zone-center optical phonon in silicon has been explained on the assumption that there is only one decay channel for the optical phonon. This involves the decay into two acoustic phonons at half the optical frequency. But the same model fails to explain the observed temperature dependence of the frequency. This instead correlates very well with Cowley's calculations which include all possible three phonon combinations throughout the Brillouin zone. In view of the present discrepancy we plan further experimental work in other simple systems and suggest that additional theoretical calculations be made to reconcile theory and experiment.

ACKNOWLEDGMENTS

We would like to thank M. Reine for several useful discussions during the course of this work, and A. S. Pine for comments on an early draft of the manuscript, and R. A. Cowley for clarifying an aspect of his paper.

PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Role of Four-Phonon Processes in the Lattice Thermal Conductivity of Silicon from 300 to 1300°K*

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(Received 14 May 1969; revised manuscript received 30 July 1969)

It is shown that the high-temperature behavior of the lattice thermal conductivity of silicon, which has been carefully remeasured recently by Fulkerson *et al.*, can be explained by the four-phonon processes. It has been also found that the major contribution to the phonon thermal conductivity at high temperatures comes from the high-frequency transverse phonons.

INTRODUCTION

MEASUREMENTS of the thermal conductivity of silicon have been performed by a number of authors.[1–8] Maycock[9] has given an account of the recent work in this field. At elevated temperatures, the contributions of electrons and photons to the total thermal conductivity are appreciable, so that the lattice thermal conductivity is obtained from the total by substracting the former two contributions.[7,8] A comparison of the theory of lattice thermal conductivity to the experimental results is possible only if the calculation of the electronic contribution[10] based on the simple parabolic band, and the calculation of the radiation contribution,[11] are considered to be valid. For silicon and germanium, Holland[12] has shown that good agreement between experimental and theoretical results can be obtained at all temperatures if one considers the separate contributions of the longitudinal and transverse phonons. His formulation has also been applied quite successfully by Bhandari and Verma[13] to explain the high-temperature thermal conductivity of Si-Ge alloys. Recently, Fulkerson *et al.*[8] have shown that their thermal conductivity data for Si in the temperature range 100–1300°K cannot be explained by Holland's model of two-mode conduction. This discrepancy becomes more obvious when one considers the plot of thermal resistivity versus temperature T. For such a plot, the lattice thermal resistivity W is slightly different from a straight line, with an upward curvature, whereas Holland's analysis gives a downward curvature. This implies that the calculated thermal conductivity does not fall with temperature as rapidly as the experimental data. In other words, this suggests that there should be some extra phonon scattering process included which increases with temperature sufficiently rapidly and is responsible for the above result. The possible processes that can take place in a real crystal include the electron-phonon interactions[8] and the four-phonon processes.[7,14] It is also possible that the optical

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phonons scatter the acoustical phonons[8] and thus contribute to the lattice thermal resistivity.

In the present work we have estimated the strength of the electron-phonon scattering relaxation time as given by Ziman,[15] and found that this is not of importance in the temperature range we have considered. It is to be noticed that the scattering of phonons by electrons, as studied by Griffin and Carruthers,[16] cannot be expected in the present case, inasmuch as this type of scattering pertains to de-ionized impurities, which do not exist in Si above room temperature. We believe that four-phonon processes should play an important part at high temperatures. This is expected since at sufficiently high temperatures the amplitude of the atomic vibrations should become so large that the quartic term in the atomic displacements, which occurs in the crystal potential, may become appreciable and cause four-phonon processes.[17,18] Such processes may also be caused by the cubic term, as has been shown by Pomeranchuk.[19] The scattering of acoustical phonons by optical phonons, however, has not been considered in the present work.

THEORY: HOLLAND'S FORMULATION

Because of the difference in the dispersion, and particularly the difference in the maximum frequencies of the longitudinal and transverse branches (the two transverse polarizations are usually not distinguished), the relaxation-time expressions and the phonon velocities are markedly different for phonons in different branches. Consideration of two-mode conduction becomes, therefore, a necessity, particularly at high temperatures where the high-frequency phonons become important. Because of the lack of an exact analytic form for the phonon velocity as a function of frequency, one is forced to use a suitably averaged velocity for different phonons. Since there is a large difference between the low- and high-frequency phonon velocities, such an average cannot be used throughout the whole frequency range. Holland has defined two frequency ranges, zero to ω_1 and ω_1 to ω_2, for the transverse phonons; for each range there is one average velocity, and ω_2 is the maximum frequency for this branch. A similar division was made for the longitudinal branch by defining frequencies ω_3 and ω_4, the latter being the maximum longitudinal phonon frequency. ω_1 and ω_3 are rather arbitrary. The thermal conductivity contribution K_T due to transverse phonons (both polarizations included) may then be written as the sum of K_{T1} and K_{T2}, where K_{T1} is due to phonons with frequency between zero and ω_1 and K_{T2} is due to the rest. Likewise, K_L, the contribution due to the longitudinal branch, divides into K_{L1} and K_{L2}. Each of these four terms may be given by an expression of the form

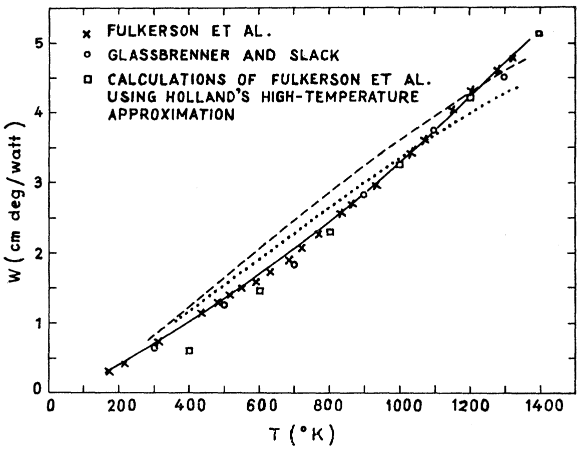

FIG. 1. Lattice thermal resistivity of Si. The curves plotted are present calculations. The solid line is obtained by making use of the parameters listed in Table I. The dashed curve is obtained by using the parameters given by Holland. The dotted curve corresponds to an arbitrary set of parameters. Four-phonon processes are not taken into consideration in getting the dashed and the dotted curves.

$$\frac{ak^4T^3}{2\pi^2vh^3}\int\tau\frac{x^4e^x}{(e^x-1)^2}dx, \tag{1}$$

where $x=\omega h/kT$, and $a=\frac{2}{3}$ for the transverse and $\frac{1}{3}$ for the longitudinal branch. The integration limits are determined by the ω_i's defined above.

In expression (1), τ is the total relaxation time given by

$$\tau^{-1}=\tau_B^{-1}+\tau_{\rm pt}^{-1}+\tau_{\rm 3ph}^{-1}, \tag{2}$$

where τ_B is the boundary scattering relaxation time, $\tau_{\rm pt}$ is due to point defects, isotopes, etc., and $\tau_{\rm 3ph}$ is due to the three-phonon processes (including both N and U processes). At the temperatures we are interested in, τ_B^{-1} is negligible. $\tau_{\rm pt}^{-1}$ has been given by $A\omega^4$. Holland has used $\tau_{\rm 3ph}^{-1}=B_L\omega^2T^3$ for the longitudinal phonons, and $\tau_{\rm 3ph}^{-1}=B_T\omega T^4$ when $0<\omega<\omega_1$, and $\tau_{\rm 3ph}^{-1}=B_{TU}\omega^2/\sinh x$ when $\omega_1<\omega<\omega_2$, for the transverse phonons. He has also given the appropriate values of the ω_i's and v's, explicitly taking into account the dispersion curves for Si.[20]

We have reanalyzed the lattice thermal conductivity of Si using the parameters of Holland,[12] the results being represented by the dashed curve in Fig. 1. In the same figure are also shown the experimental results of Glassbrenner and Slack[7] and those of Fulkerson *et al.*[8] For the sake of comparison, we have also plotted in the figure the calculations of Fulkerson *et al.*, who have used the high-temperature approximation due to Holland. Comparison of the dashed curve with the experimental results shows that the agreement is not good, and that the dashed curve has a downward curva-

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ture, whereas the experimental results exhibit an upward trend. That one cannot inprove the agreement by altering the values of the parameters can be seen from the study of the dotted curve, which we have obtained by using values of the parameters slightly different from that of Holland (the changed values are not reported here, since they are of little importance). Since at higher temperatures K_{T2} is the dominant term, it appears that there should be an extra term in τ, which causes the integral appearing in the expression for K_{T2} to fall with T as rapidly as required. This extra scattering mechanism may also affect K_{T1}, K_{L1}, and K_{L2}.

ELECTRON-PHONON SCATTERING

With an increase in temperature, there is an increase in the number of electrons in the conduction band. These electrons can interact with the phonons which carry the thermal energy and thereby decrease the phonon conductivity. Ziman[15] has given the following expression for the electron-phonon scattering relaxation time:

$$\tau_{\mathrm{eph}}{}^{-1}=DT\ln\left(\frac{1+\exp(\eta^*-N/T-PTx^2+\frac{1}{2}x)}{1+\exp(\eta^*-N/T-PTx^2-\frac{1}{2}x)}\right), \quad (3)$$

where the various terms involved have been defined elsewhere.[21] The reduced Fermi energy η^* can be obtained from the experimental results[8] for the thermoelectric power Q and the theory.[22] Gaur *et al.*[23] have calculated the variation of Q with η^* as given by theory. To estimate $\tau_{\mathrm{eph}}{}^{-1}$ one also needs a knowledge of the deformation potential constant and density-of-states effective mass that are available in the literature.[24–27] What we have observed is that $\tau_{\mathrm{eph}}{}^{-1}$ is appreciable for very small values of x but is, at most, of the same order as $\tau_B{}^{-1}$ which we have already neglected. This type of scattering, therefore, does not affect the high-temperature lattice thermal conductivity to any appreciable extent.

FOUR-PHONON PROCESSES

The relaxation-time expressions for four-phonon processes were initially derived by Pomeranchuk.[17–19] As the number of phonons taking part in the process increases, the complexity of the scattering time expressions also increases. Nevertheless, the dispersive nature of the phonon frequency becomes less important for such processes since conservation laws can now be more easily satisfied, that is, they become less restrictive.[28] Pomeranchuk started with a potential function for the crystal including the quartic term in the atomic displacements. This term leads to a reciprocal relaxation time that is quadratic in the phonon frequency and temperature.[18] Four-phonon processes may also be caused by the cubic term through second-order perturbation. Pomeranchuk has shown that the corresponding relaxation time is independent of the phonon frequency but quadratic in temperature.[19] We believe that at higher temperatures the quartic term occurring in the crystal potential function is more important, and we therefore use for the four-phonon relaxation time an expression given by

$$\tau_{4\mathrm{ph}}{}^{-1}=B_H\omega^2T^2. \quad (4)$$

This should be included in the total relaxation time τ, B_H being constant.

If one supposes that B_H is of the same order (if not the same) for all phonons, irrespective of the frequency and polarization state, its value should be small and will not affect K_{L1}, K_{L2}, and K_{T1}. We therefore include this term in the integral for K_{T2} only, and obtain

$$K_{L1}=\frac{\hbar}{6\pi^2v_{L1}T}\int_0^{\Theta_3/T}\frac{x^4}{(Ax^4+BTx^2)}\frac{e^x}{(e^x-1)^2}dx, \quad (5)$$

$$K_{L2}=\frac{\hbar}{6\pi^2v_{L2}T}\int_{\Theta_3/T}^{\Theta_4/T}\frac{x^4}{(Ax^4+BTx^2)}\frac{e^x}{(e^x-1)^2}dx, \quad (6)$$

$$K_{T1}=\frac{\hbar}{3\pi^2v_{T1}T}\int_0^{\Theta_1/T}\frac{x^4}{(Ax^4+CTx)}\frac{e^x}{(e^x-1)^2}dx, \quad (7)$$

$$K_{T2}=\frac{\hbar}{3\pi^2v_{T2}T}\int_{\Theta_1/T}^{\Theta_2/T}\frac{x^4}{(Ax^4+Dx^2/T^2\sinh x+Ex^2)} \times\frac{e^x}{(e^x-1)^2}dx, \quad (8)$$

where $\Theta_i=\omega_i\hbar/k$, the v's are the appropriate phonon velocities mentioned previously, and

$$B=B_L\hbar^2/k^2,\quad C=B_T\hbar^3/k^3,$$
$$D=B_{TU}\hbar^2/k^2,\quad E=B_H\hbar^2/k^2.$$

The parameters used in analyzing the high-temperature lattice thermal conductivity should provide a good fit to the low-temperature data as well. In other words, the choice of the parameters should be consistent with the analysis at low temperatures. This condition can easily be maintained during the analysis. This is because of the fact that at lowest temperatures the phonon conductivity is decided by boundary scattering,

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and that at comparatively high temperatures Ax^4 is the dominant term. We therefore use the same parameter A as that used by Holland.[12] In Table I, we have given the parameters which lead to the best fit to the experimental data of Fulkerson *et al.*[8] These parameters are expected to be consistent with the low-temperature analysis. Figure 1 shows that a reasonably good fit has been obtained. One feature is that our calculations can be represented by two almost straight lines with different slopes, one below and the other above about 670°K, with a slope change at this temperature. This behavior is in agreement with the experimental results. However, there is disagreement between theory and experiment at about 670°K: The experimental results lie below the calculated values. According to Fulkerson *et al.*,[8] Godfrey *et al.*[29] have tried to explain the peculiar behavior at 670°K by including an exponential factor in the three-phonon relaxation-time expression. Such an explanation is not valid, since this exponential factor should be appreciable for only low temperatures,[30] whereas the above temperature is quite high. We think that there is a point of inflection at about 670°K in the experimental results. Such behavior cannot be explained by using relaxation-time expressions, whose derivatives with respect to temperature are smoothly varying functions of T and always positive as in the present case. In other words, we conclude that the structures of the relaxation times are not simple in reality. However, a practical derivation of the relaxation-time expressions in an exact form is almost an impossibility. The above behavior is thus left unexplained.

With the present choice of the parameters, the main contribution to the thermal conductivity comes from K_{T2}. The Ax^4 term in the integrands of the expressions for K_{L1}, K_{L2}, and K_{T1} is quite small compared with the other term, so that neglecting it leads to simple power expressions for K_{L1}, K_{L2}, and K_{T1}. Thus, K_{L1} plus K_{L2} may be approximated by $K_L = 2.2\times10^7/T^3$ W cm^{-1} deg^{-1} and K_{T1} is given by $1.95\times10^9/T^4$ W cm^{-1} deg^{-1}. In the expression for K_{T2}, however, all three terms Ax^4, $Dx^2/T^2 \sinh x$, and Ex^2 are comparable in magnitude for values of x within the integration limits. Since the second term is inversely proportional to T^2, at higher temperatures the third term dominates the second in magnitude. These two terms are roughly of equal magnitudes at about 500°K, but at lower temperatures the second is larger than the third.

TEMPERATURE DEPENDENCE OF RELAXATION TIMES

Recently, Guthrie[31] has studied the temperature dependence of the three-phonon processes. According to him, the temperature dependence of the relaxation time may be expressed as T^m, where m is an exponent that varies with temperature and phonon frequency ω. Because of the dependence of m on ω, m has upper and lower limits, and, accordingly, an averaged intermediate value of m may be used to express the temperature dependence of this relaxation time for all phonons. Since m depends on T, a given value of m cannot be used for all temperatures; a continuously varying value is required. For Si, Guthrie has given $m<2$ for $T>282$°K and has argued that the T^4 and T^3 laws are not valid for T above 43 and 55°K, respectively, whether the phonon concerned belongs to the transverse or to the longitudinal branch, and whether the scattering process is normal or umklapp. At high temperatures $m=1$ should be valid. This latter result is in agreement with the temperature dependence that has been derived by Herring.[32]

TABLE I. Values of the parameters used in the analysis of the lattice thermal conductivity of Si at high temperatures. Relaxation times used are $\tau_{3\text{ph}}^{-1}=B_L\omega^2T^3$ for the longitudinal, $\tau_{3\text{ph}}^{-1}=B_T\omega T^4$ for the nondispersive transverse, and $\tau_{3\text{ph}}^{-1}=B_{TU}\omega^2/\sinh x$ for the dispersive transverse phonons; $\tau_{\text{pt}}^{-1}=A\omega^4$ and $\tau_{4\text{ph}}^{-1}=B_H\omega^2T^2$ for all phonons.

A	1.32×10^{-44} sec^3 [a]
B_L	2.57×10^{-24} sec deg^{-3}
B_T	1.12×10^{-13} deg^{-4}
B_{TU}	1.61×10^{-18} sec
B_H	1.58×10^{-23} sec deg^{-2}

[a] Reference 12.

We have analyzed the conductivity in view of the aforesaid temperature dependence of the three-phonon relaxation times. Their frequency dependence is expected to be the same as used by Holland and given by Herring[32] for normal processes. We take the following expressions for $\tau_{3\text{ph}}^{-1}$:

$$\begin{aligned}\tau_{3\text{ph}}^{-1}&=B_L'\omega^2T \quad \text{(long. branch)},\\ \tau_{3\text{ph}}^{-1}&=B_T'\omega T \quad \text{for} \quad 0<\omega<\omega_1\\ &=B_{TU}\omega^2/\sinh x \quad \text{for} \quad \omega_1<\omega<\omega_2\\ &\qquad\qquad \text{(trans. branch)}. \quad (9)\end{aligned}$$

The form of the integrands in Eqs. (5)–(8) will be changed accordingly. We have to replace BTx^2 by $B'x^2/T$ and CTx by $C'x/T$, where the new primed constants B' and C' are related to the parameters of Eq. (9). If the four-phonon term is not used, then each of the integrals varies approximately inversely with temperature. The resulting lattice thermal resistivity will be almost proportional to T. The slope of the W-versus-T curve is as shown in Fig. 2. This behavior differs very much from the experimental results. In such a case, the inclusion of higher phonon processes becomes very necessary.[14] We have assumed that the strength of the four-phonon term is almost the same in each integral. We retain the value of A that has been previously used. In order to fit the experimental curve,

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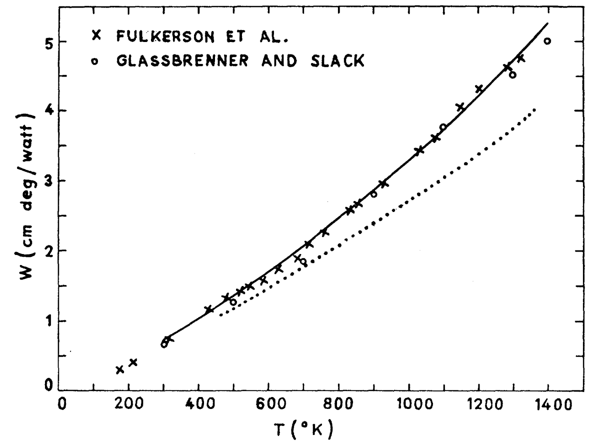

FIG. 2. Lattice thermal resistivity of Si. The solid line is obtained by making use of the parameters listed in Table II. The dotted curve shows the possible behavior when four-phonon processes are not taken into consideration.

values of the parameters are such that in K_{L1} and K_{L2} the four-phonon term is negligible. Since the behavior of K_{T1} and that of K_{T2} are more or less the same at high temperatures, the analysis becomes to some extent arbitrary. For example, the values of C' and D' can be varied without changing total resistivity. Using the parameters given in Table II, the fit to the experiment shown in Fig. 2 is obtained. Comparison of Figs. 1 and 2 shows that the present fit is similar to that of Fig. 1 and is in no way better. The behavior of W near 670°K is still not explained by this analysis. A difficulty in the present analysis is that it cannot be easily extended to lower temperatures. This is because the temperature dependence that we assume for the relaxation times is not valid at lower temperatures. We should use a varying exponent of T in Eq. (9). An extension of the analysis to lower temperatures is possible if one takes a T^3 factor in Eq. (9) in place of T for temperatures below 300°K, with a value of the parameter such that at 300°K the two relaxation times given by the expressions used for $T<300$°K and $T>300$°K are equal. The frequency dependence may, however, be assumed to be the same throughout.

TABLE II. Values of the parameters used in the analysis of the lattice thermal conductivity of Si at high temperatures. Relaxation times used are $\tau_{3\mathrm{ph}}^{-1}=B_L'\omega^2T$ for the longitudinal, $\tau_{3\mathrm{ph}}^{-1}=B_T'\omega T$ for the nondispersive transverse, and $\tau_{3\mathrm{ph}}^{-1}=B_{TU}\omega^2/\sinh x$ for the dispersive transverse phonons; $\tau_{\mathrm{pt}}^{-1}=A\omega^4$ and $\tau_{4\mathrm{ph}}^{-1}=B_H\omega^2T^2$ for all phonons.

A	1.32×10^{-44} sec^3 [a]
B_L'	1.71×10^{-18} sec deg^{-1}
B_T'	6.73×10^{-7} deg^{-1}
B_{TU}	5.74×10^{-18} sec
B_H	4.46×10^{-23} sec deg^{-2}

[a] Reference 12.

CONCLUSION

In the present analysis we find that the contribution to the thermal conductivity due to high-frequency transverse phonons is much larger than that due to others. Such a result has been obtained recently by Hamilton and Parrott[33] in the case of Ge. That the transverse phonons play an important role in thermal transport was suggested by Parrott[34] and Holland.[12] We conclude that at high temperatures multiphonon processes should be considered in calculating thermal resistivity. A rigorous analysis of the relaxation-time expressions of such processes will prove to be of some help to explain the high-temperature thermal conductivity data. An exact form of the temperature exponent in the three-phonon relaxation-time expressions should be investigated. We expect that if an exponent m that varies with T continuously is used in these expressions, better results will be obtained. This means that m should be expressed as a function of T that tends to unity at high temperatures and to 3 or 4 at low temperatures. Further, Holland's method of taking account of the dispersive nature of phonon frequency by defining a suitably averaged velocity for the phonons should be modified by assuming an empirical relation between phonon frequency ω and wave vector q, say, an expression that involves linear and quadratic terms in q such that the constants appearing are related to the velocity of low-frequency phonons and the total number of phonon states available for the concerned branch.

ACKNOWLEDGMENTS

Two of the authors (YPJ and MDT) are grateful to the Council of Scientific and Industrial Research, New Delhi, for financial assistance. Thanks are due to Professor K. S. Singwi, Professor Vachaspati, and Professor B. Dayal for their interest in the present work.

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