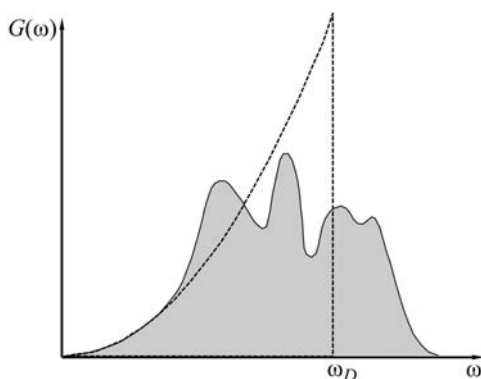## 2. SYMMETRY ASPECTS OF EXCITATIONS

Fig. 2.1.2.8. Schematic representation of the true phonon density of states (solid line) along with the Debye approximation (dotted line). Note that the areas under the two curves are identical.

Consequently, the heat capacity turns out to be

$$c_V^{\text{Einstein}} = 3NN_Z k \left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T)-1]^2}, \qquad (2.1.2.56)$$

where we use the abbreviation

$$\Theta_E = \hbar\omega_E/k, \qquad (2.1.2.57)$$

which is the *Einstein temperature.*

At low temperatures, this model predicts an exponential temperature dependence of the heat capacity [$c_V \propto \exp(\Theta_E/T)$], which does not correspond to the experimental findings in most substances. Here, the *Debye model* provides a significant improvement.

(2) *The Debye model.*

In contrast to the Einstein model, which takes only one optic mode into account, the Debye model is restricted to acoustic modes that exhibit a linear dispersion close to the Γ point (see Section 2.1.2.4). Neglecting any deviation from linear behaviour, we get the simple result that the density of states is proportional to the square of the phonon frequency. The total number of phonon states is, however, given by $3NN_Z$, which is the number of all dynamical degrees of freedom of the whole system. Consequently, the frequency spectrum is assumed to be limited to frequencies below a particular value ω_D according to

$$3NN_Z = \int_0^{\omega_D} G^{\text{Debye}}(\omega)\, d\omega. \qquad (2.1.2.58)$$

This limiting frequency is called the *Debye frequency* and is related to an appropriate average of (longitudinal and transverse) sound velocities and exhibits large values for hard materials. Fig. 2.1.2.8 compares schematically the true phonon density of states with the Debye approximation. The density of phonon states may thus be represented by

$$G^{\text{Debye}}(\omega) = 9NN_Z(\omega^2/\omega_D^3) \qquad (2.1.2.59)$$

and, correspondingly, the heat capacity is

$$c_V^{\text{Debye}} = 9NN_Z k \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{[\exp(x)-1]^2}\, dx, \qquad (2.1.2.60)$$

yielding a temperature dependence as shown in Fig. 2.1.2.9. Θ_D is the *Debye temperature*, which is defined as

$$\Theta_D = \hbar\omega_D/k. \qquad (2.1.2.61)$$

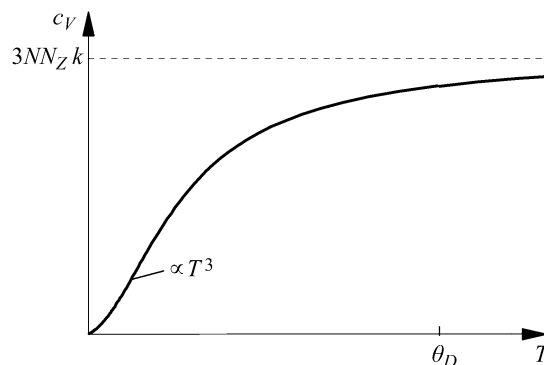At low temperatures, the heat capacity is proportional to T^3, in excellent agreement with most experiments:

Fig. 2.1.2.9. Temperature dependence of the heat capacity at constant volume according to the Debye model.

$$c_V^{\text{Debye}} \xrightarrow[T\to 0]{} \tfrac{12}{5}\pi^4 NN_Z k(T/\Theta_D)^3. \qquad (2.1.2.62)$$

It is not surprising that the Debye model provides a reasonable description of the low-temperature heat capacity, since in this temperature regime well below the Debye temperature, optical phonons are hardly excited and the heat capacity is dominated by the low-frequency acoustic modes which are modelled exactly. At higher temperatures it is, however, necessary to take into account the thermal excitation of (in general less dispersive) optic modes. This can be achieved either by introducing a temperature dependence of the Debye temperature or by mixing a Debye term like (2.1.2.60) and Einstein terms like (2.1.2.56).

As an example, we consider the case of GaAs, the density of states of which is shown in Fig. 2.1.2.7. Obviously there are two very pronounced peaks at high frequencies, which are due to nearly dispersionless optical phonon branches. These modes may therefore be regarded as Einstein oscillators. The remaining acoustic branches lead to the more continuous part of the spectrum at lower frequencies, which may be approximated by a Debye law.

2.1.2.8. *Thermal expansion, compressibility and Grüneisen parameters*

So far, we have always assumed that the crystal volume is constant. As long as we are dealing with harmonic solids, the thermal excitation of phonons does not result in a mean displacement of any atom. Consequently, thermal expansion cannot be understood in the harmonic approximation. It is due to the fact that there are anharmonic contributions to the lattice energy, *i.e.* third- and higher-order terms in the expansion with respect to atomic displacements [equation (2.1.2.4)]. Moreover, in an anharmonic lattice phonons are no longer independent elementary excitations. Rather, different lattice vibrations interact with each other leading to temperature-dependent frequency shifts, damping *etc.* Quantitatively, anharmonic effects may be analysed by means of perturbation theory, which is, however, beyond the scope of the present article. Details may be found, for example, in the monograph *The Physics of Phonons* (Reissland, 1973).

Some aspects of anharmonicity can, however, be discussed on the basis of the *quasi-harmonic model*. This approach makes use of the fact that the atomic interactions vary with the interatomic spacing and, hence, with the volume or, more generally, with any type of lattice deformation. The phonon frequencies will therefore depend on the deformation as well. Using the deformed lattice as a new reference frame for lattice dynamical calculations, the corresponding frequencies may be obtained again on the basis of a harmonic model with modified effective force constants. The comparison of phonons of both the original and the (arbitrarily) deformed lattice finally yields the partial derivatives of the frequencies $\omega_{\mathbf{q},j}$ with respect to the components ε_{kl} of the strain tensor.