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THERMAL CONDUCTIVITY

The thermal conductivity coefficient K of a solid is most easily defined with respect to the steady-state flow of heat down a long rod with a temperature gradient dT/dx:

$$Q = K\frac{dT}{dx} , \tag{54}$$

where Q is the flux of thermal energy (energy transmitted across unit area per unit time).

The form of the equation (54) which defines the conductivity implies that the process of thermal energy transfer is a random process. The energy does not simply enter one end of the specimen and proceed directly in a straight path to the other end, but rather the energy diffuses through the specimen, suffering frequent collisions. If the energy were propagated directly through the specimen without deflection, then the expression for the thermal flux would not depend on the temperature gradient, but only on the difference in temperature ΔT between the ends of the specimen, regardless of the length of the specimen. The random nature of the conductivity process brings the temperature gradient and a mean free path into the expression for the thermal flux.

From the kinetic theory of gases we find below in a certain approximation the following expression for the thermal conductivity:

$$K = \tfrac{1}{3}Cv\ell , \tag{55}$$

where C is the heat capacity per unit volume, v is the average particle velocity, and ℓ is the mean free path of a particle between collisions. This result was applied first by Debye to describe thermal conductivity in dielectric solids, with C as the heat capacity of the phonons, v the phonon velocity, and ℓ the phonon mean free path. Several representative values of the mean free path are given in Table 3.

We give first the elementary kinetic theory which leads to (55). The flux of particles in the x direction is $\frac{1}{2}n\langle|v_x|\rangle$, where n is the concentration of molecules; in equilibrium there is a flux of equal magnitude in the opposite direction. The $\langle\cdots\rangle$ denote average value. If c is the heat capacity of a particle, then in moving from a region at local temperature $T + \Delta T$ to a region at local temperature T a particle will give up energy $c\,\Delta T$. Now ΔT between the ends of a free path of the particle is given by

$$\Delta T = \frac{dT}{dx}\ell = \frac{dT}{dx}v_x\tau , \tag{56}$$

where τ is the average time between collisions.

The net flux of energy (from both senses of the particle flux) is therefore

$$Q = n\langle v_x{}^2\rangle\, c\tau\frac{dT}{dx} = \tfrac{1}{3}n\langle v^2\rangle\, c\tau\frac{dT}{dx} . \tag{57}$$

Table 3 Phonon mean free paths.

[Calculated from (55), taking $v = 5 \times 10^5$ cm/sec as a representative sound velocity. The ℓ's obtained in this way refer to the umklapp processes defined by (61)].

Crystal	T, °C	C, in J cm^{-3}deg^{-1}	K, watt cm^{-1}deg^{-1}	ℓ, in Å
Quartz*	0	2.00	0.13	40
	−190	0.55	0.50	540
NaCl	0	1.88	0.07	23
	−190	1.00	0.27	100

* Parallel to optic axis.

If, as for phonons, v is constant, we may write (57) as

$$Q = \tfrac{1}{3} C v \ell \frac{dT}{dx} , \qquad (58)$$

with $\ell \equiv v\tau$ and $C \equiv nc$. Thus $K = \frac{1}{3} C v \ell$.

Lattice Thermal Resistivity

The phonon mean free path ℓ is determined principally by two processes, geometrical scattering and scattering by other phonons. If the forces between atoms were purely harmonic, there would be no mechanism for collisions between different phonons, and the mean free path would be limited solely by collisions of a phonon with the crystal boundary, and by lattice imperfections. There are situations where these effects are dominant. With anharmonic lattice interactions such as (48) there is a coupling between different phonons which limits the value of the mean free path. The exact normal modes of the anharmonic system are no longer like pure phonons. We consider first the thermal resistivity from lattice interactions.

The theory of the effect of anharmonic coupling on thermal resistivity is a complicated problem. An approximate calculation has been given by Debye,[11] and Peierls[12,13] has considered the problem in great detail. They both show that ℓ is proportional to $1/T$ at high temperatures, in agreement with many experiments. We can understand this dependence in terms of the number of

[11] P. Debye, "Zustandsgleichung und Quantenhypothese mit einem Anhang über Wärmeleitung." In *Vorträge über die kinetische Theorie der Materie und der Elektrizität*, von M. Planck et al. (Mathematische Vorlesungen an der Universität Göttingen: VI.) Leipzig, Teubner, 1914, pp. 19–60.

[12] R. Peierls, Ann. Physik **3**, 1055 (1929).

[13] C. Herring, Phys. Rev. **95**, 954 (1954); J. Callaway, Phys. Rev. **113**, 1046 (1959); R. E. Nettleton, Phys. Rev. **132**, 2032 (1963); and the reviews cited at the end of the chapter. The Callaway and Nettleton papers contribute to an understanding of the combined effects of lattice and impurity scattering; see also M. G. Holland, Phys. Rev. **132**, 2461 (1963); P. Erdös, Phys. Rev. **138**, A1200 (1965).