[1] For references to early work on Ge and Si, see E. Burstein, G. Picus, and N. Sclar, in *Photoconductivity Conference*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (Wiley, New York, 1956).

[2] W. G. Spitzer and J. M. Whelan, Phys. Rev. 114, 59 (1959).

[3] M. D. Sturge, Phys. Rev. 127, 768 (1962).

[4] I. Balslev, Phys. Rev. 173, 762 (1968).

[5] R. Braunstein and E. O. Kane, J. Phys. Chem. Solids 23, 1423 (1962).

[6] I. Balslev, Phys. Rev. 177, 1173 (1969).

[7] W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, J. Appl. Phys. 32, 2102 (1961).

[8] W. G. Spitzer, J. Appl. Phys. 34, 792 (1963).

[9] E. Haga and H. Kimura, J. Phys. Soc. Japan 18, 777 (1963); 19, 471 (1964); 19, 658 (1964).

[10] E. Haga, J. Phys. Soc. Japan 19, 2030 (1964); 20, 735 (1965).

[11] S. Perkowitz, J. Appl. Phys. 40, 3751 (1969).

[12] J. W. Allen and J. W. Hodby, Proc. Phys. Soc. (London) 82, 315 (1963).

[13] J. W. Hodby, Proc. Phys. Soc. (London) 82, 324 (1963).

[14] K. Osamura and Y. Murakami, J. Phys. Soc. Japan 26, 1063 (1969).

[15] Y. S. Chen, W. Shockley, and G. L. Pearson, Phys. Rev. 151, 648 (1966).

[16] W. G. Spitzer, M. Gershenzon, C. J. Frosch, and D. F. Gibbs, J. Phys. Chem. Solids 11, 339 (1959).

[17] W. Paul, J. Appl. Phys. 32, 2082 (1961).

[18] R. Zallen and W. Paul, Phys. Rev. 134, A1628 (1964).

[19] A. D. Remenyuk, L. G. Zabelina, Yu. I. Uklianov, and Yu. V. Shmartsev, Fiz. Tekh. Poluprov. 2, 666 (1968); 2, 671 (1968) [Soviet Phys. Semicond. 2, 557 (1968); 2, 561 (1968)].

[20] J. D. Wiley and M. DiDomenico, Jr., Phys. Rev. B 1, 1655 (1970).

[21] P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, J. Appl. Phys. 38, 3551 (1967).

[22] D. A. Kleinman and W. G. Spitzer, Phys. Rev. 118, 110 (1960).

[23] A. S. Barker, Jr., Phys. Rev. 165, 917 (1968).

[24] A. H. Kahn, Phys. Rev. 97, 1647 (1955).

[25] E. O. Kane, J. Phys. Chem. Solids 1, 82 (1956).

[26] H. Y. Fan, W. Spitzer, and R. S. Collins, Phys. Rev. 101, 566 (1956).

[27] R. Rosenberg and M. Lax, Phys. Rev. 112, 843 (1958).

[28] H. J. G. Meyer, Phys. Rev. 112, 298 (1958).

[29] S. Visvanathan, Phys. Rev. 120, 376 (1960); 120, 379 (1960).

[30] W. Dumke, Phys. Rev. 124, 1813 (1961).

[31] L. M. Foster and J. Scardefield, J. Electrochem. Soc. 116, 494 (1969). Also see J. M. Dishman, M.. DiDomenico, Jr., and R. Caruso, Phys. Rev. B 2, 1988 (1970).

[32] H. C. Casey, F. Ermanis, and K. B. Wolfstirn, J. Appl. Phys. 40, 2945 (1968).

[33] J. S. Blakemore, *Semiconductor Statistics* (Pergamon, London, 1962).

[34] T. S. Moss, *Optical Properties of Semiconductors* (Butterworth, London, 1961).

[35] W. L. Bond, J. Appl. Phys. 36, 1674 (1965).

[36] A. S. Barker (private communication).

[37] J. D. Wiley and M. DiDomenico, Jr., Phys. Rev. B 2, 427 (1970).

[38] R. A. Faulkner (private communication). These parameters were calculated by Faulkner using the pseudopotentials of M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

[39] R. L. Bowers and G. D. Mahan, Phys. Rev. 185, 1073 (1969).

[40] O. G. Lorimor, J. Appl. Phys. 41, 5035 (1970).

[41] J. M. Dishman and M. DiDomenico, Jr. (unpublished).

[42] The anomalous wavelength dependence of sample *B* at short wavelengths is not understood but was present in two samples of the same material.

[43] G. Lucovsky, Solid State Commun. 3, 299 (1965).

[44] H. B. Bebb and R. A. Chapman, J. Phys. Chem. Solids 28, 2087 (1967); H. B. Bebb, Phys. Rev. 185, 1116 (1969).

[45] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. GPO, Washington, D. C., 1964).

PHYSICAL REVIEW B VOLUME 3, NUMBER 2 15 JANUARY 1971

Phonon Conductivity of II-VI Semiconductors

K. C. Sood, M. P. Singh, and G. S. Verma
Physics Department, Banaras Hindu University, Varanasi-5, India

(Received 22 July 1970)

It is shown in the present work that the change in the slope of K-vs-T curve, which occurs in CdS and CdTe at a temperature beyond the conductivity maximum, can be explained by considering the separate contributions of longitudinal phonons and transverse phonons. The values of the limits of the different conductivity integrals for the different acoustic branches are taken from the theoretical work of Nusimovici and Birman for CdS and from Hayes's work for CdTe. The present work also establishes that transverse phonons make a major contribution towards phonon conductivity.

I. INTRODUCTION

It is now well established that in several semiconductors there occurs a change in the slope of K-vs-T curve in the high-temperature region and that this cannot be explained by one conductivity integral as given in Callaway's[1] theory of phonon conductivity. The well-known examples are Si and Ge.[2] Holland[2] explained the high-temperature results in the semiconductors on the basis of two-mode conduction. The distinction between longitudinal phonons and transverse phonons as carriers of thermal energy leads to different conductivity integrals, and hence there is a possibility of explaining the phonon-conductivity results consistently both in the high-temperature as well as in low-temperature regions. The temperature dependence of phonon conductivity of II-VI semiconductors (Cds and CdTe) is also similar to what is observed in Si or Ge. Both in CdS and CdTe,[3] there occurs a change in the slope of K-vs-T curve, which cannot be explained on the basis of Callaway's theory based on Debye's approximation.

Recently, Moore and Klein[4] have studied the phonon conductivity of pure and doped CdS and arrived at certain conclusions regarding the scattering of phonons by impurity and by themselves. Since the experimental results are confined to the temperature range 1.4–80 °K and they have not made any attempt to explain the earlier results of Holland,[3] who studied the phonon conductivity of CdS in the temperature range 1.3–300 °K, their conclusions regarding phonon-phonon scattering are not valid for the entire temperature range. Holland[3] also could not explain his experimental results in CdS and CdTe in the entire temperature range on the basis of Callaway's theory.

Recently Hamilton and Parrott[5] have shown that the thermal transport in Ge in the temperature range 1–400 °K is mostly due to transverse phonons. Transverse phonons thus deserve special consideration. It has been shown in the present work that the previously unexplained phonon-conductivity results of CdS and CdTe can be accounted for quite successfully in the entire temperature range if one considers the separate contributions of transverse phonons and longitudinal phonons. The values of the phase velocity and the limits of the conductivity integrals for the different acoustic branches for CdS are taken from the theoretical work of Nusimovici and Birman.[6] Similarly for CdTe, we have relied on the results of Hayes.[7]

II. PHONON CONDUCTIVITY

The phonon conductivity, according to Holland,[2] can be expressed as

$$\kappa = \tfrac{1}{3}\kappa_L + \tfrac{2}{3}(\kappa_{T1} + \kappa_{T2}) \ ,$$

where

$$\kappa_L = \frac{k_B}{2\pi^2}\left(\frac{k_B}{\hbar}\right)^3 \frac{T^3}{(v_L)_{0<\omega<\omega_3}} \int_0^{\Theta_3/T} \frac{e^x x^4 (e^x-1)^{-2}\, dx}{\tau_B^{-1} + \tau_{pt}^{-1} + \tau_{pp}^{-1}} \ ,$$

$$\kappa_{T1} = \frac{k_B}{2\pi^2}\left(\frac{k_B}{\hbar}\right)^3 \frac{T^3}{(v_{T1})_{0<\omega<\omega_1}} \int_0^{\Theta_1/T} \frac{e^x x^4 (e^x-1)^{-2}\, dx}{\tau_B^{-1} + \tau_{pt}^{-1} + \tau_{pp}^{-1}} \ ,$$

$$\kappa_{T2} = \frac{k_B}{2\pi^2}\left(\frac{k_B}{\hbar}\right)^3 \frac{T^3}{(v_{T2})_{\omega_1<\omega<\omega_2}} \int_{\Theta_1/T}^{\Theta_2/T} \frac{e^x x^4 (e^x-1)^{-2}\, dx}{\tau_B^{-1} + \tau_{pt}^{-1} + \tau_{pp}^{-1}} \ .$$

Here k_B is the Boltzmann constant and v_T and v_L are transverse and longitudinal phonon velocities. Θ_1, Θ_2, and Θ_3 are given by

$$\omega_1(\tfrac{1}{2}q_{\max}, T_A) = k_B\Theta_1/\hbar,$$

$$\omega_2(q_{\max}, T_A) = k_B\Theta_2/\hbar,$$

and

$$\omega_3(q_{\max}, L_A) = k_B\Theta_3/\hbar.$$

We have relied on the theoretical values of ω_1, ω_2, and ω_3 as we could not come across any experimental data in both cases of CdS and CdTe, although the values of phonon frequencies near the zone boundary have been estimated from infrared spectra by some workers.[8-10]

The relaxation rate due to the boundary scattering of phonons is given by the expression $\tau_B^{-1} = C/L$, where C is the average phonon velocity as given by

$$1/C = \tfrac{1}{3}(1/v_L + 2/v_T) \ .$$

L is the effective scattering length and, according to Casimir,[11] is given by $L = 1.12\sqrt{S}$, where S is the area of the rectangular cross section of the crystal. The value of τ_B is further corrected by a factor F, which, according to Ziman,[12] measures the effect of finite sample length.

The relaxation rate due to the scattering of phonons by point defects is

$$\tau_{pt}^{-1} = A\omega^4 = (V_0\Gamma/4\pi v^3)\omega^4$$

$$= (V_0/4\pi v^3)\ \left|\textstyle\sum_i f_i (1 - m_i/\bar{m})^2\right| \omega^4 \ .$$

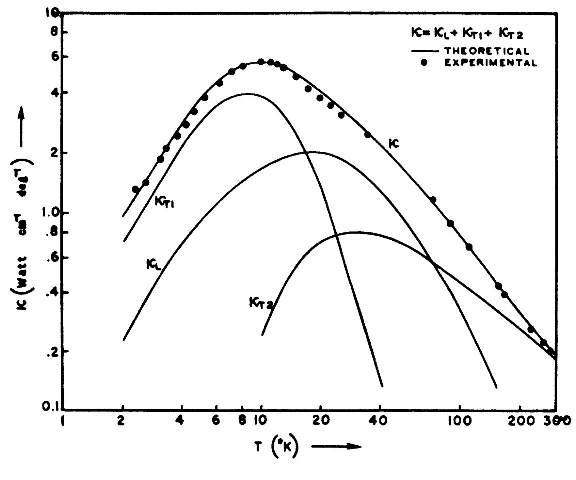

FIG. 1. Comparison of the theoretical values of the phonon conductivity of CdS with the experimentally obtained values in the temperature range 1–300 °K. Theoretical values are represented by solid lines and experimental values by circles.

TABLE I. Phonon frequencies at zone boundary and at $\frac{1}{2}q_{\max}$.

Substance	T_A (cm^{-1})	L_A (cm^{-1})	T_A at $\frac{1}{2}q_{\max}$ (cm^{-1})
CdS	42	175	32
CdTe	50	122	32

TABLE III. Values of τ_B and A obtained theoretically and also by adjustment for the best fit between experiment and theory.

Substance	τ_B(theor) (10^{-6}sec)	τ_B(expt) (10^{-6}sec)	A(theor) (10^{-44}sec^3)	A(expt) (10^{-44}sec^3)
CdS	1.6	1.0	6.21	10.2
CdTe	2.32	2.78	9.8	22.5

Here V_0 is the atomic volume, f_i is the relative abundance of the ith isotope of m_i, and $\bar{m}$ is the average mass of the species.

The relaxation rates due to phonon-phonon scattering for the transverse acoustic phonons are given by

$$\tau_N^{-1}\begin{pmatrix}\text{3-phonon, } T_A\\ 0<\omega<\omega_1\end{pmatrix}=B_{T1}\omega T^4 ,$$

$$\tau_N^{-1}\begin{pmatrix}\text{3-phonon, } T_A\\ \omega_1<\omega<\omega_2\end{pmatrix}=(B_{T2N})\omega^2 T ,$$

$$\tau_U^{-1}\begin{pmatrix}\text{3-phonon, } T_A\\ \omega_1<\omega<\omega_2\end{pmatrix}=(B_{T2})_U\omega^2 T ,$$

so that

$$\tau_N^{-1}+\tau_U^{-1}(T_A,\, \omega_1<\omega<\omega_2)=[(B_{T2})_N+(B_{T2})_U]\omega^2 T =B_{T2}\omega^2 T,$$

and for longitudinal acoustic phonons[13]

$$|\tau_N^{-1}+\tau_U^{-1}|_{(L_A,\,0<\omega<\omega_3)}=B_L\omega^2 T^3 .$$

Thus, the conductivity integrals take the form

$$\kappa_L=\frac{k_B}{2\pi^2}\left(\frac{k_BT}{\hbar}\right)^3\frac{1}{(v_L)_{0<\omega<\omega_3}}\times\int_0^{\Theta_3/T}\frac{e^x x^4(e^x-1)^{-2}\,dx}{\tau_B^{-1}+A(k_B/\hbar)^4T^4x^4+B_L(k_B/\hbar)^2T^5x^2},$$

$$\kappa_{T1}=\frac{k_B}{2\pi^2}\left(\frac{k_BT}{\hbar}\right)^3\frac{1}{(v_{T1})_{0<\omega<\omega_1}}\times\int_0^{\Theta_1/T}\frac{e^x x^4(e^x-1)^{-2}\,dx}{\tau_B^{-1}+A(k_B/\hbar)^4T^4x^4+B_{T1}(k_B/\hbar)T^5x},$$

$$\kappa_{T2}=\frac{k_B}{2\pi^2}\left(\frac{k_BT}{\hbar}\right)^3\frac{1}{(v_{T2})_{\omega_1<\omega<\omega_2}}\times\int_{\Theta_1/T}^{\Theta_2/T}\frac{e^x x^4(e^x-1)^{-2}\,dx}{A(k_B/\hbar)^4T^4x^4+B_{T2}(k_B/\hbar)^2T^3x^2}.$$

Here B_{T1}, B_{T2}, and B_L are treated as adjustable parameters, which can be evaluated from the best fit between the theoretical and experimental values of phonon conductivity in the entire temperature range.

III. RESULTS AND DISCUSSION

The values of the various parameters in the analysis of phonon-conductivity results in CdS and CdTe in the temperature range 1–300 °K are given in Tables I–IV. Table I gives the values of the phonon frequencies at the zone boundary of CdS and CdTe, respectively. CdS exists in two structures: wurtzite and sphalerite. For these two structures of CdS, the values of $q_{\max}$ for the first Brillouin zone are different in the required direction. However, if one considers Jones zone, the value of $q_{\max}$ in the required direction is the same for both structures. Comparing the dispersion curves in the [111] direction of sphalerite and the [0001] direction of wurtzite, Nusimovici and Birman found that (i) there is complete degeneracy in transverse branches and (ii) a little nondegeneracy in case of the longitudinal phonons (see Fig. 10 of Ref. 6). So for convenience of the calculations, we have taken the average value of zone-boundary phonon frequency in the case of longitudinal phonons. For CdTe, we have taken the values of ω at the Brillouin-zone boundary, as it exists only in one dominant zinc-blende structure. The values theoretically calculated by Hayes[7] and by Mani[14] are approximately the same, so we have taken the values given by Hayes. In Table I the values of

TABLE II. Values of phonon velocities and limits of the conductivity integrals.

Substance	v_L (10^5cm/sec)	v_{T1} (10^5cm/sec)	v_{T2} (10^5cm/sec)	Θ_1 (°K)	Θ_2 (°K)	Θ_3 (°K)	F[a]
CdS	4.42[b]	2.68	0.84	45.9	60.3	250.4	0.84
CdTe	2.97[c]	2.32	1.30	45.9	72.0	175.6	0.80

[a] Reference 12.

[b] From A. R. Hutson, J. Appl. Phys. 32, 2287 (1961).

[c] See D. G. Thomas, J. Appl. Phys. 32, 2298 (1961).

TABLE IV. Values of adjustable parameters.

Substance	B_{T1} [(°K)$^{-4}$]	B_{T2} [sec (°K)$^{-1}$]	B_L [sec (°K)$^{-3}$]
CdS	8.2×10^{-11}	1.76×10^{-19}	$2.6\ \times10^{-23}$
CdTe	6.3×10^{-11}	5.22×10^{-19}	1.86×10^{-22}

the phonon frequencies at $\frac{1}{2}q_{\max}$ are also given. The values of transverse phonon velocities in the two regions have been evaluated by the ratio of the slopes of the dispersion curve in the two regions.

IV. CONCLUSION

It may be seen from Figs. 1 and 2 that the present approach explains the temperature dependence of the phonon conductivity of CdS and CdTe in the entire range 1–300 °K. The present approach consists in the consideration of separate contributions of longitudinal and transverse phonons towards thermal conductivity as outlined by Holland for Si and Ge. The present calculations, which are based on the relaxation-time approach, further establish that transverse phonons make a major contribution towards phonon conductivity of II-VI semiconductors such as CdS and CdTe. This conclusion is in agreement with the result of Hamilton and Parrott in Ge, obtained on the basis of variation treatment. The change in the slope of K-vs-T curve for CdS and CdTe is explained very well on the basis of two-mode conduction. However, K-vs-T curves show slight dips just after the conductivity maximum, which are due to the resonance scattering of phonons due to impurities. No attempt has been made in the present work to explain these dips in the phonon-conductivity curves.

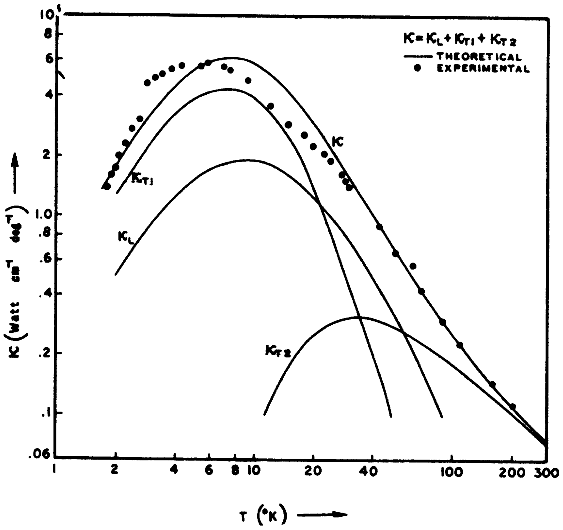

FIG. 2. Comparison of the theoretical values of the phonon conductivity of CdTe with the experimentally obtained values in the temperature range 1–300 °K. Theoretical values are represented by solid lines and experimental values by circles.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor B. Dayal and Professor K. S. Singwi for their interest in this work. One of us (K. C. S.) is indebted to CSIR, India for the award of a Junior Research Fellowship.

---

[1] J. Callaway, Phys. Rev. 113, 1046 (1959).

[2] M. G. Holland, Phys. Rev. 132, 2461 (1963).

[3] M. G. Holland, Phys. Rev. 134, 471 (1964).

[4] G. E. Moore, Jr. and M. V. Klein, Phys. Rev. 179, 722 (1969).

[5] R. A. H. Hamilton and J. E. Parrott, Phys. Rev. 178, 1284 (1969).

[6] M. A. Nusimovici and J. L. Birman, Phys. Rev. 157, 925 (1967).

[7] W. Hayes and A. R. L. Spray, J. Phys. C 2, 1129 (1969); C. T. Sennet, D. R. Bosomworth, W. Hayes, and A. R. L. Spray, *ibid.* 2, 1137 (1969).

[8] R. Marshall and S. S. Mitra, Phys. Rev. 134, 1019 (1969).

[9] G. L. Bottger, J. Chem. Phys. 47, 4858 (1967).

[10] G. A. Slack, F. S. Ham, and R. M. Chrenko, Phys. Rev. 152, 376 (1966).

[11] H. B. G. Casimir, Physica 5, 595 (1938).

[12] R. Berman, F. E. Simon, and J. M. Ziman, Proc. Roy. Soc. (London) A220, 171 (1953).

[13] Here it has been found that the ω^2T dependence for longitudinal phonons does not explain the thermal conductivity in the entire temperature range.

[14] K. K. Mani (unpublished).