1. Introduction

The volume coefficients of thermal expansion in Si, Ge, C (diamond),  $\alpha$ -Sn, InSb, ZnSe, GaAs and CdTe (Gibbons 1958, Novikova 1959, 1960, 1961) exhibit qualitatively similar behaviour. The magnitudes of  $\alpha$  are lower in these semiconductors than those of many materials, lying between 12 and 22 in the high temperature limit, to be compared with representative values lying between 92 and 119 ( $\times 10^{-6} \text{ degC}^{-1}$ ) in the face-centred cubic alkali halides. The temperature dependence of  $\alpha$  in each shows a characteristic dip to negative values at low temperatures, i.e. *large* deviations from the Mie-Gruneisen equation of state. Data are available for many of the properties of germanium and silicon and in particular the pressure dependence of the elastic constants has been measured. We therefore restrict the quantitative aspects of our discussion to these two substances. We shall discuss the thermal expansion in Ge and Si for a general continuum model and a model in which structure in the actual lattice vibrational spectrum is taken into account. We treat the thermal expansion in terms of the dimensionless quantity, Gruneisen's gamma,  $\gamma_{Gr} \equiv \alpha B_T V / C_V$  in which  $\alpha$  is the volume coefficient of thermal expansion,  $B_T$  the isothermal bulk modulus,  $V$  the volume per mole, and  $C_V$  the molar heat capacity at constant volume. If the Mie-Gruneisen equation of state were obeyed, Gruneisen's gamma would be independent of temperature. The treatment will involve throughout a quasi-harmonic approximation, i.e. one in which the interaction between various normal modes of the crystal is assumed to be negligibly small, but that the normal mode frequencies  $\nu_j$  have a volume dependence  $\gamma_j \equiv -\partial(\ln \nu_j)/\partial(\ln V)$  (Slater 1939). Straightforward statistical

mechanics then yields the expression

$$\frac{\alpha B_T V}{C_V} = \gamma_{Gr} = \frac{\sum_{j=1}^{3N} \gamma_j C_{Vj}}{\sum_{j=1}^{3N} C_{Vj}} \quad (1)$$

in which  $C_{Vj}$  is the heat capacity of the  $j$ th normal mode of the crystal at the temperature of observation, and the sum is over all normal modes. Thus each individual mode  $\gamma$  is seen to be weighted by the heat capacity of that mode. It is the changes of these weighting factors with temperature along with differences of mode gammas which give rise to a temperature dependence of  $\gamma_{Gr}$ .

In the limit of temperatures high compared with  $h\nu_{\max}/k$  where  $\nu_{\max}$  is the highest frequency of the distribution, each mode has a heat capacity  $k$  and the expression for  $\gamma_{Gr}$  reduces to

$$\gamma_{\infty} = \frac{\sum \gamma_j}{3N}$$

the simple average of the  $\gamma_j$  over all normal modes. If one had a knowledge of the frequency distribution of the  $3N$  normal modes, and of the value of  $\gamma_j$  associated with each, it would be possible to calculate the value of the  $\gamma_{Gr}$  or of the thermal expansion at any temperature (within the small changes expected in  $B_T$  and  $V$  as well as the fundamental limitations of a quasi-harmonic oscillator model). It would be possible in principle to do very careful neutron diffraction studies on samples at high pressures to measure the pressure dependence of the normal mode frequencies and thence the volume dependences. A complete set of these data would of course provide the crucial test of the model. In practice the difficulties associated with such a procedure seem formidable, especially for such materials as germanium and silicon which are relatively incompressible, e.g. a mode whose  $\gamma_j$  had the large value 2 would exhibit a total change of less than 3% in 10 kbar for Ge, 2% in Si, which would push present neutron diffraction techniques near their limit to see the change, even without the problems associated with the additional background scattering due to the thick walled pressure vessel. The implication is that the check on the limitations of the quasi-harmonic model used had best be made on one of the more compressible materials such as rubidium iodide which should exhibit interesting behaviour, or on the very compressible sodium.

Since we do *not* know the numerical values of all the  $\gamma_j$ , let us review the information which is available about the volume dependence of various normal mode frequencies. Consider the dispersion curve, frequency  $\nu$  plotted against wave vector  $\mathbf{k}$  for waves propagating in a particular direction in the reciprocal lattice.

The curve may change as pressure is applied to the crystal, reducing its volume. The frequency of a normal mode  $j$  (defined as a wave having an intergral number of wavelengths per unit distance fixed to the lattice, i.e. compressing with the lattice) changes for two reasons: (i) the value of  $k$  changes due to dimensional change of the lattice, (ii) the curve proper shifts due to changes in the interatomic interactions. Since the slope of the curve in the non-dispersive region is the velocity of sound waves of the appropriate polarization  $-\gamma_j = d(\ln \nu)/d(\ln V) + d(\ln k_j)/d(\ln V)$  applies to modes in the non-dispersive region of the spectrum.

## 2. Gamma of an anisotropic continuum

Recently measurements have been made (McSkimmin 1957, Chapman 1959) of the pressure dependence of all three independent elastic constants of germanium and silicon, making it possible to eliminate two of the assumptions of the Slater model, the assumption of elastic isotropy and that of independence of Poisson's ratio of volume. For each direction of propagation in the crystal an expression for the velocities of each of the three independent polarizations of sound waves will appear in the form  $v = (C/\rho)^{1/2}$ , where  $C$  is an elastic stiffness,  $\rho$  is the crystal density.

The gamma of each of these modes then appears in the form  $\gamma = -\frac{1}{2}d(\ln C)/d(\ln V) - \frac{1}{6}$ . The quantities  $d(\ln C)/d(\ln V)$  are related to the measured pressure derivatives of the elastic constants by the relation  $d(\ln C)/d(\ln V) = -(B_T/C)(dC/dP)$  where  $B_T$  is the isothermal bulk modulus. The high temperature limit of  $\gamma_{Gr}$  on the anisotropic continuum model is an average of the  $\gamma$ 's of the longitudinal and two transverse modes over all directions of propagation in the crystal. This averaging process has been carried out by Sheard (1958) using a machine calculation for a number of crystals. The averaging may be performed approximately by using a process such as that of Houston (1948). Values obtained in Ge and Si using the Houston approximation and data on pressure dependence of elastic constants of Ge by McSkimmin (1957) and of Si by Chapman (1959) yield  $\gamma_\infty = 0.72$  in Ge, 0.51 in Si, comparing almost too well with the experimental values of  $\gamma_{Gr}$  found by Gibbons, 0.73 in Ge, 0.45 in Si in the high temperature limit. Table 1 contains the individual values of  $\gamma$  for modes propagating along [100], [110] and [111] in Ge and Si. Note that the Slater gamma is much higher than the average gamma because of the excessive weight it gives to the longitudinal modes.

Table 1.  $\gamma$ 's of long wavelength acoustic modes propagating along various crystallographic directions.

Direction of propagation	$\gamma_L$	$C_{11}'$	$\gamma_{T1}$	$C_{T1}$	$\gamma_{T2}$	$C_{T2}$
Si [100]	1.37	(1.67)	0.33	(0.80)	0.33	(0.80)
Si [110]	1.33	(1.96)	0.33	(0.80)	-0.12	(0.51)
Si [111]	1.32	(2.05)	0.08	(0.61)	0.08	(0.61)
		$\rho N_L^2$		$\rho N_{1T}^2$		$\rho N_{2T}^2$
	$\gamma_L$	$C_{11}'$	$\gamma_{T1}$	$C_{T1}$	$\gamma_{T2}$	$C_{T2}$
Ge [100]	1.29	(1.29)	0.584	(0.67)	0.584	(0.67)
Ge [110]	1.28	(1.56)	0.584	(0.67)	0.170	(0.40)
Ge [111]	1.27	(1.65)	0.36	(0.49)	0.36	(0.49)

To obtain the low temperature limit  $\gamma_0$  of  $\gamma_{Gr}$  on this continuum model, one must weight the individual mode gammas by the inverse cube of the velocity of waves of that mode type, and again average over all directions of propagation. This is equivalent to determining  $-d(\ln \Theta_0)/d(\ln V)$  where  $\Theta_0$  is the low temperature limit of the Debye temperature. This may most easily be accomplished by using de Launay's (1960) tables of  $\Theta_0$  ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ,  $\rho$ ) together with the values of  $dC_{ij}/dP$ , with the results  $\gamma_0 = 0.49$  in Ge, 0.25 in Si (Daniels 1962). These points are plotted on the  $T = 0$  ordinate of figures 1 and 2. Note the high degree of similarity then apparent between the behaviour of Ge and Si. It might seem then as if the continuum model fits quite well the behaviour of

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 monotonic increase of  $\gamma_{Gr}$  from  $\gamma_0$  to  $\gamma_\infty$  as the

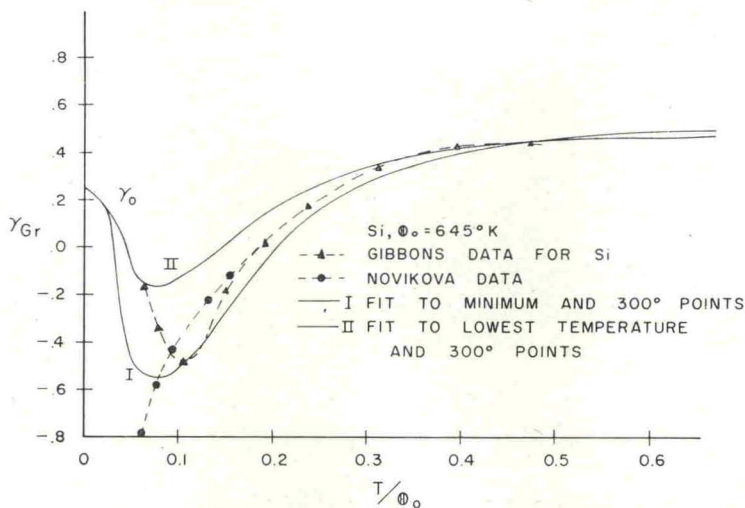


Figure 1.  $\gamma_{Gr}$  plotted against  $T$  in Si, showing experimentally determined values and synthetic values.

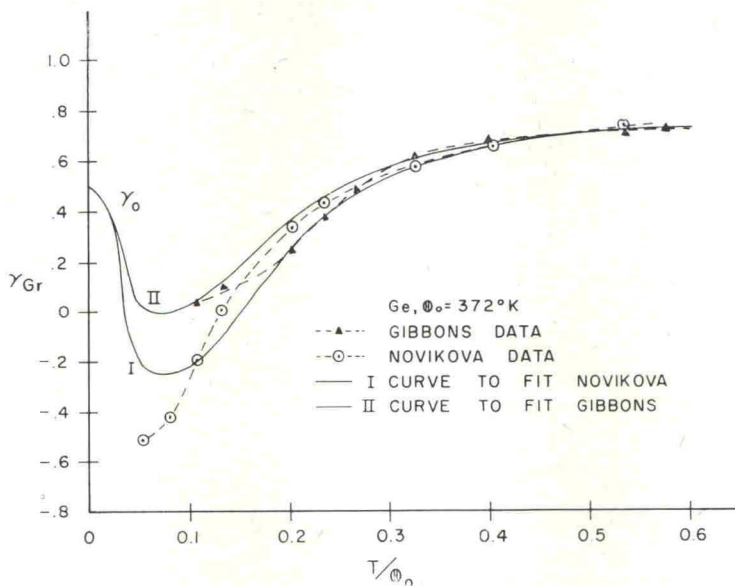


Figure 2.  $\gamma_{Gr}$  plotted against  $T$  in Ge showing experimentally determined values and synthetic values.

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  $\gamma_{Gr} \approx -0.5$  in Si when the lowest mode  $\gamma \approx -0.1$ .

It must be then that some of the modes in the dispersive region have important negative  $\gamma$ 's, since such negative values of  $\gamma_j$  do not occur strongly enough in the non-dispersive region. We can conclude that the agreement of  $\gamma_\infty$  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  $\gamma_j$  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
$\gamma_{TA}$	-21	-7.2
$\gamma_{LALO}$	+8.1	+1.7
$\gamma_{TO}$	+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 ( $\gamma_{Gr}$ , 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

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 ( $\Theta_D, T$ ) data computed from this spectrum agree very well with the data of Flubacher, Leadbetter and Morrison (1959), our computed values of  $\Theta_D$  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 $\Theta_D$	72 ( $6.48 \times 10^{-3}$ )	125 ( $6.48 \times 10^{-3}$ )
Longitudinal continuum $\Theta_D$	288 ( $4.95 \times 10^{-2}$ )	499 ( $4.95 \times 10^{-2}$ )
TA $\Theta_E$	120 (0.3267)	217 (0.3267)
LALO $\Theta_E$	327 (0.2838)	567 (0.2838)
TO $\Theta_E$	396 (0.3333)	687 (0.3333)

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

Figures 1 and 2 show the curves of  $\gamma_{Gr}$  in germanium and silicon as measured by Gibbons, and curves of  $\gamma_{Gr}$  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  $\gamma_j$  associated with each element of spectral structure were found as follows. The  $\gamma_T$  and  $\gamma_L$  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  $\gamma$  must not be considered as more than an approximate average over the two mode types. That average, and the average  $\gamma$  of the TA peaks, were found by fitting to two points on the experimental ( $\gamma_{Gr}, T$ ) curve. Values of the gammas obtained are as follows:

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

$$\gamma_T = 0.398 \quad \gamma_L = 1.28 \quad \gamma_{TA} = -0.36 \quad \gamma_{LALOTO} = 1.42$$

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

$$\gamma_T = 0.398 \quad \gamma_L = 1.28 \quad \gamma_{TA} = -0.09 \quad \gamma_{LALOTO} = 1.21$$

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

$$\gamma_T = 0.120 \quad \gamma_L = 1.34 \quad \gamma_{TA} = -0.69 \quad \gamma_{LALOTO} = 1.17$$

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

$$\gamma_T = 0.120 \quad \gamma_L = 1.34 \quad \gamma_{TA} = -0.26 \quad \gamma_{LALOTO} = 0.86$$

### 5. Discussion of results

It is clear that at best this type of analysis can yield only values of  $\gamma$ '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  $\gamma$  is taken to be  $\gamma_{Gr}$ , 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  $\gamma$  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  $\gamma_{Gr}$ , 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  $\gamma_{Gr}$ . On this basis a better average might be made over  $\gamma_j^2$ . Performing this average over the  $\gamma$ 's found in curves I of figures 1 and 2 leads to

$$(\overline{\gamma_j^2})^{1/2} = \begin{array}{l} 1.17 \text{ in Ge} \\ 1.05 \text{ in Si} \end{array}$$

to be compared with the high temperature limiting value of  $\gamma_{Gr}$ ,  $\gamma_\infty = 0.74$  in Ge, 0.45 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  $\gamma_\infty$  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  $\gamma_j$ , 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  $\gamma$  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

cryogenic equipment problems, and expected to have data at this time, but the usual difficulties have intervened.

Examination of the data of Chynoweth, Logan and Thomas (1962) reveals that in Ge one has reasonable hope of determining the  $\gamma$ 's for all mode types with the  $\mathbf{k}$  at the zone edge in the [111] direction.

The situation in Si is not quite so clear, because the pressure shift of the characteristics will be due to both the pressure dependence of the phonon energies at constant  $\mathbf{k}$  plus a shift due to the change in  $\mathbf{k}$  of the conduction band minimum with pressure. This second contribution will probably not be critical in the case of the TA and TO modes which have little  $\mathbf{k}$  dependence near the zone edge.

With a knowledge of the volume dependences of the frequencies at a few symmetry points from these experiments, coupled with the measured volume dependences of the slopes of the dispersion curves at  $\mathbf{k} = 0$  from measurements of the pressure dependences of the elastic constants, one should be able to use Cochran's theory of the lattice vibrations in Ge to construct an entire set of dispersion curves at different volumes. The detailed knowledge of the anharmonicities, i.e. of the  $\gamma_j$ , will enable one to reconstruct accurately the temperature dependence of  $\gamma_{Gr}$ , or of the thermal expansion coefficient independently of thermal measurements, as well as to provide material for the theory of thermal conductivity in these structures.

### Acknowledgments

This work was supported in part by the Army Research Office, Durham.

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