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Pressure dependence of the thermal conductivity and ultrasonic attenuation of non-metallic solids†

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Abstract. The pressure dependence of the thermal conductivity is determined for the case of a perfect crystal and for the extreme case of high point-defect concentrations. Also the dependence of the ultrasonic attenuation on pressure for a perfect crystal is considered. All expressions depend upon the Grueneisen constant and its derivatives.

Introduction

The dilatation dependence of the thermal conductivity and ultrasonic attenuation in dielectric materials is of potential interest in geophysics. Expressions for the dilatation dependence of these quantities are obtained. Since ultrasonic attenuation is also related to thermal conductivity, simultaneous measurements of the dilatation dependence of the thermal conductivity and of the attenuation of ultrasonic waves would yield the Grueneisen constant and its dilatation derivatives, and would thus provide information about the equation of state.

In these considerations it is assumed that no phase transitions occur in the range of dilatation under consideration. The dilatation dependence of thermal conductivity is calculated both for the case of a crystal free from defects and for the extreme case of high point-defect concentrations. The temperature range considered is the 'high temperature' region at or above the Debye temperature.

Thermal conductivity

When the temperature T is much greater than the Debye temperature θ, the thermal conductivity K of a crystal free from defects is given by

$$K \sim \frac{24}{10} \times \frac{4}{\gamma^2}\left(\frac{k}{h}\right) Ma \frac{\theta^3}{T},$$

where γ is the Grueneisen constant, k is the Boltzmann constant, a is the interatomic spacing, and h is Planck's constant (Klemens, 1958). In the same approximation

$$\theta \propto \frac{c}{a},$$

where c is the velocity of sound in the crystal. Thus, at a fixed temperature the thermal conductivity may be expressed as

$$K = \frac{Ac^3}{\gamma^2 a^2}, \tag{1}$$

where A is a constant combining all other factors.

Now we may take the velocity of sound to be

$$c = c_0(1 - \gamma(\Delta)\Delta),$$

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where Δ, the dilatation, is defined by

$$\Delta = \frac{V - V_0}{V_0} .$$

V and V_0 refer to the volumes of the compressed and uncompressed crystal respectively. c, γ, and a are all expressible as functions of Δ and

$$K = K(c(\gamma(\Delta), \Delta), a(\Delta)) .$$

One may express K in a power series expansion

$$K \approx K_0 + \frac{dK}{d\Delta}\bigg|_{\Delta=0} \Delta + \tfrac{1}{2}\frac{d^2K}{d^2\Delta}\bigg|_{\Delta=0} \Delta^2 ,$$

and letting

$$\gamma_0' \equiv \frac{d\gamma}{d\Delta}\bigg|_{\Delta=0}$$

one obtains

$$K \approx K_0\left\{1 - \left(3\gamma_0 + \tfrac{2}{3} + 2\frac{\gamma_0'}{\gamma}\right)\Delta + \tfrac{1}{2}\left[\left(3\gamma_0 + \tfrac{2}{3} + 2\frac{\gamma_0'}{\gamma}\right)^2 - 3\gamma_0^2 + 2\left(\frac{\gamma_0'}{\gamma_0}\right)^2 - 6\gamma_0' - 2\frac{\gamma''}{\gamma_0} + \tfrac{4}{9}\right]\Delta^2\right\} , \qquad (2)$$

In the case of strong point-defect scattering in addition to anharmonic scattering when $T > \theta$ an expression for the thermal conductivity K_d is given by Klemens (1960) to be

$$K_d \propto \frac{\theta^2}{\gamma}$$

which by a similar expansion yields

$$K_d \approx K_{d0}\left[1 - \left(2\gamma_0 + \tfrac{2}{3} + \frac{\gamma_0'}{\gamma_0}\right)\Delta + \tfrac{1}{2}D\Delta^2\right] ,$$

where

$$D \equiv \left[\left(2\gamma_0 + \tfrac{2}{3} + \frac{\gamma_0'}{\gamma_0}\right)^2 - 2(2\gamma_0' + \gamma_0^2) - \frac{\gamma_0''}{\gamma_0} + \left(\frac{\gamma_0'}{\gamma_0}\right)^2 + \tfrac{4}{9}\right] .$$

The terms of first order in Δ are comparable but not identical to the corresponding term for a perfect crystal.

Ultrasonic attenuation

The ultrasonic attenuation Γ of a perfect crystal is of the form

$$\Gamma = \frac{\gamma^2 \Omega^2 TK}{\rho c^5} \qquad (3)$$

where Ω is the angular frequency of the ultrasonic sound being attenuated, and ρ the density of the crystal (Woodruff and Ehrenreich, 1961). This expression applies when the wavelength is greater than the mean free paths of the thermal phonons and is thus appropriate at all but very low temperatures. Substituting Equation (1) into Equation (3) one obtains at a fixed temperature

$$\Gamma = B\frac{a}{c^2} \qquad (4)$$

where B stands for all terms which do not vary with dilatation. Using a procedure

similar to the one used earlier, one can write

$$\Gamma = \Gamma(c(\gamma(\Delta), \Delta), a(\Delta))$$

and obtain

$$\Gamma \approx \Gamma_0[1 + (2\gamma_0 + \tfrac{1}{3})\Delta + \tfrac{1}{2}(6\gamma_0^2 + \tfrac{4}{3}\gamma_0 - \tfrac{2}{9} + 4\gamma_0')\Delta^2] .$$

Note that Γ of Equation (4) is independent of γ_0, so that its dilatational derivative is independent of γ_0' to first order.

Determination of $\gamma_0'(\Delta)$ for sodium chloride

The only measurement of thermal conductivity of a simple crystal under large hydrostatic pressures appears to be that on sodium chloride by Bridgman (1932). He expressed the dilatation as a function of pressure in the form

$$-\Delta = \alpha p - \beta p^2$$

and found $\alpha = 41{\cdot}82 \times 10^{-7}$ cm^2 kg^{-1}, $\beta = 50{\cdot}4 \times 10^{-12}$ cm^4 kg^{-2}, while the pressure dependence of K was found to be

$$K = 8{\cdot}80 \times 10^{-3} + 3{\cdot}17 \times 10^{-7} p . \qquad (5)$$

Expressing Equation (2) to first order in pressure one has

$$K = K_0 + \left(3\gamma_0 + \tfrac{2}{3} + 2\frac{\gamma_0'}{\gamma_0}\right) K_0 \alpha p . \qquad (6)$$

Using a value of $\gamma_0 = 1{\cdot}61$ and comparing Equation (6) with Equation (5) one obtains $\gamma_0'(\Delta) = 2{\cdot}5$ (Leibfried, 1955).

Conclusion

The thermal conductivities for both pure and highly defected materials exhibit approximately the same fractional increase with dilatation; the fractional change is slightly smaller in the presence of extreme point-defects.

To first order in dilatation the thermal conductivity depends on both γ_0 and γ_0' while for the perfect material the attenuation of elastic waves depends only on γ_0. A simultaneous measurement of both quantities over a wide range of Δ could determine both γ_0 and γ_0'. Also, if γ_0 is known from thermal expansion measurements, a single measurement of the thermal conductivity could determine γ_0'. For dilatations of over 3% the linear dependence of the thermal conductivity with pressure can no longer be trusted.

While the present theoretical considerations may be of value in pointing out how the pressure dependence of the thermal conductivity or the ultrasonic attenuation could be used to study anharmonic properties of simple solids, one must be cautious in applying them to geophysical situations. Most rocks should be regarded as solids with large defect concentrations. We conclude that these should show pressure dependences similar to pure crystals. On the other hand, Bridgman found in some cases that the pressure coefficient of the thermal conductivity is strongly temperature dependent. This is not explained by our theory. Either one must invoke defects whose nature and concentrations are both temperature and strain sensitive, or one must consider the possibility that grain boundaries add to the thermal resistivity in a manner which depends on both pressure and temperature.

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