5.2 Lattice thermal conductivity

The lattice component of thermal conductivity (k) refers to the conduction of heat via the vibrations of lattice ions in a solid. The study of the underlying physics of the heat-conduction process can provide a deep and detailed understanding of the nature of lattice vibrations in solids. The thermal conductivity of a solid is one of its most fundamental and important physical parameters. Understanding thermal conductivity is important to the thermal management of mechanical, electrical, chemical, and nuclear systems. Thermal conductivity also relates to thermal barriers and thermal insulating materials.

5.2.1 Inverse proportionality to distance

The law of heat conduction, also known as Fourier's law, states that the rate of heat transfer through a material is proportional to the negative gradient of temperature and area through which the heat flows. Fourier's law can be written as:

$$q = -k(dT/dx) \qquad (5.2.1.1)$$

where q is the heat flux, dT is the temperature (T) difference, and dx is area. This can also be written in term of distance (x) and T gradient (ΔT):

$$q = -k(\Delta T/x) \qquad (5.2.1.2)$$

However, the origin of the inverse proportionality to the distance is not obvious. An example of the lack of relation between q and x, related to the heat transfer between surfaces A and B in space, is illustrated as follows:

$$q = -\sigma \Delta T \cdot T_{AB}^3 \qquad (5.2.1.3)$$

where q is a function of ΔT but not of x. Thus, the thermal conductivity of space [k(x)] cannot be defined. The inverse proportionality to the distance is the central issue of the lattice component of thermal conductivity.

5.2.2 Thermal resistance

At the interface region of nonmetals, the electron contribution to the heat flux can be neglected with respect to the lattice contribution. In a perfectly crystalline nonmetal, the heat flux can be expressed in terms of levels of vibrational energy, also known as phonons. A phonon incident on the interface has a certain probability of being transmitted to the other side. The probability of transmission depends on the phonon mode, its polarization, wave vector and frequency (Antidormi and Colombo, 2018). The net heat transfer across the interface is due to the net balance of incoming, transmitting and reflected phonon flux (Swartz and Pohl, 1989; Chen, 2005). In the case of two materials with unlike thermal transport properties, a thermal bias occurs at the meeting interface of the two materials. This results in a sudden drop in temperature ΔT at the interface region. The effect of thermal resistance is illustrated in Fig.1.

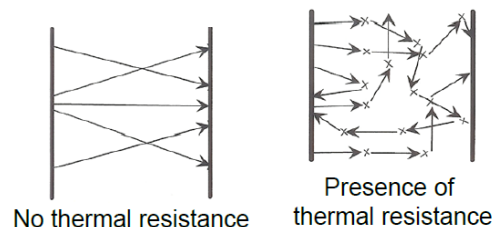No thermal resistance   Presence of thermal resistance

Fig.1. Diagram of heat transfer across an interface of a homogenous thermal property, without thermal resistance, (left) and inhomogeneous thermal properties, with thermal resistance, (right).

5.2.3 Mean free path

The mean free path (ℓ) is a property defined by the distance a particle can travel without colliding with any obstacle ($q \propto \ell$). In quantum mechanism, the lattice component of thermal conductivity can be written as:

$$k \propto nc\nu\ell \qquad (5.2.3.1)$$

where n is the number of phonons per volume, c is the heat capacity per phonon, and ν is the average velocity of phonons. The heat capacity per volume is defined as C=nc.

5.2.4 Thermal resistance in lattice thermal conductivity

In a harmonic oscillation, the atomic force is perfectly proportional to the displacement while the propagating lattice vibration goes straightly and is not attenuated. Intersecting oscillations, or waves, may also continue straightly without interacting or causing thermal resistance. The energy potential of the harmonic oscillator is illustrated in Fig.2.
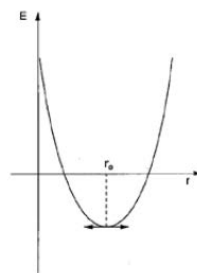

Fig.2. Diagram of harmonic oscillation, where interacting oscillations no do interact, illustrated in a potential well. At temperature (T), the potential energy (E) extends to higher distances (r).

Thermal resistance occurs due to defects in the lattice (i.e., vacancy, impurity, dislocation, stacking fault). In this case, the thermal resistance is relatively significant at low temperatures and thus not essential for geophysical applications. Thermal resistance may also occur from anharmonicity of the atomic potential. The force between atoms is not proportional to the displacement, which is also the cause of thermal expansion. This case is significant at high temperatures and for geophysical applications. The energy potential of the anharmonic oscillator is illustrated in Fig.3.
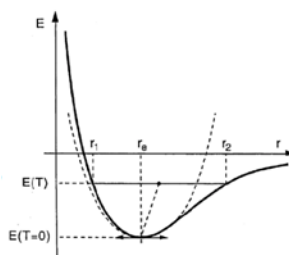

Fig.3. Diagram of anharmonic oscillation, where interacting oscillations interact, illustrated in a potential well. At temperature (T), the potential energy (E) is almost null at higher distances (r).

5.2.5 Atomic vibration in the anharmonic potential

In the case of the anharmonic oscillator, the atomic potential U(x) as a function of the displacement from the equilibrium position x (referred to as E and r in Fig.3. respectively) can be expressed as:

$$U(x) = a_1 x^2 + a_2 x^3 \qquad (5.2.5.1)$$

where a_1 and a_2 are constants that will be solved for. If it were harmonic, the second term would be neglected. In that case, the equation of motion for the atom is simplified to:

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$$m\frac{d^2x}{dt^2} = F = -\frac{dU}{dx} = -2a_1 x \qquad (5.2.5.2)$$

where m is the mass of the atom. The solution to this equation is $x(t) = A\cos(\omega t)$, where $\omega = \sqrt{2a_1/m}$. In the case of the anharmonic oscillation, the second term of equation 5.2.5.1 is important and leads to the following equation of motion:

$$m\frac{d^2x}{dt^2} = F = -\frac{dU}{dx} = -2a_1 x - 3a_2 x^2 \qquad (5.2.5.3)$$

Using the previous definition of ω and $\phi = -3a_2/m$, the following expression can be written:

$$m\frac{d^2x}{dt^2} = F = -\frac{dU}{dx} = -\omega^2 x - \phi x^2 \qquad (5.2.5.4)$$

Here, we assume a much smaller contribution of the higher-order term $|\omega^2 x| \gg |\phi x^2|$. For the first approximation, the solution of the previous relationship is assumed to have a formula with a slightly different angular frequency ω', $\omega^2 \gg |\omega^2 - \omega'^2|$ such that $x(t) = B\cos(\omega' t)$. Then, modifying the previous equations accordingly gives:

$$\frac{d^2x}{dt^2} + \omega'^2 x = -(\omega^2 - \omega'^2)x + \phi x^2 \qquad (5.2.5.5)$$

Substitution for x(t) gives:

$$\frac{d^2x}{dt^2} + \omega'^2 x = -(\omega^2 - \omega'^2)B\cos(\omega' t) + \phi(B\cos(\omega' t))^2 =$$
$$= -(\omega^2 - \omega'^2)B\cos(\omega' t) + \phi B^2(\cos(2\omega' t) + 1)/2 \qquad (5.2.5.6)$$

The solution to this equation has the form $x_a(t) = C_1\cos(\omega' t) + C_2\cos(2\omega' t) + C_0$. Substituting this solution back into the previous equation gives:

$$\frac{d^2x}{dt^2} + \omega'^2 x$$
$$= -2\omega'^2 C_2\cos(2\omega' t) - \omega' C_1\cos(\omega' t) + \omega'^2 C_2\cos(2\omega' t) + \omega' C_1\cos(\omega' t) \qquad (5.2.5.7)$$
$$+ \omega'^2 C_0$$
$$= -(\omega^2 - \omega'^2)B\cos(\omega' t) + \phi B^2(\cos(2\omega' t) + 1)/2$$

Where the $\cos(2\omega' t)$ term can be written as $-3\omega'^2 C_2 = \phi B^2/2$, and the $\cos(\omega' t)$ term can be written as $0 = -(\omega^2 - \omega'^2)B$. Since $\omega^2 - \omega'^2 \approx 0$, then B≠0. Thus, one solution to the anharmonic oscillation is $x_a(t) = C_1\cos(\omega' t) + \frac{\phi B^2}{6\omega'}\cos(2\omega' t) + \frac{\phi B^2}{2\omega'^2}$. Assuming a similarity with the solution of 5.2.5.4, then $C_1 \approx B$ and $x_a(t) = B\cos(\omega' t) + \frac{\phi B^2}{6\omega'}\cos(2\omega' t) + \frac{\phi B^2}{2\omega'^2}$. Then, the higher term (second one in previous solution) of the potential produces a higher harmonic oscillation. The amplitude of the harmonic oscillation increases with the amplitude squared of the base wave. When two waves with the same amplitude intersect, the amplitude at the intersection becomes twice larger, and the amplitude of the higher harmonics becomes four times larger. The intersection of waves produces a larger magnitude of higher harmonic oscillation.

5.2.6 Umklapp scattering

Scattering caused by phonon-phonon interactions is defined as the formation of a new lattice wave due to the intersection of two lattice waves. When two propagating waves intersect, the amplitude increases, and the new wave is generated and propagates in the opposite direction. This is defined as Umklapp scattering and is at the origin of the thermal resistance of lattice thermal conductivity. The difference between normal and Umklapp scattering is illustrated in Fig.4.
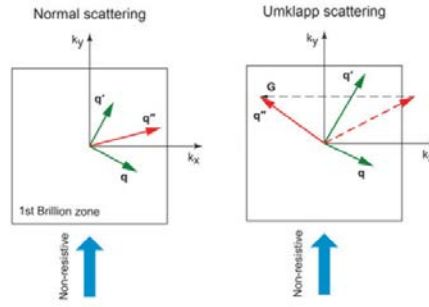
Fig.4. Diagram of normal scattering (left) and Umklapp scattering (right). The new wave generated q" is propagated in the opposite direction of q.

5.2.7 Temperature, pressure and structural dependance of lattice thermal conductivity

The amplitude of the harmonic oscillation is proportional to the amplitude of the original wave squared. The more intense the lattice vibration is, the higher the production of harmonic oscillations is. Thus, the rate of Umklapp scattering can be written as $\frac{\phi B^2}{6\omega'}/B = \frac{\phi B}{6\omega'}$, which suggests that k $\propto \left(\frac{\phi B}{6\omega'}\right)^{-1}$. The amplitude of the lattice wave is proportional to temperature, such that $\frac{\phi B}{6\omega'} \propto T$ and k $\propto \frac{1}{T}$. As temperature increases, the amplitude of the oscillation increases, the production of harmonic oscillation increases, the intensity of Umklapp scattering increases, the thermal resistance increases and thus the lattice thermal conductivity decreases. Therefore, the lattice thermal conductivity decreases with temperature. Thermal resistance (Umklapp scattering) and the thermal expansion are caused by the anharmonicity of lattice vibration. Thermal conductivity and thermal expansion have an opposite dependence. As atomic distances increases the anharmonicity increases and thermal conductivity decreases. A summary of this analysis is illustrated in Fig.5.

	Thermal conductivity	Thermal expansion
Temperature ↑	↓	↑
Compression ↑	↑	↓
Coordination number ↑	↓	↑

Fig.5. Summary of temperature, pressure (compression) and structure (coordination number) effects on thermal conductivity and thermal expansion.

For example, Fig.6. illustrates the thermal conductivity of olivine, wadsleyite and ringwoodite (Xu et al., 2004) as a function of temperature. It can be noted that thermal conductivity decreases with temperature and increases with pressure. The high-pressure phases have higher conductivity (k $\propto$ $Cvℓ$) and higher sound velocity.
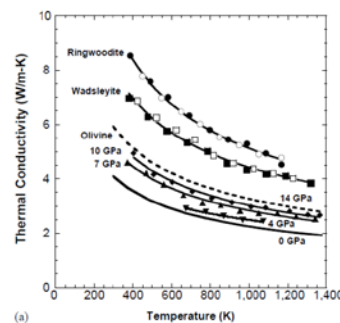

Fig.6. Thermal conductivity of Olivine, Wadsleyite, Ringwoodite as a function of temperature (Xu et al., 2004).

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Similarly, thermal conductivity decreases as the coordination number increases. The B1-B2 transition in KCl consists of the coordination number increasing from 6 to 8. This transition takes place around 20 kbar (2 GPa) which coincides with the drop of thermal conductivity, see Fig. 7. Thus, the atomic distance increases while the lattice thermal conductivity decreases.
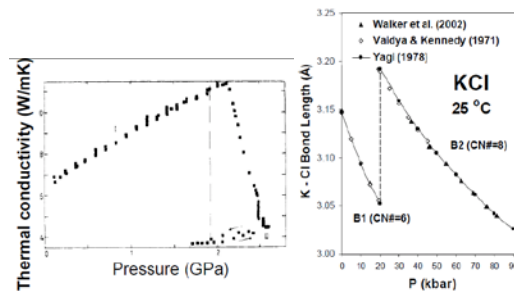

Fig.7. Thermal conductivity of KCL as a function of pressure (left) and structure of K-CL bonds as a function of pressure (right) at ambient temperature.

5.2.8 References

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