Thermal Conductivity and Seebeck Coefficient of InP

I. KUDMAN AND E. F. STEIGMEIER

RCA Laboratories, Princeton, New Jersey

(Received 28 October 1963)

The thermal conductivity and the Seebeck coefficient of two undoped InP crystals were measured between 300 and 800°K. Computed values of the Seebeck coefficient, assuming pure polar scattering, are in excellent agreement with the experimental data. The electronic thermal conductivity was found to be negligible in InP. The interpretation of the lattice thermal resistivity provides strong evidence for the influence of optical mode scattering on the thermal resistivity of III–V compounds, which was postulated earlier by the authors.

INTRODUCTION

THE electrical properties of InP have been investigated by several authors.[1-5] Values of the room-temperature thermal conductivity and Seebeck coefficient were reported by Weiss[6] and Newman,[7] respectively. High-temperature measurements of these transport phenomena are of considerable theoretical and practical interest. The lattice thermal conductivity is useful in determining the mechanisms of phonon scattering, while the Seebeck coefficient provides information concerning the electron scattering. However, to our knowledge these high-temperature data are not available in the literature. The present work is an experimental investigation of the thermal conductivity and the Seebeck coefficient of InP between 300 and 800°K.

In an earlier paper,[8] the authors gave evidence for the effect of optical mode scattering on the lattice thermal resistivity of III–V compounds. InP represents a particularly suitable material in which to investigate this effect because of the large mass ratio of its constituent elements. This work provides new experimental results, and supports the previous interpretation.

The measurements of the Seebeck coefficients were analyzed to determine the importance of polar scattering of the electrons.

EXPERIMENTAL

The InP specimens were large grain polycrystals, grown by the horizontal Bridgman technique. They were cut to the size of $6\times6\times42$ mm. Both samples were n type, undoped. Their carrier concentrations were determined from Hall measurements at 300°K, using the relation $n=1/eR_H$. The resulting carrier concentrations are given in Table I.

The apparatus described by Abeles *et al.*[9] was used to measure the thermal diffusivity κ/c_p of InP between 300 and 800°K at frequencies of 12 cycles/min (IPB-18), and 5 and 12 cycles/min (L2-26). The measurements were made in a vacuum of better than 1×10^{-5} mm mercury. Measurements above 800°K were not possible because of the increasing phosphorus vapor pressure.[10] The diffusivity method eliminates radiation losses; however, it requires knowledge of the specific heat c_p to determine the thermal conductivity κ.

Piesbergen[11] reports measurements of the specific heat of InP at room temperature and below. However, high-temperature data were not available. Therefore, they were derived in the same manner as for InAs in Fig. 1 of Ref. 8. The curve, which can be expressed for InP as

$$c_p = c_{p300°K} + 6.5\times10^{-4}(T\text{-}300)[J/cm^3 \text{ deg}],$$

passes through the measured[11] room-temperature value of InP (parallel to the curve for InAs in Fig. 1 of Ref. 8), and is believed to be a good approximation to c_p of InP at high temperatures. More justification for this procedure was given in Ref. 8. A Debye temperature, $\theta_D = 321°K$, was used.[12]

RESULTS

Figure 1 shows the measured thermal resistivities. The results of the two samples of different carrier concentration agree within 5%. Identical values of the

TABLE I. The carrier concentration and Hall mobilities of InP crystals.

Crystal	Carrier concentrations		Hall mobilities	
	300°K (cm^{-3})	77°K (cm^{-3})	300°K (cm^2/ Vsec)	77°K (cm^2/ Vsec)
IPB-18	7.1×10^{15}	6.3×10^{15}	4190	6270
L2-26[a]	2.1×10^{17}	1.9×10^{17}	3310	3000

[a] This crystal was bought from Monsanto Chemical Company, St. Louis, Missouri.

[1] O. G. Folberth and H. Weiss, Z. Naturforsch. **10a**, 615 (1955).
[2] F. J. Reid and R. K. Willardson, J. Electron. **5**, 54 (1958).
[3] M. Glicksman and K. Weiser, J. Electrochem. Soc. **105**, 728 (1958).
[4] M. Glicksman and K. Weiser, Phys. Chem. Solids **10**, 337 (1959).
[5] For further references see C. Hilsum and A. C. Rose-Innes, *Semiconducting III–V Compounds* (Pergamon Press, Inc., New York, 1961), p. 134.
[6] H. Weiss, Ann. Physik **4**, 121 (1959).
[7] R. Newman, Phys. Rev. **111**, 1518 (1958).
[8] E. F. Steigmeier and I. Kudman, Phys. Rev. **132**, 508 (1963).

[9] B. Abeles, G. D. Cody, and D. S. Beers, J. Appl. Phys. **31**, 1585 (1960).
[10] D. Richman, Phys. Chem. Solids (to be published).
[11] U. Piesbergen, Ph.D. thesis, University of Zurich, 1960 (unpublished); Z. Naturforsch. **18a**, 141 (1963).
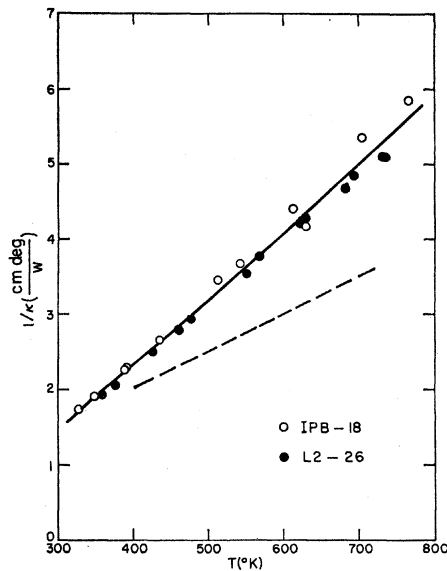[12] E. F. Steigmeier, Appl. Phys. Letters **3**, 6 (1963).

FIG. 1. The thermal resistivity of InP as a function of the absolute temperature. The dashed line represents the function $1/\kappa = \text{const } T^1$.

thermal resistivity were obtained for sample L2–26 at 5 and 12 cycles/min. The thermal conductivity determined from Fig. 1 for 300°K is 0.68 W/cm deg; the value reported by Weiss[6] is 10% higher.

The possibility of a photon contribution to the thermal conductivity[13,14] was investigated. It was found to be negligible for InP at the frequencies used.

Figures 2 and 3 give the measurements of the electrical resistivity ρ and the Seebeck coefficient Q which were obtained simultaneously with the thermal diffu-
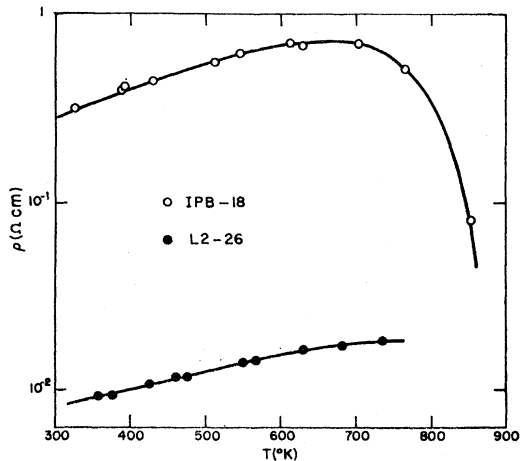

FIG. 2. The electrical resistivity of InP as a function of the absolute temperature.

[13] 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.

[14] G. D. Cody, B. Abeles, and D. S. Beers, Bull. Am. Phys. Soc. 8, 296 (1963).

sivity. Newman[7] reported a value of $Q = -400$ μV/deg at room temperature for a sample of 5×10^{15} cm^{-3}; this disagrees with our results of $Q = -595$ μV/deg on sample IPB-18 which has an almost identical carrier concentration.

DISCUSSION

The thermal resistivity given in Fig. 1 is the total thermal resistivity. The electronic contribution, including the ambipolar part, was computed and found to be negligible for both samples and all temperatures below 800°K. Therefore, the thermal resistivity shown in Fig. 1 represents the lattice thermal resistivity as well.

In an earlier paper,[8] the lattice thermal resistivities of some III-V compounds, including some preliminary data of InP, were interpreted. An outline of this inter-
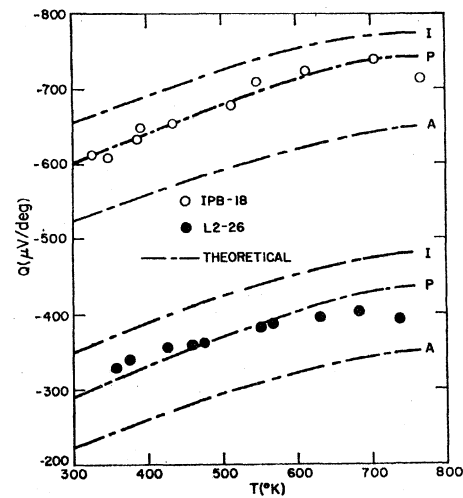

FIG. 3. The absolute Seebeck coefficient of InP as a function of the absolute temperature. The curves are theoretical values, computed for the assumption of pure polar scattering (curve P), pure acoustical scattering (curve A), and pure impurity scattering (curve I).

pretation shall be given here: The anharmonicity parameter γ was calculated from a modification[15] of the formula given by Leibfried and Schloemann[16] for the lattice thermal resistivity. The anharmonicity parameters of different III-V compounds were compared, and a correlation between γ and the mass ratio of the constituent elements of the compounds was found, which was interpreted in terms of scattering of the acoustical by the optical phonons. This effect depends on the separation of the optical and acoustical branches of the lattice frequency spectrum, which changes monotonically with the mass ratio. InP is an important material in this argument, since it is the only one with a mass ratio larger than 1.5 for which we were able to secure high-temperature data.

[15] See Ref. 17 of Ref. 8.

[16] G. Leibfried and E. Schloemann, Nachr. Akad. Wiss. Goettingen, Math. Physik. Kl. IIa 4, 71 (1954).

An anharmonicity parameter $\gamma = 0.75$ was calculated for InP at $T = \theta$. This agrees with the preliminary value used earlier.[8] This more detailed experimental investigation, therefore, provides additional support for the earlier interpretation. According to the model used, the scattering of the acoustical by the optical phonons is ruled out in InP to a large extent, and the small anharmonicity parameter results from the predominance of the scattering of the acoustical by the acoustical phonons.

The temperature dependence of the anharmonicity parameter, observed earlier in other materials[8] and attributed to higher order processes, not considered by Leibfried and Schloemann, is also verified here. It is seen in Fig. 1 that the temperature dependence of the thermal resistivity does not follow the relation $1/\kappa$ $= $ const T^1. The temperature dependence of the anharmonicity parameter at $T > \theta$ can be expressed by $\gamma^2 = 0.36 + 0.21 T/\theta$.

The Seebeck coefficient can be calculated in the extrinsic case from the expression

$$Q = k/e[\eta - B(\eta, r)],$$

where η is the reduced Fermi level and B is the transport term which depends on η and the scattering mechanism. It was assumed here that the case of pure polar scattering applies, and that a relaxation time $\tau = \tau_0 E^r$ may be used,[17] where r is temperature-dependent in the manner given by Ehrenreich (Fig. 5 of Ref. 17). The transport term B was computed and tabulated for these assumptions by Amith.[18] An optical characteristic temperature[19] $\theta_E = 504°K$ was used for the determination of $r(T/\theta_E)$. A temperature-independent effective mass, $m_n^* = 0.073$ m, was assumed[20] for the calculation of the Fermi level η using the formula for the Hall coefficient

$$R_H = f(\eta, r)/e n_0 F_{\frac{1}{2}}(\eta),$$

---

[17] H. Ehrenreich, J. Appl. Phys. Suppl. **32**, 2155 (1961).
[18] A. Amith (private communication).
[19] M. Hass and B. W. Henvis, Phys. Chem. Solids **23**, 1099 (1962).
[20] T. S. Moss and A. K. Walton, Physica **25**, 1142 (1959).

where

$$n_0 = 2.85 \times 10^{19} [(m_n^*/m)(T/300)]^{3/2}$$

and $F_{1/2}$ is the Fermi integral. $f(\eta, r)$ has a value close to unity and was also tabulated by Amith.[18] It was assumed that the Hall coefficient R_H is temperature independent which is a good approximation[1] up to $700°K$ for the carrier concentrations considered.

The justification for using pure polar scattering above $300°K$ is derived from a comparison of the measured Hall mobilities (Table I) with the results of Glicksman and Weiser.[3] It follows that sample L2-26 might be influenced slightly by impurity scattering while sample IPB-18 is sufficiently pure for the polar scattering to be dominant.

The Seebeck coefficients calculated in this manner, using the values of the parameters given above, are shown in Fig. 3 by the curve P; no adjustments were made. For comparison the same calculations have been carried out under the assumptions of pure acoustical lattice scattering and of pure impurity scattering. The results are shown in Fig. 3 by the curves A and I, respectively. Excellent agreement is found for sample IPB-18 between the experimental points and curve (P) computed for polar scattering. This confirms that polar scattering is dominant in this sample, and is sufficient to explain the experimental results. Good agreement with the curve for polar scattering (P) is found also for sample L2–26. A slight deviation at low temperatures is believed to be due to the increased influence of impurity scattering as might be expected from the temperature dependence of the carrier mobility. The deviations from the calculated curves above $700°K$ are attributed to the onset of intrinsic conduction.

ACKNOWLEDGMENTS