5 Thermal Properties

In Sect. 4.2 we saw how the $3rN$ equations of motion of a periodic solid can be largely decoupled by means of the plane-wave ansatz and the assumption of harmonic forces. With (4.7) we arrived at a system of equations that, for a given wave vector $\boldsymbol{q}$, couples the wave amplitudes of the atoms within a unit cell. It can be shown mathematically that within the harmonic approximation the equations of motion, even for a nonperiodic solid, can be completely decoupled by means of a linear coordinate transformation to so-called normal coordinates. We thereby obtain a total of $3rN$ independent forms of motion of the crystal, each with a harmonic time dependence and a specific frequency which, in the case of a periodic solid, is given by the dispersion relation $\omega(\boldsymbol{q})$. Any one of these "normal modes" can gain or lose energy independently of the others. The amount of energy that can be exchanged is quantized, however, as for a single harmonic oscillator:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\,\omega \qquad n = 0, 1, 2, \ldots \,. \tag{5.1}$$

Classically, the quantum number n corresponds to the amplitude of the vibration according to

$$M\,\omega^2\,\langle s^2\rangle_t = \left(n + \frac{1}{2}\right)\hbar\,\omega. \tag{5.2}$$

where $\langle s^2\rangle_t$ denotes the time average. If, for example, one wishes to calculate in the harmonic approximation the thermal energy per unit volume of a solid, one needs to know firstly the eigenfrequency spectrum of the solid, and secondly the energy of a harmonic oscillator in equilibrium with a heat bath. We begin by considering how to obtain, in principle at least, the frequency spectrum of the solid.

5.1 The Density of States

The $3rN$ equations of motion (4.4) have exactly $3rN$, in general distinct, solutions. In contrast, the plane-wave ansatz (4.5) for the periodic solid would appear to give a continuous manifold of solutions. This contradiction stems from the assumptions, on the one hand, of complete translational

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symmetry, i.e., an infinitely extended lattice, and, on the other hand, of a finite number N of unit cells. We can overcome this problem by considering a finite crystal of volume V containing N unit cells, which, however, we imagine to be part of an infinitely extended periodic continuation of the same. In this way we obtain a finite crystal while simultaneously preserving the full translational symmetry that is a prerequisite for the plane-wave solutions. If we were to consider only the finite crystal, this would lead to complications due to the additional localized solutions that are produced by its surfaces. For very small crystals, where the number of surface atoms is comparable with the number of bulk atoms, it is indeed necessary to consider such localized solutions when calculating the thermal properties.

The requirement that all properties of the lattice should be repeated in each direction after every $N^{1/3}$ unit cells means that the displacements of the atoms $\boldsymbol{s}_n$ must also repeat. According to (4.5) this leads to the condition

$$e^{iN^{1/3}\boldsymbol{q}\cdot(\boldsymbol{a}_1+\boldsymbol{a}_2+\boldsymbol{a}_3)} = 1 \ . \tag{5.3a}$$

If the wave vector $\boldsymbol{q}$ is separated into components in terms of the basis vectors of the reciprocal lattice $\boldsymbol{g}_i$ (3.21), the individual components q_i must satisfy the equation

$$q_i = \frac{n_i}{N^{1/3}} \quad \text{with}$$

$$\begin{cases} n_i = 0, 1, 2, \dots N^{1/3} - 1 \\ n_i = 0, \pm 1, \pm 2, \dots \quad \text{with the condition} \quad \boldsymbol{G}\cdot\boldsymbol{q} \le \frac{1}{2}G^2 \ . \end{cases} \tag{5.3b}$$

The series of integers n_i can either be chosen so that $\boldsymbol{q}$ takes values within the unit cell of the reciprocal lattice, or such that it always lies within the first Brillouin zone introduced in Sect. 3.5, which indeed has the same volume as the unit cell. In the latter case the maximum values of n_i are determined by the condition $\boldsymbol{G}\cdot\boldsymbol{q} \le \frac{1}{2}G^2$ (Fig. 3.8). This procedure of introducing a finite lattice while retaining the full translational symmetry thus leads to discrete $\boldsymbol{q}$-values. The total number of $\boldsymbol{q}$-values is equal to the number of unit cells N. The density of allowed $\boldsymbol{q}$-values in reciprocal space is N divided by the volume of the unit cell of the reciprocal lattice $\boldsymbol{g}_1\cdot(\boldsymbol{g}_2\times\boldsymbol{g}_3)$. On applying (3.25) one obtains the density of states in reciprocal space to be $V/(2\pi)^3$. In a cubic lattice the separation of allowed $\boldsymbol{q}$-values is thus simply $2\pi/L$ $(=g/N^{1/3})$ where L is the repeat distance in real space. This result can also be deduced directly from (5.3) (Fig. 5.1).

For the large N, the states in $\boldsymbol{q}$-space are densely packed and form a homogeneous *quasicontinuous* distribution. The number of states in a frequency interval $d\omega$ is then given by the volume of $\boldsymbol{q}$-space between the surfaces $\omega(\boldsymbol{q}) = \text{const}$ and $\omega(\boldsymbol{q}) + d\omega(\boldsymbol{q}) = \text{const}$, multiplied by the $\boldsymbol{q}$-space density of states

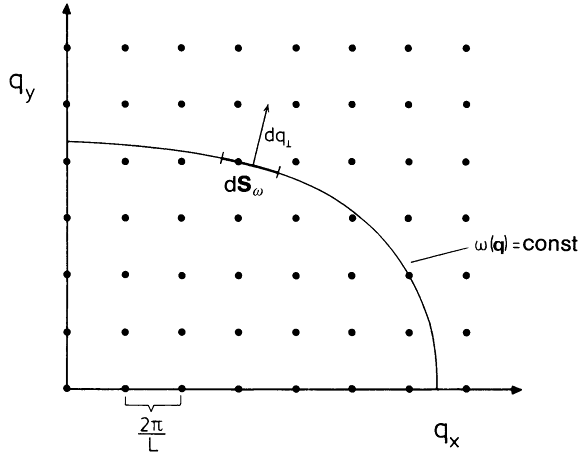

Fig. 5.1. Allowed values of $\boldsymbol{q}$ in reciprocal space for a square lattice. L is the repeat distance in real space

$$Z(\omega)d\omega = \frac{V}{(2\pi)^3} \int_{\omega}^{\omega+d\omega} d\boldsymbol{q} \,. \tag{5.4}$$

The function $Z(\omega)$ is also called the density of states. The density of states is a concept of central importance in solid-state physics, also for electronic properties (Sect. 6.1). We separate the wave vector volume element $d\boldsymbol{q}$ into a length perpendicular to the surface $\omega(\boldsymbol{q}) = \text{const}$ and an element of surface area

$$d\boldsymbol{q} = df_{\omega}\, dq_{\perp} \,.$$

With $d\omega = |\text{grad}_{\boldsymbol{q}}\, \omega| dq_{\perp}$ one obtains

$$Z(\omega)\, d\omega = \frac{V}{(2\pi)^3} d\omega \int_{\omega=\text{const}} \frac{df_{\omega}}{|\text{grad}_{\boldsymbol{q}}\, \omega|} \,. \tag{5.5}$$

The density of states is high in regions where the dispersion curve is flat. For frequencies at which the dispersion relation has a horizontal tangent, the derivative of the density of states with respect to frequency has a singularity (van Hove singularity; Fig. 5.2). For the case of a linear chain, even the density of states itself is singular. We note that the concept of density of states does not presuppose a periodic structure. Amorphous solids also have a density of states, which is usually not very different from that of the corresponding periodic solid. However, in the case of amorphous solids there are no van Hove singularities.

As an example we shall calculate the density of states for an *elastic isotropic medium* with sound velocity c_{L} for longitudinal waves and c_{T} for the two (degenerate) transverse branches. For each branch the surface

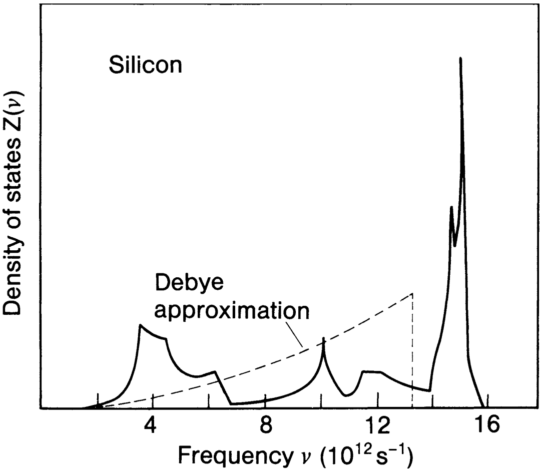

Fig. 5.2. Phonon density of states of Si [5.1] (Fig. 4.4). The dashed line is the density of states that one would obtain for an elastic isotropic continuum (Debye approximation with $\Theta = 640$ K; Sect. 5.3)

$\omega(\boldsymbol{q}) = \text{const}$ is a sphere. Thus $|\text{grad}_{\boldsymbol{q}}\omega|$ is equal to the sound velocity c_i for each branch i and is independent of $\boldsymbol{q}$. The surface integral in (5.5) is therefore simply the surface area of the sphere $4\pi q^2$. For each branch we then have the result

$$Z_i(\omega)\,d\omega = \frac{V}{2\pi^2}\frac{q^2}{c_i}\,d\omega = \frac{V}{2\pi^2}\frac{\omega^2}{c_i^3}\,d\omega \tag{5.6}$$

and for the total density of states

$$Z(\omega)\,d\omega = \frac{V}{2\pi^2}\left(\frac{1}{c_\mathrm{L}^3} + \frac{2}{c_\mathrm{T}^3}\right)\omega^2\,d\omega\,. \tag{5.7}$$

Thus the density of states for an elastic isotropic medium, and likewise for a crystal at small frequencies and wave vectors, increases quadratically with frequency. With increasing frequency it would become ever larger. However, using the example of the linear chain (Fig. 4.3), we can see that for every solid there is a maximum possible frequency. This is also true for nonperiodic structures.

5.2 The Thermal Energy of a Harmonic Oscillator

We now consider an oscillator in equilibrium with a heat bath at temperature T. The oscillator cannot be assumed to be in a fixed and known quantum state n with energy $E_n = (n + \frac{1}{2})\hbar\omega$. Instead one can only state the probability P_n that the oscillator is found in state n. The appropriate probability is given by the *Boltzmann distribution* (known also as the *canonical distribution*)

$$P_n \propto \mathrm{e}^{-E_n/kT} \quad (k\text{: Boltzmann constant})\,. \tag{5.8}$$

The constant of proportionality is given by the condition that the oscillator must be in one of the possible states

$$\begin{aligned}\sum_{n=0}^{\infty} P_n &= 1\ ,\\ \sum_{n=0}^{\infty} \mathrm{e}^{-E_n/kT} &= \mathrm{e}^{-\hbar\omega/2kT}\sum_{n=0}^{\infty}(\mathrm{e}^{-\hbar\omega/kT})^n\\ &= \mathrm{e}^{-\hbar\omega/2kT}(1-\mathrm{e}^{-\hbar\omega/kT})^{-1}\ .\end{aligned} \tag{5.9}$$

Therefore we have

$$P_n = \mathrm{e}^{-n\hbar\omega/kT}(1-\mathrm{e}^{-\hbar\omega/kT})\ . \tag{5.10}$$

The average energy $\varepsilon(\omega, T)$ is thus given by

$$\varepsilon(\omega, T) = \sum_{n=0}^{\infty} E_n P_n = (1-\mathrm{e}^{-\hbar\omega/kT})\,\hbar\omega\sum_{n=0}^{\infty}\left(n+\frac{1}{2}\right)(\mathrm{e}^{-\hbar\omega/kT})^n\ . \tag{5.11}$$

By differentiating the summation formula for the geometric series

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \tag{5.12}$$

to give

$$\sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2}\ , \tag{5.13}$$

it can be shown that the mean energy is

$$\varepsilon(\omega, T) = \hbar\omega\left(\frac{1}{2}+\frac{1}{\mathrm{e}^{\hbar\omega/kT}-1}\right)\ . \tag{5.14}$$

This expression has a form similar to the energy levels (5.1) of a single oscillator. Thus one can write

$$\langle n\rangle_T = \frac{1}{\mathrm{e}^{\hbar\omega/kT}-1} \tag{5.15}$$

for the expected value of the quantum number n of an oscillator in thermal equilibrium at temperature T.

As was discussed in Sect. 4.3, it is possible to regard the wave-like motion of the atoms as noninteracting particles (phonons) whose state is determined by the wave vector $\boldsymbol{q}$ and the branch j. The number n then corresponds to the number of particles in a state $\boldsymbol{q},j$, and $\langle n\rangle_T$ is the expected value of this number. The statistics of such noninteracting particles for situations where there is no limit on the number of particles in a given state is called *Bose statistics*. The wave quanta therefore behave as Bose particles (bosons).

It should be noted that the two different statistical distributions P_n in (5.8) and $\langle n \rangle_T$ in (5.15), i.e., the Boltzmann and the Bose distributions, result from two different ways of examining the problem: the Boltzmann distribution gives us the probability that a single particle occupies a certain state; Bose statistics, on the other hand, tells us the average number of noninteracting particles to be found in a certain state that can be occupied by any number of particles.

5.3 The Specific Heat Capacity

We now know the thermal energy $\varepsilon(\omega, T)$ of an oscillator with frequency ω. This also gives us the energy content of a normal vibration of the solid of frequency ω. The total energy of the solid in thermal equilibrium, i.e., the internal energy $U(T)$, is obtained by summing over all the eigenfrequencies. Using the density of states Z introduced in Sect. 5.1, the internal energy may be written

$$U(T) = \frac{1}{V} \int_0^\infty Z(\omega)\, \varepsilon(\omega, T)\, d\omega \,. \tag{5.16}$$

The derivative of the internal energy with respect to temperature is the specific heat capacity. We should immediately remark that, in the harmonic approximation, the specific heats at constant volume and at constant pressure are identical, and thus it is not necessary to consider any additional parameters in the derivatives.

The thermal energy of a crystal and its corresponding specific heat capacity can thus be calculated from the density of states $Z(\omega)$ using (5.16). In turn, the density of states can be deduced, in principle, from the coupling matrices. In order to understand the qualitative behavior of the specific heat as a function of temperature, it is sufficient to consider a simple model for the density of states. For this we will take the previously calculated density of states of the elastic isotropic medium. The dispersion relation is then simply $\omega = cq$ and the typical dispersion due to the discrete lattice is neglected. Using (5.7) and (5.16) this model leads to

$$c_v(T) = \frac{1}{2\pi^2} \left(\frac{1}{c_\mathrm{L}^3} + \frac{2}{c_\mathrm{T}^3} \right) \int_0^{\omega_\mathrm{D}} \omega^2 \frac{d}{dT} \varepsilon(\omega, T)\, d\omega \,. \tag{5.17}$$

The Debye cutoff frequency ω_D is determined by the requirement that the total number of states is equal to $3rN$, i.e.,

$$3rN = \frac{V}{2\pi^2}\left(\frac{1}{c_\mathrm{L}^3}+\frac{2}{c_\mathrm{T}^3}\right)\int\limits_0^{\omega_\mathrm{D}}\omega^2\,d\omega\,. \tag{5.18}$$

The imposition of a common cutoff frequency for all three acoustic modes represents a certain inconsistency of the model. Nonetheless, it actually leads to a better agreement with the experimental values of $c_v(T)$ than is obtained by the introduction of separate cutoff frequencies for the longitudinal and two transverse branches.

From (5.14, 5.17) we have

$$c_v = \frac{9rN}{V}\frac{1}{\omega_\mathrm{D}^3}\frac{d}{dT}\int\limits_0^{\omega_\mathrm{D}}\frac{\hbar\omega^3\,d\omega}{\mathrm{e}^{\hbar\omega/kT}-1}\,. \tag{5.19}$$

Introducing the Debye temperature Θ according to the definition

$$\hbar\omega_\mathrm{D} = k\Theta \tag{5.20}$$

we obtain, with the integration variable $y = \hbar\omega/kT$,

$$c_v = \frac{3rNk}{V}3\left(\frac{T}{\Theta}\right)^3\int\limits_0^{\Theta/T}\frac{y^4\,\mathrm{e}^y\,dy}{(\mathrm{e}^y-1)^2}\,. \tag{5.21}$$

The form of $c_v(T)$ is depicted in Fig. 5.3. As is readily seen from (5.19), for $kT > \hbar\omega_\mathrm{D}$, the specific heat is given by

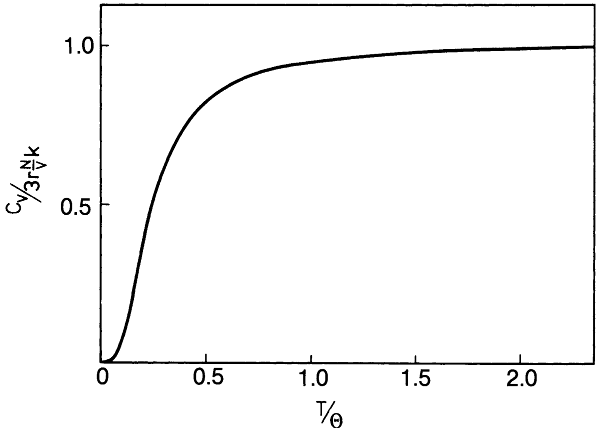

Fig. 5.3. The specific heat capacity per unit volume according to the Debye model. The specific heat is normalized to the Boltzmann constant k, the density of unit cells N/V and the number of atoms in the unit cell r. In this model different materials are only distinguished by their values of Debye temperature Θ

Table 5.1. Debye temperatures of selected materials in K [5.2]

Cs	38	In	108	ZnS	315	C	420	Fe	467
Hg	72	Te	153	NaCl	321	Ir	420	Cr	630
Se	90	Au	165	Cu	343	LiCl	422	Si	640
K	91	KCl	235	Li	344	Al	428	LiF	732
Ar	93	Pt	240	Ge	370	Mo	450	Be	1440
Pb	105	Nb	275	W	400	Ni	450	C	2230

$$c_v = \frac{1}{V} 3\,rNk$$

and is thus temperature independent. In relation to the density it is also identical for all solids since the characteristic temperature Θ is no longer involved. This is only true however within the framework of the harmonic approximation. Experimentally, one observes an additional slight increase in the specific heat roughly proportional to T. For low temperatures the integration limit Θ/T in (5.21) can be replaced by $+\infty$ and one obtains the result

$$c_v(T) = \frac{1}{V} 3\,rNk\,\frac{4\pi^4}{5}\left(\frac{T}{\Theta}\right)^3 \qquad T \ll \Theta\,. \tag{5.22}$$

Since at sufficiently low temperatures only elastic waves are excited, for which the density of states in real solids actually varies as $\propto \omega^2$, the T^3-law is valid for the vibrational contribution to the specific heat for all solids. The temperature range for which the T^3-law holds can however lie below 1 K.

Within the Debye approximation, the specific heat of a solid is completely determined at all temperatures by the characteristic temperature Θ. Thus to compare various materials with one another a knowledge of their Debye temperatures is useful (Table 5.1). Since in reality the specific heat deviates from that of the Debye model, it is not quite clear how best to define Θ. It is usual to determine Θ according to (5.22) using the experimentally measured value of c_v at low temperatures. This Θ-value, however, can differ markedly from the value obtained for higher temperatures from (5.20).

5.4 Effects Due to Anharmonicity

Until now we have only considered the atomic motion within the harmonic approximation. Higher terms in the expansion of the potential (4.1) have been neglected. However, many important properties of the solid are not described by this approximation. Some examples are the thermal expansion, the temperature dependence of the elastic constants, and the (weak) increase in the specific heat above Θ. A perfectly "harmonic" solid would also have an infinitely large thermal conductivity. This arises from the fact that a wave packet of elastic waves, once created, would have an infinite lifetime. The associated heat transport would thus proceed unhindered.

Unfortunately, the description of anharmonic effects is not simple. An exact treatment as in the harmonic case is not possible since one no longer has the nice decoupling of the equations of motion with the plane-wave ansatz. Thus in the anharmonic case one considers the solutions for the harmonic potential, the phonons, as a first approximation to the true solution. The phonons, however, are now no longer the exact eigensolutions to the equations of motion. Even if one could describe the state of motion of the crystal at a particular time by a plane wave (a phonon), this description would, in contrast to the harmonic case, become progressively less accurate with time. Instead, one would have to describe the time development by introducing a spectrum of other phonons. This feature is also known as "phonon decay".

A phonon can decay into two or more other phonons. An exact quantum mechanical treatment of this problem using perturbation theory shows that the decay of one phonon into two phonons, and also the corresponding inverse process, derive from the inclusion of the third term in the expansion of the potential. Processes that involve four phonons stem from the next highest term, and so on. Since the magnitude of higher terms generally decreases monotonically, the probability for such multiphonon processes also becomes very small. This is important for example in the inelastic interaction of phonons with light or particle waves (Sect. 4.4): the largest inelastic cross section is that for the excitation of a single phonon. The first anharmonic term of the expansion allows the simultaneous excitation of two phonons. Absorption involving the excitation of three phonons is very weak in comparison. It is only because of this that is it possible to make measurements of dispersion curves such as those shown in Fig. 4.4; these measurements rely on the predominance of single phonon excitation and absorption.

Another interesting question in this context is whether stationary solutions are also possible for nonlinear force laws. In certain special cases it is indeed possible to find such stationary solutions, known as solitons. Solitons are important particularly for the electrodynamics of nonlinear media [5.3].

In the following two sections we discuss the two most important anharmonic effects, the thermal expansion and the thermal conductivity due to phonons, and present models to describe these.

5.5 Thermal Expansion

All substances change their volume or dimensions with temperature. Although these changes are relatively small for solids, they are nonetheless of great technical importance, particularly in situations where one wishes to permanently join materials with differing expansion coefficients. In order to arrive at a definition that is independent of the length l of the sample, one defines the linear expansion coefficient, α, by

$$\alpha = \frac{1}{l}\frac{dl}{dT}\ . \tag{5.23}$$

For isotropic substances and cubic crystals, α is equal to one-third of the volume expansion coefficient

$$\alpha_V = 3\,\alpha = \frac{1}{V}\frac{dV}{dT}\ . \tag{5.24}$$

Typical values for linear expansion coefficients of solids are of the order of $10^{-5}\ \mathrm{K}^{-1}$. The expansion coefficient can clearly only be measured if the sample is kept in a stress-free state. Thermodynamically, this means that the derivative of the free energy with respect to the volume, i.e., the pressure p, must be equal to zero for all temperatures:

$$-\left(\frac{\partial F}{\partial V}\right)_T = p = 0\ . \tag{5.25}$$

This equation can be used to calculate the thermal expansion coefficient: Provided one can express the free energy as a function of the volume, then the condition of zero stress for every temperature yields a relation between volume and temperature and thus the thermal expansion. We will use this approach and begin by considering the free energy of a single oscillator. The generalization to a lattice is then straightforward.

The free energy of a system can be expressed in terms of the partition function Z

$$F = -k T \ln Z \quad \text{with} \quad Z = \sum_i \mathrm{e}^{-E_i/k T}\ . \tag{5.26}$$

The index i runs over all the quantum mechanically distinct states of the particular system. For a harmonic oscillator we have

$$Z = \sum_n \mathrm{e}^{-\hbar\omega(n+1/2)/k T} = \frac{\mathrm{e}^{-(\hbar\omega/k T)/2}}{1 - \mathrm{e}^{-\hbar\omega/k T}}\ . \tag{5.27}$$

The vibrational contribution to the free energy is therefore

$$F_s = \frac{1}{2}\hbar\omega + k T \ln\left(1 - \mathrm{e}^{-\hbar\omega/k T}\right)\ . \tag{5.28}$$

The total free energy also includes the value Φ of the potential energy in the equilibrium position

$$F = \Phi + \frac{1}{2}\hbar\omega + k T \ln\left(1 - \mathrm{e}^{-\hbar\omega/k T}\right)\ . \tag{5.29}$$

For a *harmonic* oscillator it is easy to convince oneself that the frequency ω is unaffected by a displacement u from the equilibrium position. Correspondingly, one finds that application of the equilibrium condition (5.25) yields no thermal expansion.

We now proceed to the case of the anharmonic oscillator in that we allow the frequency to change with a displacement from the equilibrium position. We assume that the energy levels are still given by $E_n = (n + \frac{1}{2}\hbar\omega)$. This procedure is known as the quasi-harmonic approximation. For a *single* oscillator it is easy to express the frequency change in terms of the third coefficient of the potential expansion (4.1). The actual calculation need not be performed here (Problem 5.6). For the simple calculation of the derivative (5.25) we consider the free energy expanded about the equilibrium position. The position of the potential minimum will be denoted by a_0. In the anharmonic case, the time-averaged position of the oscillator is no longer equal to a_0, and will be denoted a. Then, with force constant f, we obtain for the expansion

$$\begin{aligned} \Phi &= \Phi_0\,(a_0) + \frac{1}{2} f (a - a_0)^2 \,, \\ F_s &= F_s\,(a_0) + \left.\frac{\partial F_s}{\partial a}\right|_{a=a_0} (a - a_0) \,. \end{aligned} \tag{5.30}$$

The equilibrium condition (5.25), together with (5.29), then yields

$$f(a - a_0) + \frac{1}{\omega}\frac{\partial \omega}{\partial a}\varepsilon\,(\omega, T) = 0 \,. \tag{5.31}$$

With this equation we already have the relation between the average displacement and the temperature. The displacement is proportional to the thermal energy $\varepsilon(\omega, T)$ of the oscillator. Thus, for the linear expansion coefficient, we obtain

$$\alpha\,(T) = \frac{1}{a_0}\frac{da}{dT} = -\frac{1}{a_0^2 f}\frac{\partial \ln \omega}{\partial \ln a}\frac{\partial}{\partial T}\varepsilon\,(\omega, T) \,. \tag{5.32}$$

To generalize this to solids we simply need to replace $\alpha = a_0^{-1}\,(da/dT)$ by $\alpha_v = V^{-1}\,(dV/dT)$ and to sum over all phonon wave vectors $\boldsymbol{q}$ and all branches j. In place of $a_0^2 f$ one has $V\kappa$, where $\kappa = V(\partial p/\partial V)$ is the bulk modulus of compressibility

$$\frac{1}{V}\frac{dV(T)}{dT} = \alpha_V = \frac{1}{V\kappa}\sum_{q,j} -\frac{\partial \ln \omega\,(\boldsymbol{q},j)}{\partial \ln V}\frac{\partial}{\partial T}\varepsilon\,[\omega\,(\boldsymbol{q},j),\; T] \,. \tag{5.33}$$

This is the thermal equation of state of a lattice. One can immediately recognize that in the low- and high-temperature limits, the expansion coefficient shows the same behavior as the specific heat capacity, i.e., it is proportional to T^3 at low temperatures, and is constant (within this approximation) at high temperatures. For many lattice types, even the "Grüneisen number"

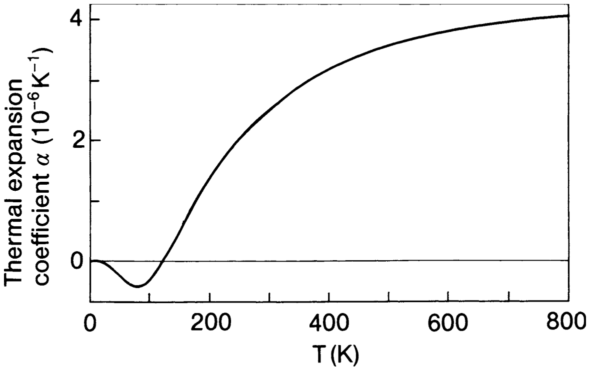

Fig. 5.4. Linear expansion coefficient of silicon as a function of temperature [5.4]

$$\gamma = -\frac{\partial \ln \omega(\boldsymbol{q},j)}{\partial \ln V} \tag{5.34}$$

shows only weak dependence on the frequency $\omega(\boldsymbol{q},j)$. The Grüneisen number can then be assigned an average value and taken out of the sum in (5.33). The expansion coefficient thereby becomes approximately proportional to the specific heat at all temperatures. Typical values of this average Grüneisen parameter $\langle\gamma\rangle$ are around 2, and are relatively independent of the material. On account of the bulk modulus appearing in the denominator of (5.33), one can claim, as a rule of thumb, that soft materials with their small bulk moduli have a high thermal expansion coefficient.

The proportionality between α_V and the specific heat does not hold, however, for all crystal classes. For structures with tetrahedral coordination, the expansion coefficient changes sign at low temperatures. The expansion coefficient of silicon shown in Fig. 5.4 serves as an example.

We have implicitly assumed in our derivation of the thermal equation of state that we are dealing with a cubic structure. Hexagonal structures have different expansion coefficients parallel and perpendicular to the c-axis. These coefficients can even have different signs as is the case for tellurium: with increasing temperature a tellurium crystal expands perpendicular to the c-axis, but shrinks – albeit only slightly – in the direction parallel to the c-axis. Crystals with triclinic, monoclinic and rhombic lattices have three different expansion coefficients.

5.6 Heat Conduction by Phonons

In solids, heat is transported by phonons and by free electrons. For metals, it is the electronic contribution that dominates the thermal conductivity. However, this does not mean that insulators are necessarily poor conductors of heat. At low temperatures the thermal conductivity of crystalline Al_2O_3

and SiO_2 is higher than that of copper. This juxtaposition of properties – electrical insulation together with good thermal conductivity – makes these materials useful for experiments in low-temperature physics.

In contrast to the thermal properties discussed so far, thermal conduction is a nonequilibrium phenomenon. A thermal current only arises in a temperature gradient and the thermal current density $\boldsymbol{Q}$ is proportional to the temperature gradient

$$\boldsymbol{Q} = -\lambda \operatorname{grad} T \tag{5.35}$$

where λ is the thermal conductivity.

The fact that we are dealing with deviations from thermal equilibrium and with spatially varying temperatures complicates the description somewhat: the thermal quantities $\varepsilon(\omega, T)$ and mean phonon number $\langle n \rangle$ (Sect. 5.2) have, until now, been defined only for systems at a single temperature. We must therefore assume that the spatial variation of T is small, such that in a sufficiently large region (i.e., one containing many atoms) the temperature can be considered homogeneous and the phonon number $\langle n \rangle$ can be defined. Neighboring regions will then have a slightly different temperature. In this way the phonon number now becomes a function of position. To calculate the thermal conductivity we must first express the thermal current density $\boldsymbol{Q}$ in terms of the properties of the phonons. As illustrated in Fig. 5.5, the thermal current passing through the area A in the x-direction in a time τ is equal to the energy density times the volume of the cylinder of length $v_x\tau$. Here v is the energy transport velocity of the phonons. This is not equal to the phase velocity ω/q of the phonon waves but, as is shown in electrodynamics text books for light and in quantum mechanical texts for electrons, it is given by the velocity of a wave packet $\partial\omega/\partial q$ (Sect. 9.1)

$$Q_x = \frac{1}{V}\sum_{\boldsymbol{q},j} \hbar\omega \langle n \rangle v_x \,, \quad v_x = \frac{\partial \omega}{\partial q_x} \,. \tag{5.36}$$

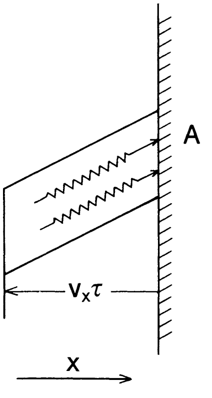

Fig. 5.5. Schematic representation of the thermal current through a cross-sectional area A. In the time interval τ all phonons travelling in the x direction within the cylinder of length $v_x\tau$ pass through the surface A

Here and in the following we shall drop the indices $\boldsymbol{q}$ and j in ω, $\langle n\rangle$ and v_x for the sake of brevity. In thermal equilibrium the thermal current density $\boldsymbol{Q}$ is of course zero. This can also be seen from the expression (5.36) for $\boldsymbol{Q}$ since, in equilibrium, the phonon occupation numbers $\langle n\rangle$ are equal for positive and negative q-values. And because of the symmetry of the dispersion curve, we have $v_x(\boldsymbol{q}) = -v_x(-\boldsymbol{q})$. Thus the summation gives a vanishing thermal current. A thermal current can therefore only arise when the phonon number $\langle n\rangle$ deviates from the equilibrium value $\langle n\rangle^0$. This gives us a further expression for the thermal current in terms of the deviation in phonon occupation numbers from their equilibrium values:

$$Q_x = \frac{1}{V}\sum_{\boldsymbol{q},j} \hbar\omega\,(\langle n\rangle - \langle n\rangle^0)\,v_x\,. \tag{5.37}$$

A time variation of $\langle n\rangle$ in a particular region can arise in two ways: More or fewer phonons may diffuse into than out of the region from neighboring regions, or phonons may decay within the region into other phonons:

$$\frac{d\langle n\rangle}{dt} = \left.\frac{\partial\langle n\rangle}{\partial t}\right|_{\text{diff.}} + \left.\frac{\partial\langle n\rangle}{\partial t}\right|_{\text{decay}}\,. \tag{5.38}$$

This is a special form of the so-called Boltzmann equation, which is also applicable to problems concerning electron transport (Sect. 9.4). We shall consider the particular case of steady-state thermal currents in which the temperature is constant in time and thus also the phonon number. The total time derivative $d\langle n\rangle/dt$ is therefore zero.

For the time variation due to phonon decay, one can introduce a relaxation time τ such that

$$\left.\frac{\partial\langle n\rangle}{dt}\right|_{\text{decay}} = -\frac{\langle n\rangle - \langle n\rangle^0}{\tau}\,. \tag{5.39}$$

According to this expression, the more the phonon number deviates from its equilibrium value, the greater its time variation. The diffusion term is related to the temperature gradient. In a time interval Δt all the phonons that were originally within the region x–$v_x\Delta t$, will arrive in the region of interest around x. We thus have

$$\begin{aligned}\left.\frac{\partial\langle n\rangle}{\partial t}\right|_{\text{diff.}} &= \lim_{\Delta t\to 0}\frac{1}{\Delta t}\left[\langle n(x - v_x\Delta t)\rangle - \langle n(x)\rangle\right]\\ &= -v_x\,\frac{\partial\langle n\rangle}{\partial x} = -v_x\frac{\partial\langle n\rangle^0}{\partial T}\frac{\partial T}{\partial x}\,.\end{aligned} \tag{5.40}$$

Because we have supposed steady-state conditions and local thermal equilibrium, having introduced the temperature gradient, we have replaced $\langle n\rangle$ by $\langle n\rangle^0$. If we now substitute (5.38–5.40) into (5.37), we obtain

$$Q_x = -\frac{1}{V}\sum_{\boldsymbol{q},j} \hbar\,\omega(\boldsymbol{q},j)\,\tau(\boldsymbol{q},j)\,v_x^2(\boldsymbol{q},j)\,\frac{\partial\langle n(\boldsymbol{q},j)\rangle^0}{\partial T}\frac{\partial T}{\partial x}\ . \tag{5.41}$$

For cubic or isotropic systems we have, in addition,

$$\langle v_x^2\rangle = \frac{1}{3}\,v^2\ . \tag{5.42}$$

Comparing this with the phenomenological equation (5.35), we obtain for the thermal conductivity

$$\lambda = \frac{1}{3\,V}\sum_{\boldsymbol{q},j} v(\boldsymbol{q},j)\,\Lambda(\boldsymbol{q},j)\,\frac{\partial}{\partial T}\,\varepsilon\,[\omega(\boldsymbol{q},j),\ T]\ . \tag{5.43}$$

Here $\Lambda = v\tau$ is the mean free path of a phonon. An analogous relation holds for the thermal conductivity of a gas and of the electron gas (Sect. 9.7). As expected, the specific heat capacity of the individual phonons plays an important role in heat transport. A further significant quantity is the group velocity: phonons close to the zone boundary and optical phonons contribute little to the thermal current. However, the temperature dependence of λ is also determined by the mean free path. Here, according to the temperature range of interest, one has to consider a variety of processes. These will be discussed in more detail in the following.

We must firstly take a closer look at phonon decay. For the decay due to anharmonic interactions that was described in Sect. 5.4, one has conservation of quasimomentum and energy:

$$\boldsymbol{q}_1 = \boldsymbol{q}_2 + \boldsymbol{q}_3 + \boldsymbol{G}\ ,\quad \hbar\,\omega_1 = \hbar\,\omega_2 + \hbar\,\omega_3\ . \tag{5.44}$$

At low temperatures, where only sound waves are thermally excited, the momentum and energy conservation can be satisfied with $\boldsymbol{G} = 0$. Such processes are illustrated in Fig. 5.6 a. One sees that the projections of $\boldsymbol{q}_1$ and of $\boldsymbol{q}_2 + \boldsymbol{q}_3$ onto an arbitrary direction are in this case equal. Since for elastic waves the magnitude of the group velocity is independent of $\boldsymbol{q}$, the thermal current is not disturbed by the decay process. Therefore, at low temperatures (in practice those below ~ 10 K) the anharmonic interaction does not influence the mean free path in (5.43). In this case only processes for which $\boldsymbol{q}$-conservation does not hold contribute to the thermal resistivity. These processes include the scattering of phonons by crystal defects, or – for a highly perfect single crystal – their scattering at the surface of the crystal. We then have the seemingly improbable, but nonetheless observed, phenomenon of the thermal conductivity that depends on the external dimensions of the crystal and the condition of its surface. The temperature dependence of λ is determined here by the specific heat and is thus proportional to T^3.

At higher temperatures, momentum and energy conservation may also involve a reciprocal lattice vector. Such processes can reverse the direction of energy transport (Fig. 5.6 b). They are therefore also known as "Umklapp" processes (from the German term for "folding over"). The con-

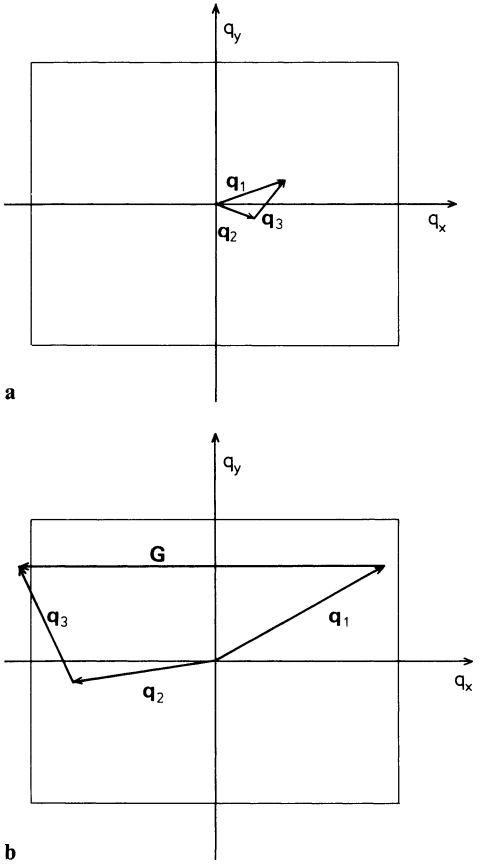

Fig. 5.6. A normal decay process (**a**) and an umklapp process (**b**) in q-space. In case (**b**) the vector $\boldsymbol{q}_1$ is split with the help of the vector $\boldsymbol{G}$ into two vectors $\boldsymbol{q}_2$ and $\boldsymbol{q}_3$, for which the group velocity is in the negative q_x-direction. This causes a reversal of the direction of energy flow

dition for their occurrence is that phonons with sufficiently large $\boldsymbol{q}$-vectors are excited. The decaying phonon must have a wave vector q_1 of roughly half the diameter of the Brillouin zone and therefore possesses an energy of $\sim \not{k}\, \Theta/2$. The probability for this is proportional to $\exp(-\Theta/bT)$, with $b = 2$. The mean free path Λ thus obeys

$$\Lambda \propto \mathrm{e}^{\Theta/bT}\,. \tag{5.45}$$

This strong exponential dependence on temperature determines the behavior of λ in the region of intermediate temperatures.

At high temperatures Λ only drops slowly with temperature ($\propto T^{-1}$). The full characteristic behavior of the thermal conductivity of a (non-conducting) single crystal is shown in Fig. 5.7 for the example of SiO_2 (quartz). For comparison the figure also displays the totally different behavior observed for the same material in the amorphous state (quartz glass). Here the scattering from defects is dominant even at the Debye temperature, and λ drops rapidly with decreasing temperature without showing the intermedi-

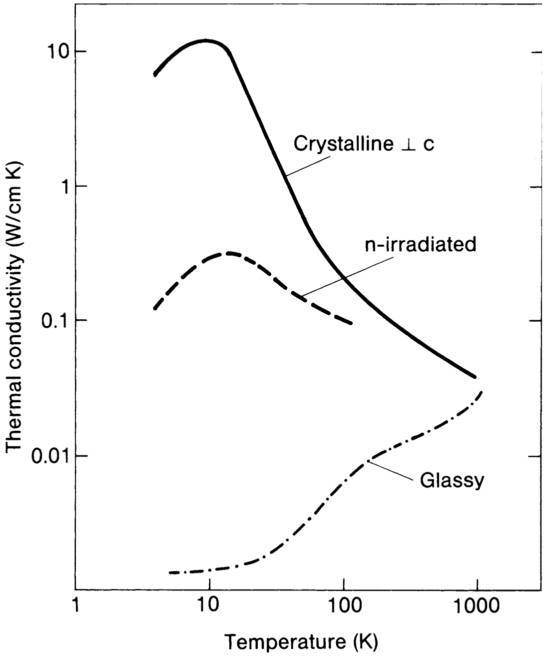

Fig. 5.7. Thermal conductivity of simple-crystal SiO_2 (quartz) perpendicular to the crystal *c*-axis. Also shown are the corresponding curves for the same crystal with defects induced by neutron bombardment, and for quartz glass [5.5, 5.6]

ate maximum typical for single crystals. Radiation damage and other defects also significantly reduce the thermal conductivity of single crystals.

Problems

5.1 Calculate the density of states and the specific heat at high and low temperatures for a one-dimensional and a two-dimensional elastic continuum. Are there physical realizations of such systems?

5.2 Calculate the thermal energy and specific heat for
a) a system of two harmonic oscillators,
b) a system with two energy levels.
Explain the difference in the two results. Are there any physical realizations of case (b)?

5.3 Assume a tetragonal lattice with a base of two atoms at (0, 0, 0) and (0, 0, $\frac{1}{2}$) carrying equal charges of opposite sign.
a) Calculate the static polarization of the lattice.
b) How large a surface charge is needed in order to compensate the static polarization?

c) Calculate the piezoelectric constant $\partial P_3/\partial \tau_3$ where τ_3 is the stress along the polar c-axis and assuming central forces to nearest neighbors.
d) For which direction of the ZnS and the wurtzite structures do you expect a longitudinal piezoeffect?

5.4 Calculate and plot the phase and group velocity of phonons for a diatomic linear chain with a mass ratio of 1:5. Estimate the contribution of the optical mode to the thermal conductivity.

5.5 Show that the equation of motion for an anharmonic oscillator

$$M\ddot{u} + fu - \frac{1}{2}gu^2 = 0$$

is solved by an approximate solution involving multiples of the harmonic frequency $\omega_0^2 = f/M$:

$$u = \sum_{n=1}^{\infty} a_n \mathrm{e}^{\mathrm{i}n\omega_0 t} .$$

Discuss the result in relation to phonon decay. What is the analogy to electrical circuits and to signal transmission in nonlinear media?

5.6 Calculate the thermal expansion of an anharmonic oscillator following the procedure of Sect. 5.5. The frequency shift for a displacement u_{stat} can be found by evoking the ansatz $u(t) = u_{\text{stat}} + u_1 \sin \omega t$.

Panel IV
Experiments at Low Temperatures

In the history of solid state physics, advances in the production and measurement of low temperatures have often been associated with the discovery of new physical phenomena. For example, in 1911, shortly after the first successful production of liquid ^{4}He in 1908, Kamerlingh Onnes discovered superconductivity [IV.1]. Indeed, it is a feature of the many-particle systems that we know as "solids", that they possess elementary excitations with very small energies. However, the quantum character of the excitation spectrum only becomes particularly noticeable when $k T$ is small compared to the quantum energies. In the endeavor to produce ever lower temperatures, modern research has reached the micro-Kelvin region (12 μK [IV.2]). To obtain such temperatures requires the simultaneous application of many sophisticated techniques. For example, the heat flow to the cold sample must not exceed 10^{-9} W. It is even necessary to avoid incident electromagnetic radiation in the radio frequency range and mechanical vibrations. Besides the application of liquid ^{4}He ($T = 4.2$–1.2 K) and ^{3}He ($T = 3.2$–0.3 K) for preliminary cooling, the chief method for the production of the lowest temperatures is the so-called "adiabatic demagnetization" of nuclear spin systems.

In this cooling process one begins with a set of nuclear spins in the milli-Kelvin range, which are split in energy by the presence of a magnetic field. The removal of heat causes the spins to adopt lower energy states. The magnetic field is then gradually reduced, which causes a corresponding reduction of the energy level splitting of the spin system. Eventually, at the appropriate temperature, a few of the spins are able to enter higher energy states of the nuclear spin system. The energy required in this process is supplied as heat from the electron and (at not too low temperatures) phonon systems of the solid.

As in all frontier areas of physics, not only the production, but also the measurement of the lowest temperatures, presents a problem. Even the equilibration of nuclear spin and electron temperatures can take hours.

In this experimental section we will introduce the reader to two experimental arrangements that allow one to measure the specific heat capacity and thermal conductivity of solids down to about 0.3 K. Compared to the work in the μK region, these are simple experiments. Nonetheless, they serve to illustrate the essential elements of low-temperature techniques.

Figure IV.1 depicts a so-called Nernst calorimeter [IV.3] used for the measurement of specific heat capacity. The calorimeter consists of an evacu-

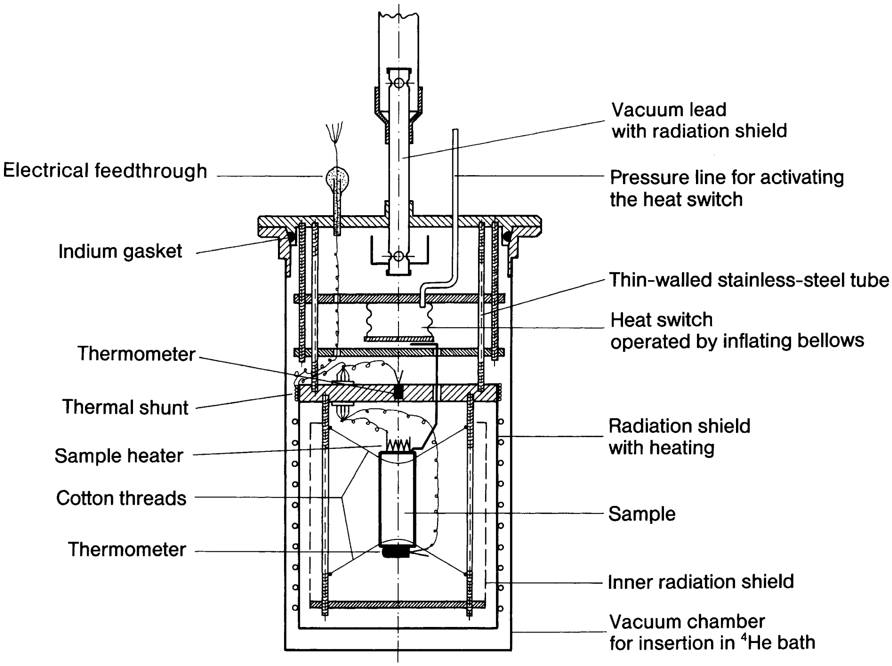

Fig. IV.1. An adiabatic Nernst calorimeter [IV.3]

ated vessel to prevent heat conduction by gas, which is submersed in the helium bath of a conventional cryostat. The helium bath in turn is surrounded by a mantle at liquid nitrogen temperature which serves to reduce thermal radiation. The principle of the specific heat measurement is to record the temperature rise of the sample upon supplying a known amount of energy, usually in the form of electrically produced heat. The main problem is the undesired extraneous heat reaching the sample. This stems from three sources: thermal conduction by the background gas in the calorimeter, thermal radiation, and conductivity of the leads. Heat conduction by the background gas can be largely avoided by evacuation, preferably at high temperatures. The influence of radiation is kept to a minimum by surrounding the sample with a radiation shield whose temperature is maintained close to that of the sample (the so-called "adiabatic" calorimeter). The sample itself is held by cotton or nylon threads which provide good thermal isolation. The conduction of heat through the leads cannot be totally avoided, but can be minimized by careful choice of materials and by ensuring good thermal contact between the leads and the outer radiation shield. To establish the desired sample temperature, particularly for cooling, one can use a heat switch. In the calorimeter of Gmelin shown in Fig. IV.1, this heat switch is a pneumatically switched heat bridge, with which the sample can be coupled to the temperature of the helium bath. The temperature of the sample is measured by the resistance of carbon resistors, or, even more reproducibly,

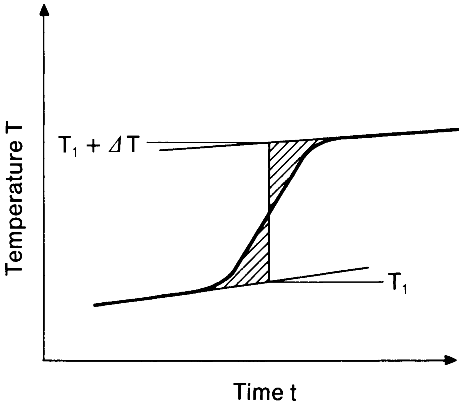

Fig. IV.2. Typical temperature variation of a sample in an experiment to measure specific heat from the temperature rise produced by supplying a known amount of heat. To determine the true temperature rise, the curves before and after the measurement must be extrapolated as shown in the figure

by the resistance of a doped germanium crystal which falls exponentially with increasing temperature (Chap. 12). Such resistance thermometers must be calibrated against the thermodynamical fixed points of ^{3}He and ^{4}He or, better still, against a vapor pressure thermometer with these gases. As a small example of the sophistication involved in the experiment of Fig. IV.1, one should note how the special form of the vacuum lead prevents the 300 K radiation from escaping from the lead into the calorimeter.

Despite careful screening, it is not possible to avoid a slight temperature drift of the sample (Fig. IV.2). After supplying a quantity of heat ΔQ one must therefore determine the true temperature rise by extrapolation (Fig. IV.2). The specific heat capacity can then be calculated from

$$c_{\mathrm{p}} = \frac{1}{m}\frac{\Delta Q}{\Delta T} . \tag{IV.1}$$

With a calorimeter of the type shown in Fig. IV.2 it is also possible, in principle, to measure the thermal conductivity of a sample. A somewhat different set-up, from the laboratory of Pohl [IV.4], developed especially for thermal conductivity measurements, is shown in Fig. IV.3. The entire apparatus can again be submerged in a bath of ^{4}He (4.2 K at atmospheric pressure), which in turn is shielded by a radiation shield at liquid nitrogen temperature. The apparatus of Fig. IV.3 possesses in addition a tank for ^{3}He. By pumping down this tank one can exploit the latent heat of evaporation of ^{3}He to obtain temperatures of about 0.3 K. This apparatus for measuring thermal conductivity contains two heating elements. One serves to set the temperature of the sample and the other sends a stationary thermal current through the crystalline sample from its upper end. The temperature difference is registered by the two carbon resistors. The thermal conductivity can then be calculated from

$$\lambda = \frac{L\dot{Q}}{F\Delta T} \tag{IV.2}$$

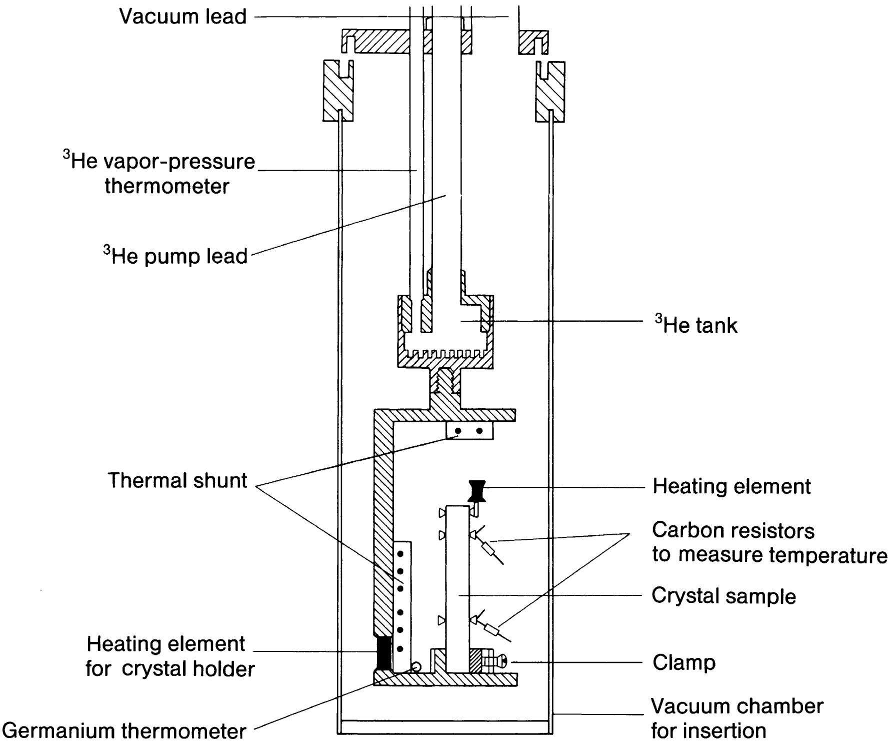

Fig. IV.3. Apparatus for the measurement of thermal conductivity (simplified) [IV.4]

where L is the distance between the carbon resistors, A is the cross-sectional area of the sample, and $\dot{Q}$ is the power of the heating element.

References

IV.1 W. Buckel: *Supraleitung*, 2nd. edn. (Physik Verlag, Weinheim 1977)

IV.2 K. Gloos, P. Smeibidel, C. Kennedy, A. Singsaas, P. Sekowski, R.M. Muelle, F. Pobell: J. Low Temp. Phys. 73, 101 (1988)

IV.3 E. Gmelin: Thermochimica Acta 29, 1 (1979)

IV.4 W.D. Seward, V. Narayanamurti: Phys. Rev. 148, 463 (1966)