

TABLE III. The theoretical electronic thermal conductivity of Si and Ge versus temperature.

Crystal	T °K	$\frac{b}{(1+b)^2}$	E_G eV	σ ohm ⁻¹ cm ⁻¹	K_{ep}	K_{eb}	K_e
					mW/cm deg		
Si	800	0.21	0.92	3.9	0.0	1.4	1.4
	1000	0.21	0.85	22.	0.3	6.2	6.5
	1200	0.21	0.78	73.	1.3	16.4	17.7
	1400	0.21	0.71	170.	3.5	31.9	35.4
	1600	0.21	0.55	315.	7.5	50.5	58.0
	1681	0.21	0.52	385.	9.6	58.2	67.8
Ge	400	0.20	0.61	0.9	0.0	0.3	0.3
	600	0.19	0.52	30.	0.3	5.0	5.3
	800	0.18	0.43	160.	1.9	18.0	19.9
	1000	0.16	0.34	440.	6.5	33.4	39.9
	1200	0.16	0.26	870.	15.5	51.9	67.4
	1210	0.16	0.25	890.	16.0	52.5	68.5

The various quantities are defined as k =Boltzmann's constant, e =electronic charge, σ =total electrical conductivity at T , b =mobility ratio at T , and E_G =indirect energy gap at T . The polar part K_{ep} is the usual Wiedemann-Franz-Lorenz contribution present in metals. The bipolar part K_{eb} is a property of semiconductors, and is caused by electron-hole pairs with energy E_G diffusing down the temperature gradient. Equation (13) has been derived for a very idealized semiconductor which is assumed to be intrinsic, to possess simple parabolic valence and conduction bands, and in which the charge carriers suffer only acoustic mode lattice scattering where the scattering probability varies with the carrier energy ϵ as $\sqrt{\epsilon}$. Neither Si nor Ge can be said to fit this model very well since they have multiple minima conduction bands, multiple valence bands, and since both acoustic mode and intervalley scattering occur. An exact calculation of K_e in which all of these effects are considered is not undertaken here. However, as will be seen, Eq. (13) yields predictions which are in reasonable agreement with the experiment.

The experimental parameters that are used in Eq. (13) are σ , b , and E_G . Representative values for these parameters and the calculated values for K_{ep} and K_{eb} are given in Table III. For Si, the $\sigma(T)$ values have been taken from Morin and Maita⁵⁶ and Mokrovskii and Regel,⁵⁷ and the values of b versus T have been estimated from an extrapolation of the mobility curves of Morin and Maita.⁵⁶ The $E_G(T)$ values⁵⁶ have been corrected for more recent values of the effective mass, and are taken from Hannay.⁵⁸ It has been assumed that E_G varies linearly with temperature and the value of $E_G = (1.21 - 4.1 \times 10^{-4}T)$ eV was used.

For Ge the $\sigma(T)$ values have been taken from Morin and Maita,⁵⁹ from Epstein,⁶⁰ and from the recent com-

TABLE IV. The experimentally determined contributions to K in solid Si and Ge at their respective melting points.

Quantity	Si 1681°K	Ge 1210°K
K_{ep}/K	5%	9%
K_{eb}/K	32%	32%
K_e/K	63%	59%
K (W/cm deg)	0.22	0.17

plication of Hamilton and Seidensticker.⁶¹ The values of b versus T have been estimated from an extrapolation of the data given by Morin and Maita.⁵⁹ The $E_G(T)$ values⁵⁹ have been corrected for better effective mass values.⁵⁸ The equation used for Ge was $E_G = (0.785 - 4.4 \times 10^{-4}T)$ eV. The computation of K_{ep} depends only on σ and is probably accurate to $\pm 5\%$. The computation of K_{eb} depends similarly on σ and is also sensitive to errors in E_G and b . The over-all accuracy in the calculation of K_{eb} is estimated to be $\pm 15\%$. Figures 12 and 13 show how the calculated theoretical value of K_e compares with the experimental determination, which is judged to be accurate to within ± 5 mW/cm deg. This uncertainty is indicated by the broad band in Figs. 12 and 13. Since the theoretical values of K_e are probably accurate to $\pm 15\%$, the agreement with theory is considered quite adequate. In view of the uncertainties in both the calculated and experimental values of K_e it does not seem worthwhile, at present, to undertake a more exact calculation of K_e in which the details of the band structure of Si and Ge are carefully taken into account.

The three contributions to the total thermal conductivity, K_{tot} , at the melting point are K_e , K_{ep} , and K_{eb} . Table IV shows the relative contributions of these three terms for Si and Ge. K_e is estimated from the extrapolated dashed curve in Figs. 2 and 3, K_{ep} is calculated from Eq. (13), and K_{eb} is taken to be equal to $K_{tot} - K_e - K_{ep}$. For both materials the lattice thermal conductivity is still dominant at the melting point and is 61% of the total, the bipolar electron-hole pair diffusion accounts for 32%, while the usual Wiedemann-Franz-Lorenz contribution is only 7% of the total.

The experimental value of K_{eb} determined from $K_{tot} - K_e - K_{ep}$ can be used to estimate E_G by means of Eq. (13). The values of b and σ at the melting point are taken from Table III, and the experimental values of K_e are taken from Figs. 12 and 13. The result is that at the melting point the thermal band gap is $E_G = 0.6 \pm 0.1$ eV for Si and $E_G = 0.26 \pm 0.08$ eV for Ge. These values are not very far from the linearly extrapolated values of 0.52 and 0.25 eV given in Table III. The K_e results show that the band gap in the solid at the melting point is nonzero. The gap thus drops discontinuously to zero upon melting, since both liquid Si and Ge are metallic in character.^{57,61}

⁶¹ D. R. Hamilton and R. G. Seidensticker, J. Appl. Phys. 34, 2697 (1963).

⁵⁶ F. J. Morin and J. P. Maita, Phys. Rev. 96, 28 (1954).

⁵⁷ N. P. Mokrovskii and A. R. Regel, Zh. Tekhn. Fiz. 23, 779 (1953).

⁵⁸ N. B. Hannay, Semiconductors (Reinhold Publishing Corporation, New York, 1959), p. 332.

⁵⁹ F. J. Morin and J. P. Maita, Phys. Rev. 94, 1525 (1954).

⁶⁰ E. A. Epstein, Ph.D. thesis, Purdue University, 1954 (unpublished).