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Analysis of the Lattice Thermal Conductivity of Germanium

M. D. Tiwari and Bal K. Agrawal
Department of Physics, University of Allahabad, Allahabad-2, India

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The lattice thermal conductivity of germanium has been analyzed on the basis of the Callaway model in the temperature range 2–1100 °K. At high temperatures four-phonon processes are seen to play an important role in the determination of the thermal resistivity of germanium. In order to take account of the nonlinear behavior of the dispersion relations of the crystal lattice, the phonon wave vector is assumed to be certain simple but different functions of the phonon frequency for longitudinal and transverse branches. Three-phonon processes having different temperature dependences in the various temperature ranges have been used in the calculations. Very good agreement with the experimental results has been obtained.

I. INTRODUCTION

The need to include four-phonon processes in explaining the lattice thermal conductivity of solids at high temperatures has already been recognized.[1-6] The thermal resistivity of a solid due to four-phonon processes for longitudinal phonons was calculated by Pomeranchuk.[2]

As an exact treatment of the lattice thermal conductivity of solids is hampered by the lack of knowledge of the crystal vibration spectra and the anharmonic forces, and by the difficulty of obtaining the exact solution of the Boltzmann equation, a simplified phenomenological model due to Callaway[7] has been widely used[8-12] at low temperatures, to explain the thermal conductivity of a number of solids. In the Callaway model we use the Debye approximation, i.e., a linear relation between phonon frequency ω and phonon wave vector $\vec{q}$, which is satisfactory only for very long-wavelength phonons, which are the main carriers of heat at very low temperatures. At high temperatures the departure of the dispersion relation from linearity should be taken into account. Further, the different behavior of longitudinal and transverse phonons should also be allowed for. Some of these points have been considered by several workers[6,13-15] to explain successfully the thermal conductivity of a number of solids.

In earlier studies no proper distinction was made between the phonon group and phonon phase velocities, which is very important especially for the case of high-frequency phonons. In order to account for the departure of the dispersion relation of phonons from a linear one, a simple function of frequency, e.g., a quadratic function for the phonon wave vector, has been used in earlier analyses.[16,17] In the case of germanium the dispersive nature of the longitudinal and the transverse phonons is nearly accounted for if one takes quadratic and cubic forms of the frequency dependence of the wave vectors. Similar functions have been used in the case of GaAs[18] to explain the experimental lattice thermal conductivity. We may, thus, express the phonon group and phase velocities as the functions of the phonon frequency. The first Brillouin zone is taken to be spherically symmetric and the two transverse branches to be degenerate. To account for the resistance incurred by the three-phonon processes, Guthrie[19] has suggested that three-phonon relaxation times can be expressed by T^{-m}, where m is an exponent which is a function of the temperature T. The different values of the exponent m are chosen to determine the relaxation rates in the different temperature ranges.

II. THEORY

Callaway's[7] model for the lattice thermal conductivity can be expressed as a sum of two integral terms. The relative magnitudes of these two terms vary from substance to substance. The contribution of the second term, which is usually called the correction term, is seen to be negligible in comparison to the first one in a majority of cases.[6,14,15] But in some cases, like helium,[9] where the normal processes are dominant, it imparts a major contribution. In germanium the normal processes are not very important, and we therefore ignore the contribution of the second term. Further, we do not consider the contribution of optical phonons, which is likely to be negligible in the case of germanium. The Brillouin zone of Ge, which has a diamond-type structure, is assumed to be spherically symmetric. The contributions of the three polarization branches, one longitudinal and two transverse, are calculated separately to obtain the thermal conductivity.

The contribution of each branch is given by an expression of the form

$$K_i=\frac{1}{6\pi^2}\int v_{gi}^2\,\tau_{ci}\,\frac{\hbar^2\omega^2}{kT^2}\,\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}\,q^2\,dq\ , \qquad (1)$$

where i denotes the transverse or longitudinal branch and the integration is to be performed over the first Brillouin zone assumed to be spherical. v_{gi} denotes the group velocity of a phonon of the ith branch, and τ_{ci} is the total relaxation time, to be discussed later. The phonon frequencies of the two transverse branches are very nearly equal and are very different from the corresponding frequencies of the longitudinal ones for most of the directions of the wave vectors in the reciprocal lattice space. We therefore assume the contributions of the two transverse branches to be equal and denote them by the same expression.

To evaluate the integral of Eq. (1) one should know the appropriate dispersion relations. In a real solid ω is a function of the magnitude as well as the direction of the wave vector $\vec{q}$. For a spherical Brillouion zone ω is a function of $|\vec{q}|$. In the earlier analyses, an acoustic approximation, i.e., a linear relation between ω and $\vec{q}$, has always been assumed but this is not a good approximation, particularly at high frequencies. Experimental study of the dispersion curves of Ge shows that at small wavelengths the ω-q curve bends gradually towards the q axis and this bending is different for the longitudinal and transverse branches. One may therefore express q as a polynomial of ω. In order to avoid the involvement of a large number of unknown parameters in the expansion, we restrict ourselves to the consideration of a few of its terms.

In the case of germanium, the following frequency-dependent functions for the wave vector have been seen to be appropriate: For longitudinal phonons

$$q_L=\omega_L\,v_L^{-1}\,(1+\alpha\omega_L)\ , \qquad (2a)$$

and for transverse phonons

$$q_T=\omega_T\,v_T^{-1}\,(1+\beta\omega_T^2). \qquad (2b)$$

In these equations v_L and v_T are the low-frequency phonon velocities. The constants α and β are evaluated by using the fact that the total number of phonon states per polarization branch in a given crystal is equal to the number of lattice points available. If n is the number of lattice points per unit volume of the solid, it may be easily shown that

$$\alpha=(1/\omega_{mL})\,[(6n\pi^2)^{1/3}\,v_L/\omega_{mL}-1] \qquad (3a)$$

and

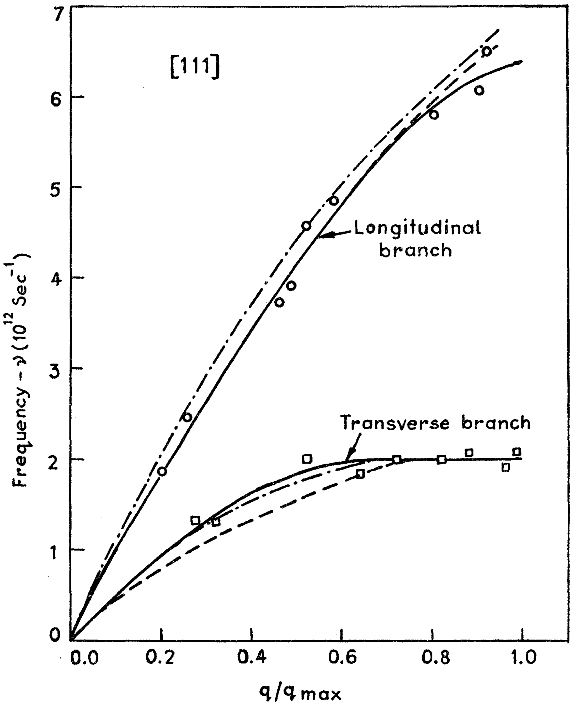

FIG. 1. Dispersion relations in Ge in the [111] direction. Squares and circles indicate the experimental results for transverse and longitudinal branches, respectively. The full curve denotes the theoretical fit by Brockhouse and Iyengar. The dashed curve shows a quadratic frequency dependence of the wave vector; the dot-dash curve, a cubic dependence.

$$\beta=(1/\omega_{mT}^2)\,[(6n\pi^2)^{1/3}\,v_T/\omega_{mT}-1]\ , \qquad (3b)$$

where the subscript m denotes the maximum value of the frequency of the branch concerned.

We have compared the dispersion relations calculated by using Eqs. (2a) and (2b) with the available experimental measurements from Brockhouse and Iyengar[20] along two symmetry directions, [111] and [100], in Figs. 1 and 2, respectively. The results, after using the cubic frequency dependence for the longitudinal branch and the quadratic dependence for the transverse ones, have also been shown. It is obvious that a quadratic dependence for longitudinal phonons and a cubic frequency dependence for the case of transverse ones are more near to the experimental results. Further, in view of the fact that these dependences involving the same values of the parameters α and β give good results in two entirely different symmetry directions, except in the case of [100] direction for transverse branch, it may also be true along other directions.

Using Eqs. (2), we may determine the phonon phase velocity V_p and phonon group velocity V_g and rewrite Eq. (1) as

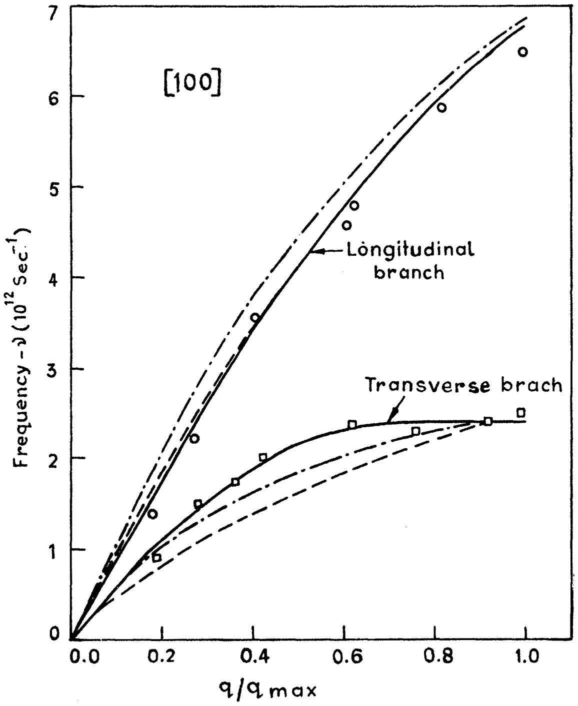

FIG. 2. Dispersion relations in Ge in the [100] direction. Squares and circles indicate the experimental results for transverse and longitudinal branches, respectively. Full curve denotes the theoretical fit by Brockhouse and Iyengar. The dashed curve shows a quadratic frequency dependence of the wave vector; the dot-dash curve, a cubic dependence.

$$K_i = \frac{k^4 T^3}{6\pi^2 \hbar^3} \int_0^{\Theta_i/T} \tau_{ci} \frac{V_g}{V_p^2} \frac{x^4 e^x}{(e^x - 1)^2}\, dx , \qquad (4)$$

where $x = \hbar\omega/kT$ and $\Theta_i = \hbar\omega_{mi}/k$.

This equation is different from that of Holland in that here we have used v_g/v_p^2 in place of $1/v$ taken by Holland. Although the dimensions of the expression v_p^2/v_g are those of velocity and are constant for a given phonon, it is not in fact the phonon velocity. According to Holland the phonon velocity v, used by him in place of v_p^2/v_g, is a sufficiently decreasing function of ω and is such that its averaged value for low-frequency phonons is more than twice the velocity of high-frequency phonons. Since v_g decreases more rapidly than v_p as ω increases, one cannot expect the value of v_p^2/v_g for high-frequency phonons to be much less than that of the low-frequency phonons. This expectation is supported by the form of expression for v_p^2/v_g obtained after using the simplified expressions of $|\vec{q}|$ given by Eqs. (2). It is seen that for germanium v_p^2/v_g is approximately constant for longitudinal phonons and for transverse phonons its value at $\omega = \omega_m$ is about 1.5 times the value at low frequencies.

The contributions to the lattice thermal conductivity from the longitudinal and transverse phonons may thus be written as

$$K_L = \frac{k^4 T^3}{6\pi^2 v_L \hbar^3} \int_0^{\Theta_L/T} \tau_{cL} \frac{x^4 e^x}{(e^x - 1)^2} \times \frac{(1 + \alpha' T x)^2}{1 + 2\alpha' T x}\, dx , \qquad (5a)$$

and

$$K_T = \frac{k^4 T^3}{6\pi^2 v_T \hbar^3} \int_0^{\Theta_T/T} \tau_{cT} \frac{x^4 e^x}{(e^x - 1)^2} \times \frac{(1 + \beta' T^2 x^2)^2}{1 + 3\beta' T^2 x^2}\, dx , \qquad (5b)$$

where $\alpha' = \alpha k/\hbar$ and $\beta' = \beta k^2/\hbar^2$.

III. PHONON-SCATTERING PROCESSES

A. Boundary Scattering

There are several phonon-scattering processes that lead to thermal resistivity in semiconductors. At very low temperatures the thermal conductivity can be very well explained on the basis of boundary scattering.[21-23] Casimir[22] has shown that the boundary-scattering relaxation time τ_b is given by L/v, where L is characteristic length associated with the specimen under study and v is the phonon velocity. The boundary scattering is important for low-frequency phonons and it is unimportant whether we use group velocity or phase velocity. It is sufficient to use a low-frequency value for v. Holland has used one weighted average value of v for all the polarization branches. We believe that it should be a better approximation if one uses the different low-frequency phonon velocities for different polarization branches. The characteristic length L is determined by the crystal dimensions and is assumed to be the same for all phonons. The value of L given by theory does not give good agreement with the experiment and therefore we treat L as an unknown parameter to which we assign a value that gives the best fit to the experimental results.

B. Scattering Due to Isotopes, Point Defects, etc.

At temperatures near the conductivity maximum, the scattering due to isotopes, point defects, etc., are the dominant relaxation processes. At such temperatures the high-frequency phonons are not excited to a large extent and it is reasonable to use $A\omega^4$ for the inverse relaxation time τ_{pt}^{-1}. This expression was initially obtained by Klemens[24] and is particularly valid for low-frequency phonons.[25,26]

C. Three-Phonon and Four-Phonon Processes

At high temperatures the three-phonon processes are the dominant relaxation processes. They can also be important at low temperatures and they give quite a substantial contribution to the thermal resistivity at the conductivity maximum. It is difficult to assign a simple and exact form for the three-phonon relaxation time $\tau_{3\text{ph}}$. However, it is evident that $\tau_{3\text{ph}}$ has different values for transverse and longitudinal branches. Many authors[13,27,28] have calculated approximate expressions for $\tau_{3\text{ph}}$. These results suggest that it is a good approximation to assume the frequency dependence of $\tau_{3\text{ph}}^{-1}$ as ω and ω^2 for transverse and longitudinal phonons, respectively. We ignore the exponential factor which appears in the expression of the relaxation rate of the umklapp processes and assume that the normal and umklapp processes have the same frequency dependence.

As a matter of fact, the thermal conductivity is not very sensitive to the frequency dependence of $\tau_{3\text{ph}}^{-1}$ at high temperatures. However, it is extremely sensitive to the temperature dependence of $\tau_{3\text{ph}}^{-1}$. Guthrie[19] has shown that a fixed temperature dependence of the type T^3 or T^4 is valid at low temperatures. He has suggested that $\tau_{3\text{ph}}^{-1}$ may be effectively taken to be proportional to T^m, where m is an exponent which has different values in different temperature ranges. At low temperatures the values of m for longitudinal and transverse phonons are 3 and 4, respectively, and tend to unity at high temperatures irrespective of the branch and the type of the processes (normal or umklapp). It is not possible to determine an exact variation of m with temperature. A possible approximation is to define a temperature range for which the values of m may be taken to be constant. This leads to a large number of parameters. These parameters are not arbitrary, because the relaxation-time expressions should be smoothly joined at temperatures which are common to the two adjacent ranges. Thus a single parameter can be associated with $\tau_{3\text{ph}}$ in one temperature range.

It is observed that at temperatures above 350 °K the calculated thermal conductivity, considering only three-phonon processes, does not decrease with the increase of temperature as rapidly as the experimental data. This suggests the occurrence of some extra phonon scattering processes whose effect increases more rapidly with temperature. Pomeranchuk[2] obtained in the first approximation a relaxation rate for longitudinal phonons which is quadratic in the phonon frequency and temperature, after considering the quartic term in the atomic displacements appearing in Taylor's expansion of the potential energy of a solid. Later Pomeranchuk[2] also showed that four-phonon processes may also occur due to the cubic term, not in the first order but in the second-order approximation of the perturbation theory. The relaxation time seen in the later case is frequency independent and smaller by a factor of $(\hbar\omega/\Theta)^2$ than the former. At high temperatures one may expect that the former mechanism is more operative than the later one. It has been seen that at high temperatures the major contribution to thermal conductivity is due to transverse phonons.[6,16,29] Pomeranchuk has made his calculations only for longitudinal phonons. As no calculation is available for the case of transverse phonons, we have used a relaxation rate for four-phonon processes similar to a longitudinal one. However, for the case of three-phonon processes Guthrie[19] has shown that for high-temperature phonons the forms of the relaxation times for longitudinal and transverse phonons are practically the same. Even for low-frequency phonons, not much difference in this dependence is observed. We presume that the same is true for the case of four-phonon processes. The relaxation time $\tau_{4\text{ph}}$ for four-phonon processes derived by Pomeranchuk[2] is given by

$$\tau_{4\text{ph}}^{-1} = B_H\,\omega^2 T^2 , \tag{6}$$

where B_H is a parameter.

The total relaxation time τ_c is thus given by

$$\tau_c^{-1} = \tau_B^{-1} + \tau_{pt}^{-1} + \tau_{3\,\text{ph}}^{-1} + \tau_{4\,\text{ph}}^{-1} . \tag{7}$$

In order to specify the polarization branches one has to apply suffix L or T to the various terms of Eq. (7).

The total lattice thermal conductivity K, after taking into account the degeneracy of the transverse branch, may be expressed as

$$K = K_L + 2K_T . \tag{8}$$

This expression differs from that of Holland[13] in the sense that only two terms are considered here against the three terms used by him.

IV. CALCULATIONS

The lattice thermal conductivity of germanium has been analyzed by numerically integrating Eqs. (5) after using the relaxation rate parameters listed in Table I. An exact estimation of the magnitude of the parameters requires simultaneous consideration of all the relaxation times and one has to perform complicated numerical integrations. We have tried to obtain the final set of parameters that lead to the best fit to the experimental results.[4,30,31] In Table II, we list all the parameters for the case of solid germanium. The values of Θ_L and Θ_T are similar to those of Holland.[13] V_L and V_T are obtained from the dispersion curves (Fig. 1) by drawing tangents at low frequencies. The number of lattice points per unit volume of germanium crystal has been calculated after taking into consideration that there are two atoms per lattice point. The values of α and β are obtained with the help of Eqs. (3a) and (3b).

The parameter A is usually evaluated by binomi-

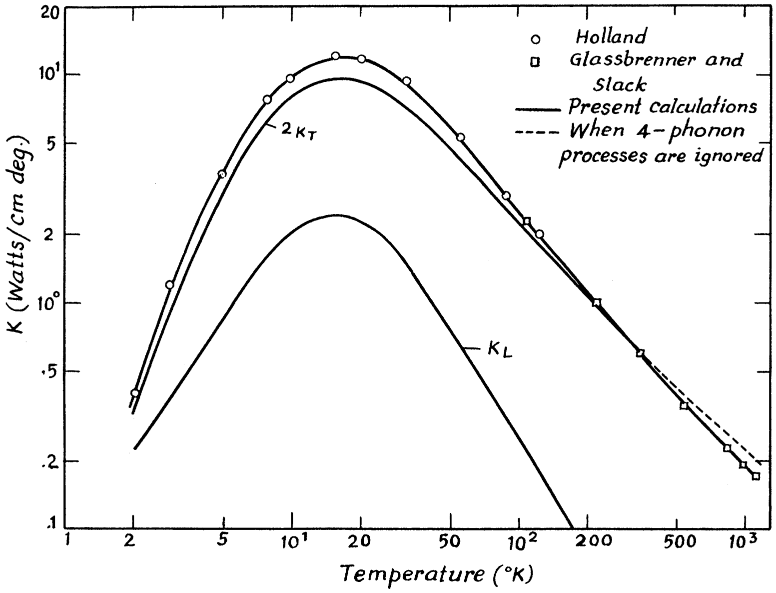

FIG. 3. Lattice thermal conductivity of germanium. The solid curve is the present analysis. The dashed curve shows the trend of the theoretical results in the absence of four-phonon processes.

ally expanding the expression for τ_c at low temperatures, treating τ_{pt}^{-1} as a small quantity compared to τ_b^{-1}. Such an expansion is not valid here due to the following considerations. First, the inequality $\tau_{pt}^{-1} < \tau_b^{-1}$ does not hold for all values of x lying within the integration limits. Second, a binomial expansion is not valid particularly when the upper limit of integration is replaced by infinity. What one should do is to evaluate the integrals numerically without taking any approximation of this type. However, binomial expansion of τ_c is valid at high temperatures where $\tau_{pt}^{-1} < \tau_{3\,ph}^{-1}$, and this inequality is satisfied for all values of x within the integration limits. The obtained value of A given in Table II leads to a good agreement with the experimental results.[4,30,31]

It is observed that up to 300 °K there is good agreement of the theory with the experimental results, but above this temperature agreement is only obtained if one includes four-phonon processes. The dotted curve in Fig. 3 shows the behavior of the thermal conductivity if four-phonon processes are ignored.

We have found that the contribution of the longitudinal phonons is small. At low temperatures K_L, the contribution due to longitudinal phonons is about one-fourth of the total contributions of the phonons of the two transverse branches. This result is not

TABLE I. Inverse relaxation times used in analyzing the lattice thermal conductivity of germanium. $B_{L_1} = 20B_L$; $B_{L_2} = 115B_{L_1}$; $B_{L_3} = 170B_{L_2}$; and B_T, B_{T_1}, B_{T_2}, and B_{T_3} are similarly related.

Type of scattering	Symbol	Longitudinal	Transverse	Temperature range (° K)
Boundary[a]	τ_b^{-1}	v_L/L	v_T/L	All temperatures
Isotope, etc.[b]	τ_{pt}^{-1}	$A\omega^4$	$A\omega^4$	All temperatures
Three-phonon[c]	$\tau_{3\,ph}^{-1}$	$B_L\omega^2T^4$	$B_T\omega T^4$	$T \leqslant 20$
		$B_{I_1}\omega^2T^3$	$B_{T_1}\omega T^3$	$20 \leqslant T \leqslant 115$
		$B_{I_2}\omega T^2$	$B_{T_2}\omega T^2$	$115 \leqslant T \leqslant 170$
		$B_{L_3}\omega^2T$	$B_{T_3}\omega T$	$T \geqslant 170$
Four-phonon[d]	$\tau_{4\,ph}^{-1}$	-	$B_H\omega^2T^2$	High temperatures

[a] Reference 22.

[b] Reference 24.

[c] References 26, 13, and 28; the temperature dependence of the three-phonon relaxation is based on the results of Ref. 19.

[d] Reference 2.

TABLE II. Paramaters used in the analysis.

a (atomic weight)	72.6
ρ (density)	5.46 gm cm^{-3} [a]
Θ_T	118 °K[b]
Θ_L	333 °K[b]
v_T	3.11×10^5 cm sec^{-1}
v_L	6.24×10^5 cm sec^{-1}
α	5.62×10^{-15} sec
β	6.43×10^{-27} deg sec^2
L[b]	0.32 (0.24) cm[c]
A	5.0×10^{-44} sec^3
B_T	1.73×10^{-12} deg^{-4}
B_L	3.50×10^{-24} sec deg^{-3}
B_H	2.91×10^{-23} sec deg^{-2}

[a] Reference 29.

[b] Reference 13.

[c] The bracketed value is used by Holland, the other by us.

unexpected, because there are two transverse branches, and the value of the phonon velocity v_T is smaller than that of v_L. This means that the transverse phonon states are more densely packed in the energy space compared to the longitudinal phonon states. At high temperatures the magnitude of K_L is lower than the corresponding transverse contribution by 10%. These results are in agreement with the recent results of Hamilton and Parrott.[29] It should be noticed that in Holland's analysis the longitudinal contribution is small compared to the transverse one at both low and high temperatures. At about 90 °K the two are comparable. In Fig. 3 we have plotted K_L and $2K_T$ separately to show their relative magnitudes.

Another point which is worth considering is that it is difficult to simplify the integrals in Eqs. (5a) and (5b) so that K may be expressed as a simple function of temperature. This is due to the fact that each of the relaxation times is dominant over all others at one temperature or another. The high temperature forms of K_L and K_T can be simplified to some extent if one approximates $x^2e^x/(e^x-1)^2$ by unity for $x<1$ and if the boundary scattering is neglected. The integrals so obtained can easily be evaluated analytically.

V. CONCLUSIONS

The thermal conductivity of solid germanium has been very successfully explained in the temperature range 2–1100 °K. The importance of the four-phonon processes has been exhibited at high temperatures since, if these are ignored, the thermal resistivities of solid germanium cannot be understood. By taking into account the nonlinear character of the dispersion relations at high frequencies, simple but different expressions for the wave vectors have been assumed for the different types of the phonons (longitudinal and transverse). Different temperature dependences in the different temperature ranges were used to yield a better approximation for the three-phonon relaxation rates. Finally, it is observed that the transverse phonons make a significant contribution to the thermal conductivity of germanium at all temperatures.

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