

Sem IV

Lattice waves and Electron states Anharmonicity and thermal expansion

The potential energy of the crystal as a Taylor series in the lattice displacements has further terms, such as

$$\psi^{(3)} = \frac{1}{3!} \sum_{\substack{j_1 j_2 j_3 \\ s_1 s_2 s_3 \\ x_1 x_2 x_3 \\ j_1' j_2' j_3'}} \left[\frac{\partial^3 \psi}{\partial u_{s_1}^{j_1} \partial u_{s_2}^{j_2} \partial u_{s_3}^{j_3}} \right]_0 \quad \text{--- (i)}$$

and so on. The actual calculation of the coefficients is a very complicated problem since they involve geometrical factors as well as third derivatives of the interatomic potentials.

Several important physical phenomena are associated with the anharmonic terms. Of these the most familiar is thermal expansion. It is not easy to derive this directly from expressions like (i), but the general physical idea is easy enough. As the temperature rises the amplitude of the lattice vibrations increases, so that the average R.M.S. values of the displacements $\bar{u}_{s_1}^{j_1}$, etc., increase. The anharmonic terms contribute to the free energy of the crystal, which is now no longer necessarily a minimum for vibrations around the assumed 'equilibrium' configuration in which each $\bar{u}_{s_1}^{j_1}$ vanishes. The whole crystal then expands (or contracts) until it finds the volume where the total free energy is a minimum.

In default of adequate information about the anharmonic terms for a 'first principle' calculation, we may assume phenomenologically that the frequency of the lattice modes is a function of volume. For simplicity it is supposed that change of volume ΔV gives rise to the same relative change of frequency of every mode:

$$\frac{\Delta \nu}{\nu} = -\gamma \frac{\Delta V}{V} \quad \text{--- (ii)}$$

The total free energy of the crystal, as a function of volume, may then be written

$$F = \frac{1}{2} \frac{1}{K} \left(\frac{\Delta V}{V} \right)^2 + K T \sum_q \log \left(2 \sinh \frac{\hbar \nu_q}{2 K T} \right) \quad \text{--- (iii)}$$

The first term in the potential energy associated with the compressibility K of the solid as an elastic continuum. The second term is the sum of the free energies in the lattice modes, as given by the conventional statistical mechanics of B.E oscillators

Differentiating with respect to volume, and using eq (ii), we find ~~that~~ the condition for minimum free energy,

$$\frac{1}{K} \left(\frac{\Delta V}{V} \right) = \sum_q \gamma \hbar \nu_q \frac{1}{2} \coth \frac{\hbar \nu_q}{2 K T}$$

$$= \gamma \bar{E}(T) \quad \text{--- (iv)}$$

where \bar{E} is the energy in the lattice modes at temperature T . We thus arrive at the Grüneisen formula; the dilatation at temperature T is proportional to the mean thermal energy density, i.e.

$$\frac{\Delta V}{V} = K \gamma \bar{E}(T) \quad \text{--- (v)}$$

The thermal expansion coefficient, being the derivative of the dilatation with temperature, is proportional to the specific heat, C_v .

This formula may be compared with experiment to yield the Grüneisen constant, γ , which is usually about 2. It is a convenient dimensionless parameter for the effects of anharmonicity. In the Debye model, we can write eq (ii) in the form

$$\gamma = - \frac{\partial \log \Theta}{\partial \log V} \quad \text{--- (vi)}$$

showing the effect of volume on the Debye temperature. In truth, this is much too simplified as a model of thermal -

expansion. Dilatation affects different modes in different ways; the value of γ for longitudinal modes is usually much larger than for transverse modes, so these must be counted as separate contributions in eqn (IV)

Another effect of anharmonicity is on the elastic constants, which vary with volume and with temperature. These are complicated phenomena, for which there is no elementary theory; they depend on a number of different parameters.

