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Phonon conductivity of II-IV Group semiconductors

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Phonon conductivity of three different samples Mg_2Ge, Mg_2Si and Mg_2Sn of II–IV group is calculated in the temperature range 4–1000°K, 3–500°K and 4–1000°K respectively. Excellent agreement has been obtained between calculated and experimental value of the phonon conductivity in the entire temperature range of investigation. The reduced contribution of transverse and longitudinal phonon is also studied and it is found that the major heat carriers are the transverse phonons.

1. Introduction

The phonon conductivity of Mg_2Ge, Mg_2Si and Mg_2Sn was calculated by Martin (1972) to explain experimental results of the phonon conductivity of the above stated samples using Holland's model (Holland 1963, 1964) of two mode conduction of phonons. He used the Herring (1954) relations for the three phonon scattering relaxation rate in the entire temperature range which are valid at low temperatures only. At the same time, he could not get good agreement between calculated and experimental values of phonon conductivity. Later, Dubey (1974, 1976) calculated phonon conductivity of above samples using Sharma, Dubey and Verma model (Sharma *et al* 1971, Dubey & Verma 1971, Dubey 1971, 1973, Dubey & Verma 1973) and he obtained good results at high as well as at low temperatures. But he could not get good agreement in the vicinity of the conductivity maxima. Recently Joshi & Verma (1970) proposed a simple expression for the three phonon scattering relaxation rate which is based on Guthrie's limits (Guthrie 1966, 1971) for the temperature exponent of the three phonon scattering relaxation rate and it is applied successfully by several workers (Tiwari & Agrawal 1971, Tiwari *et al* 1971, Misho & Dubey 1976) to explain phonon conductivity of different samples. The four phonon processes (Pomeranchuk 1941, 1941a, 1942) are also playing an important role towards lattice thermal resistivity of a crystal at high temperatures. The previous calculations on the lattice thermal resistivity of the above stated samples do not include the contribution of the four phonon processes.

In the present work, we have calculated phonon conductivity of the above stated samples using the three phonon scattering relaxation rate expression proposed by Joshi & Verma (1970). The contribution of the four phonon processes is also included in the present calculations of the phonon conductivity of Mg_2Ge,

Mg_2Si and Mg_2Sn for the first time. The present calculations show excellent agreement between calculated and experimental values of phonon conductivity in the entire temperature range of investigation. We have also used a better dispersion relation given by $q = (w/v)(1 + rw^2)$ to calculate group and phase velocities inside the conductivity integral whereas Martin used $q = w/v$, which is a very crude approximation. (Terms are explained in section 2). The present work also includes a study of the reduced contribution of transverse and longitudinal phonons for their separate contributions towards total phonon conductivity. It is found that at high temperatures, the transverse phonons are the main heat carriers. The paper is divided into six sections. Section 2 deals with the phonon conductivity integral whereas section 3, 4 and 5 are devoted to the phonon conductivity of Mg_2Ge, Mg_2Si and Mg_2Sn respectively. Section 6 deals with the results and their discussions.

2 Phonon Conductivity Integral

The contribution of each branch of phonons towards total phonon conductivity K at any temperature T can be expressed as (Callaway 1959, Holland 1963)

$$K_i = (1/6\pi^2) \int \tau_{c,i}\, v_{qi}^3 (\hbar w)^2 / k_B T^2) e^{\hbar w/k_B T} (e^{\hbar w/k_B T} - 1)^{-2} q^2 dq \qquad (1)$$

where k_B is the Boltzmann constant, $\hbar$ is the Planck constant divided by 2π, v_{qi} is the group velocity, q is the phonon wave vector having frequency w, suffix i refers to the modes of phonons and τ is the combined scattering relaxation time and it can be expressed as

$$\tau_c^{-1} = \tau_B^{-1} + \tau_{pt}^{-1} + \tau_{3ph}^{-1} + \tau_{4ph}^{-1} + \tau_r^{-1}$$

where τ_B^{-1}, τ_{pt}^{-1}, τ_{3ph}^{-1}, τ_{4ph}^{-1} and τ_r^{-1} are the boundary scattering (Casimir 1938), point defect scattering (Klemens 1955), three phonon scattering (Joshi & Verma 1970), four phonon scattering (Pomeranchuk 1941, 1941a, 1942) and resonance phonon scattering (Kwock 1966, Griffins & Carruthers 1963, Kumar *et al* 1970, Kumar 1970) relaxation rates respectively. The used expression for these scattering relaxation rates are reported in table 1. In writing the above expression for K, the correction term due to the three phonon normal processes has been neglected due to its negligibly small contribution (Dubey & Verma 1972, Agarwal & Verma 1962, Dubey 1976, Callaway & Baeyer 1960) towards total phonon conductivity K. Martin used Holland's model to calculate phonon conductivity of above stated samples in which a crude approximation $q = w/v$ is used to calculate group and phase velocities. The above stated approximation does not make any difference between group and phase velocities of the phonon. Following Sharma *et al* (1971a), we have used a better dispersion relation

$$q = (w/v)(1 + rw^2) \qquad \ldots (2)$$

Table 1. The scattering relaxation rate expressions used in the present calculations L is the Casimir length of the sample, A is the point defect scattering strength, B's are the three-phonon scattering strengths, B_H and H are the four-phonon and resonance scattering strengths respectively, V_S is the average phonon velocity, V is the atomic volume, f_i is the fractional concentration of the i-th species, m_i is the mass of the i-th species, m is the mass of the host lattice atom, $f_0(T)$ and $f(T)$ are the population of the ground state and next higher energy state, $F(q)$ is the form factor, r_0 is the average radius of donor orbit.

Scattering processes	Expression		Remarks
Boundary scattering	$\tau_B^{-1} = v_s/L$		Casimir (1938)
Point defect scattering	$\tau_{pt}^{-1} = Aw^4$; $A = \frac{V}{4\pi v_s^3} \sum_i f_i(1-m_i/m)^2$		Klemens (1955)
Resonance scattering	$\tau_r^{-1} = HF^4(q)w^2(f_0(T)+f(T))$		Kumar & Verma (1970)
	$F(q) = (1+r_0^2w^2/4v_s^2)^{-2}$		
Four-phonon scattering	$\tau_{4ph}^{-1} = B_H w^2 T^2$		Pomeranchuk (1941, 1941a, 1942)
Three-phonon scattering	$\tau_{3ph,T}^{-1}$	$\tau_{3ph,L}^{-1}$	Joshi & Verma (1970)
	$B_T wT^3$	$B_L w^2 T^3$	$T < T_1$
	$B_{T_1} wT^3$	$B_L w^2 T^3$	$T_1 < T < T_2$
	$B_{T_2} wT^2$	$B_{L_1} w^2 T^2$	$T_2 < T < T_3$
	$B_{T_3} wT$	$B_{L_2} w^2 T$	$T > T_3$
	$B_{T_1} = T_1 B_T$	$B_{L_1} = T_2 B_L$	
	$B_{T_2} = T_2 B_{T_1}$	$B_{L_2} = T_3 B_{L_1}$	
	$B_{T_3} = T_3 B_{T_2}$		

where r is a constant and can be calculated with the help of dispersion curve of the sample under study Using eq (2) and dividing the conductivity integral into two integrals corresponding to $0-\frac{1}{2}q_{max}$ and $\frac{1}{2}q_{max}-q_{max}$, the total lattice thermal conductivity of a crystal can be expressed as

$$K = K_T + K_L \qquad \ldots (3)$$

where K_T and K_L are the contributions of transverse and longitudinal phonons respectively and those contributions are given by

$$K_T = C_{T_1} \int_0^{\theta_1/T} x^4 e^x (e^x-1)^{-2}(1+R_1x^2T^2)^2(1+3R_1x^2T^2)^{-1}\tau_{c,T}\,dx$$

$$+C_{T_2} \int_{\theta_1/T}^{\theta_2/T} x^4 e^x (e^x-1)^{-2}(1+R_2x^2T^2)^2(1+3R_2x^2T^2)^{-1}\tau_{c,T}\,dx \qquad \ldots (4)$$

$$K_L = C_{L_1} \int_0^{\theta_3/T} x^4 e^x (e^x-1)^{-2} (1+R_1 x^2 T^2)^2 (1+3R_3 x^2 T^2)^{-1} \tau_{c,L}\, dx$$

$$+ C_{L_2} \int_{\theta_3/T}^{\theta_3/S} x^4 e^x (e^x-1)^{-2} (1+R_3 x^2 T^2)^2 (1+3R_3 x^2 T^2)^{-1} \tau_{c,L}\, dx \qquad (5)$$

where $C_{Ti} = (k_B/3\pi^2)(k_B T/\hbar)^3 (1/v_{Ti})$, $C_{Li} = (k_B/6\pi^2)(k_B T/h)^3 (1/v_{Li})$, $i = 1$ and 2, v_{T_1} and v_{T_2} are the transverse phonon velocities in the region $0 \to \frac{1}{2}q_{max}$ and $\frac{1}{2}q_{max} \to q_{max}$ of the first Brillouin zone respectively, v_{L_1} and v_{L_2} are the same for longitudinal phonons $\theta_i = \hbar w_i/k$; $i = 1, 2, 3$ and 4, w_1 and w_2 are the transverse phonon frequencies at $\frac{1}{2}q_{max}$ and q_{max} respectively, whereas w_3 and w_4 are the same for longitudinal phonons $R_i = \tau_i (k_B/\hbar)^2$, $i = 1, 2, 3$ and 4

The reduced contribution of transverse and longitudinal phonon can be expressed as

$$K_{R,T} = K_T/(K_L + K_L) \text{ and } K_{R,L} = K_L/(K_T + K_L)$$

3. Phonon Conductivity of Mg_2Ge

The constants related to the dispersion curve are calculated with the help of the experimental dispersion curve of Mg_2Ge measured by Chung *et al* (1965) We are interested in calculating the phonon conductivity of Mg_2Ge sample no 1 of Martin Therefore the resonance phonon scattering relaxation rate is ignored in the calculation due to the fact that Martin (1972) has reported sample no 1 displayed no neutral donor scattering The constants and parameters used in the calculations are listed in table 2 We know that at very low temperatures the entire thermal resistivity is due to the boundary scattering alone and one can calculate the Casimir (1938) length of the crystal at these temperatures Thus, $(\tau_{B,T}^{-1})$ and $(\tau_{B,L}^{-1})$ are found at 4°K by calculating the Casimir length of the crystal The point defect scattering strength A is adjusted at 8°K The three phonon scattering strength B_T and B_L are adjusted at 20°K (near the conductivity maxima).

Knowing the value of B_T and B_L and other constants, phonon conductivity of the said sample is calculated and it is found that the calculated values of the lattice thermal resistivity is smaller than the experimental values of it at high temperatures. It is due to the contribution of the four phonon processes The difference of calculated and experimental values of the lattice thermal resistivity is balanced by including the contribution of the four-phonon processes and four-phonon scattering strength B is calculated at 400°K The value of the critical temperature T_1, T_2 and T_3 is calculated using the Guthrie (1966) expression for the temperature exponent of the three-phonon scattering relaxation rate

Table 2. Constants and parameters used in the calculation of phonon conductivity of Mg_2Ge, Mg_2Si and Mg_2Sn.

Constants	Mg_2Ge	Mg_2Si	Mg_2Sn
v_{T1} (cm/sec)	$3{\cdot}9\times10^{5}$	$4\,6\times10^{5}$	$3\,19\times10^{5}$
v_{T2} (cm/sec)	$1{\cdot}8\times10^{5}$	$1\,4\times10^{5}$	$1\,16\times10^{5}$
v_{L1} (cm/sec)	$5{\cdot}8\times10^{5}$	$6{\cdot}4\times10^{5}$	$4\,30\times10^{5}$
v_{L2} (cm/sec)	$2\,4\times10^{5}$	$5\,1\times10^{5}$	$2\,05\times10^{5}$
θ_1 (°K)	140	154	90
θ_2 (°K)	210	224	118
θ_3 (°K)	306	392	176
θ_4 (°K)	210	254	138
T_1 (°K)	62	80	36
T_2 (°K)	80	103	46
T_3 (°K)	119	150	68
r_1 (sec^2)	$1{\cdot}240\times10^{-26}$	$3{\cdot}250\times10^{-26}$	$1{\cdot}788\times10^{-27}$
r_2 (sec^2)	$5\,534\times10^{-28}$	$6{\cdot}428\times10^{-28}$	$3{\cdot}776\times10^{-27}$
r_3 (sec^2)	$2\,660\times10^{-28}$	$8{\cdot}804\times10^{-29}$	$1{\cdot}388\times10^{-27}$
r_4 (sec^2)	$6\,518\times10^{-29}$	$1\,019\times10^{-29}$	$3{\cdot}363\times10^{-28}$
*a (cm^{-1})	$6{\cdot}387\times10^{-8}$	$6{\cdot}351\times10^{-8}$	$6{\cdot}763\times10^{-8}$
$(\tau_B^{-1})_T$ (sec^{-1})	$1{\cdot}77\times10^{6}$	$5\,68\times10^{5}$	$1\,21\times10^{6}$
$(\tau_B^{-1})_L$ (sec^{-1})	$2{\cdot}63\times10^{6}$	$7\,90\times10^{5}$	$1\,21\times10^{6}$
A (sec^3)	$1{\cdot}40\times10^{-41}$	$3\,90\times10^{-44}$	$5\,60\times10^{-44}$
B_H (sec deg^{-3})	$3{\cdot}0\times10^{-22}$	$2{\cdot}0\times10^{-24}$	$3{\cdot}0\times10^{-22}$
B_T (deg^{-4})	$3\,51\times10^{-21}$	$1{\cdot}86\times10^{-21}$	$1{\cdot}07\times10^{-20}$
B_L (sec deg^{-3})	$6\,2\times10^{-23}$	$1{\cdot}0\times10^{-24}$	$3\,23\times10^{-22}$
r_0 (Å)			40
4Δ (ov)			$5{\cdot}0\times10^{-4}$
ρ (gm cm^{-3})			3·592
η_{ex}			$2\,4\times10^{-19}$
H (sec^{-1} deg^{-2})			$2{\cdot}7\times10^{6}$

* a is the lattice constant.

Thus, knowing all the constants and parameters as reported in table 2 and using scattering relaxation rate expressions reported in table 1, phonon conductivity of Mg_2Ge is calculated in the entire temperature range 4–1000°K and is shown in figure 1. The reduced phonon conductivity $K_{R,T}$ and $K_{R,L}$ due to

transverse and longitudinal phonons respectively are also calculated in the entire temperature range of study and results are also shown in figure 1.

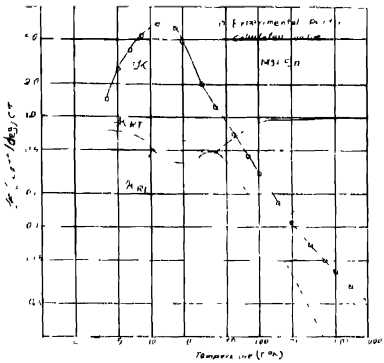

Fig. 1 Phonon conductivity of Mg_2Ge in the temperature range 4–1000°K. Solid line is the calculated value and circles are experimental points. $K_{R,T}$ and $K_{R,L}$ are the reduced contributions of transverse and longitudinal phonons respectively toward total phonon conductivity K.

4 Phonon Conductivity of Mg_2Si

The constants related to the dispersion curve are calculated with the help of experimental findings of Whitten *et al* (1965). This sample also does not contain resonance producing impurities and therefore the resonance scattering relaxation rate has been ignored in the calculation of phonon conductivity of this sample too. The Casimir length of the sample is calculated at 3°K. The point defect scattering strength A and three phonon scattering strength B_T and B_L are adjusted at 8°K and 20°K respectively similar to Mg_2Ge. The four-phonon scattering strength B_H has been calculated at 300°K. The critical temperatures T_1 etc. are also calculated similar to the Mg_2Ge. The constants and parameters used in the calculation are reported in table 2. The phonon conductivity of Mg_2Si and reduced contributions due to the transverse and longitudinal phonons are calculated in the temperature range 3–500°K and results are shown in figure 2.

5 Phonon Conductivity of Mg_2Sn

Martin & Denielson (1968) tried to explain the experimental data of phonon conductivity of Mg_2Sn measured by themselves on the basis of the Holland model of phonon conductivity. But they failed to get good agreement specially at low temperatures where the resonance scattering relaxation rate is playing

dominating role. They used ω^4--frequency dependence for resonance phonon scattering relaxation rate which is not valid for $\hbar\omega \gg 4\Delta$, where 4Δ is the energy separation between the ground state and the next higher energy state. In the present calculations, we have used modified expression of Kumar & Verma (1970) for the resonance scattering relaxation rate which has been successfully applied to explain phonon conductivity of number of samples having such

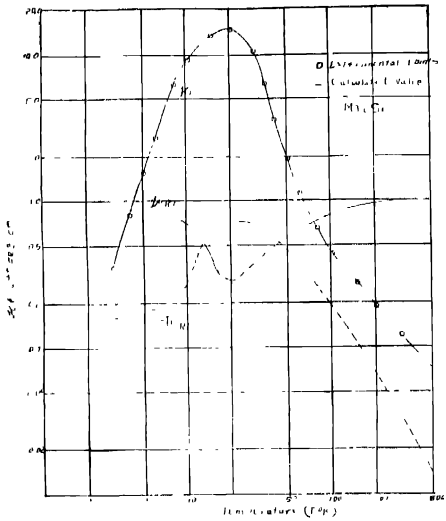

Fig. 2 Phonon conductivity of Mg_2Si the temperature range 3-500°K Solid line is the calculated value and circles the experimental points $K_{R\text{-}T}$ and $K_{R\text{-}L}$ are the reduced contributions of transverse and longitudinal phonons respectively towards total phonon conductivity K

impurities For the simplicity of calculations τ_B^{-1} and resonance scattering strength H are taken to be the same for both of the polarisation branches in the calculations and these two parameters have been adjusted at 4°K and 6°K respectively The constant H is treated as an adjustable parameter due to lack of data regarding the deformation potential etc The values of constants A, B_T, B_L and B_H are found similar to Mg_2Ge The constants related to the dispersion curve are calculated with the help of the dispersion curve of the sample reported by Kearney *et al* (1970) The other constants regarding to the resonance scattering are taken from the earlier report of Dubey (1974) The used constants and parameters are stated in table 2 Using constants and parameters reported in table 2 and including the resonance scattering relaxation rate as stated in table 1, phonon conductivity of Mg_2Sn is calculated in the entire temperature

range 4–1000°K and results are shown in figure 3. The reduced contributions due to each mode of phonons are also calculated in the above said temperature range and reported in figure 3.

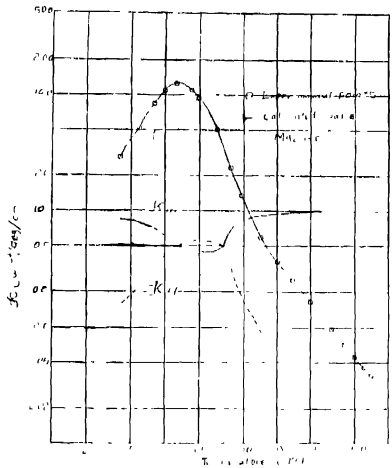

Fig. 3. Phonon conductivity of Mg_2Sn in the temperature range 4–1000°K. Solid line is the calculated value and circles are experimental points. $K_{R,T}$ and $K_{R,L}$ are the reduced contributions of transverse and longitudinal phonons respectively towards total phonon conductivity K.

6. Discussions

From figures 1, 2 and 3, one can see that agreement between calculated and experimental values of lattice thermal conductivity of all the three samples is excellent in the entire temperature range of study. At high temperatures, $K_{R,T}$ becomes unity which tells us that almost all the heat is carried by the transverse phonons alone at high temperatures i.e., one can conclude that at high temperatures, transverse phonons are major carriers of heat similar to the previous findings of Hamilton & Parrott (1969) for Ge based on the variational techniques. It is also similar to the previous report of Sharma *et al* (1971) and Dubey & Verma (1971, 1973) for Ge, Si, InSb and GaAs based on Sharma, Dubey and Verma model. At low temperatures, $K_{R,T} \gg K_{R,L}$ because the lattice thermal resistivity is mainly due to the boundary scattering alone at these temperatures. If one calculates K_T and K_L due to boundary scattering alone, he gets

$$K_T = C\,L/(3v_{T_1}^2) \quad \text{and} \quad K_L = C\,L/(6v_{L_1}^2),$$

where $C = (k_B/\pi^2)(k_BT/\hbar)^3$ which gives us

$$K_{R,T} = (1+\tfrac{1}{2}(v_{T_1}/v_{L_1})^2)^{-1} \text{ and } K_{R,L} = (1+\tfrac{1}{2}(v_{L_1}/v_{T_1})^2)^{-1}$$

The above stated expression tells us that the phonon conductivity depends on the square of velocity at very low temperatures The velocity of transverse phonon is less than the velocity of longitudinal phonon. Therefore, at low temperatures, $K_{R,T} \gg K_{R,L}$, which is similar to our results reported in figures 1, 2 and 3. At the same time, it is also similar to earlier report of Sharma *et al* (1971a).

At a little higher temperature towards the conductivity maxima, $K_{R,T}$ is tending to decrease with increase of temperature upto a certain temperature and opposite nature is observed for longitudinal phonons This nature of $K_{R,T}$ and $K_{R,L}$ stops at a certain temperatures and $K_{R,T}$ begins to increase and tends to unity at high temperatures and *vice versa* is also true for $K_{R,L}$. The contribution of transverse and longitudinal phonons in the kink region depends totally on the limit of integration of the conductivity integral and it is known as point defect scattering region because phonon conductivity of a sample is mainly governed by defects present inside the crystal lattice The θ_3 (upper limit of longitudinal phonon conductivity integral) is much greater than θ_2 (upper limit of the transverse phonon conductivity integral), therefore $K_{R,T} \ll K_{R,L}$ at these temperatures Similar nature is also observed by Sharma *et al* (1971a) based on the Holland model of two mode conduction of phonons

Thus, one can conclude that the present work shows excellent agreement between calculated and experimental values of phonon conductivity of Mg_2Ge, Mg_2Si and Mg_2Sn in the entire temperature range 4–1000°K, 3-500°K and 4–1000°K respectively The reduced contribution due to transverse and longitudinal phonons is also calculated and it is found that at high temperatures, almost all the heat is carried by transverse phonons alone At very low temperatures, the lattice thermal resistivity is governed by boundary scattering alone and contribution of each of the mode depends on the square of velocity of the particular mode In the vicinity of conductivity maxima, the lattice thermal resistivity is mainly due to point-defect scattering and it depends on the limits of the conductivity integral The contribution of the four-phonon processes towards total lattice thermal resistivity of II–IV group semiconductors is included for the first time

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