Thermal Conductivity of Ge-Si Alloys at High Temperatures*

B. ABELES, D. S. BEERS, G. D. CODY AND J. P. DISMUKES
RCA Laboratories, Princeton, New Jersey

(Received August 16, 1961)

The thermal conductivity of several Ge-Si alloys was determined in the temperature range 300° to 1200° K. A strikingly large decrease in the lattice thermal conductivity in the entire temperature range was found upon alloying. The temperature dependence and magnitude of the thermal conductivity can be obtained from current theory if it is modified to permit the dependence of anharmonic scattering on alloy composition. Justification for this dependence is given in terms of second order processes involving simultaneous two-phonon point defect scattering and three-phonon anharmonic scattering. The low-thermal conductivity, the high-thermal stability, and the low mass of the Ge-Si alloys makes these materials very useful for high-temperature thermoelectric power generation. A couple made up of heavily doped n- and p-type Ge-Si alloys, operated over a temperature range 300°–1140°K, had an energy conversion efficiency of 10%.

SOLID solution alloys of germanium and silicon constitute the simplest semiconductor system upon which to study the effect of point defects on the phonon thermal conductivity. Ge-Si alloys may be regarded as an isotropic mixture[1] with mass fluctuation scattering, which is the simplest and so far best understood form of point-defect scattering. Recent theories[2,3] of phonon thermal conductivity κ_{ph} in dielectric crystals with point defects indicate a strong dependence of κ_{ph} on the Debye temperature and mean atomic mass and volume. The above quantities vary considerably in going across the alloy system from Ge to Si. The theory can thus be tested over a wide range of the parameters. Previous studies[1,2,4,5] of κ_{ph} in Ge-Si alloys have been confined to $T \lesssim 300$°K. In the present work the measurements and the theoretical analysis of the results have been extended to 1200°K.

I. EXPERIMENTAL

The alloys, grown by a horizontal zone method were single-phase large-grain polycrystals and had compositional variations of less than 1%.

The measurements, accurate to 2%, were made on bars of dimensions $\frac{1}{4}$ in.$\times\frac{1}{4}$ in.$\times 2$ in. The thermal conductivity κ was determined from measurements of the diffusivity κ/c, thus avoiding experimental difficulties due to radiation.[6] The experimental technique was described in detail previously.[7]

The specific heat per unit volume at constant pressure, c, was computed from the Debye specific heat $C_v(\Theta/T)$ and the atomic volume[8] δ^3. The error introduced by neglecting anharmonic contributions to c, in Ge and Si, is negligible at[9] 300°K and is less than 7% at 1200°K.[10] The error is not expected to be significantly larger in the alloys. The Debye temperatures Θ for the alloys were interpolated from those of pure[9] Ge and Si at 0°K, using Lindemann's rule[11] in the form

$$\Theta = a + bT_m^{\frac{1}{2}}\delta^{-1}M^{-\frac{1}{2}}, \quad (1)$$

where T_m is the melting point[12] and M the mean atomic weight of the alloys. The constants a and b were determined by fitting Eq. (1) to Ge and Si.

The lattice thermal resistivity $1/\kappa_{ph}$, plotted in Fig. 1, as a function of temperature for several p-type alloy

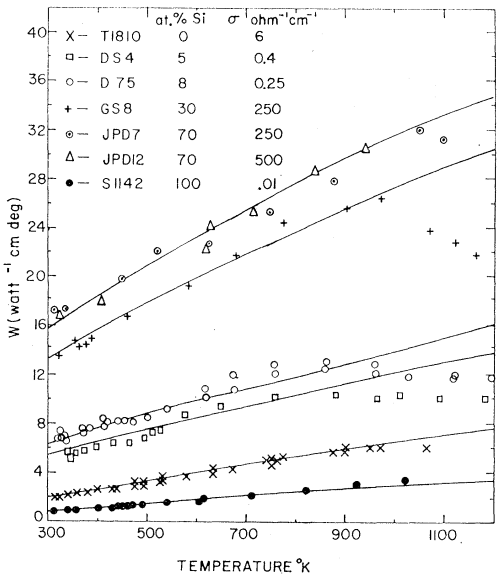

FIG. 1. The variation of the phonon thermal resistance W of Ge-Si alloys with temperature and alloying. The compositions and room temperature electrical conductivities are indicated. The full curves were computed from Eqs. (1)–(5).

* Work supported by Naval Bureau of Ships.

[1] A. M. Toxen, Phys. Rev. **122**, 450 (1961).
[2] P. G. Klemens, Phys. Rev. **119**, 507 (1960).
[3] J. Callaway and H. C. von Baeyer, Rev. **120**, 1149 (1960).
[4] A. V. Joffe and A. R. Joffe, Izvest. Akad. Nauk. S. S. S. R. Ser. Fiz. **20**, 65 (1956).
[5] M. C. Steele and F. D. Rosi, J. Appl. Phys. **29**, 1517 (1958).
[6] P. H. Sidles and G. C. Danielson, J. Appl. Phys. **25**, 58 (1954).
[7] B. Abeles, G. D. Cody, and D. S. Beers, J. Appl. Phys. **31**, 1585 (1960).
[8] E. R. Johnson and S. M. Christian, Phys. Rev. 95, 560 (1954).
[9] P. Flubacher, A. L. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959).
[10] In Si, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), p. 4-43, the measured value of c at 1200°K is only 7% higher then the Dulong–Petit specific heat. In Ge, E. S. Greiner, J. Metals **4**, 1044 (1952), this difference appears to be negligible.
[11] J. K. Roberts and A. R. Miller, *Heat and Thermodynamics* (Interscience Publishers, Inc., New York, 1954), p. 552. We have found that Eq. (1) also fits most of the III–V compounds.
[12] H. Stohr and W. Klemm, Z. anorg. Chem. **241**, 305 (1939).

compositions was obtained by subtracting from κ the Wiedemann–Franz part of the electronic thermal conductivity $\kappa_{W.F}=L\sigma T$. Measured values of σ and $L=4(k/e)^2$ appropriate to impurity scattering were used in the computation. The above electronic effect was at most 10% for the most heavily doped sample. The ambipolar electronic contribution[13] to κ was negligible below 900°K for all the specimens and was not taken into account.

We have also made direct measurements of κ on several alloys and obtained good agreement with κ derived from the diffusivity measurements. The present results for κ at 300°K agree very well with those of Joffe and Joffe[4] but are lower than those of Steele and Rosi.[5]

II. INTERPRETATION OF THE EXPERIMENTAL RESULTS

To interpret our experimental results we assumed that the Ge–Si alloy may be considered an isotopic mixture.[1] We used the phenomenological theory of Klemens[2] and Callaway and von Baeyer[3] for phonon-phonon and phonon-isotopic point-defect scattering at $\Theta/T<1$. We have expressed the scattering parameter[3] C in terms of the thermal conductivity due to phonon-phonon scattering[14] and we used the Debye expression[15] for the sound velocity v_s. The expression for the phonon thermal resistance[3] W can then be written in the form

$$W=U/(\kappa_p \tan^{-1}U), \tag{2}$$

where

$$U=8.7\times10^{-2}\Gamma^{\frac{1}{2}}M^{\frac{1}{2}}\delta\Theta\gamma^{-1}T^{-\frac{1}{2}}, \tag{3}$$

$$\kappa_p=5.7\times10^{-8}M\delta\Theta^3\gamma^{-2}T^{-1}\text{w deg}^{-1}\text{ cm}^{-1}, \tag{4}$$

and

$$\Gamma=\sum_i f_i[(M_i-M)/M]^2. \tag{5}$$

Here γ is the Grüneisen anharmonicity parameter, Γ is the disorder parameter, f_i is the fractional concentration of mass M_1 and δ is in A units.

The solid curves in Fig. 1 were computed from Eqs. (1)–(5). The only undetermined quantity, the anharmonicity factor γ, was used as an adjustable parameter[16] to obtain best fit between the computed curve and the experimental data in the temperature range where the ambipolar contribution is negligible. Estimated values of the ambipolar contribution are of the right magnitude to account for the deviations of the experimental points from the computed curves above 900°K.

The γ values, determined in this manner, vary with alloy composition in a simple manner. In Fig. 2 we show the variation of γ with Γ which can be described by $\gamma^2=3.6+40\Gamma$. Toxen[1] observed a similar effect in the temperature range 2°–50°K on alloys with low Si content. One can interpret the variations in his $\beta_1+\beta_2$ as $\gamma^2\approx1.3+50\Gamma$.

The increase of γ with Γ suggests that second-order processes[17] are important in determining phonon scattering in highly disordered systems. First-order perturbation theory leads to umklapp (U) and normal (N) three-phonon processes due to anharmonicity, and to two-phonon momentum-nonconserving processes due to point defects. The major contribution of second order perturbation will be five-phonon processes, which result from the simultaneous occurrences of three- and two-phonon processes. In second-order perturbation these five processes lead to an effective three-phonon interaction which has the same temperature dependence as the ordinary U or N process, is linear in the quantity Γ and does not conserve momentum. The effect of the second-order processes can be interpreted as an enhancement of the anharmonic three-phonon interaction, and a linear dependence fo the quantity γ^2 on Γ. The magnitude of the contribution to γ^2 has been roughly estimated in terms of an integration over final states. This calculation gives a variation of γ^2 with Γ in order of magnitude agreement with experiment. A more detailed treatment will be given in a subsequent paper.

III. THERMOELECTRIC POWER GENERATION

The thermoelectric properties, thermoelectric power Q and electrical conductivity σ, of heavily doped germanium[18] and silicon[19] are well suited for thermoelectric devices. However, due to their high thermal conductivities, the figures of merit $Q^2\sigma/\kappa$ are low. Heavily doped Ge-Si alloys have similar Q and σ as

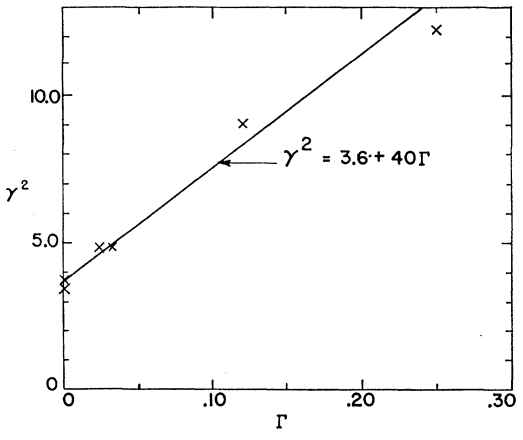

FIG. 2. Variation of the anharmonicity parameter γ with the disorder parameter Γ.

[13] P. J. Price, Phil. Mag. **46**, 1252 (1955).
[14] G. Leibfried and E. Schlömann, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. IIa, Math.-physik-chem. Abt. No. 4, 71 (1954).
[15] Reference 11 p. 514.
[16] Ge and Si ($\Gamma\approx0$) have $\gamma\approx1.9$ and we have found the same value in six different III–V compounds. This value is considerably larger than that computed from thermal expansion and compressibility, D. F. Gibbons, Phys. Rev. **112**, 136 (1958). A theoretical explanation for such a discrepancy has been proposed by T. H. K. Barron, Nature **178**, 871 (1956).
[17] P. Carruthers, Revs. Modern Phys. **33**, 92 (1961).
[18] R. Wolfe and R. L. Moore, Bull. Am. Phys. Soc. **6**, 155 (1961).
[19] T. H. Geballe and G. W. Hull, Phys. Rev. **98**, 940 (1955).

heavily doped Ge and Si; however, their thermal conductivities are much lower so that alloys with very high figures of merit are attainable.

We have prepared n-type and p-type Ge-Si alloys with figures of merit as high as 0.95×10^{-3} deg^{-1} and 0.55×10^{-3} deg^{-1}, respectively, averaged over a temperature range 700°–1200°K. We have measured 7.3% power conversion efficiency on a couple made up of bars of n-type and p-type alloys with dimensions $\frac{1}{4}$in.$\times\frac{1}{4}$in.$\times\frac{1}{2}$in. The cold junction temperature was 300°K and the hot junction temperature was 1140°K. The output current and voltage, into a matched load, were 12 amp and 0.19v. The efficiency predicted from the material properties was 10%. The difference between the theoretical and measured efficiencies could be entirely accounted for by electrical contact resistance and radiation losses.

ACKNOWLEDGMENTS

We thank S. M. Christian for supplying several Ge-Si crystals, E. V. Fitzke and H. E. Temple for their assistance in the material preparation, R. J. Paff for the x-ray analysis and R. W. Cohen for the power conversion measurements.

PHYSICAL REVIEW VOLUME 125, NUMBER 1 JANUARY 1, 1962

Two-Phonon Transitions in the Impurity Conduction in Semiconductors

JERZY MYCIELSKI
Institute of Physics, Polish Academy of Sciences, Warsaw, Poland
(Received July 10, 1961)

The two-phonon transition rate for carrier transfer from an occupied impurity center to an empty one was calculated on the basis of the formalism given by Gummel and Lax for the multiphonon processes in the Born-Oppenheimer and deformation-potential approximations. The general formula for the two-phonon transition rate was investigated in detail in the case of simple parabolic band in two regions of temperature. Numerical data are given for n- and p-type Si and Ge. It is shown that two-phonon transitions can play a role in impurity conduction in materials with low mobility of carriers and low impurity concentration.

I. INTRODUCTION

IMPURITY conduction in semiconductors at low concentrations of impurities is due to tunnelling of carriers from the ground state of occupied impurity centers to the ground state of empty ones. Unoccupied majority centers are present because of compensation. The transition rate depends on the overlap of the wave functions of the carrier in the neighboring impurity centers and decreases rapidly with decreasing impurity concentration. The ionized majority and minority centers give an electrostatic potential which varies from center to center. Thus hopping of carriers from occupied impurity centers to empty ones can occur only with absorption or emission of phonons. In this way the observed activation energy of impurity conduction can be explained.[1,2] The trapping of the carrier on an impurity center can occur also because of interaction with the deformed crystal lattice.[3]

The transition rate for phonon-accompanied carrier transfer from one center to another was obtained theoretically by the use of the resonance energy[3] or the deformation potential[1,2] as perturbation. The last method gave satisfactory agreement with the experimental data but only one-phonon processes were investigated in detail in this way.

The purpose of the present work is to obtain the ratio of the transition rates for two-phonon and one-phonon processes by the use of the deformation-potential approximation. As in references 1 and 2, only longitudinal acoustic phonons are taken into account. We use the general formalism for multiphonon transitions developed by Gummel and Lax[4] (to be referred to in the following as GL) in the Born-Oppenheimer and deformation-potential approximations. This formalism is a first-order perturbation theory, so that we do not have here transitions through intermediate states, as was proposed in reference 1. The perturbing operator is linear in the elastic wave amplitudes, and the possibility of multiphonon transitions occurs because of the dependence of the equilibrium position of the lattice atoms on the state of the carrier.

Phonons may be visualized to be involved in a transition for two reasons: firstly, because of the failure of the carrier to adjust instantaneously to the atomic positions (so-called kinetic phonons, K), and secondly, as the result of the deformed lattice relaxation (lattice-relaxation phonons, LR). It is well known that the multiphonon processes can be obtained also by taking into account the nonlinear terms in the perturbing operator.[5] This was not done here, because it is difficult

[1] T. Kasuya and S. Koide, J. Phys. Soc. Japan **13**, 1287 (1958).
[2] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
[3] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **23**, 378 (1960).
[4] H. Gummel and M. Lax, Ann. Phys. **2**, 28 (1957).
[5] S. Koshino, Progr. Theoret. Phys. (Kyoto) **18**, 23 (1957).