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Pressure Dependence of the Grüneisen Parameters of KCl, KI, LiF, NaCl, and RbBr

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A new expression has been obtained, using the Callaway integral equation for thermal conductivity, which relates the pressure dependence of thermal conductivities, average phonon velocities, and average Grüneisen parameters. Using this technique for the first time, we calculated the pressure dependence of the Grüneisen parameters of KCl, KI, LiF, NaCl, and RbBr at 310 K and zero pressure.

Introduction

The Grüneisen parameter, γ, is an important quantity in the study of anharmonic, dielectric, elastic, and thermal properties of solids. This quantity has been extensively studied both experimentally and theoretically for many solid materials. Grüneisen has shown by examining experimental data that γ remains constant over a wide range of temperatures for solids. However, it is expected that pressure will be the dependent variable, as phonon velocities are strongly pressure-dependent quantities (*1*).

Romain *et al.* (*2*) developed a theory for the calculation of γ for metals. This technique takes into consideration the volume dependence of Poisson's ratio and may be extrapolated to high pressures. Shankar and Singh (*3*) used the same technique to calculate the Grüneisen parameters of the alkali halides with NaCl structure. However, neither of the investigators extrapolated their calculations to high pressures.

Recently, we calculated the pressure dependence of Grüneisen parameters and thermal conductivities for silver chloride (*4*) and silver bromide (*5*), using the Callaway integral technique for the first time.

In the present work, using the Callaway integral equation for thermal conductivity, we derive a new equation which relates the isothermal pressure derivatives of the Grüneisen parameters with those of phonon velocities and thermal conductivities. The advantage of this work over our previous technique is that the new method does not require knowledge of the absolute values of the phonon velocities and thermal conductivities.

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Theory

The Callaway integral (*6*) for the thermal conductivity of a nonmetallic solid is given by

$$K = \frac{k}{2\pi^2 v}\left(\frac{kT}{\hbar}\right)^3 \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2 \tau^{-1}}\, dx \qquad (1)$$

where k, v, T, and θ are Boltzmann's constant, the average phonon velocity, the absolute temperature, and the Debye temperature, respectively. $\hbar = h/2\pi$, where h is Planck's constant. $x = \hbar\omega/kT$, where ω is the phonon frequency. τ^{-1}, the total inverse relaxation time, is the sum of all inverse relaxation times due to phonon scattering by the boundary, τ_B^{-1}; phonon scattering by point defects, τ_{pt}^{-1}, and phonon scattering by phonons, τ_{ph-ph}^{-1}:

$$\tau^{-1} = \tau_B^{-1} + \tau_{pt}^{-1} + \tau_{ph-ph}^{-1}.$$

τ_B^{-1} and τ_{pt}^{-1} are significant at fairly low temperatures, below 40 K. As the temperature is increased the phonon–phonon scattering, τ_{ph}^{-1}, dominates τ_B^{-1} and τ_{pt}^{-1}. At room temperature and above, τ_B^{-1} and τ_{pt}^{-1} are negligible compared to τ_{ph-ph}^{-1} (*5, 13*); therefore,

$$\tau^{-1} = \tau_{ph}^{-1}.$$

τ^{-1} is the phonon–phonon relaxation rate (*4*) given by

$$\tau^{-1} = A\omega^2 T = A\left(\frac{k}{\hbar}\right)^2 x^2 T^3 \qquad (2)$$

where A is given by (*7*)

$$A = \frac{4\pi k a \gamma^2}{\sqrt{2} M v^3}. \qquad (3)$$

Here a is the lattice constant, γ is the Gruneisen parameter, and M is the mass per unit cell.

Combining Eqs. (1)–(3), we obtain

$$K = \frac{M(k)(v)^2}{4\sqrt{2}\pi^3 a(\hbar)(\gamma)^2} \int_0^{\theta/T} \frac{x^2 e^x}{(e^x - 1)^2}\, dx. \qquad (4)$$

We now differentiate Eq. (4) with respect to the volume at constant temperature, using the Leibnitz rule, to obtain

$$\left(\frac{\partial K}{\partial V}\right)_T = \frac{-M}{4\sqrt{2}\pi^3 a^2}\left(\frac{\partial a}{\partial V}\right)_T \left(\frac{k}{\hbar}\right)\left(\frac{v}{\gamma}\right)^2 I\left(\frac{\theta}{T}\right) + \frac{2M}{4\sqrt{2}\pi^3 a}\left(\frac{k}{\hbar}\right)\left(\frac{v}{\gamma}\right)\left[\frac{\partial\left(\frac{v}{\gamma}\right)}{\partial V_2}\right] I\left(\frac{\theta}{T}\right) + \frac{M}{4\sqrt{2}\pi^3 a}\left(\frac{k}{\hbar}\right)\left(\frac{v}{\gamma}\right)^2 \left[\frac{\left(\frac{\theta}{T}\right)^2 e^{\theta/T}}{T(e^{\theta/T} - 1)^2}\left(\frac{\partial\theta}{\partial V}\right)_T\right].$$

Here $I(\theta/T)$ is the integral in Eq. (4). Dividing both sides of this equation by K, we obtain

$$\frac{1}{K}\left(\frac{\partial K}{\partial V}\right)_T = -\frac{1}{a}\left(\frac{\partial a}{\partial V}\right)_T + 2\left(\frac{\gamma}{v}\right)\left[\frac{\partial\left\{\left(\frac{\gamma}{v}\right)^{-1}\right\}}{\partial V}\right]_T + \frac{\left(\frac{\theta}{T}\right)^2 e^{\theta/T}}{T(e^{\theta/T} - 1)^2 I\left(\frac{\theta}{T}\right)}\left(\frac{\partial\theta}{\partial V}\right)_T. \qquad (5)$$

But since

$$\left(\frac{\partial\theta}{\partial V}\right) = -\frac{\theta}{V}\left(-\frac{\partial\ln\theta}{\partial\ln V}\right)_T = -\frac{\theta}{V}\gamma,$$

and after expanding the second term on the right hand side of Eq. (5), we obtain

$$\frac{1}{K}\left(\frac{\partial K}{\partial V}\right)_T = -\frac{1}{a}\left(\frac{\partial a}{\partial V}\right)_T + \frac{2}{v}\left(\frac{\partial v}{\partial V}\right)_T - \frac{2}{\gamma}\left(\frac{\partial\gamma}{\partial V}\right)_T - \frac{\left(\frac{\theta}{T}\right)^3 e^{\theta/T}}{V(e^{\theta/T} - 1)^2 I\left(\frac{\theta}{T}\right)}\gamma.$$

Now using

$$\left(\frac{\partial}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial}{\partial P}\right)_T,$$

we get

$$\frac{1}{K}\left(\frac{\partial K}{\partial P}\right)_T = -\frac{1}{a}\left(\frac{\partial a}{\partial P}\right)_T + \frac{2}{v}\left(\frac{\partial v}{\partial P}\right)_T - \frac{2}{\gamma}\left(\frac{\partial \gamma}{\partial P}\right)_T - \frac{\left(\frac{\theta}{T}\right)^3 e^{\theta/T}}{V(e^{\theta/T} - 1)^2 I\left(\frac{\theta}{T}\right)}\left(\frac{\partial V}{\partial P}\right)_T \gamma.$$

But we have

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

and

$$-\frac{1}{a}\left(\frac{\partial a}{\partial P}\right)_T = -\frac{1}{3V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{k_T}{3}$$

where k_T is the isothermal compressibility. Therefore,

$$\frac{1}{K}\left(\frac{\partial K}{\partial P}\right)_T = \frac{k_T}{3} + \frac{2}{v}\left(\frac{\partial v}{\partial P}\right)_T - \frac{2}{\gamma}\left(\frac{\partial \gamma}{\partial P}\right)_T + \frac{\left(\frac{\theta}{T}\right)^3 e^{\theta/T}\gamma k_T}{(e^{\theta/T} - 1)^2 I\left(\frac{\theta}{T}\right)}$$

or

$$\frac{1}{\gamma}\left(\frac{\partial \gamma}{\partial P}\right)_T = \frac{k_T}{2}\left[\frac{\left(\frac{\theta}{T}\right)^3 e^{\theta/T}\gamma}{(e^{\theta/T} - 1)^2 I\left(\frac{\theta}{T}\right)} + \frac{1}{3}\right] + \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T - \frac{1}{2K}\left(\frac{\partial K}{\partial P}\right)_T. \quad (6)$$

Results and Discussion

Using Eq. (6), we have calculated $(\partial\gamma/\partial P)_T$ for KCl, KI, LiF, NaCl, and RbBr at 310 K and zero pressure. Table I shows the results along with the different quantities used in our calculations. The values of θ and k_T are obtained from the "American Institute of Physics Handbook" (*8*). Values of γ, which are based on thermodynamic data, are from Smith and Cain (*9*). The quantities $(1/v)(\partial v/\partial P)_T$ are obtained from the pressure dependence of average phonon velocities. These, in turn, are calculated by using densities and the data on second-order elastic constants and their pressure derivatives (*10*). Phonon velocities at each pressure are first averaged over the acoustic polarization modes and then over different crystal directions (*5*). The values of $(1/K)(\partial K/\partial P)_T$ are obtained from Averkin *et al.* (*11*).

Our calculated value of $(\partial\gamma/\partial P)_T$ for NaCl is in good agreement with that obtained from the experimental work of Voronov and Grigorev (*12*), using (*4*)

$$\gamma_i = \frac{1}{3} + \frac{1}{K_T}\left(\frac{\partial \ln v_i}{\partial P}\right)_T$$

and

$$\gamma = (\tfrac{1}{3}\gamma_l^2 + \tfrac{2}{3}\gamma_t^2)^{1/2}$$

where the subscript *i* stands for l or t, the

TABLE I

CALCULATED ISOTHERMAL PRESSURE DERIVATIVES OF THE GRÜNEISEN PARAMETERS FROM EQ. (6) AND VARIOUS QUANTITIES USED FOR THEIR CALCULATIONS AT 310 K AND ZERO PRESSURE

	θ (K)	$I\left(\frac{\theta}{T}\right)$	K_T (10^{-3} kbar^{-1})	γ	$\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$ (10^{-3} kbar^{-1})	$\frac{1}{K}\left(\frac{\partial K}{\partial P}\right)_T$ (10^{-3} kbar^{-1})	$\left(\frac{\partial \gamma}{\partial P}\right)_T$ (10^{-3} kbar^{-1})
KCl	235	0.7462	5.200	1.49	6.843	0.047	−0.0179
KI	132	0.4237	9.200	1.53	12.569	0.105	−0.0481
LiF	732	2.0484	1.467	1.63	1.837	0.018	−0.0098
NaCl	321	1.0056	3.700	1.61	5.378	0.035	−0.0140
RbBr	131	0.4205	10.800	1.42	7.523	0.068	−0.0243

longitudinal or transverse modes, respectively. $(\partial\gamma/\partial P)_T$ for NaCl obtained in this way is -0.0115 kbar^{-1}. In order to further check the validity of our theory, we also calculated $(\partial\gamma/\partial P)_T$ for silver chloride by the technique developed in this work at zero pressure and 238 and 296 K. These values are -0.0127 and -0.0125 kbar^{-1}, respectively, which are also in good agreement with the value of -0.0194 kbar^{-1} which is based on the experimental work of Voronov and Grigorev as described above. It is worth noting that our calculated values of $(\partial\gamma/\partial P)_T$ at 238 and 296 K indicate that this quantity is independent of temperature for silver chloride, as it should be if γ is independent of temperature.

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