TABLE VII. Comparison between theoretical and experimental values for various transitions. All transitions originate from the state $^6A_{1g}$. The values are given in cm^{-1}.

Transition	Theoretical	Experimental	Experimental values for Fe^{3+} in beryl
$^6A_{1g} \rightarrow {}^4T_1t^4e$	16 700	not observed	14 200
$\rightarrow {}^4T_2t^4e$	17 700	17 200 17 800	17 500
$\rightarrow {}^4Et^3e^2$ ${}^4A_1t^3e^2$	24 000	25 600	23 600
$\rightarrow {}^4T_1t^3e^2$	24 500	not observed	26 500

compares well with the experimental value of 1650 cm^{-1} obtained by McClure.[7]

Table VII shows the comparison between our calculated values [for position (b)] of the energy levels and those obtained experimentally by McClure.[7] The last column in Table VI gives the values for Fe^{3+} in beryl.[14] We quote these values because in beryl also Fe^{3+} is coordinated with six oxygen ions and the average Al–O distance is 1.94 Å which is fairly close to the Al—O distance in corundum.

[14] M. Duir and W. Low, Phys. Rev. **119**, 1587 (1960).

DISCUSSION

Though our calculations are in good agreement with the experimental results, it is obvious that the present model will not lead to the correct spectra of other transition metal ions in Al_2O_3 because of the strong Z_{eff} dependence of $\langle r^k \rangle$ [See Eq. (6)]. The alternative method of calculating is to use Watson's[15] functions. The values so obtained vary less strongly from one transition metal ion to the other, but are unrealistically low, for example, for Fe^{3+} Watson's functions give $\langle r^2 \rangle = 0.32\times10^{-16}$ cm^2, $\langle r^4 \rangle = 0.22\times10^{-32}$ cm^4, and $Dq = 300$ cm^{-1}. A recent note by Artman and Murphy[16] on ruby takes into account the shift of the neighboring O^{2-} ions due to the shift of the Cr^{3+} ion along the C axis. One should really expect different amounts of displacements for different ions substituted in Al_2O_3. This effect, along with the fact that the changes in the configuration of the surrounding ions are caused due to the substitutional ion being in an excited state, might lead to a model which gives good results for all the transition metal ions.

[15] R. E. Watson, Technical Report No. 12, 1959, Solid State and Molecular Theory Group MIT, Cambridge, Massachusetts.

[16] J. O. Artman and J. C. Murphy, Bull. Am. Phys. Soc. **8**, 313 (1963).

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Thermal Conductivity of III-V Compounds at High Temperatures*

E. F. STEIGMEIER AND I. KUDMAN
RCA Laboratories, Princeton, New Jersey

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The thermal conductivity of intrinsic and heavily doped InAs crystals was determined between 300 and 900°K using the diffusivity technique. The electronic contribution was computed using the measured electrical conductivity and the Seebeck coefficient. Adding 3×10^{19} donors and acceptors cm^{-3} to the intrinsic InAs increases the lattice thermal resistivity appreciably. Thermal conductivity data are given also for GaAs and InP. The anharmonicity parameters χ of the III-V compounds, obtained by comparing the experimental thermal conductivities with the theoretical values of Leibfried and Schlömann for 3-phonon processes, are found to be temperature- and mass-ratio-dependent. The temperature dependence is believed to be caused by higher order processes. The correlation between the anharmonicity parameters and the mass ratios of the constituent elements of the compounds is ascribed to an effect of optical-mode scattering on the lattice thermal resistivity.

A. INTRODUCTION

THE III-V compounds represent particularly suitable materials for studying the high-temperature thermal conductivity since they cover a wide range of values of the parameters influencing this property.

The present work is a detailed experimental investigation of the thermal conductivity of InAs. Previous measurements of this substance have been made by Bowers *et al.*[1] and Stuckes.[2] This study was undertaken to extend the measurements on intrinsic material to higher temperatures as well as to investigate the effect of donor and acceptor impurities on the lattice thermal conductivity of InAs. This latter effect was observed earlier[3] in Ge.

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[1] R. Bowers, R. W. Ure, J. E. Bauerle, and A. J. Cornish, J. Appl. Phys. **30**, 930 (1959).

[2] A. D. Stuckes, Phil. Mag. **5**, 84 (1960).

[3] D. S. Beers, G. D. Cody, and B. Abeles, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and The Physical Society, London, 1962), p. 41.

The lattice thermal conductivity of InAs and those of other III-V compounds are compiled and correlated to gain more insight into the important scattering mechanisms in this class of materials. The data are interpreted in terms of the theory of Leibfried and Schlömann[4] for 3-phonon processes, and the possible occurrence of higher order processes is investigated. The interesting question of how the optical-mode scattering effects the lattice thermal conductivity of the III-V compounds is also studied.

B. InAs

Experimental

The InAs specimens were large grain polycrystals grown by the horizontal Bridgman technique. They were cut to the size of 6 mm×6 mm×50 mm. Samples *LE* 29 and 42 were undoped, n type, hereinafter to be referred to as "intrinsic"; their carrier concentrations were 2.6×10^{16} cm^{-3} and 2.1×10^{16} cm^{-3}, respectively, at 77°K. The sample *I*-92 was n type, sulfur doped to a carrier concentration of 3×10^{19} cm^{-3}. The sample *I*-95 was p type, zinc doped to a carrier concentration of 3×10^{19} cm^{-3}.

The apparatus described by Abeles *et al.*[5] was used to measure the thermal diffusivity c_p/κ of InAs between 300 and 900°K. This method has the advantage of eliminating radiation losses. However, knowledge of the specific heat is required.

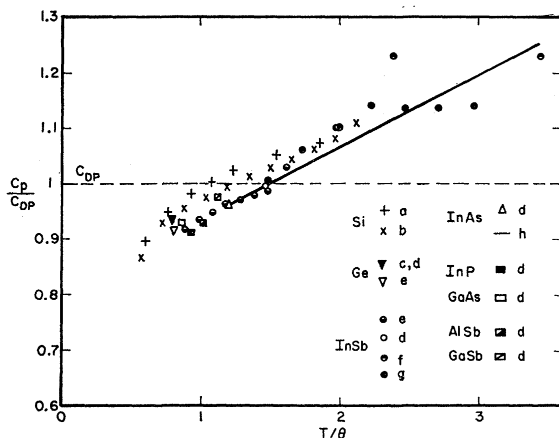

FIG. 1. The reduced specific heats of Group IV and III-V semiconductors as a function of the reduced temperatures. (a) Data from *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957). (b) D. H. Dennison (private communication), quoted in H. R. Shanks, P. D. Maycock, P. H. Sidles, and G. C. Danielson, Phys. Rev. **130**, 1743 (1963). (c) P. Flubacher, A. L. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959). (d) Ref. 9. (e) P. V. Gul'tyaev and A. V. Petrov, Fiz. Tverd. Tela. **1**, 368 (1959) [translation: Soviet Phys.—Solid State **1**, 330 (1959)]. (f) N. H. Nachtrieb and N. Clement, J. Phys. Chem. **62**, 876 (1962). (g) From a combination of κ/c of B. Abeles D. S. Beers, and G. D. Cody (private communication), with κ of Ref. 18. (h) Extrapolation from room temperature measurements of Ref. 9. $c_p=c_{p300°\mathrm{K}}+7.7\times10^{-4}(T-300)$[j/cm^3 deg].

TABLE I. The influence of optical mode scattering on the lattice thermal conductivity of group IV and group III-V semiconductors.

	M_1/M_2	M	a (Å)	Θ (°K)	$\kappa_l^{300°\mathrm{K}\,c}$ (w/cm deg)	γ $T=\Theta$
Si	1	28.1	5.431	647.8[a]	1.412[d]	0.94
Ge	1	72.6	5.6576	374.0[a]	0.606[d]	0.95
InSb	1.06	118.4	6.4789	202.5[a]	0.166[e]	0.97
GaAs	1.07	72.3	5.6535	344.2[a]	0.455[f]	0.98
InAs	1.53	94.8	6.0585	249.0[a]	0.273[g]	0.91
GaSb	1.75	95.7	6.0955	265.5[a]	0.378[h]	0.86
GaP	2.25	50.4	5.4506	435.0[b]	...	...
InP	3.70	72.9	5.8688	321.5[b]	0.670[f]	0.76
AlSb	4.51	74.4	6.1356	292.0[a]	0.463[i]	0.79

[a] Computed from elastic constants after Ref. 6, using elastic constants given by H. J. McSkimin, J. Appl. Phys. **24**, 988 (1955); D. I. Bolef and M. Menes, *ibid.* **31**, 1426 (1960); D. Gerlich, Bull. Am. Phys. Soc. **8**, 472 (1963).
[b] Estimated Ref. 7.
[c] Isotope effect subtracted.
[d] Ref. 3.
[e] Ref. 18.
[f] Ref. 19.
[g] This work.
[h] Ref. 20.
[i] Ref. 21.

High-temperature measurements of the specific heat of InAs are not available. Figure 1 shows the assumptions which were made to obtain this information. This graph gives a plot of the reduced values of the measured specific heats versus the reduced temperatures of Si, Ge, and all III-V compounds available; the Debye temperatures used for the reduction were computed[6,7] from elastic constants and are given in Table I. In this plot all the materials fall on one curve with some spread. Recent measurements of Gerlich[8] on Si and Ge also confirm this fact. The full curve in Fig. 1 represents the assumed temperature dependence of the specific heat of InAs. The curve, which can be expressed as $c_p=c_{p300°\mathrm{K}}+7.7\times10^{-4}(T\text{-}300)$ [j/cm^3 deg], passes through the measured[9] room-temperature value of InAs and is believed to be a good approximation to c_p at elevated temperatures. Furthermore, it was assumed that the specific heat does not change with doping.

In Fig. 2 are plotted the measured thermal resistivities and, for comparison, the previous results of Stuckes[2] and Bowers *et al.*[1] Excellent agreement is found between the values for our two intrinsic samples, which differ from each other by less than 2%, and the data of Stuckes for the same carrier concentration; the curve of Bowers *et al.* deviates slightly from our results. The thermal resistivity of the heavily doped p-type sample is not much different from the intrinsic material. The heavily doped n-type sample, however, exhibits a much smaller thermal resistivity for the same carrier concentration. This is due to the large electron to hole mobility ratio of InAs which effects the electronic thermal conductivity.

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[7] E. F. Steigmeier, Appl. Phys. Letters **3**, 6 (1963).
[8] D. Gerlich (private communication).
[9] U. Piesbergen, Z. Naturforsch. **18a**, 141 (1963).

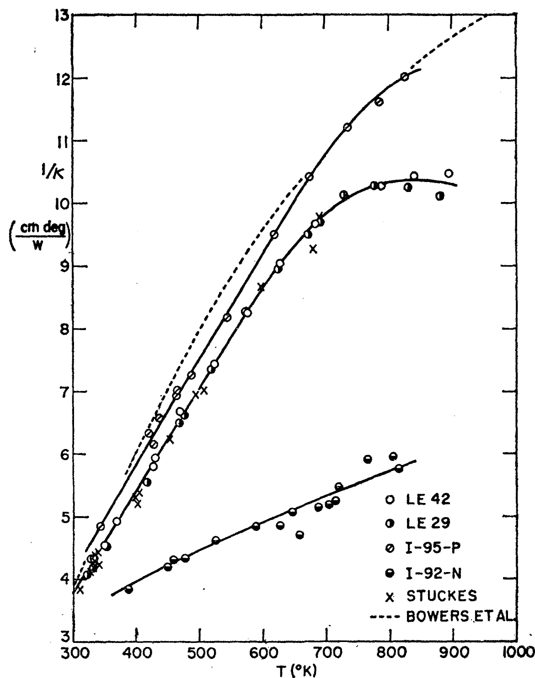

FIG. 2. The thermal resistivity of intrinsic and heavily doped InAs as a function of the absolute temperature.

Seebeck coefficients and electrical resistivities of all the above samples are shown in Figs. 3 and 4.

Electronic Thermal Conductivity

The electronic thermal conductivity of the intrinsic samples was computed by using the formula[10]

$$\kappa_{\mathrm{el}}=\frac{k^2}{e^2}\sigma T\left\{\frac{A_n\sigma_n+A_p\sigma_p}{\sigma}+\frac{npb}{(nb+p)^2}\left[\frac{E_g^T}{kT}+B_n+B_p\right]^2\right\}, \quad (1)$$

where n and p refer to electrons and holes, respectively; E_g^T is the band gap at the temperature T, σ the electrical conductivity, and b the mobility ratio. For Boltzmann statistics,

$$A_{n,p}=r+\tfrac{5}{2}, \quad B_{n,p}=r+\tfrac{5}{2}. \quad (2)$$

r is given by $\tau=\tau_0E^r$. Ehrenreich[11] has treated the failure of the relaxation time approximation for polar scattering at intermediate temperatures. He has shown that, in the limit of Boltzmann statistics and no screening effects, a relaxation time of the above form fits the results of the variational technique if r is allowed to be temperature-dependent. These assumptions, and specifically $r(T/\Theta_E)$ given by Ehrenreich, were used for this calculation of the electronic thermal conductivity. This seems to be satisfactory since the electronic contribution is small compared to the lattice part of intrinsic InAs at all temperatures below 800°K. An optical characteristic temperature,[12] $\Theta_E=350$°K, was used to compute r from the function $r(T/\Theta_E)$. The relation[13] $E_g^T=0.45-3.5\times10^{-4}T$(eV) was assumed to calculate the energy gap E_g^T. The mobility ratio b and the product np of the electron and hole concentrations, n and p, were taken from electrical measurements of Folberth *et al.*[14] The values of b range from $b=175$ at 350°K to $b=350$ at 700°K and higher.

For heavily doped samples the procedure of Beers *et al.*[3] was used. To take into account the optical scattering[11] the relaxation time was modified to

$$\tau^{-1}=\mathrm{const}\,(E^{-r(T)}+qE^{-3/2}) \quad (3)$$

with q as an adjustable parameter. The numbers A and B of Eq. (1) have been computed and tabulated by Amith[15] for Eq. (3) with q and the Fermi level η as parameters. q and η could be determined from measurements of the Seebeck and Hall coefficient. At each temperature the tables[15] for the appropriate r values[11] were used. The mobility ratio $b=25$ was assumed for the degenerate samples; this is the ratio of the electron mobility in n type to the hole mobility in p-type InAs

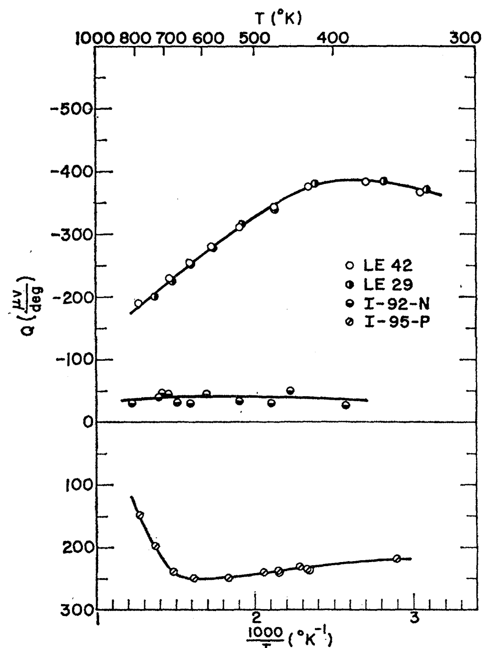

FIG. 3. The absolute Seebeck coefficient of InAs as a function of the reciprocal absolute temperature.

[10] See, e.g., O. Madelung, in *Handbuch der Physik,* edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 88; or see Ref. 24, p. 427.

[11] H. Ehrenreich, Suppl. J. Appl. Phys. **32**, 2155 (1961).

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[14] O. G. Folberth, O. Madelung, and H. Weiss, Z. Naturforsch. **9a**, 954 (1954).

[15] A. Amith (private communication).

with impurity concentrations of 3×10^{19} cm^{-3}, according to Schilling.[16]

Lattice Thermal Conductivity

The lattice thermal conductivity κ_l is obtained by subtracting the electronic contribution κ_{el} from the total thermal conductivity κ. The results are shown in Fig. 5. The effect of isotope scattering on the thermal conductivity was calculated and found to be negligible in InAs. The lattice conductivity of the intrinsic samples is discussed in the next section in connection with other III-V compounds.

The samples containing large amounts of impurities show an increase in the lattice thermal resistivity confirming the measurement of Stuckes[2] on an n-type sample. The change in lattice resistivity of the p-type samples is 10% at 400°K and 4% at 600°K compared to 27% at 400°K and 63% at 600°K for the n-type material of the same carrier concentration. This is similar to the behavior found by Beers *et al.*[3] in Ge, where the thermal resistivity of n-type material also changes more markedly. It is, therefore, very likely that the same mechanisms are involved. Since data for changes of bond strength and neighbor distances for sulfur and zinc impurities in InAs were not available, only the increase in lattice resistivity due to mass difference $[\Gamma=\sum_i f_i(\Delta M_i/M)^2]$ was estimated. It results in a 4% increase for the n-type and only a 1% increase for the p-type sample, which is not sufficient to explain the observed effect. It is probable that phonon-electron scattering contributes considerably to the change in the lattice thermal resistivity, as in Ge.

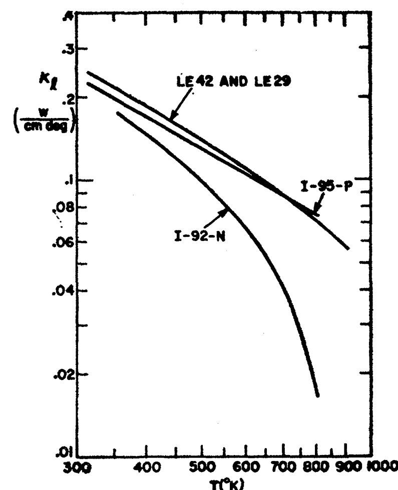

Fig. 5. The lattice thermal conductivity of intrinsic and heavily doped InAs as a function of the absolute temperature.

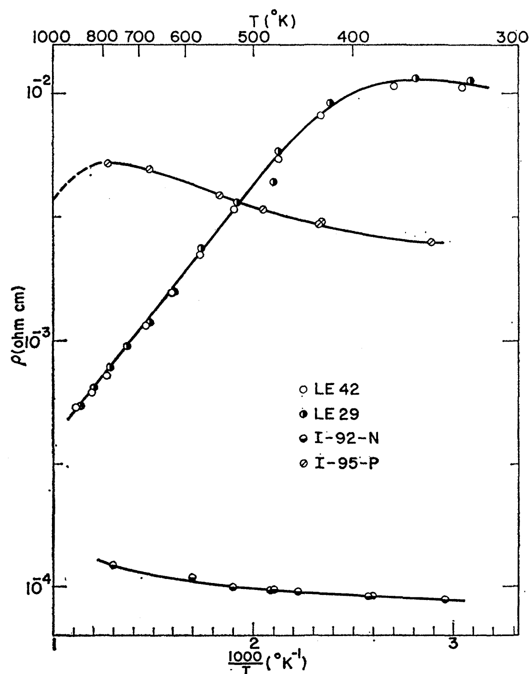

Fig. 4. The electrical resistivity of InAs as a function of the reciprocal absolute temperature.

C. III-V COMPOUNDS

Leibfried and Schlömann[4] calculated the lattice thermal conductivity for 3-phonon processes at high temperatures and obtained[17]

$$\kappa_l=\tfrac{3}{5}4^{1/3}\left(\frac{k}{h}\right)^3\frac{M\delta\Theta^3}{\gamma^2 T}, \tag{4}$$

where M is the mean atomic mass, δ is the cube root of the atomic volume, and γ is the Grüneisen anharmonicity parameter.

In order to check the agreement between experiment and theory, γ^2 was calculated from Eq. (4) using the experimental values of the lattice thermal conductivity and Debye temperatures computed[6,7] from elastic constants and listed in Table I. This was done for all group IV and III-V materials for which data were available, namely, for Si,[3] Ge,[3] InSb,[18] GaAs,[19] InP,[19] GaSb,[20] and AlSb.[21] The resulting anharmonicity parameters are given in Fig. 6 for temperatures $T\leq\Theta\leq2\Theta$.

Two striking results show up in Fig. 6: First, the anharmonicity parameters depend on the temperature. Second, they depend on the material.

The temperature dependence of γ^2 indicates that for none of these materials does the thermal resistivity follow a simple T^1 relationship as postulated by

[16] E. Schilling, Z. Naturforsch. **11a**, 463 (1956).

[17] Equation (4) is a modification of the original formula of Leibfried and Schlömann by a factor 4 which arises from the fact that they approximated their Eq. (23) by Eq. (23a) using $\gamma=2$ while a value $\gamma=0.5$ seems to be more appropriate according to Gibbons (see Ref. 25), McCammon and White (see Ref. 26). This results in a change of a factor 4 in Eq. (38) of Leibfried and Schlömann's paper (see Ref. 4).

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[19] I. Kudman and E. F. Steigmeier (to be published).

[20] M. G. Holland, Bull. Am. Phys. Soc. **8**, 15 (1963); and private communication.

[21] D. A. Wright, Electron. Eng. **31**, 659 (1959).

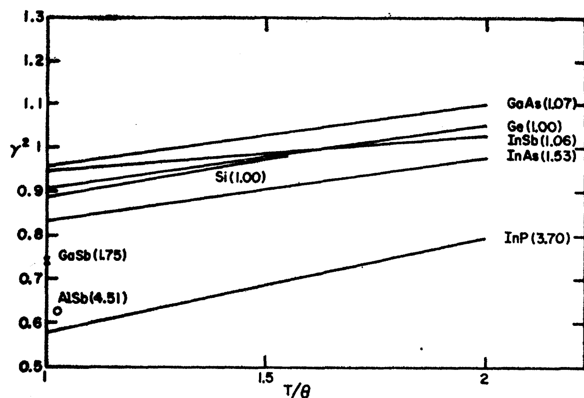

FIG. 6. The square of the anharmonicity parameter of Si, Ge, InSb, GaAs, InAs, GaSb, InP, and AlSb, calculated from Eq. (4), as a function of the reduced temperature. The mass ratios of the constituent elements are given in parentheses.

Leibfried and Schlömann [Eq. (4)] for 3-phonon processes. This is believed to be caused by the occurrence of higher order processes which were not considered by Leibfried and Schlömann. It may be mentioned in this connection that Pomeranchuk[22] computed a T^2 dependence of $1/\kappa_l$ for 4-phonon processes; but no conclusive experimental evidence had been given thus far.

The dependence of γ^2 on the material is related to the mass ratio of the constituent elements of the compounds and is shown in Fig. 7 for $T=\Theta$. With increasing mass ratio, γ^2 first increases slightly, goes through a maximum, and then decreases again. This behavior can be understood in terms of scattering of the acoustical phonons (A) by the optical phonons (O).

Blackman[23] (cf. also Ref. 24) has treated this scattering process for a simple Einstein-Debye model (the acoustical modes having only one velocity and the optical modes having only one frequency ω_E). The number of 3-phonon U processes of the type $A+A=0$ can be shown to increase with increasing ratio ω_E/ω_D, where ω_D is the limiting acoustical frequency. For $\omega_E/\omega_D>2$, the number of U processes of this type goes to zero again since no more phonons are available to fulfill the conservation rules. Therefore, the thermal resistivity due to these processes is expected to go through a maximum with increasing mass ratio which changes monotonically with the frequency ratio. Hence, the observed variation of γ^2 with the mass ratio is in agreement with the model of Blackman.

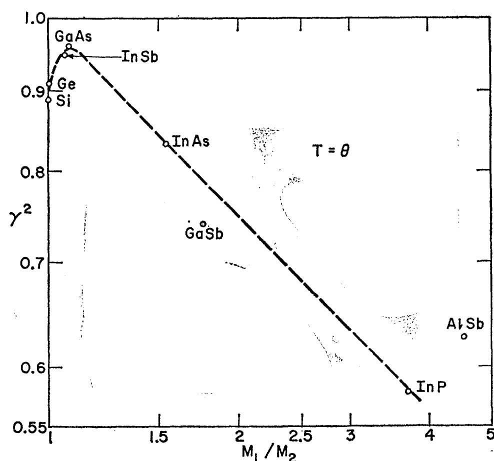

FIG. 7. The square of the anharmonicity parameter of group IV and III–V semiconductors at $T=\Theta$ as a function of the mass ratio of the constituent elements.

The maximum anharmonicity parameter is seen to occur close to a mass ratio of one. The exact location of this maximum could be derived only from a more detailed analysis of the actual frequency spectrum which is more complex than the assumed Einstein-Debye model.

The anharmonicity parameter $\gamma\approx0.95$, resulting for Si and Ge (Fig. 7), compare reasonably well with the values of 0.5 to 0.7 obtained by Gibbons,[25] and McCammon and White[26] from thermal expansion, compressibility and specific heat. The values of γ derived by Daniels[27] from the volume dependence of the elastic constants is 0.25 for Si and 0.49 for Ge. Assuming the lattice parameter dependence of the elastic constants established by Keyes[28] for Si and Ge, one obtains[7,29] $\gamma=0.5$ both for Si and Ge.

It is recognized that, due to the experimental difficulties in carrying out accurate measurements of the thermal conductivity at high temperatures as well as due to the crudeness of the theory, these relations are at the moment only qualitative. However, it is believed, that this does represent the first strong evidence for an appreciable influence of the optical phonons on the lattice thermal conductivity of III-V semiconductors. Thus far, no detailed theoretical treatment of this problem is known. Measurements on other III-V compounds will be necessary for more definitive interpretations.

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