

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, α -Sn, InSb, GaAs, ZnSe and CdTe for which data are available, are unusual in the following respects: (i) the magnitude of α 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 γ , $\gamma_{Gr} = \alpha B_T V/C_V$ 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), α -Sn, InSb, ZnSe, GaAs and CdTe (Gibbons 1958, Novikova 1959, 1960, 1961) exhibit qualitatively similar behaviour. The magnitudes of α 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 α 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 α 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 ν_j have a volume dependence $\gamma_j \equiv -\partial(\ln \nu_j)/\partial(\ln V)$ (Slater 1939). Straightforward statistical