1

Physical Basis of Thermal Conduction

Xian Zhang[1], Ping Zhang[2], Chao Xiao[1], Yanyan Wang[1], Xin Ding[1],
Xianglan Liu[1], and Xingyou Tian[1]

[1]*Chinese Academy of Sciences, Institute of Solid State Physics, Hefei Institutes of Physical Science,*
350 Shushanhu Road, Hefei, 230031, Anhui, P. R. China
[2]*School of Materials Science & Engineering, Anhui University, 111 Jiulong Road, Hefei, 230601, Anhui,*
P. R. China

1.1 Basic Concepts and Laws of Thermal Conduction

1.1.1 Description of Temperature Field

The difference in temperature drives the heat transfer from the high-temperature zone to the low-temperature zone; it is therefore important to understand the temperature distribution of the object for studying the heat transfer. The temperature distribution can be expressed in mathematical equations and image forms using a scalar temperature field, which is a function of time (t) and space coordinates (x, y, z):

$$T = f(t, x, y, z) \tag{1.1}$$

According to the temperature variation with time, the temperature field can be divided into steady temperature field and unsteady temperature field. In the steady-state temperature field, the temperature of the object is only related to space but not to time change. It can be expressed by

$$T = f(x, y, z), \frac{\partial T}{\partial t} = 0 \tag{1.2}$$

According to the dimensional correlation with the spatial coordinates, the temperature field can be divided into one-dimensional, two-dimensional, and three-dimensional temperature fields, that is, the object temperature is only related to one, two, or three coordinates of space. For example, one-dimensional steady temperature field can be expressed by

$$T = f(x), \frac{\partial T}{\partial y} = \frac{\partial T}{\partial z} = \frac{\partial T}{\partial t} = 0 \tag{1.3}$$

When the temperature field is described by an image, the image formed by connecting the same points of temperature is called an isothermal surface. By analogy, a cluster of curves is formed in the two-dimensional temperature field, which is

Thermal Management Materials for Electronic Packaging: Preparation, Characterization, and Devices,
First Edition. Edited by Xingyou Tian.

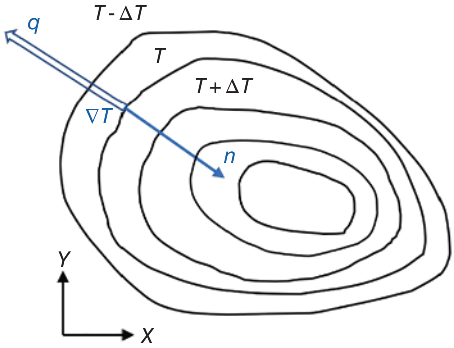

Figure 1.1 Temperature field and temperature gradient.

called an isotherm. As shown in Figure 1.1, there is no temperature difference on an isotherm, so heat can only transfer between different isotherms.

1.1.2 Temperature Gradient

As shown in Figure 1.1, the temperature difference between isotherms is the same. However, the ratio limit of the temperature difference to the distance of a point in different directions is different. The limit of the ratio of the temperature difference to the distance in the normal direction of the point is the maximum. The maximum limit value is defined as the temperature gradient, which is recorded as ∇T, it is a vector whose direction points to the direction of temperature rise along the isotherm normal and can be expressed by

$$\nabla T = \lim_{\Delta n \to \infty} \left(\frac{\Delta T}{\Delta n} \right) \tag{1.4}$$

1.1.3 Fourier's Law

In 1882, French scholar Fourier proposed the basic law of heat conduction process, namely Fourier's law. The expression is [1]

$$q = -k\nabla T \tag{1.5}$$

where q is the heat flow density in $\mathrm{W/m^2}$ and k is the thermal conductivity in W/m K. Formula (1.5) shows that q is a vector, and its direction lies on the same normal of the temperature gradient isotherm, pointing to the direction of temperature reduction.

1.1.4 Heat Flux Density Field

In the space coordinate system, the heat flux expression is

$$q = q_x\bar{\boldsymbol{x}} + q_y\bar{\boldsymbol{y}} + q_z\bar{\boldsymbol{z}} \tag{1.6}$$

where $\bar{\boldsymbol{x}}, \bar{\boldsymbol{y}}, \bar{\boldsymbol{z}}$ are unit vectors in x-, y-, z-directions, respectively. The heat flux distribution inside the object constitutes a heat flux field, which is a vector field. As shown in Figure 1.2, the solid line represents the isotherm, and the dotted line represents the isochore. Isothermal streamline is a set of curves perpendicular to the isotherm everywhere. The heat flux density on the isothermic streamline is equal everywhere, the direction of the heat flux density at any point is always tangent to the isothermic

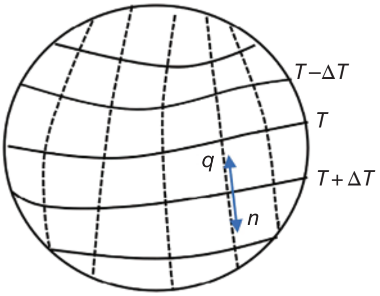

Figure 1.2 Isotherms and heat flux.

streamline, and the heat flux transmitted between two adjacent dotted lines is equal everywhere.

1.1.5 Thermal Conductivity

According to Formula (1.5),

$$k = -\frac{q}{\nabla T} = \frac{Q \cdot d}{S \cdot t \cdot \Delta T} = \frac{q \cdot d}{S \cdot \Delta T} \tag{1.7}$$

where S is the area, Q is the heat transferred through the area S in t time, and d is the distance of heat transfer. Thermal conductivity is a proportional coefficient in Fourier's law, which reflects the thermal conductivity of an object, that is, the heat flow that can be transferred through a unit area under the action of a unit temperature gradient.

The thermal conductivity of object usually varies with temperature. When the temperature range of the objective is small, the thermal conductivity is linearly related to the temperature:

$$k = k_0(1 + bT) \tag{1.8}$$

where k_0 is the thermal conductivity under a certain reference state and b is the constant determined experimentally. Due to the difference of heat conduction mechanism, the thermal conductivity of object in different forms is quite different. The heat conduction of objects is the collision and transfer of microscopic particles, including the thermal movement of molecules, the phonon movement formed by lattice vibration, and the movement of free electrons. Generally, the thermal conductivity of solid is the highest, while that of gas is the lowest.

1.2 Heat Conduction Differential Equation and Finite Solution

1.2.1 Heat Conduction Differential Equation

Figure 1.3 shows a cube element with side lengths of dx, dy, dz. Here, the density ρ, specific heat C_p, and thermal conductivity k are constants.

According to the law of conservation of energy, the sum of the net heat flowing into the cube unit in a certain time ΔQ_i and the heat generated by the cube unit itself ΔQ_p is equal to the increase in the enthalpy ΔE of the infinitesimal cube.

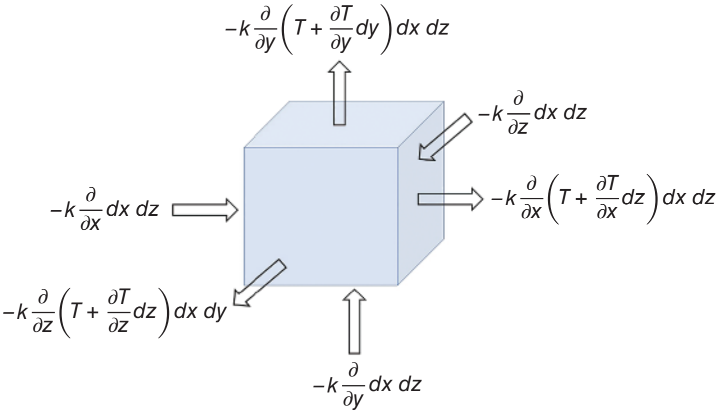

Figure 1.3 Cube element.

During $d\tau$ time, the total net inflow heat in the x-, y-, z-directions is

$$\Delta Q_i = k\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}\right)dx\,dy\,dz\,d\tau \tag{1.9}$$

The heat generated by the heat source in the cube unit in time $d\tau$ is

$$\Delta Q_p = q_1 dx\,dy\,dz\,d\tau \tag{1.10}$$

where $q_1$is the calorific value of the heat source per unit time and volume, and the unit is W/m^3.

The increase in enthalpy of the heat source of the cube unit in time $d\tau$ is

$$\Delta E = \rho c\frac{\partial T}{\partial \tau}dx\,dy\,dz\,d\tau \tag{1.11}$$

According to the conservation of energy,

$$\rho c\frac{\partial T}{\partial \tau} = k\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}\right)+q_1 \tag{1.12}$$

It can also be written as

$$\frac{\partial T}{\partial \tau} = \alpha\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}\right)+\frac{q_1}{\rho c} = \nabla^2 T+\frac{q_1}{\rho c} \tag{1.13}$$

where ∇^2 is Laplace operator, and α is the thermal diffusion coefficient with unit of m^2/s. Formulas (1.12) and (1.13) are the differential equations of heat conduction, which describes the variation of temperature field in the heat conduction system with time and space.

Thermal diffusion coefficient ($\alpha = k/\rho c$) is a physical parameter related to the type of material, and the value depends on the thermal conductivity, density, and specific heat of the object. It reflects the ability of the object to transmit temperature changes.

For the steady-state temperature field with constant thermal conductivity, the thermal conductivity differential equation becomes

$$0 = \frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}+\frac{q_1}{k} = \nabla^2 T+\frac{q_1}{\rho c} \tag{1.14}$$

For steady-state temperature field with constant thermal conductivity and no internal heat source, the thermal conductivity differential equation is expressed as

$$0 = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \tag{1.15}$$

The above equation is called Laplace equation, which is the most basic differential equation for studying the steady-state temperature field.

1.2.2 Definite Conditions

The differential equation of heat conduction is a universal equation for heat conduction problems. For specific heat conduction problems, the eigenvalue conditions of the corresponding problem must be given. These conditions include initial conditions (initial state of heat conduction system) and boundary conditions (interface characteristics, relationship between system and environment), where the initial condition expression is

$$T = f(x, y, z, 0) \tag{1.16}$$

If the initial temperature is uniform and constant ($T = T_i$), the initial condition is not required for the steady-state heat conduction problem. There are three common types of boundary problems.

The first boundary condition is that the boundary temperature distribution of the system is known:

$$T = f(x, y, z, 0) \tag{1.17}$$

The second boundary condition is that the heat flux distribution on the boundary is known:

$$q = q(x, y, z) \tag{1.18}$$

The third boundary condition is that the convective heat transfer coefficient and fluid temperature between the object and the surrounding fluid are known:

$$-k\frac{\partial T}{\partial n} = \alpha(T - T_\infty) \tag{1.19}$$

1.3 Heat Conduction Mechanism and Theoretical Calculation

The heat transfer of gases relies on the thermal motion and collision of molecules and atoms. The heat transfer in liquids relies on irregular elastic vibrations (or similar gases). In solids, heat energy is transferred through electrons and lattice vibrations. In metal solids, heat conduction is mainly realized by the interaction and collision of electrons. On the contrary, in dielectric solids including semiconductors and insulators, heat is mainly transferred through quantized lattice vibration. Among these heat conduction mechanisms, the speed of heat transfer through electron collision is the highest, while the one by molecular or atomic collision is the lowest.

1.3.1 Gases

The heat conduction mechanism of gases involves the heat transfer caused by the thermal movement of molecules and the collision between molecules. According to the theory of ideal gas molecular motion, the mathematical expression of molecular heat conduction mechanism can be deduced as [1]

$$k = \frac{1}{3}\overline{C_v}v\bar{l} \tag{1.20}$$

where k is the thermal conductivity, $\overline{C_v}$ is the heat capacity per unit volume of gas, v is the average velocity of gas molecules, and $\overline{l}$ is the average free path of gas molecules. Because the heat capacity of the gas and the average speed of molecular motion increase with the increase in temperature, the thermal conductivity of the gas also increases with the increase in temperature.

Chapman and Cowling [2] associate the thermal conductivity of simple gas with viscosity and specific heat at constant volume, and the expression is

$$k = f\eta C_v \tag{1.21}$$

where f is constant, 2.5 for smooth spherically symmetric molecules and 2.522 for rigid elastic spheres; η is the kinematic viscosity with a unit of kg/(m s); and c_v is the specific heat of constant volume with a unit of W/(kg K).

Eucken [3] correlated the thermal conductivity of monatomic gas with viscosity and specific heat at atmospheric pressure and 0 °C:

$$k = \frac{9r - 5}{4} \cdot \eta \cdot c_v \times 420(\mathrm{W/(m\,K)}) \tag{1.22}$$

Hirschfelder et al. [4] later modified the Euken equation:

$$k = \left(\frac{H}{v}\right) \eta/M(c_v + 9R/4) \tag{1.23}$$

where H and v are the complex interaction coefficients between molecular pairs, M is the molecular weight, and R is the ideal gas constant.

1.3.2 Solids

The lattice in solid is fixed and can only vibrate slightly near its equilibrium position. The heat conduction in solids is mainly realized by the lattice wave of lattice vibration and the movement of free electrons. According to quantum theory, the energy of lattice vibration is quantized, and the quantum of lattice vibration is usually called phonon [5]. Therefore, phonons can be regarded as free “gas” particles by analogy with gas heat conduction [6]. The contribution of phonons or electrons to heat conduction varies greatly depending on the type of solid.

1.3.2.1 Metals

There are a large number of unbound free electrons with light mass in metals. The electrons move like “electron gas.” The interaction or collision between electrons is the main mechanism of metal heat conduction, that is, electronic heat conduction. Metals are also crystals; hence, lattice vibration (phonon) also contributes to the heat transfer in metals. Therefore, the thermal conductivity k of metal can be expressed by the following formula:

$$k = k_e + k_p \tag{1.24}$$

where k_e is the thermal conductivity representing the contribution of free electrons, and k_p is the thermal conductivity representing the contribution of phonon.

Based on the results of the kinetic theory of gas molecules, the mathematical expression of k_e is

$$k_e = \frac{1}{3} C_{ve} \cdot \overline{V_e} \cdot \bar{l}_e = \frac{1}{3} C_{ve} \cdot \overline{V_e^2} \cdot \tau \tag{1.25}$$

where C_{ve} is the heat capacity of electrons per unit volume, $\overline{V}_e$ is the average velocity of electrons, and $\bar{l}_e$ is the average free path of the electron.

Free electrons in metals serve as both the carrier of heat and the carrier of electricity, so metal heat conduction and conductivity are closely related. The relationship between thermal conductivity and conductivity of metals follows Wiedman–Franz law:

$$\frac{k}{\sigma T} = \frac{\pi^2 {k_B}^2}{3e^2} \tag{1.26}$$

where σ is the electrical conductivity, e is the absolute value of electronic charge, and k_B is the Boltzmann constant. The law shows that the thermal conductivity of metal is proportional to the electrical conductivity.

The law of electron heat conduction in metal changing with temperature is shown in Figure 1.4. At very low temperatures, the electron thermal conductivity increases linearly with temperature; at medium temperatures, the electron thermal conductivity is almost constant and does not change with temperature; and at very high temperatures, the electron thermal conductivity decreases slightly with the increase in temperature.

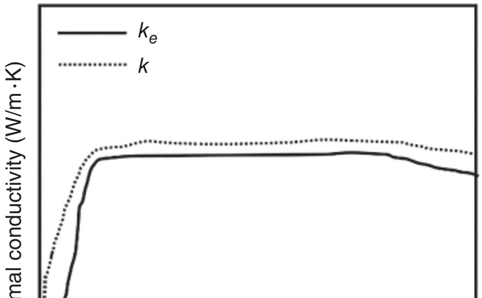

Figure 1.4 Relationship between metal thermal conductivity and temperature.

1.3.2.2 Inorganic Nonmetals

Crystal In dielectric crystals, heat energy is transferred by lattice vibration. Therefore, the propagation of lattice waves is regarded as the movement of phonons. The scattering encountered by lattice waves in the crystal is regarded as the collision between phonons, phonons and grain boundaries, and lattice defects. The thermal resistance in an ideal crystal is attributed to the collision between phonons.

According to Debye's assumption, by analogy with gases, it is considered that the mathematical expression of thermal conductivity in dielectric crystals should be the similar to that in gases. Therefore, the expression of phonon thermal conductivity can be expressed by

$$k_{pn} = \frac{1}{3} C_{vpn} \cdot \overline{V}_{pn} \cdot \bar{l}_{pn} \tag{1.27}$$

where $C_{vpn}, \overline{V}_{pn}$, and $\bar{l}_{pn}$ are the volume heat capacity, average velocity, and average free path of phonons, respectively.

According to the Klemens model, the lattice thermal conductivity of blocky solid is given by

$$k_{pn} = \frac{1}{3} \int \frac{\partial E_i(q, T)}{\partial T} v_i^2(q) \tau_i(q) dq \tag{1.28}$$

where i is the index of phonons, v is the group velocity of phonons, τ is the relaxation time, and q is the wave vector.

The curve of thermal conductivity of dielectric crystal changing with temperature is shown in Figure 1.5 [7]. At very low temperatures, the phonon-specific heat capacity is proportional to T^3. It means that heat conduction of crystal increases proportionally with the third power of temperature [8]. At higher temperatures, on the one hand, the phonon heat capacity does not change with temperature and is close to a constant 3R. On the other hand, the mean free path of phonons decreases gradually with the increase in temperature, and the mean free path of phonons is inversely proportional to the temperature ($l \propto 1/T$). Therefore, the thermal conductivity of the dielectric crystal at a higher temperature decreases [9].

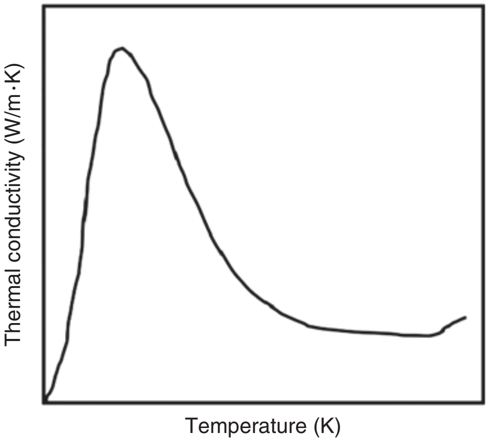

Figure 1.5 Relationship between thermal conductivity and temperature of dielectric crystals.

The formulas for calculating the theoretical thermal conductivity of dielectric crystals are summarized below:

Debye formula

$$k = \frac{1}{16\pi^3} \cdot \frac{3}{3\alpha^2 + 1} \cdot \frac{\rho v^5}{x_0 v^4} \cdot \frac{C}{k_B T} \tag{1.29}$$

where ρ is the density, v is the propagation velocity of phonons, C is the heat capacity, x_0 is the compression coefficient, v is the frequency, k_B is the Boltzmann constant, T is the absolute temperature, and α is the correlation coefficient.

Compton formula

$$k = bn^2 dRv \frac{2 - C_0 T e^{-\frac{\beta v}{2T}}}{{C_0}^2 T} \tag{1.30}$$

where $b = 4m_1 m_2/(m_1 + m_2)$, m is the mass of different atoms, n^2 is the number of atoms per unit area perpendicular to the heat flow, d is the atomic spacing parallel to the heat flow, R is the gas constant of a single molecule, v is the atomic vibration frequency, C_0 is the constant determined by thermal conductivity at a given temperature, T is the absolute temperature, and β is a constant.

Pell formula

$$\frac{1}{k} = AT + AT^B e^{-\frac{\Theta}{2T}} \tag{1.31}$$

where Θ is the Debye temperature, T is the absolute temperature, and A and B are constants.

Papapecchu formula

$$k = \frac{l_0 u_0 v}{3V} \left(\frac{C}{u} + \frac{u}{3RT^2} \right) \tag{1.32}$$

where V is the gram atomic volume; $l = l_0 u_0/u$ is the average free path; R is the gas constant; $u = 3LE$, E is the average energy of a wave and L is the Loschmidt constant; v is the average propagation speed; C is the specific heat of gram atom; and T is the absolute temperature.

Entuo formula

$$k = \frac{3nk\pi vNd}{2} \left(\frac{hv}{kT} \right)^2 \left[\frac{e^{\frac{hv}{k_B T}}}{\left(e^{\frac{hv}{k_B T}} - 1 \right)^{\frac{3}{2}}} \right] \tag{1.33}$$

where k_B is the Boltzmann constant, n is a factor determined by the type of spatial lattice, N is the number of atoms per unit area, d is the atomic spacing, R is the gas constant, h is Planck constant, v is the natural vibration frequency, and T is the absolute temperature.

Noncrystal Inorganic amorphous materials have a long-range disorder and short-range ordered structure. To analyze their heat conduction mechanism, they are generally treated as a "crystal" composed of very fine grains with only a few lattices spacing sizes. Allen and Feldman [10] studied the heat transfer mechanism in amorphous materials using lattice dynamics calculations and divided the vibration modes into three different categories: plane wave propagator, diffuser, and locator. The relative contribution of each mode determines the thermal conductivity of the material, including its value, dependence on sample size, and temperature [11]. In 1911, Einstein [12], first proposed the "amorphous limit" model to predict the minimum lattice thermal conductivity of amorphous solids. In 1979, Slack [13] further developed the "amorphous Limit" model, which equates the minimum mean free path of phonons with the wavelength of lattice waves and is called the "minimum thermal conductivity" model.

Cahill–Pohl model [14] simulates the thermal conductivity of amorphous solids by assuming that the average free path of each vibration mode is half of its wavelength. Agne et al. [15] simplified the Cahill–Pohl model results to

$$k = 1.21k_B\frac{1}{3}(2v_T + v_L)n^{2/3} \tag{1.34}$$

where k_B is the Boltzmann constant, n is the atomic number density, v_T is the lateral propagation velocity, and v_L is the longitudinal speed. In 1992, Cahill et al. [15] further modified the "minimum thermal conductivity" model.

For the relationship between thermal conductivity and temperature of inorganic amorphous, the contribution of photonic heat conduction should be considered at higher temperatures, and it will be mainly determined by the relationship between heat capacity and temperature in other temperature ranges. The thermal conductivity of inorganic amorphous materials changes with temperature as shown in Figure 1.6 [17]. At low temperatures, the thermal conductivity of inorganic amorphous increases monotonously with the increase in temperature. At this time, the change of phonon heat conduction with temperature is determined by

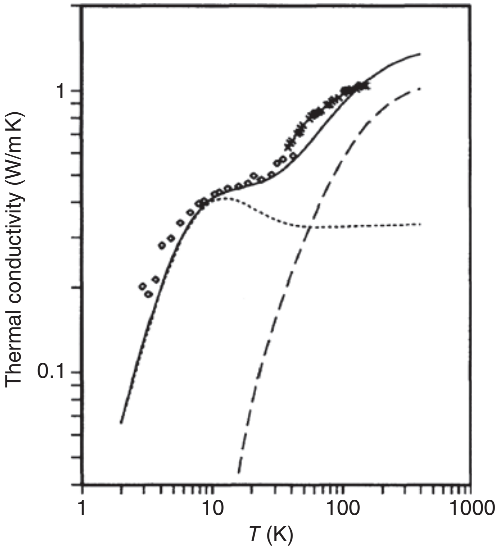

Figure 1.6 Relationship between thermal conductivity and temperature of inorganic amorphous solids. Source: Reproduced with permission from Ref. [16]; ©1993 American Physical Society.

the change rule of phonon heat capacity with temperature. As the temperature increases, the phonon heat capacity increases, so the thermal conductivity of the amorphous increases accordingly. From medium temperature to high temperature, although the temperature increases, the phonon heat capacity no longer increases but gradually becomes constant. Therefore, the phonon heat conduction no longer varies with temperature, and the thermal conductivity curve presents a straight line nearly parallel to the horizontal axis. Above the high temperature, the phonon heat conduction changes little with the further increase in temperature. As the average free path of photons increases significantly, the thermal conductivity of inorganic amorphous is proportional to the third power of temperature.

1.3.3 Liquids

The heat conduction mechanism of liquids is still controversial. One view is that the heat conduction mechanism of liquids is similar to that of gases. However, the unreasonable thing is that the distance between liquid molecules is relatively close, and the intermolecular force has a greater impact on the collision process than in gases. Another point is that the heat conduction mechanism of liquid is similar to that of non-metallic solids, mainly due to the effect of elastic waves.

The simplest equation applicable to all organic liquids is [18]

$$k = A\left[1 + B(1 - T/T_c)^{1/3} + C(1 - T/T_c)^{2/3} + D(1 - T/T_c)\right] \tag{1.35}$$

where T_c is the critical temperature, B, C, D are constants, A is the pseudo-critical thermal conductivity.

Bridgman [19] provides a simple formula that can accurately calculate the thermal conductivity of some liquids:

$$k = \frac{2k_B v_s}{d^2} = 2k_B v_s n^{2/3} \tag{1.36}$$

where v_s is the longitudinal speed of sound in a liquid, d is the mean distance between the centers of molecules and can be calculated from $d = n^{-1/3}$, and n is the number density of molecules in the liquid.

Chapman–Enskog [20] gives the thermal conductivity of liquids as follows:

$$k = \frac{k_0}{g(D)}\left[1 + \frac{2}{5}\pi\rho D^3 g(D)\right]^2 + \frac{3k_B}{2m}\mathrm{II} \tag{1.37}$$

where D is the effective diameter of the molecule, m is the mass of a liquid molecule, ρ is the density of the liquid (kg/m^3), and T is the absolute temperature.

van Elk vet al. [21] developed an equation for the correlation between the components of binary mixed liquids and thermal conductivity, and verified various types of mixed liquids:

$$k_m = w_1 k_1 + w_2 k_2 - 0.72 w_1 w_2 (k_2 - k_1) \tag{1.38}$$

The components are so selected that $k_2 \geq k_1$; the constant 0.72 may be replaced by an adjustable parameter when $k_2 < k_1$.

In 1974, Saksena and Harminder [22, 23] also successively proposed and improved the calculation formula for thermal conductivity of binary mixed liquids; Jamieson suggested that the thermal conductivity of binary mixture can be calculated by the following formula:

$$k = w_1k_1 + w_2k_2 - \alpha(k_2 - k_1)\left[1 - (w_2)^{1/2}\right] w_2 \tag{1.39}$$

The components are so selected that $k_2 \geq k_1$; α is an adjustable parameter that is set equal to unity if mixture data are unavailable for regression purposes. Equation (1.39) enables one to estimate m within about 7% for all types of binary mixtures with or without water.

In 1982, Rowley Method [24] proposed the thermal conductivity equation for multi-component mixed liquids using the two liquid theory modeling:

$$k_m = \sum_{i=1}^{n} w_i \sum_{j=1}^{n} w_{ji} k_{ji} \tag{1.40}$$

where k_m is the liquid mixture thermal conductivity, W/(m K); w_i is the weight fraction of component; w_{ji} is the local weight fraction of component j relative to a central molecule of component i; and k_{ji} is the characteristic parameter for the thermal conductivity that expresses the interactions between j and i, W/(m K).

In 1976, Li [25] provided a new idea for the calculation of thermal conductivity of multi-component mixed liquids:

$$k_m = \sum_{i=1}^{n} \sum_{j=1}^{n} \varphi_i \varphi_j k_{ji} \tag{1.41}$$

$$k_{ji} = 2\left(k_i^{-1} + k_j^{-1}\right)^{-1}$$

$$\varphi_i = \frac{X_i V_i}{\sum_{j=1}^{n} X_i V_j}$$

where X_i is the mole fraction of component i and φ_i is the superficial volume fraction of i. V_i is the molar volume of the pure liquid.

1.4 Factors Affecting Thermal Conductivity of Inorganic Nonmetals

1.4.1 Temperature

After summarizing the measurement results of the thermal conductivity of a large number of dielectric crystals and amorphous solids, Eueken [26] concluded that (i) the thermal conductivity of single crystals increases with the decrease of temperature, while the thermal conductivity of amorphous solids shows inverse trend; (ii) the thermal conductivity is inversely proportional to the absolute temperature of the crystal; and (iii) the thermal conductivity of amorphous solids is roughly proportional to the specific heat.

Except for lead oxide, the thermal conductivity of inorganic non-metallic crystals is almost proportional to the reciprocal of absolute temperature above room temperature [10]:

$$k = \frac{A}{T};\ k = \frac{A}{T} + B \tag{1.42}$$

where T is the absolute temperature, and A and B are constants determined experimentally.

For inorganic amorphous, the thermal conductivity increases approximately in direct proportion to the temperature [27]:

$$k = CT \tag{1.43}$$

where T is the absolute temperature, and C is the constant determined experimentally.

For the mixture of inorganic crystal and amorphous, the relationship between thermal conductivity and temperature can be expressed as

$$k = \frac{1}{AT + B + C/T} \tag{1.44}$$

1.4.2 Pressure

Under pressure, the correlation between thermal conductivity and pressure can be divided into increasing, decreasing, independent, and abnormal trends.

For example, the thermal conductivity of an object can increase sharply under pressure. This is because the strain generated by pressure enhances the atomic interaction and compresses the bond, changing the phonon dispersion, thus greatly increasing the propagation speed of phonons. Such enhancement is nonlinear in some cases, which can be attributed to the combined effect of decreasing phonon relaxation time and increasing phonon group velocity [28].

In addition, the thermal conductivity of the object can also be reduced under pressure, because phonon anharmonicity and phonon softening induced by pressure increase [29]. The first-principle calculation shows that the reduced thermal conductivity under pressure is mainly due to the stronger cubic anharmonic interaction, large mass ratio, and significant acousto-optic frequency gap [30].

In some cases, the thermal conductivity is independent of the pressure, which may be caused by the strong electron correlation effect driven by the electronic topological transition [31].

Several mechanisms have been proposed to understand abnormal thermal conductivity changes under pressure. The abnormal decrease of thermal conductivity of some materials under pressure can be ascribed to the large phonon frequency gap of materials under high pressure. The contribution of the inherent three-phonon scattering process is smaller than that of other cases, and the complex scattering process between more phonons dominates and increases the overall phonon scattering [32]. In the case of another non-monotonic behavior, the thermal conductivity first increases and then decreases with the increase in pressure. The possible mechanism of this behavior is the competitive scattering process of three phonons interacting with four phonons under high pressure [33] or the interaction between group velocity and phonon relaxation time under pressure [34]. When some rare earths show different pressure dependences of thermal conductivity, the pressure dependence is determined by the competition between the enhancement of phonon group velocity and the reduction of phonon relaxation time [35].

1.4.3 Crystal Structure

The more complex the crystal structure, the lower the thermal conductivity. For example, the structure of magnesia alumina spinel ($MgAl_2O_4$) is similar to that of alumina (Al_2O_3) and magnesium oxide (MgO), and their thermal solubility, thermal expansion coefficient, and elastic modulus are similar. However, due to the complex structure of the former, its thermal conductivity is much lower than the latter two. In addition, the mean free path of phonons of materials with complex structures is easy to approach or reach its minimum limit value, that is, the lattice size value, at high temperatures to obtain lower thermal conductivity.

The structural integrity and regularity of polycrystals are worse than that of single crystals. In addition, the influence of impurities and distortion on the grain boundary increases the phonon scattering, which is more significant at higher temperatures. In different crystal axis directions, the thermal conductivity of single crystals is also different, with anisotropy, and the phonon scattering is different. The difference of thermal conductivity of single crystals in different crystal axis directions decreases with the increase in temperature, because anisotropic crystals tend to improve or enhance their symmetry with the increase in temperature.

1.4.4 Thermal Resistance

As we all know, the smaller the thermal resistance, the greater the thermal conductivity. The main factor affecting thermal resistance is Debye temperature. The Debye temperature is closely related to atomic weight, theoretical density, and compressibility. The total thermal resistance in the crystal is

$$r = \frac{AT^m}{\left(e^{\frac{\Theta}{2T}} - 1\right)} + BNT^n + 1/(VLT^3) \tag{1.45}$$

where A is the atomic weight, Θ is the Debye temperature, ρ is the theoretical density, and X is the compression coefficient. Generally, the smaller the theoretical density is, the greater the Debye temperature is. The greater the Debye temperature, the smaller the thermal resistance. Therefore, lighter substances usually have higher thermal conductivity. The smaller the compression coefficient or the larger the Young's modulus, the higher the Debye temperature. The higher the Debye temperature, the smaller the thermal resistance. Therefore, materials with higher binding energy usually have higher thermal conductivity. The smaller the atomic weight, the higher the Debye temperature. Therefore, materials with large atomic weights have high thermal conductivity.

1.4.5 Others

Defects and impurities have a great influence on the thermal conductivity of materials, which is determined by the phonon heat conduction mechanism of dielectric crystals [10]. They are the center of phonon scattering, which will reduce the mean free path and thermal conductivity of materials [7]. Because the thermal conductivity of gas in the porosity is far lower than that of materials, porosity always reduces the thermal conductivity of the materials. Peierls-Boltzmann [36] revealed the process of strain affecting thermal conductivity and found the power law scaling relationship between thermal conductivity and temperature and strain. Strain first affects the speed of phonon propagation and then affects the relaxation time, while temperature only affects the relaxation time.

The experimental work of Krupskii and Manzhelli on the unconstrained argon sample revealed that the thermal conductivity has a deviation in addition to the inverse temperature dependence predicted theoretically [37]. They attributed the bias to the higher-order four-phonon interaction, while Clayton and Batchelder attributed it to the thermal expansion effect [38]. Dugdale and MacDonald assumed that micro-area lattice expansion would occur due to thermal expansion resulting from the temperature gradient [39]. For example, for a material with a positive thermal expansion coefficient, the relative expansion of the hotter region and the compression of the cooler region produces additional heat transfer sources, which further reduce the thermal conductivity.

References

1 Zhao, A.Z., Wingert, M.C., Chen, R. et al. (2021). Phonon gas model for thermal conductivity of dense, strongly interacting liquids. *Journal of Applied Physics* 129 (23): 235101.

2 Chapman, S. and Cowling, T.G. (1952). *The Mathematical Theory of Nonuniform Gases*. New York: Cambridge Univ. Press.

3 Hirschfelder, J.O., Bird, R.B., and Spotz, E.L. (1948). The transport properties for non-polar gases. *The Journal of Chemical Physics* 16 (10): 968–981.

4 Maloka, I.E., Hashim, E.T., and Ibrahim, S.Y. (2004). Effect of molecular weight on thermal conductivity of gases. *Petroleum Science and Technology* 22 (11–12): 1507–1511.

5 Peierls, R. (1929). The kinetic theory of thermal conduction in crystals. *Annalen der Physik* 3 (8): 1055–1101.

6 Lv, W. and Henry, A. (2016). Examining the validity of the phonon gas model in amorphous materials. *Scientific Reports* 6: 37675.

7 Chen, Y., Lukes, J.R., Li, D. et al. (2004). Thermal expansion and impurity effects on lattice thermal conductivity of solid argon. *The Journal of Chemical Physics* 120 (8): 3841–3846.

8 Klemens, P.G. and Simon, F.E. (1951). The thermal conductivity of dielectric solids at low temperatures (Theoretical). *Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences* 208 (1092): 108–133.

9 Kittel, C. (1956). *Introduction to Solid State Physics*, 2e.

10 Kingery, W.D. and McQuarrie, M.C. (1954). Thermal conductivity: I, concepts of measurement and factors affecting thermal conductivity of ceramic materials. *Journal of the American Ceramic Society* 37 (2): 67–72.

11 Wingert, M.C., Zheng, J., Kwon, S. et al. (2016). Thermal transport in amorphous materials: a review. *Semiconductor Science and Technology* 31 (11): 113003.

12 Einstein, A. (1911). Über den Einfluß der Schwerkraft auf die Ausbreitung des Lichtes. *Annalen der Physik* 340 (10): 898–908.

13 Slack, G.A. (1979). The thermal conductivity of nonmetallic crystals. In: *Solid State Physics*, vol. 34 (ed. H. Ehrenreich, F. Seitz, and D. Turnbull), 1–71. Academic Press.

14 Cahill, D.G., Watson, S.K., and Pohl, R.O. (1992). Lower limit to the thermal conductivity of disordered crystals. *Physical Review B: Condensed Matter* 46 (10): 6131–6140.

15 Agne, M.T., Hanus, R., and Snyder, G.J. (2018). Minimum thermal conductivity in the context of diffuson-mediated thermal transport. *Energy & Environmental Science* 11 (3): 609–616.

16 Feldman, J.L., Kluge, M.D., Allen, P.B. et al. (1993). Thermal conductivity and localization in glasses: numerical study of a model of amorphous silicon. *Physical Review B* 48 (17): 12589–12602.

17 Kittel, C. (1949). Interpretation of the thermal conductivity of glasses. *Physical Review* 75 (6): 972–974.

18 Jamieson, D.T. (1979). Thermal conductivity of liquids. *Journal of Chemical and Engineering Data* 24 (3): 244–245.

19 Bridgman, P.W. (1923). The thermal conductivity of liquids. *Proceedings of the National Academy of Sciences* 9 (10): 341–345.

20 Huber, M.L., Perkins, R.A., Friend, D.G. et al. (2012). New international formulation for the thermal conductivity of H_2O. *Journal of Physical and Chemical Reference Data* 41 (3): 033102.

21 van Elk, E.P., Arendsen, A.R.J., and Versteeg, G.F. (2009). A new flowsheeting tool for flue gas treating. *Energy Procedia* 1 (1): 1481–1488. https://doi.org/10.1016/j.egypro.2009.01.194.

22 Harminder, M.P.S.a. (1974). Thermal Conductivity of binary liquid mixture. *Chemical Physics Letters* 25 (3): 445–446.

23 Harminder, M.P.S.a. (1974). Thermal conductivity of binary liquid mixtures. 27 (3): 448–449.

24 Rowley, R.L. (1982). A local composition model for multicomponent liquid mixture thermal conductivities. *Chemical Engineering Science* 37 (6): 897–904.

25 Maloka, I.E. (2007). Thermal conductivities of liquid mixtures. *Petroleum Science and Technology* 25 (8): 1065–1072.

26 Eucken, A. (1911). Über die Temperaturabhängigkeit der Wärmeleitfähigkeit fester Nichtmetalle. *Annalen der Physik* 339 (2): 185–221.

27 Berman, R. and Simon, F.E. (1951). The thermal conductivities of some dielectric solids at low temperatures (Experimental). *Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences* 208 (1092): 90–108.

28 Sun, Z., Yuan, K., Zhang, X. et al. (2018). Pressure tuning of the thermal conductivity of gallium arsenide from first-principles calculations. *Physical Chemistry Chemical Physics* 20 (48): 30331–30339.

29 Zhou, Y., Dong, Z.-Y., Hsieh, W.-P. et al. (2022). Thermal conductivity of materials under pressure. *Nature Reviews Physics* 4 (5): 319–335.

30 Wang, L., Tian, F., Liang, X. et al. (2019). High-pressure phases of boron arsenide with potential high thermal conductivity. *Physical Review B* 99 (17).

31 Saha, P., Mazumder, A., and Mukherjee, G.D. (2020). Thermal conductivity of dense hcp iron: Direct measurements using laser heated diamond anvil cell. *Geoscience Frontiers* 11 (5): 1755–1761.

32 Lindsay, L., Broido, D.A., Carrete, J. et al. (2015). Anomalous pressure dependence of thermal conductivities of large mass ratio compounds. *Physical Review B* 91 (12): 121202(R).

33 Ravichandran, N.K. and Broido, D. (2019). Non-monotonic pressure dependence of the thermal conductivity of boron arsenide. *Nature Communications* 10 (1): 827.

34 Yuan, K., Zhang, X., Tang, D. et al. (2018). Anomalous pressure effect on the thermal conductivity of ZnO, GaN, and AlN from first-principles calculations. *Physical Review B* 98 (14): 144303.

35 Lan, G., Ouyang, B., and Song, J. (2015). The role of low-lying optical phonons in lattice thermal conductance of rare-earth pyrochlores: a first-principle study. *Acta Materialia* 91: 304–317.

36 Bhowmick, S. and Shenoy, V.B. (2006). Effect of strain on the thermal conductivity of solids. *The Journal of Chemical Physics* 125 (16): 164513.

37 Krupskii, I.N. and Manzhely, V.G. (1967). Thermal conductivity of solid argon. *Physica Status Solidi B* 24 (1): K53–K56.

38 Clayton, F. and Batchelder, D.N. (1973). Temperature and volume dependence of the thermal conductivity of solid argon. *Journal of Physics C: Solid State Physics* 6 (7): 1213.

39 Dugdale, J.S. and Macdonald, D.K.C. (1955). Lattice thermal conductivity. *Physical Review* 98 (6): 1751–1752.