

7. THERMAL PROPERTIES OF SOLIDS.

Aim: To provide an overview of the description of thermal properties of solids, particularly insulators, using the dynamics of lattice vibrations.

In this lecture we discuss the specific heat and thermal conductivity of crystalline solids. We make use of the density of vibrational states and the concept of phonons that were covered in the previous lecture.

1. Classical model of the specific heat.

Consider a monatomic ideal gas of N atoms. The inner energy is given by the kinetic energy of the atoms. Each atom has three degrees of freedom, so the energy is given by,

$$U = 3Nk_B T/2,$$

where k_B is Boltzmann's constant and T is temperature. The heat capacity is given by $C = (\partial U / \partial T)$. In the case of a crystalline solid, we must add the potential energy, resulting from three additional degrees of freedom. Hence

$$U = 3 RT, \text{ where } R = Nk_B \text{ is the gas constant.}$$

Dulong and Petit's law:

$$C = 3R \approx 25 \text{ J / mole K.}$$

This value is a fair approximation at high temperatures, as we will see below.

2. Quantum mechanical model (K p. 107-108).

We take each vibrational mode to be described by a harmonic oscillator occupied with $\langle n \rangle$ phonons. The total energy is the sum of $U_{k,p}$ over all vibrational modes. The index k labels all allowed k -vectors and the index p enumerates all branches of modes (TA, LA, TO, LO). The sum over k is then transformed to an integral over the phonon density of states (Kittel eq. (9) and (10), p. 108). The exact formula is cumbersome and one usually resorts to certain approximations.

a) Einstein model (K p. 114-117).

Here we assume that all atoms vibrate with the same frequency. Given a monatomic solid with three branches in the dispersion relation we just sum over $3N$ identical harmonic oscillators. This approximation is especially good for the case of optical phonon modes.

The resulting expression shows discrepancies from experimental data (fig. 11, p. 117) at low temperatures. Acoustic modes, which are the ones excited at low temperatures have a very different dispersion relation.

b) Debye model (K p. 112-114).

In the Debye model it is assumed that the group velocity is constant and that the dispersion relation is given by $\omega = vk$. Hence the frequency contours in k -space have a spherical symmetry and the density of states is

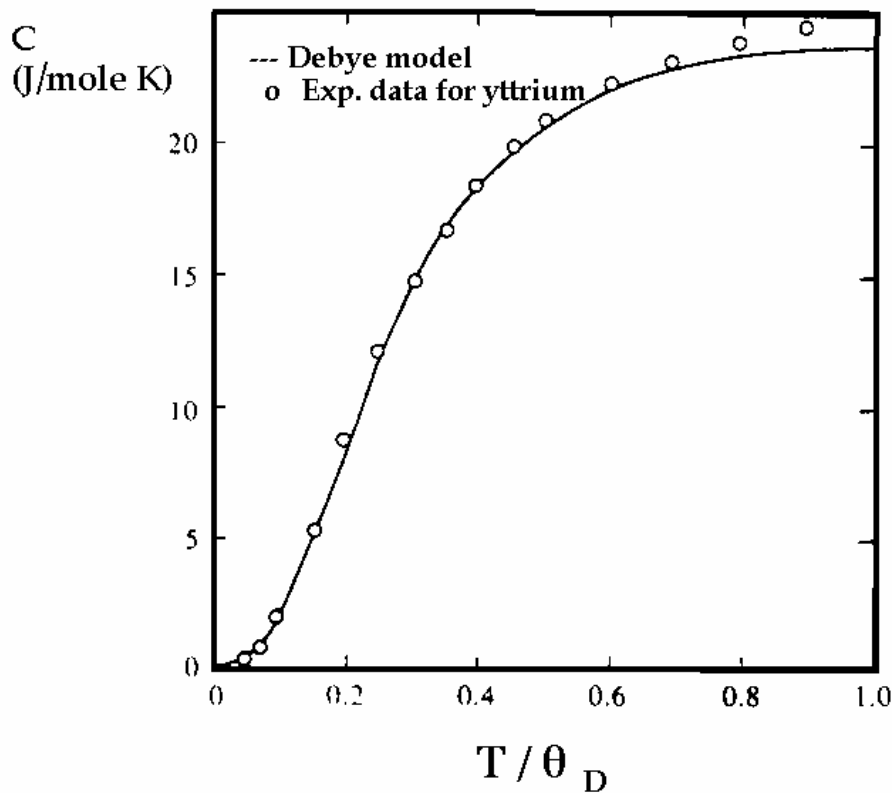
$$D(\omega) = V\omega^2/2\pi^2v^3,$$

The upper cutoff frequency is chosen so that the number of modes per branch is N . It is also assumed that v is independent of the branch. The resulting expressions for the heat capacity are somewhat complicated (K p. 112-113). At high temperatures C approaches the value $3R$, while at low temperatures it is found that

$$C \approx 234 Nk_B(T/\theta)^3,$$

where θ is a characteristic temperature, the Debye temperature, which depends on the cutoff frequency. A simple argument for this "law" is given in fig. 10, p. 115 in Kittel. The Debye temperatures are tabulated on p. 116.

Agreement with experiments is generally good, as demonstrated below for the case of Yttrium.



3. Anharmonic effects (K p. 119-121).

So far we have used the harmonic approximation. We have assumed that the potential energy only has terms quadratic in the atomic displacements from equilibrium. This leads to a force proportional to the displacements (cf. Hooke's law). However there exist anharmonic terms in the potential energy. They have higher powers than two in the dependence on the atomic displacements. Physical effects of the anharmonicity are:

- Phonon-phonon interactions. Two phonons may interact to produce a third etc.
- Thermal expansion. The average atomic displacement (hence the lattice constant) is proportional to temperature.
- The heat capacity of solids is not constant at high T, but gradually increases over the Dulong-Petit value.
- Thermal conductivity by phonons. We look at this more in detail below.

4. Thermal Conductivity (K p. 121-128).

The thermal conductivity of a solid is defined as the proportionality coefficient between the flux of thermal energy (heat) and the temperature gradient. We consider a one-dimensional case, i.e. a long rod. The phonons in the solid are treated as a gas where the particles frequently collide with one another. It is assumed that they have a mean free path, l , between collisions. The flux of phonons in the positive and negative x-directions is equal. However, phonons moving towards lower T lose an energy $c\Delta T$, while the others gain the energy $c\Delta T$. The energy transport takes place by diffusion. The kinetic theory of gases yields for the thermal conductivity

$$K = Cvl / 3$$

Here C is the heat capacity of the material, and v is the phonon velocity (of the order of the velocity of sound). The mean free path is limited by collisions of phonons with other phonons, defects, impurities, ..., and for very pure specimens even the sample boundaries. The phonon mechanism is the dominating one in non-metals. It is "umklapp" processes (K p. 125-126) of the form $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$, that cause thermal resistance and give rise to the mean free path. For temperatures lower than the Debye temperature θ , the probability of Umklapp processes is proportional to $\exp(-\theta/2T)$, hence $l \sim \exp(\theta/2T)$. At higher temperatures the mean free path is proportional to the inverse of the phonon concentration.

At low temperatures there are few phonons excited. The mean free path is large and K is limited by the heat capacity. From the Debye approximation $K \sim C \sim T^3$.

At high temperatures many phonons are present and the mean free path limits K. The high-temperature limit of Planck's law gives that the average phonon number is proportional to T. We obtain $K \sim l \sim \langle n \rangle^{-1} \sim 1/T$.

At intermediate temperatures K exhibits a peak. The height of the peak depends on the purity of the sample. For very pure materials it may even be limited by the size of the sample. The limiting process is scattering of phonons by lattice imperfections, grain boundaries, impurities... Above the peak a region with $\exp(\theta/2T)$ dependence can often be seen.

The figure below (adapted from Myers) gives a schematic illustration of the temperature dependence of the thermal conductivity. Experimental data for LiF with different amounts of the isotope ^6Li , which acts as an impurity is also shown. The impurity content is lowest for the curve with the highest peak and vice versa.

