

Free-Carrier Absorption in *p*-Type PbTe

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Infrared absorption measurements have been made on *p*-type PbTe at wavelengths ranging from 4 to 28 μ and at temperatures ranging from 300 to 77°K. Absorption by three different mechanisms was observed. At short wavelengths, the dominant absorption is caused by transitions across the forbidden energy gap. In the long-wavelength region, commencing at a temperature-dependent short-wavelength limit, the absorption resembles intraband free-carrier absorption and is of the form $\alpha = c\lambda^q$, where α is the absorption coefficient, λ is the wavelength, and $q = 2.0 \pm 0.2$ at all temperatures studied. At intermediate wavelengths, additional absorption is observed. Both the long-wavelength absorption and the additional absorption are proportional to carrier density and decrease with decreasing temperature at all wavelengths observed. In contrast, *n*-type material shows no additional absorption structure.

I. INTRODUCTION

THE present paper represents an attempt to establish the relationship between infrared absorption, carrier density, and temperature for pulled single crystals of PbTe. Free-carrier absorption in PbTe has been reported previously by Gibson.¹ From his analysis of the data, Gibson suggests the presence of additional absorption superimposed on intraband free-carrier absorption. However, Gibson's measurements were limited to a rather small range of carrier density, and it appears that sample inhomogeneity was serious enough to make accurate quantitative analysis difficult. Recently developed crystal-growing and heat-treatment techniques have made it possible to produce very homogeneous samples over a relatively large range of carrier density. The lower carrier density samples permit measurements at longer wavelengths than those attainable by Gibson.

II. EXPERIMENTAL

Optical samples were prepared by grinding and polishing crystals of PbTe to thicknesses ranging from approximately 0.1 to 1 mm depending upon their carrier density. The samples were attached with silver paint to the low-temperature tip of an optical cryostat similar to that described by Duerig and Mador.² The cryostat was placed at the exit slit of a Perkin-Elmer model-112 infrared spectrometer equipped with either a NaCl or a CsBr prism,

With one exception, the PbTe used was pulled from the melt by the Czochralski method by B. B. Houston and R. F. Bis of this laboratory.³ Carrier densities of the pulled crystals were changed by vacuum annealing using the data of Scanlon⁴ and by a heat-treatment method described by Brebrick and Allgaier.⁵ The one exception was an *n*-type sample grown by sublimation from a lead-rich melt onto the cool end of an evacuated quartz ampule.

The absorption coefficient (α) was calculated from

the transmission (T) using the formula⁶

$$T = (1-R)^2 / (e^{\alpha l} - R^2 e^{-\alpha l}), \quad (1)$$

where l is the sample thickness and R is the reflectivity. A constant value of R equal to 0.48 and was assumed true for all carrier densities and wavelengths used in the present measurements. This value of R was calculated from the room-temperature index of refraction at 6 μ reported by Avery.⁷ Dixon has studied the variation in R as a function of wavelength and carrier density for *p*-type PbTe having lightly worked or etched surfaces.⁸ The maximum error in our value of α resulting from using a constant R is estimated on the basis of Dixon's results, to be less than 10% and relatively independent of wavelength. The error is expected to be considerably smaller than 10% since the polishing techniques used in this work produced a heavily worked surface, and the reflectivities associated with such surfaces have been found in this laboratory to be approximately 48% and independent of wavelength in the range covered by the present measurements.

Values of the carrier density p and the Hall mobility μ_H were calculated using values of the Hall constant R_H and the conductivity σ , measured at liquid-nitrogen temperature and the relations $p = (eR_H)^{-1}$ and $\mu_H = |R_H| \sigma$.

TABLE I. The electrical characteristics of the PbTe samples used for optical transmission studies.

Sample	Type	Carrier density (77°K) (cm ⁻³)	Hall mobility (300°K) (cm ² /v-sec)	Hall mobility (77°K) (cm ² /v-sec)
A	<i>p</i>	5.0×10^{17}	7.4×10^2	2.3×10^4
B	<i>p</i>	9.1×10^{17}	8.4×10^2	2.3×10^4
C	<i>p</i>	3.7×10^{18}	9.2×10^2	1.6×10^4
D	<i>p</i>	7.0×10^{18}	9.4×10^2	1.3×10^4
E	<i>n</i>	3.9×10^{17}	1.5×10^3	3.2×10^4
F	<i>n</i>	2.5×10^{18}	1.6×10^3	1.4×10^4

¹ A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).

² W. W. Duerig and I. L. Mador, Rev. Sci. Instr. **23**, 421 (1952).

³ B. B. Houston, Jr., Bull. Am. Phys. Soc. **5**, 166 (1960).

⁴ W. W. Scanlon (to be published).

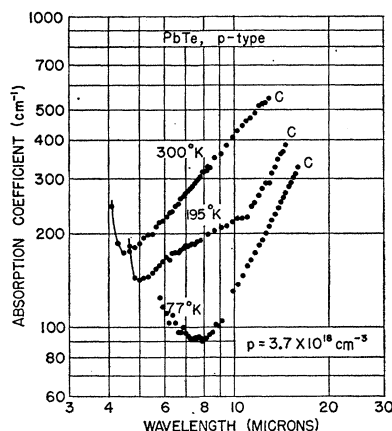
⁵ R. F. Brebrick and R. S. Allgaier, J. Chem. Phys. **32**, 1826 (1960).

⁶ H. Y. Fan, *Reports on Progress in Physics* (The Physical Society, London, 1956), Vol. 19, p. 107.

⁷ D. G. Avery, Proc. Phys. Soc. (London) **B67**, 2 (1954).

⁸ J. R. Dixon, Bull. Am. Phys. Soc. **6**, 312 (1961).

FIG. 1. The absorption coefficient as a function of wavelength and temperature for a PbTe sample with hole density equal to $3.7 \times 10^{18} \text{ cm}^{-3}$.



III. RESULTS

Table I lists the carrier densities and carrier mobilities of the PbTe samples used.

A. *p*-Type

The absorption coefficient as a function of wavelength and temperature for a sample having a hole density of $3.7 \times 10^{18} \text{ cm}^{-3}$ is shown in Fig. 1. The wavelength and temperature dependences of the absorption for this sample are typical of all of the *p*-type samples measured. The data taken at 195°K distinctly show three absorption regions. The steep rise in the absorption coefficient

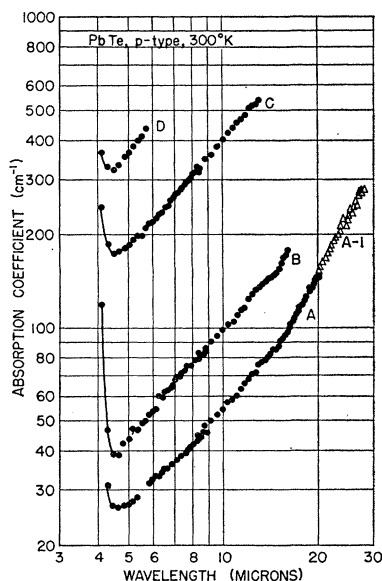
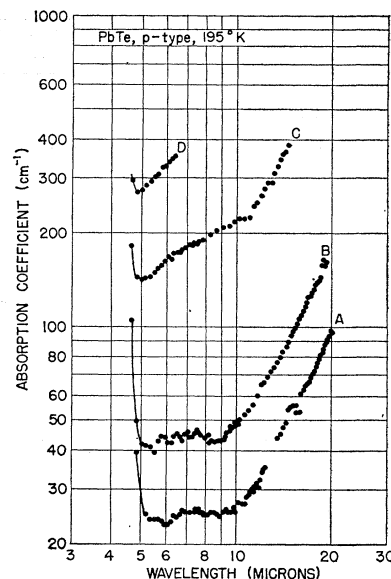


FIG. 2. The absorption coefficient at 300°K as a function of wavelength and carrier density for *p*-type PbTe. In order to extend the data obtained from sample A to wavelengths beyond 20 μ , a thinner sample, A-1, was taken from the same single-crystal ingot as sample A. The samples were of slightly different carrier density and consequently the absorption curves were displaced from one another in the overlapping wavelength region. The absorption curve of sample A-1 was shifted upward by 20%. The absorption curve of sample A-1 was shifted upward by 20% in order to more clearly show the approximate λ -squared dependence.

FIG. 3. The absorption coefficient at 195°K as a function of wavelength and carrier density for *p*-type PbTe.



at short wavelengths is due to transitions across the gap, and has been studied previously.^{1,9,10} In the long-wavelength range beyond 10 μ , absorption resembling intraband free-carrier absorption is observed. At intermediate wavelengths, extending from the absorption edge to approximately 10 μ , the absorption is due to a combination of intraband free-carrier absorption and an additional absorption.

Figures 2-4 show the absorption coefficient as a function of wavelength and carrier density for samples at 300, 195, and 77°K, respectively.

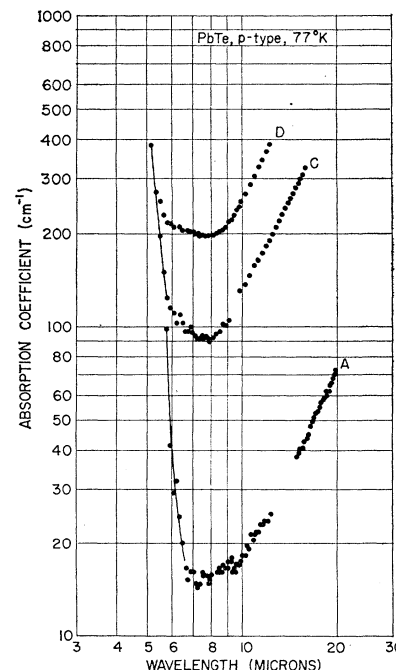


FIG. 4. The absorption coefficient at 77°K as a function of wavelength and carrier density for *p*-type PbTe.

⁹ M. A. Clark and R. J. Cashman, Phys. Rev. **85**, 1043 (1952).

¹⁰ W. W. Scanlon, J. Phys. Chem. Solids **8**, 423 (1959).

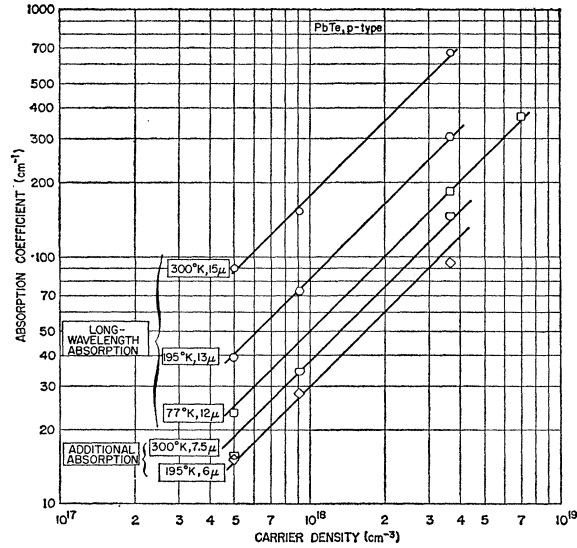


FIG. 5. The absorption coefficient in the long-wavelength region (top three lines), and the maximum additional absorption coefficient (bottom two lines), as a function of carrier density. The solid lines are of unit slope.

1. Long Wavelengths

At wavelengths beyond approximately 15, 10, and 9 μ at temperatures of 300, 195, and 77°K, respectively, the absorption resembles intraband free-carrier absorption.

The classical expression for free-carrier absorption is

$$\alpha = 5.26 \times 10^{-17} (\lambda^2/n) [N\mu^{-1}(m^*/m)^{-2}] \text{ cm}^{-1}, \quad (2)$$

where α is the absorption coefficient, λ is the wavelength in microns, n is the index of refraction at wavelength λ , N is the carrier density in cm^{-3} , m^* is the conductivity effective mass, m is the free electron mass, and μ is the mobility in $\text{cm}^2/\text{V}\cdot\text{sec}$. According to this equation, the absorption coefficient is proportional to N/μ and varies as λ^2 . Table II shows that the wavelength dependence of the long-wavelength absorption is very close to that given by expression (2). In Fig. 5 the absorption coefficients at 15 μ for 300°K, at 13 μ for 195°K, and at 12 μ for 77°K have been plotted against carrier density. (Data at a common wavelength are not available.) The

TABLE II. The wavelength dependence of the long-wavelength absorption for *p*-type PbTe. This absorption is proportional to λ^2 .

Sample	q	Temperature (°K)
A	1.9	300
A	2.0	195
A	2.2	77
B	2.0	195
C	1.9	195
C	2.0	77
D	2.1	77

points lie close to a line of unit slope showing a proportionality between α and N . This is not in agreement with Eq. (2) since the mobilities of the samples used are not independent of carrier density. The corresponding absorption cross sections are $18 \times 10^{-17} \text{ cm}^2$ at 15 μ and 300°K, $8.1 \times 10^{-17} \text{ cm}^2$ at 13 μ and 195°K, and $5.0 \times 10^{-17} \text{ cm}^2$ at 12 μ and 77°K. Equating these cross sections to the appropriate factor in Eq. (2), and using the mobilities given in Table I yields values for the effective mass ratio, m^*/m , of 0.1 and 0.04 at 300 and 77°K, respectively, for sample C. The effective mass ratio of 0.1 is in reasonable agreement with the value estimated from infrared reflectivity studies on a sample of approximately the same carrier density as that of sample C.⁸

2. Intermediate Wavelengths

At intermediate wavelengths there is a definite departure from the λ^2 dependence, suggesting additional absorption superimposed on intraband absorption. Extrapolating the long-wavelength absorption to short wavelengths and subtracting it from the observed absorption given in Figs. 2 and 3 yields the additional absorption curves shown in Fig. 6. The shape of the observed additional absorption changes with temperature. It is not clear, however, whether the additional absorption has moved to higher energy with decreasing temperature, or merely decreased with decreasing temperature to a greater degree at long wavelengths than at short wavelengths, or both. At 77°K, the additional absorption is almost completely gone, as shown in Fig. 4.

The maximum value of the additional absorption occurs at approximately 7.5 and 6 μ at 300 and 195°K, respectively. This maximum value is plotted as a function of carrier concentration in Fig. 5 (the two bottom lines). The points lie close to a straight line of unit slope, showing that the absorption is proportional to the carrier density. The corresponding absorption cross sections are $3.6 \times 10^{-17} \text{ cm}^2$ at 300°K and $2.9 \times 10^{-17} \text{ cm}^2$ at 195°K.

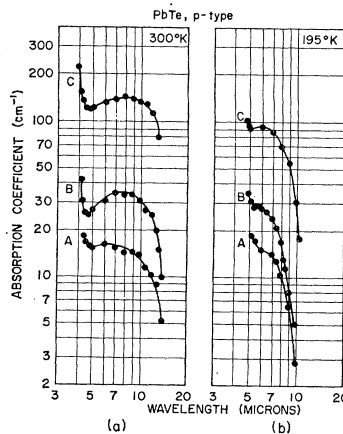


FIG. 6. The additional absorption at 300°K (a) and 195°K (b) as a function of carrier density for *p*-type PbTe. The rise at short wavelengths is the fundamental absorption edge.

B. *n*-Type

The results for *n*-type samples are shown in Fig. 7 and the electrical data for these samples are given in Table I. At wavelengths beyond the fundamental absorption edge, the absorption increases as approximately the square of λ in both samples. The absorption cross sections at $12\ \mu$ are $8.5 \times 10^{-17}\ \text{cm}^2$ and $5.9 \times 10^{-17}\ \text{cm}^2$ at 300°K for samples *E* and *F*, respectively, and $5.4 \times 10^{-17}\ \text{cm}^2$ and $2.9 \times 10^{-17}\ \text{cm}^2$ for sample *E* at 195°K and 77°K, respectively. The corresponding effective mass ratios (m^*/m) calculated from Eq. (2) are 0.1 for both samples at 300°K and 0.04 for sample *E* at 77°K, values which are similar to those found for the *p*-type material. However, the results on the *n*-type samples should be considered only qualitatively, since only two samples were available for study. The curves are shown to illustrate the absence of any strong absorption structure in this region of the spectrum in *n*-type PbTe.

C. Fundamental Absorption Edge

Figure 8 shows a portion of the edge of PbTe at 300°K for *p*-type samples ranging in carrier density from $5.0 \times 10^{17}\ \text{cm}^{-3}$ to $3.7 \times 10^{18}\ \text{cm}^{-3}$ and an *n*-type sample having a carrier density of $2.5 \times 10^{18}\ \text{cm}^{-3}$. Absorption beyond the edge has been extrapolated to shorter wavelengths and subtracted out. It is clear from the figure that no shift is observable within the limits of the reso-

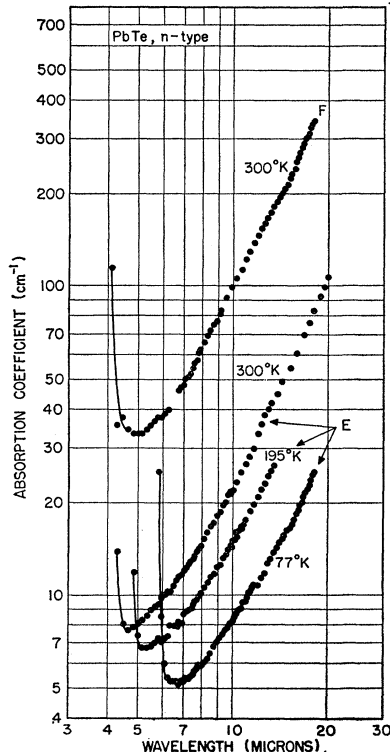


FIG. 7. The absorption coefficient as a function of wavelength, carrier density, and temperature for two samples of *n*-type PbTe.

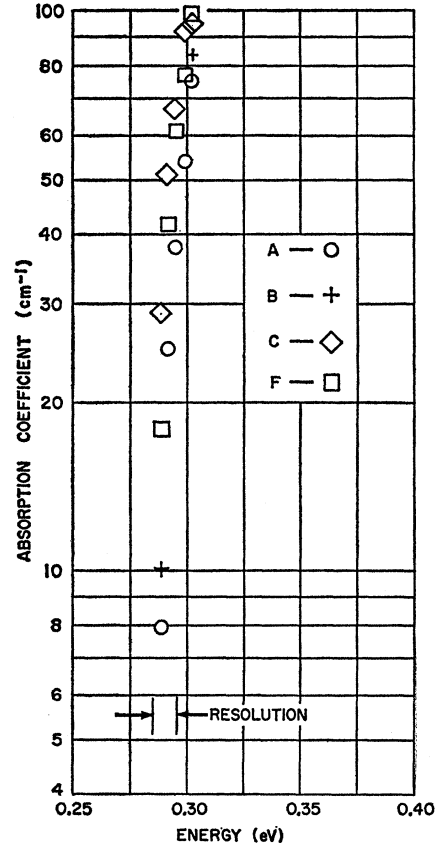


FIG. 8. The fundamental absorption edge at 300°K for three *p*-type samples of varying carrier density and one *n*-type sample.

lution. These results are consistent with the results of Gibson,¹ and indicate that lower temperature or a wider range of carrier density is required in order to observe the Burstein shift.¹¹

IV. DISCUSSION AND CONCLUSION

The origin of the additional absorption which is superimposed on the intraband absorption in *p*-type PbTe is of particular interest. Additional absorption structure in the free-carrier region suggesting the existence of auxiliary conduction or valence bands have been seen in Ge, Si, and various III-V compound semiconductors.¹² If the additional absorption in PbTe were the result of direct transitions, the absorption would be expected to increase with decreasing temperature,¹³ since carrier freeze-out is not observed in the temperature range used for the optical measurements. The additional absorption observed, however, decreases with decreasing temperature, suggesting indirect transitions.

¹¹ E. Burstein, Phys. Rev. **93**, 632 (1954).

¹² For reviews see T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications, London, 1959); H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961); F. Stern, *ibid.* **2166** (1961); W. Paul, *ibid.* **2082** (1961).

¹³ F. Matossi and F. Stern, Phys. Rev. **111**, 472 (1958).

A theoretical treatment of the contribution of intervalley scattering between nonequivalent valleys to infrared absorption in semiconductors has been reported by Risken and Meyer.¹⁴ Since not all of the parameters required by the theory are known for PbTe and the theory applies to nondegenerate material, a rigorous comparison between theory and experiment could not be made. Qualitative comparison yielded only fair agreement. The theory indicated, however, that at 300°K and possibly at 195°K the experimentally observed long-wavelength absorption may also include a significant contribution from interband absorption.

To interpret the additional absorption in PbTe as being due to indirect transitions between valence band extrema separated by approximately 0.1 eV would be consistent with results of the electrical measurements of Allgaier¹⁵ and the optical reflectivity measurements of Dixon.⁸ However, the possibility that the additional absorption is due to some other absorption mechanism cannot be ruled out. The additional absorption, for instance may be due to transitions from a valence band to deep lying levels in the forbidden energy gap. In all of the samples used, the free-carrier density was controlled by the deviation from stoichiometric composition. In PbTe

an excess Te atom may dissociate as $\text{Te}=\text{Te}^+=2$ holes, thereby contributing two energy levels. One of these levels is shallow and contributes to the free-carrier density. The other level may be a deep level in the forbidden gap. In this case, the free-carrier density would be equal to the density of deep levels,¹⁶ and it is likely that the absorption would be proportional to the free-carrier density as was observed. The validity of this model could be checked experimentally by compensating the hole density caused by deviations from stoichiometric composition with various donor impurities. This would serve to determine whether the magnitude of the additional absorption is proportional to the net density of free carriers, or proportional to the density of free carriers produced by deviations from stoichiometric composition.

ACKNOWLEDGMENTS

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¹⁴ H. Risken and H. J. G. Meyer, *Phys. Rev.* **123**, 416 (1961).

¹⁵ R. S. Allgaier, *J. Appl. Phys.* **32**, 2185 (1961).

¹⁶ Assuming compensation by excess Pb to be negligible.