Longitudinal phonons and high-temperature heat conduction in germanium

K C Sood and M K Roy†

Department of Physics, Banaras Hindu University, Varanasi-221 005, India

Abstract. Using the relaxation time approach, we present a new analysis of phonon conductivity which shows that at high temperature ($T > \theta_D$, the Debye temperature), the longitudinal phonons are the dominant heat carriers in germanium. The present result, which is a consequence of the effect of phonon dispersion on the Callaway integral for lattice thermal conductivity, is contrary to the general belief that transverse phonons carry heat at $T > \theta_D$. A qualitative justification has also been given for the three-phonon scattering parameters obtained.

1. Introduction

After Parrott's [1] paper on Si–Ge alloys, many workers [2–7] except Guthrie [8,9] concluded that at temperatures greater than the Debye temperature, the phonon conductivity 'K' is chiefly dominated by transverse phonons. Guthrie [9], however, could not give any quantitative justification for his doubts. In fact, this result was the consequence of an inappropriate inclusion of phonon dispersion in the Callaway integral [10] for phonon conductivity. For example, Parrott [1] introduced the idea of two-mode conduction without considering any nonlinearity in the phonon dispersion curves. He could arrive at the above-mentioned result only qualitatively by exploiting the correction term of the Callaway model [10]. On the other hand, Holland [2], guided by Callaway's failure in interpreting the high-temperature phonon transport, included a partial effect of phonon dispersion in the conductivity integral by splitting the transverse acoustic (TA) branch into two approximately linear regions. Neglecting the correction term of the Callaway model, he wrote

$$K = K_l(03) + K_t(02) + K_t(23) \tag{1}$$

where [3]

$$K_\lambda(nm) = \frac{k_B}{2\pi^2} \left(\frac{k_B}{\hbar}\right)^3 T^3 b_\lambda \int_{\theta_\lambda(n)/T}^{\theta_\lambda(m)/T} \frac{v_{g\lambda}(x)}{v_{p\lambda}^2(x)} \tau_c(x,\lambda) J_4(x) \, dx \tag{1a}$$

† Permanent address: Department of Physics, University of Chittagong, Chittagong, Bangladesh.

with

$$J_4(x) = \frac{x^4 e^x}{(e^x - 1)^2} \qquad \tau_c^{-1} = \tau_b^{-1} + \tau_{pt}^{-1} + \tau_u^{-1} + \tau_n^{-1} \qquad (1b)$$

where, from figure 1, $0 \equiv \{q = 0\}$, $2 \equiv \{q = 0.5q_m\}$, and $3 \equiv \{q = q_m\}$. Also $\theta_\lambda(n) = \hbar\omega_\lambda(n)/k_B$, λ being the polarization index, $x = \hbar\omega/k_B T$, $b_1 = \frac{1}{3}$ and $b_t = \frac{2}{3}$. $v_{g\lambda}$ and $v_{p\lambda}$ are the phonon group and phase velocities. τ_b^{-1}, τ_{pt}^{-1}, τ_u^{-1} and τ_n^{-1} are the relaxation rates, respectively, due to phonon-boundary, phonon-point-defect, umklapp and normal three-phonon scattering processes. In the Holland model, the inclusion of phonon dispersion was partial because (i) phonon-point-defect scattering processes were not supposed to be influenced by it and (ii) $v_{g\lambda}/v_{p\lambda}^2$ was approximated by $1/v_{g\lambda}$ in all the integrals.
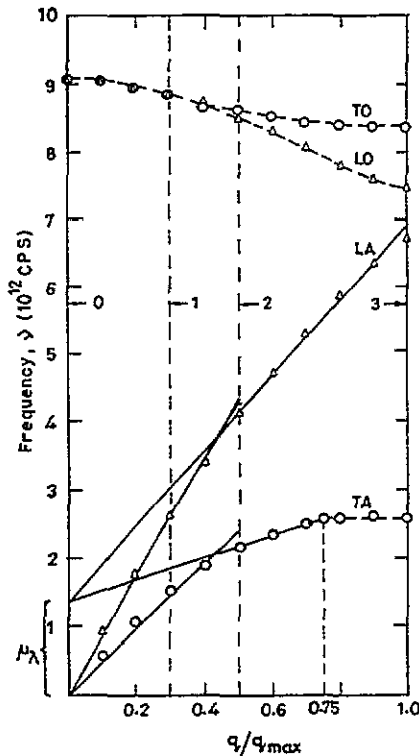

Figure 1. Mean phonon dispersion curves in germanium, after [14].

Holland neglected the correction term in his model and explained the high-temperature K of Ge only through the short-wave transverse acoustic (SWTA) phonons belonging to the strongly dispersive region of the transverse branch, i.e. $K_t(23)$. Many workers [4–7], basically following the Holland model with some variations, obtained similar results. These results were also supported by Hamilton and Parrott [11]
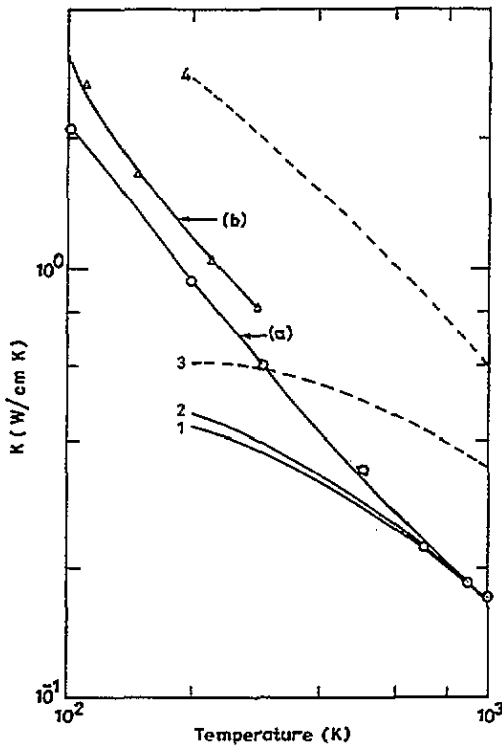
Figure 2. Experimental curves for the phonon conductivity of normal ($\bigcirc$) and enriched ($\triangle$) Ge. Curves 1 and 2 are obtained from $[K_l(23) + K_t(23)]$. For curve 1, $B_{ln}(23) = 5.09 \times 10^{-7}$ deg^{-1}; $B_{lu}(23) = 2.04 \times 10^{-20}$ s deg^{-1}; and for curve 2, $B_{ln}(23) = 2.80 \times 10^{-8}$ deg^{-1}; $B_{lu}(23) = 3.61 \times 10^{-20}$ s deg^{-1} (small normal process). Curves 3 and 4 are the theoretical curves obtained, respectively, for normal and enriched Ge, after adjusting K at 300 K for normal Ge with $B_{lu}(23) = 1.16 \times 10^{-20}$ s deg^{-1} and $B_{ln}(23) = 2.80 \times 10^{-8}$ deg^{-1}.

who, with the use of the variational principle for solving the phonon Boltzmann equation, showed the dominance of the transverse phonons almost in the entire temperature range. This result was also obtained within the framework of a non-dispersive isotropic model.

After an adequate inclusion of phonon dispersion in the calculations of phonon conductivity, the present work reconsiders the role of longitudinal and transverse phonons at high temperatures. The approach of the calculation is given in section 2 and the results, which contradict the general belief regarding the dominance of transverse phonons at high temperatures, are discussed in section 3.

2. Theory

2.1. Phonon conductivity: the general expression

We observe that Holland's expression for phonon conductivity in the two-mode conduction model is incomplete in the sense that it ignores the correction term,

which appears in the Callaway model [10] due to the special treatment of momentum conserving three-phonon normal processes. The complete expression was provided by Parrott [12] for the non-dispersive isotropic model. A direct view of the contribution of LA and TA parts of the correction term cannot be taken from Parrott's expression, which is as follows:

$$K = \left(\sum_{\lambda=1,t} K_\lambda \right) + K_c \tag{2}$$

where K_λ has the same form as defined in (1a) and the correction term

$$K_c = \frac{k_B}{6\pi^2} \left(\frac{k_B T}{\hbar} \right)^3 \left(\sum_\lambda \frac{1}{v_\lambda^3} \int_0^{\theta\lambda/T} \frac{\tau_{n\lambda}^{-1}(x)}{\tau_{c\lambda}^{-1}(x)} J_4(x) \, dx \right)^2$$

$$\times \left(\sum_\lambda \frac{1}{v_\lambda^5} \int_0^{\theta\lambda/T} \frac{\tau_{n\lambda}^{-1}(x)\tau_{r\lambda}^{-1}(x)}{\tau_{c\lambda}^{-1}(x)} J_4(x) \, dx \right)^{-1}. \tag{2a}$$

In Parrott's [12] work, $v_\lambda = v_{g\lambda} = v_{p\lambda}$. It would be in our interest to write this expression in the presence of phonon dispersion, i.e. when $v_{g\lambda} \neq v_{p\lambda}$. In equation (4) of Parrott's paper [12], if we convert q to ω, we get $\int d^3q = 4\pi \int q^2 dq = 4\pi \int (\omega^2/v_{p\lambda}^2)/v_{g\lambda} d\omega$. Here $v_{p\lambda} = \omega/q$ and $v_{g\lambda} = d\omega/dq$. Putting $x = \hbar\omega/k_B T$, $\check{N} = (e^x - 1)^{-1}$ and using this conversion in equation (4) of [12] we can easily obtain

$$K_c = \frac{k_B}{6\pi^2} \left(\frac{k_B T}{\hbar} \right)^3 \left(\sum_\lambda \int_0^{\theta\lambda/T} \frac{1}{v_{p\lambda}^3(x)} \tau_{c\lambda}(x)\tau_{n\lambda}^{-1}(x) J_4(x) \, dx \right)^2$$

$$\times \left(\sum_\lambda \int_0^{\theta\lambda/T} \frac{1}{v_{p\lambda}^4(x)v_{g\lambda}(x)} \tau_{c\lambda}(x)\tau_{n\lambda}^{-1}(x)\tau_{r\lambda}^{-1}(x) J_4(x) \, dx \right)^{-1}. \tag{2b}$$

Here $\tau_{r\lambda}^{-1}$ is the total relaxation rate of all the processes which do not conserve the crystal momentum. We next study the effect of phonon dispersion on various quantities in the integrals defined in equation (2–2b).

2.1.1. Phonon-point defect relaxation rate. According to Carruthers [13]

$$\tau_{pt}^{-1} = \frac{\omega_{q\lambda}^2 \Omega_0 \Gamma}{16\pi^2} \sum_{\lambda'} \int d^3q' \delta(\omega_{q\lambda} - \omega_{q'\lambda'})(\hat{e}_{q\lambda} \cdot \hat{e}_{q'\lambda'})^2 \tag{3}$$

where $\Gamma = \Sigma_i f_i (1 - M_i/M)^2$, f_i being the fractional abundance of the isotopes and M_i their atomic mass. q and q' are, respectively, the incoming and outgoing phonons; $\hat{e}_{q\lambda}$ is the polarization vector and Ω_0 the atomic volume. To simplify equation (3), we replace $(\hat{e}_{q\lambda} \cdot \hat{e}_{q'\lambda'})^2$ by its angular average, which is $\frac{1}{3}$. Further, figure 1 shows that the energy conservation condition would roughly allow a particular incoming phonon to be scattered only through those processes which are given in table 1. Keeping these processes in view and integrating the RHS of equation (3), expressions for τ_{pt}^{-1} are obtained for the incoming phonons (q, λ), lying in the different domains of figure 1. All these expressions are also given in table 1.

Table 1. Possible point defect scattering processes for an incoming phonon and corresponding expressions for the relaxation rate. $\eta_\lambda(nm) = v_{g\lambda}(nm)v_{p\lambda}^2(nm)$ and $A_0 = \Omega_0\Gamma/4\pi$.

Region	Domain	Incoming phonon	Possible outgoing phonon	$\tau_{pt}^{-1}, \lambda = 1$ or t
01	$0 \leqslant q \leqslant 0.3q_m$	l	l and t both	$\frac{1}{3}A_0\left(\frac{1}{\eta_l(01)} + \frac{2}{\eta_t(01)}\right)\omega_\lambda^4$
		t	l and t both	$\frac{1}{3}A_0\left(\frac{1}{\eta_l(01)} + \frac{2}{\eta_t(01)}\right)\omega_\lambda^4$
12	$0.3q_m \leqslant q \leqslant 0.5q_m$	l	l only	$\frac{1}{3}A_0\frac{\omega_\lambda^4}{\eta_l(12)}$
		t	l and t both	$\frac{1}{3}A_0\left(\frac{1}{\eta_l(12)} + \frac{2}{\eta_t(12)}\right)\omega_\lambda^4$
23	$0.5q_m \leqslant q \leqslant q_m$	l	l only	$\frac{1}{3}A_0\frac{\omega_\lambda^4}{\eta_l(23)}$
		t	l and t both	$\frac{1}{3}A_0\left(\frac{1}{\eta_l(02)} + \frac{2}{\eta_t(23)}\right)\omega_\lambda^4$

2.1.2. Relaxation rates for phonon scattering by the crystal surface and other phonons.
Phonon scattering by the crystal surface is effective only at low temperatures $(T < 10$ K) where low-frequency phonons dominate. So τ_b^{-1} would, more or less, remain uninfluenced by phonon dispersion; the three-phonon relaxation rates are, of course, strongly affected by it. This will, however, automatically be taken care of since their scattering strengths are usually treated as adjustable parameters.

2.1.3. The factor $v_{g\lambda}/v_{p\lambda}^2$. Phonon dispersion affects the phonon conductivity integral through the changes in $v_{g\lambda}$ and $v_{p\lambda}$ with $|q|$. From figure 1, values of $v_{g\lambda}(\omega)$ can be easily calculated from the relation $v_{g\lambda}(q) = v_{g\lambda}(02)m_{23}/m_{02}$, where $v_{g\lambda}(02)$ (the mean group velocity of the phonons in the region (02)) is given in [2]; and m_{23} and m_{02} are, respectively, the mean slopes of the dispersion curves in regions (23) and (02). In the domain (02), $v_{p\lambda}(\omega) = v_{g\lambda}(\omega)$, while in the domain (23) we introduce the following relation:

$$v_{p\lambda}(\omega, 23) = v_{g\lambda}(23)/(1 - \overline{\delta}_\lambda/\omega_\lambda) \tag{4}$$

where $\overline{\delta}_\lambda$ $(= 2\pi\mu_\lambda)$ is clearly shown in figure 1.

2.2. An appropriate expression for K under dispersion effects

In this paper, the Holland model has been improved by dividing all the integrals from equation (2) in such a way that the group velocity as well as the prefactor of the phonon-point-defect scattering rates remain almost independent of ω in a given subintegral. Thus table 1, together with figure 1, suggests that the longitudinal branch should also be divided into three parts. Consequently, the expression for the phonon conductivity in equation (2) becomes

$$K = K_l(0 \leqslant q \leqslant 0.3q_m) + K_l(0.3q_m \leqslant q \leqslant 0.5q_m) + K_l(0.5q_m \leqslant q \leqslant q_m)$$

$$+ K_t(0 \leqslant q \leqslant 0.5q_m) + K_t(0.5q_m \leqslant q \leqslant 0.75q_m) + K_c$$
$$= K_l(01) + K_l(12) + K_l(23) + K_t(02) + K_t(23) + K_c$$
$$= K_r + K_l(23) + K_t(23) + K_c. \tag{5}$$

In $K_t(23)$, the region above $0.75q_m$ has been neglected because, there, v_{gt} is nearly zero for all directions [14].

2.3. Three-phonon relaxation rates: the high-temperature limits

To calculate various terms in equation (5), we require the high-temperature parametric forms for various $\tau_{u\lambda}^{-1}$ and $\tau_{n\lambda}^{-1}$, which, in turn, strongly depend upon the phonon polarization, frequency and temperature. The relaxation rates for $\tau_{ul}^{-1}(23)$, $\tau_{nl}^{-1}(23)$ and $\tau_{nt}^{-1}(23)$ are not available in the literature. On the basis of previous work [1, 2, 8], however, we can derive the following information for various three-phonon relaxation rates.

(i) The exponent of frequency for umklapp processes is higher than that for normal processes.

(ii) The exponent of frequency for longitudinal phonons is higher than that for transverse phonons.

(iii) At high temperatures the exponent of temperature is unity for all the phonons involved in any type of three-phonon processes.

In table 2, only the high-temperature forms of all the three-phonon relaxation rates along with their references are given. While some of the expressions are being proposed by us, most of them have been derived by Parrott [1] for low-frequency phonons. Following Klemens [15] and Sharma *et al* [16] the relaxation rates of umklapp processes have been multiplied by the factor $e^{-\theta/\alpha T}$ where θ is the mean value of θ_λs corresponding to their zone boundary values for all phonon dispersion branches. α depends upon the particular 'scattering process' as well as 'dispersion effects'; and it is assumed to be an adjustable parameter.

A comment is needed for the expression $\tau_{nt}^{-1}(23)$ proposed on the basis of the available form of $\tau_{ut}^{-1}(23)$, which tends to $B_{tu}(23)\omega T$ at very high temperatures. This, on the basis of point (i), suggests that in $\tau_{nt}^{-1}(23)$ the exponent of ω should be less than one. This would make $\tau_{nt}^{-1}(23)$ a very slowly varying function of ω which in itself changes very little in the region (23) of the TA branch. Therefore the factor, which depends upon ω in $\tau_{nt}^{-1}(23)$, has been absorbed in the parameter $B_{tn}(23)$ itself.

Similarly, the other proposed forms are also consistent with the above written statements; we do not claim them to be very accurate. These semiphenomenological expressions for $\tau_{n\lambda}^{-1}$ and $\tau_{u\lambda}^{-1}$ (see table 2) are actually replacements of general integrals which become very cumbersome due to the anisotropic as well as dispersive nature of the crystal. The forms of $\tau_{n\lambda}^{-1}$ and $\tau_{u\lambda}^{-1}$ depend upon phonon polarization, frequency and temperature. In fact the detailed workout for these expressions is not attempted because some variation in their form is not going to affect our final conclusion.

It should not be forgotten that the expressions for three-phonon relaxation rates chosen by us ignore interactions with optic phonons. In fact the existence of optic phonons cannot be overlooked at high temperatures and, due to their low group

Table 2. Three-phonon relaxation rates and corresponding parameters used for theoretical calculations of K in figures 3 and 4. c indicates that the expression is obtained by multiplying the factor $\exp(-\theta/\alpha T)$ in Parrott's [1] results. p stands for our own proposals.

Region	Relaxation rate		B
Longitudinal branch			
01	$\tau_{\rm nl}^{-1} = B_{\rm ln}(01)\theta_{\rm l}^2\omega^2 T$	[1]	6.91×10^{-23} s deg^{-3}
	$\tau_{\rm ul}^{-1} = B_{\rm lu}(01)\theta_{\rm l}\omega^3 T \exp(-\theta/\alpha T)$	[c]	$\simeq 0$
12	$\tau_{\rm nl}^{-1} = B_{\rm ln}(12)\theta_{\rm l}^2\omega^2 T$	[1]	3.55×10^{-25} s deg^{-3}
	$\tau_{\rm ul}^{-1} = B_{\rm lu}(12)\theta_{\rm l}\omega^3 T \exp(-\theta/\alpha T)$	[c]	1.80×10^{-35} s^2 deg^{-2}
23	$\tau_{\rm nl}^{-1} = B_{\rm ln}(23)\omega T$	[p]	see captions for figures
	$\tau_{\rm ul}^{-1} = B_{\rm lu}(23)\omega^2 T \exp(-\theta/\alpha T)$	[p]	3 and 4
Transverse branch			
02	$\tau_{\rm nt}^{-1} = B_{\rm tn}(02)\theta_{\rm t}^3\omega T$	[1]	1.01×10^{-11} deg^{-4}
	$\tau_{\rm ut}^{-1} = B_{\rm tu}(02)\theta_{\rm t}^2\omega^2 T \exp(-\theta/\alpha T)$	[c]	5.57×10^{-23} s deg^{-3}
23	$\tau_{\rm nt}^{-1} = B_{\rm tn}(23) T$	[1]	8.0×10^4 s^{-1} deg^{-1}
	$\tau_{\rm ut}^{-1} = B_{\rm tu}(23)\omega^2 / \sinh(x) \qquad x = \dfrac{\hbar\omega}{k_{\rm B}T}$	[2]	1.54×10^{-16} s

velocity, they are bound to enhance the total scattering quite considerably. However, according to Logachev and Yurev [17], this interaction still gives $\tau_{\rm ph-ph}^{-1} \propto T$ at $T \gg \theta_{\rm D}$, and so it would not be irrelevant to assume that three-phonon scattering parameters, in particular, will automatically take care of these processes when adjustments are made for the phonon conductivity data.

3. Results and discussion

3.1. Role of SWTA and optic phonons

Following the work of Berman and Brock [18], we neglect $K_{\rm c}$ at the first instance whilst calculating the phonon conductivity at high temperatures. Similarly $K_{\rm l}(01)$, $K_{\rm l}(12)$ and $K_{\rm t}(02)$, which correspond to low-frequency phonons, are also neglected on the basis of [2, 5, 7]. Thus initially the phonon conductivity data were attempted to be fitted only with $[K_{\rm l}(23) + K_{\rm t}(23)]$. The values of various physical constants used are given in table 3. Figure 2 gives the experimental [2, 19] as well as the theoretical curves obtained from $\{K_{\rm l}(23) + K_{\rm t}(23)\}$ in the temperature range 200–1000 K. Parameters used for the calculations are given in the figure caption. The parameter 'A_0' is obtained from Holland's value [2] for the long-wave phonon-point-defect scattering parameter in Ge.

According to these calculations, we find that $K_{\rm t}(23) = 0.03$ W cm^{-1} K^{-1} at $T = 1000$ K, even if $\tau_{\rm ut}^{-1}(23)$ is totally neglected. This result is very small compared with the experimental value for K (= 0.17 W cm^{-1} K^{-1}) at $T = 1000$ K. The addition of $\tau_{\rm ut}^{-1}(23)$ in $\tau_{\rm c}^{-1}(23)$ will cause a further decrease in $K_{\rm t}(23)$. Holland [2] and others [3, 5] obtained high values for $K_{\rm t}(23)$ due to the following reasons.

(i) While Holland's replacement of $[v_{\rm g}(23)v_{\rm pt}^{-2}(23)]$ by $v_{\rm gt}^{-1}(23)$ is true only in the non-dispersive model, the approximation of Sharma *et al* [5] gives $[v_{\rm gt}(23)v_{\rm pt}^{-2}(23)]$

Table 3. Values for some calculated physical quantities used in the calculation of phonon conductivity.

$L_c = 0.193$ cm (normal)	$v_{gl}(02) = 4.92 \times 10^5$ cm s^{-1}
$\quad = 0.27$ cm (enriched)	$v_{gl}(23) = 3.25 \times 10^5$ cm s^{-1}
$A_0 = 1.355\,78 \times 10^{-27}$ cm^3	$v_{gt}(02) = 3.55 \times 10^5$ cm s^{-1}
$\theta_l = 333$ K	$v_{gt}(23) = 1.13 \times 10^5$ cm s^{-1}
$\theta_t = 125$ K	$\bar{\delta}_l = \bar{\delta}_t = 8.32 \times 10^{12}$ cps
$\theta = 194$ K	$\alpha = 2$

somewhat larger than $v_{gt}^{-1}(23)$. On the other hand, from figure 1, it is obvious that as $v_{gt}(23) \to 0$, $v_{pt}(23)$ becomes much larger than $v_{gt}(23)$ and consequently one gets $[(v_{gt}(23)v_{pt}^{-2}(23)]$ to be less than $v_{gt}^{-1}(23)$. Thus, the above-mentioned approximations are unrealistic. In this work, a much more realistic approximation for $v_{p\lambda}$, defined through equation (4) gives

$$v_{g\lambda}(\omega)/v_{p\lambda}^2(\omega) = (1 - \bar{\delta}_\lambda/\omega)^2/v_{g\lambda}.$$

This factor obviously becomes very small for TA phonons in region (23).

(ii) Holland [2] and others [5, 7] neglected the dispersion effects on τ_{pt}^{-1} also. For TA phonons in region (23), the corrected values for $v_{gt}(23)$ and $v_{pt}(23)$ very much enhance the rate $\tau_{pt}^{-1}(23)$ which, in turn, decreases $K_t(23)$ to a large extent.

(iii) It is well known that the three-phonon processes for strongly dispersive TA phonons are much stronger than LA phonons. So, $\tau_{ut}^{-1}(23)$ must be chosen at least an order of magnitude higher than $\tau_{ul}^{-1}(23)$. This results in a value for $\tau_{ut}^{-1}(23)$ much higher than the one chosen by Holland [2] and ultimately it makes $K_t(23)$ negligible in the present model.

We therefore conclude that $K_t(23)$ or the high-frequency TA phonons cannot contribute much to the high-temperature phonon conductivity of germanium.

Little participation in K can be expected from the optic phonons on similar grounds. For optic phonons, generally, v_{po} is very large and v_{go} small (see figure 1). As a result, v_{go}/v_{po}^2 becomes too small to allow any significant contribution from these phonons in the total K. Only short-wave LO phonons may become controversial as their group velocity is somewhat larger. Still, in this case also, v_{glo}/v_{plo}^2 should be much smaller than its value for short-wave LA phonons and, ultimately, we believe that this contribution can also be neglected. In the absence of any exclusive work regarding three-phonon relaxation rates for optic phonons, a complete check does not seem possible. Nevertheless, our analysis is in line with the estimates of Logachev and Yurev [17] and the two-fluid model of Armstrong [20] who assume that the phonons belonging to the strongly dispersive regions do not participate in the heat transport.

3.2. Role of SWLA ($K_l(23)$) phonons

If K_r and K_c are to be ignored in equation (5), one is left only with short-wave LA phonons, which can explain the heat transport in Ge at high temperatures. Figure 2 shows that, through a proper choice of $B_{lu}(23)$, a reasonable fit to the experimental data can be given above 600 K. Figure 2 also shows that there is an increasing discrepancy between the theory and experiment towards lower

temperatures. Therefore, it can be argued that a much lower value for $B_{lu}(23)$ (i.e. $\tau_{ul}^{-1}(23)$) and the inclusion of four-phonon processes is a more relevant way of explaining the high-temperature data for K and, in fact, this procedure was adopted by a few workers [4, 21]. However, figure 2 shows that the low value of $B_{lu}(23)$ obtained through such an attempt overestimates the phonon conductivity of enriched Ge a little too much. Thus, this approach would make a simultaneous explanation of K in both normal and enriched germanium almost impossible. Secondly, τ_{4ph}^{-1} proportional to $\omega^2 T^2$ [22–24] should give $K \propto T^{-2}$ at high temperatures while the experimental data for both Ge and Si reveal that beyond $T = 800$ K, K varies even more slowly than T^{-1} (see figure 2). This ascertains that four-phonon processes do not influence phonon transport much.

3.3. Role of low-frequency phonons and the correction term

Now the discrepancy below 600 K has to be attributed to the omitted terms from equation (5). If all the terms in equation (5) are included, table 2 suggests that many parameters have to be estimated for such a calculation. This causes the adjustment of the correction term to be very difficult in a two-mode conduction model. To our knowledge, no one has made any attempt to do this. Here, however, we try to give a rough estimate for K_c and K_r above 200 K by choosing the high-temperature limits of all the three-phonon relaxation rates given in table 2. For the normal processes in $K_1(01)$ and $K_t(02)$, we start with the parameters used by Holland [2], and the rest have been adjusted for the best fit. The parameters used are given in table 2 and the results obtained after adopting this scheme are depicted in figure 3. Figure 3 shows that a reasonable fit between theoretical and experimental values for K can be obtained in Ge, even when longitudinal phonons are chosen to be the dominant heat carriers at high temperatures. Further, figure 4 shows that the values for phonon conductivity obtained for enriched Ge with the same set of parameters are also reasonably good.

Although, unless the analysis is done in the entire temperature range, nothing can be said about the uniqueness of the adjusted parameters, we still try to give some justification for their obtained values. In $K_1(23)$, a large amount of normal processes ($\simeq$ umklapp processes) results in a larger discrepancy between theory and experiment at lower temperatures (see figure 3) in normal Ge. On the other hand, in enriched Ge, the results are improved (see figure 4). Thus, we believe that large normal processes in $K_1(23)$ will go against the possibility of simultaneous fitting of the phonon conductivity data for both normal and enriched Ge with the same set of three-phonon parameters. Thus, for a better fit, the normal processes are assumed to be decreasing with $|q|$ in order to reduce their value in region (23). Theoretically, this result is not unexpected as the area of integration in the integrals for τ_n^{-1} [11, 25] decreases with $|q|$. In the case of umklapp process for longitudinal phonons, we find that $\tau_{ul}^{-1}(23)$ does not increase with $|q|$ very sharply beyond $q \geqslant q_m/2$. This result seems to be somewhat abnormal because in τ_u^{-1} the area of integration must increase with $|q|$. The possible explanation for this can be given on the basis of the diminishing probability of the processes LA + TA $\rightleftarrows$ 0 + G, when $|q|$ becomes greater than $|q_m/2|$ (see figure 1).

These calculations show that Holland's assumption [2] of connecting the high-temperature phonon conductivity with high-frequency phonons only is not justified. Low-frequency phonons also play some role at $T > \theta_D$ through $K_t(02)$, $K_1(01)$,
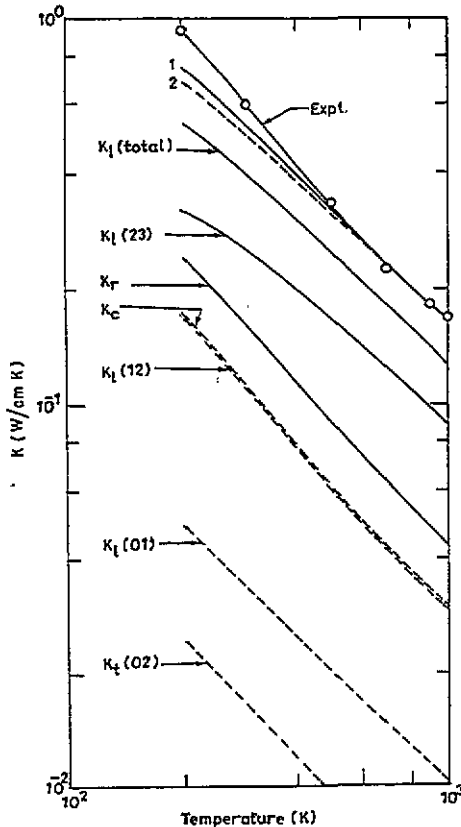
Figure 3. Experimental points for normal Ge (O). Curves 1 and 2 are obtained values for the phonon conductivity from equation (5). For curve 1, $B_{ln}(23) = 1.69 \times 10^{-7}$ deg^{-1}, $B_{lu}(23) = 7.29 \times 10^{-20}$ s deg^{-1}; and for curve 2, $B_{ln}(23) = 3.98 \times 10^{-6}$ deg^{-1}, $B_{lu}(23) = 6.53 \times 10^{-20}$ s deg^{-1} (large normal process). K_c, K_r, $K_l(01)$, $K_l(12)$, $K_l(23)$, $K_t(02)$ and K_l(total) are defined in the text.

$K_l(12)$, and K_c, whose individual contributions are also plotted in figure 3. Thus, even though $K_t(23)$ is bound to be negligible (see section 3.1), transverse phonons do give some contribution at $T > \theta_D$ via $K_t(02)$ and K_c.

Despite the fact that the relative importance of different terms in equation (5) is subject to the accuracy of the various parametric forms of the relaxation rates used in this paper, we believe that the dominance of the longitudinal phonons beyond $T = \theta_D (\simeq 376$ K) looks almost certain as their net contribution K_l(total) = $K_l(01) + K_l(12) + K_l(23)$ in total K is more than 75% beyond $T \geqslant \theta_D$. Here the contribution of longitudinal phonons via K_c is not included. This conclusion can be controversial only in the unlikely situation where K_r and K_c may become the dominant terms, even at high temperatures.

It is also obvious from figure 3 that there is still some discrepancy between theoretical and experimental values below $T = 400$ K. The results could be improved by choosing $B_{tu}(02)$ and $B_{lu}(12)$ somewhat lower and $B_{lu}(23)$ a little higher. But then the fitting beyond $T = 500$ K is disturbed. As a matter of fact, this

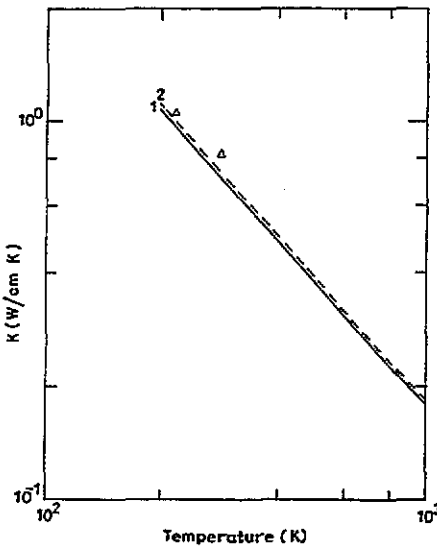**Figure 4.** Theoretical and experimental values for K for enriched Ge with $A'_0 = A_0/15$. For curve 1, $B_{ln}(23) = 1.69 \times 10^{-7}$ deg^{-1}, $B_{lu}(23) = 7.29 \times 10^{-20}$ s deg^{-1}; and for curve 2, $B_{ln}(23) = 3.98 \times 10^{-6}$ deg^{-1}, $B_{lu}(23) = 6.53 \times 10^{-20}$ s deg^{-1}. The remaining parameters are given in tables 2 and 3.

discrepancy is, actually, not unexpected because the three-phonon relaxation rates will in general not obey a T^1 dependence below $T \simeq 300$ K (see section (2.3) and [8]). An exact explanation at lower temperatures would not only require the modified parametric forms of the three-phonon relaxation rate expressions, but also a thorough readjustment of all concerned parameters. In fact, in our opinion, a reliable estimate for the relative scattering strength of various three-phonon processes can be made only through a simultaneous explanation of the phonon conductivity of both normal and enriched Ge in the entire temperature range. This may be treated as a separate problem and the main conclusion of the present paper, that at high temperatures longitudinal phonons should carry the main part of lattice heat, is convincingly drawn without going into all these details.

Although we have not made an attempt to do the calculations for Si, GaSb, GaAs, etc the result can be extended for these also because they have similar phonon dispersion curves.

References

[1]   Parrott J E 1963 *Proc. Phys. Soc.* **81** 726
[2]   Holland M G 1963 *Phys. Rev.* **132** 2461
[3]   Tiwari M D and Agrawal B K 1971 *Phys. Rev.* B **4** 3527
[4]   Joshi Y P, Tiwari M D and Verma G S 1970 *Phys. Rev.* **1** 642
[5]   Sharma P C, Dubey K S and Verma G S 1971 *Phys. Rev.* B **3** 1985
[6]   Logachev Y A and Vasilev L N 1973 *Sov. Phys.–Solid State* **15** 1081
[7]   Sood K C, Singh M P and Verma G S 1971 *Phys. Rev.* B **3** 385
[8]   Guthrie G L 1966 *Phys. Rev.* **152** 801
[9]   Guthrie G L 1971 *Phys. Rev.* B **3** 3573
[10] Callaway J 1959 *Phys. Rev.* **113** 1046
[11] Hamilton R A H and Parrott J E 1969 *Phys. Rev.* **178** 1284
[12] Parrott J E 1971 *Phys. Status Solidi* b **48** K159
[13] Carruthers P 1961 *Rev. Mod. Phys.* **33** 92
[14] Nilsson G and Nelin G 1971 *Phys. Rev.* B **3** 364
[15] Klemens P G 1951 *Proc. R. Soc.* A **208** 108
[16] Sharma P C, Dubey K S and Verma G S 1971 *Phys. Rev.* B **4** 1306
[17] Logachev Y A and Yurev M S 1973 *Sov. Phys.–Solid State* **14** 2826
[18] Berman R and Brock J C F 1965 *Proc. R. Soc.* A **289** 46
[19] Geballe T H and Hull G W 1958 *Phys. Rev.* **110** 773
[20] Armstrong B H 1981 *Phys. Rev.* B **23** 883
[21] Fulkerson W, Moore J P, Williams R K, Graves R S and McElroy D L 1968 *Phys. Rev.* **167** 765
[22] Pomeranchuk I 1941 *Phys. Rev.* **60** 820
[23] Pomeranchuk I 1941 *J. Phys. USSR* **4** 259
[24] Pomeranchuk I 1942 *J. Phys. USSR* **7** 197
[25] Strivastava G P 1970 *Phil. Mag.* **34** 795