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Temperature Dependence of the Optical Absorption Edge of *p*-Type SnTe

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The optical-absorption coefficient and index of refraction of SnTe were measured at 300, 77, and 12°K over the photon energy range between 0.14 and 0.64 eV. The specimen was a single-crystal SnTe film with a hole concentration of 3.6×10^{19} cm^{-3}. The threshold of absorption by bound carriers at 12°K occurs at a photon energy less than 0.38 eV. This suggests that the smallest direct gap is considerably less than the gap of 0.30 eV which Esaki and Stiles have deduced from tunneling measurements. In contrast to the temperature dependence of the tunneling gap, the temperature dependence of the absorption edge suggests that the temperature coefficients of the direct gaps that lie in the photon energy range investigated are *positive*. However, these coefficients decrease rapidly with decreasing photon energy, suggesting that direct gaps between states sufficiently close to the band edge will have negative temperature coefficients. The electric-susceptibility effective mass was also determined. Its variation from $0.066m_0$ at 300°K to $0.057m_0$ at 12°K is consistent with the observation of direct gaps having positive temperature coefficients. We propose new features for the band structure of SnTe which account for these results, as well as previously reported results for the PbTe-SnTe alloy system.

I. INTRODUCTION

Tin telluride (SnTe) is a semiconductor which crystallizes in the NaCl structure and always contains a significant excess of tellurium.[1,2] Each extra tellurium atom creates two holes in the valence band.[3] Consequently, all samples of SnTe behave as heavily doped degenerate *p*-type semiconductors. For instance, Czochralski-grown material typically has a hole concentration of about 5×10^{20} cm^{-3}.

Despite the fact that SnTe has attracted a significant amount of attention within the last several years, few details of its band structure are well established. Shubnikov–de Haas measurements[4,5] on bulk single crystals have shown that the Fermi surface consists of complicated $\langle111\rangle$ prolate surfaces for hole concentrations less than about 2×10^{20} cm^{-3}, and that a second band becomes populated at higher concentrations. Three band calculations for this material have been reported. Two[6,7] of these place the primary conduction- and valence-band extrema at the L points of the Brillouin zone. The third[8] indicates that the valence-band maxima are slightly displaced from the L points in the $\langle111\rangle$ directions. In addition, a band model at the L points has been developed by fitting a $\mathbf{k}\cdot\mathbf{p}$ calculation[9] to experimental data.

A number of measurements of the infrared optical properties of SnTe have been made on samples having hole concentrations in the range 3.6×10^{19} to about 1×10^{21} cm^{-3} (Refs. 10–14). The electric-susceptibility effective mass is surprisingly small for material having this many carriers, and it decreases with decreasing hole concentration.[14] The absorption edge exhibits a large Burstein shift,[11,12] and the corresponding absorption threshold energies are on the order of a few tenths of an electron volt.[10,11]

Tunneling studies,[15–17] carried out on polycrystalline films having a hole concentration of about 5×10^{20} cm^{-3}, have detected a thermal gap which varies from about 0.3 eV at 4.2°K to about 0.2 eV at 300°K. The contrast between this negative temperature coefficient for SnTe, and the positive coefficient of the forbidden gap of PbTe,[18] combined with the results of optical absorption[19] and laser emission studies[20] on PbTe-SnTe alloys, led to the proposal[20] that there is a zero band gap at some alloy composition. Studies of the temperature dependence of the resistivity of these alloys are consistent with this interpretation.[21]

The main purpose of this investigation was to determine the temperature dependence of the direct optical gap in SnTe, and to compare the results with the thermal gap which Esaki and Stiles obtained from tunneling

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measurements. The direct optical gap and the tunneling gap may or may not be simply related. Defining this relationship would be very helpful in understanding the band structure of SnTe.

In order to minimize the difference between the optical gap (by optical gap we will always mean direct optical gap) and the smallest direct gap, we chose a single-crystal film having the lowest concentration available (3.6×10^{19} cm^{-3}). The absorption coefficient and index of refraction were measured at 300, 77, and 12°K over the photon energy range between 0.14 and 0.64 eV. In addition, the temperature dependence of the free carrier electric-susceptibility effective mass and the optical dielectric constant were also obtained. The results led us to propose new features for the energy-band structure of SnTe near the L points of the Brillouin zone.

We did not consider the effects upon our data of a possible phase change occurring in the temperature range investigated. Such a phase change, based upon thermal expansion measurements in single-crystal bulk SnTe,[22] has been proposed. However, subsequent thermal expansion,[23] as well as neutron diffraction[24] measurements on material with the same chemical composition, and most likely the same hole concentration, have failed to confirm this result. In addition, the film used in the present studies was at all times attached to the NaCl substrate upon which it was epitaxially grown. If a phase change had occurred, or if one were prevented from occurring by the substrate, it seems likely that the film would have been noticeably damaged from the resulting stresses. No such damage was observed after repeated temperature cycling.

II. OPTICAL PROPERTIES

Measurements were made on a single-crystal film, epitaxially deposited to a thickness of 1.2 μ on a NaCl substrate. This film was heat treated by a method previously described[25] to lower the hole concentration to 3.6×10^{19} cm^{-3}. Transmittance data taken at 300 and 77°K are shown in Fig. 1. Data were also taken at 12°K, but are not shown because they are almost identical with those obtained at 77°K. The oscillations are the result of interference phenomena in the film.

The complex dielectric constant $\tilde{\epsilon}$ is given by

$$\tilde{\epsilon}=n^2-k^2+i(2nk), \tag{1}$$

where n is the refractive index, and k is the extinction coefficient. Both n and k were determined from the transmittance data in a manner similar to that previously described by Schoolar and Dixon.[11] The absorption coefficient α is related to k and the wavelength λ by

$$\alpha=4\pi k/\lambda. \tag{2}$$

The dependence of α on photon energy is shown in Fig. 2. The room-temperature data are in good agreement with those obtained by Schoolar and Dixon.[11] The dashed line shows their results at energies higher than those investigated here. The sharp rise on the high-energy side of the absorption minima, and the large values of absorption coefficient, are characteristic of direct transitions across an energy gap. The rise in absorption

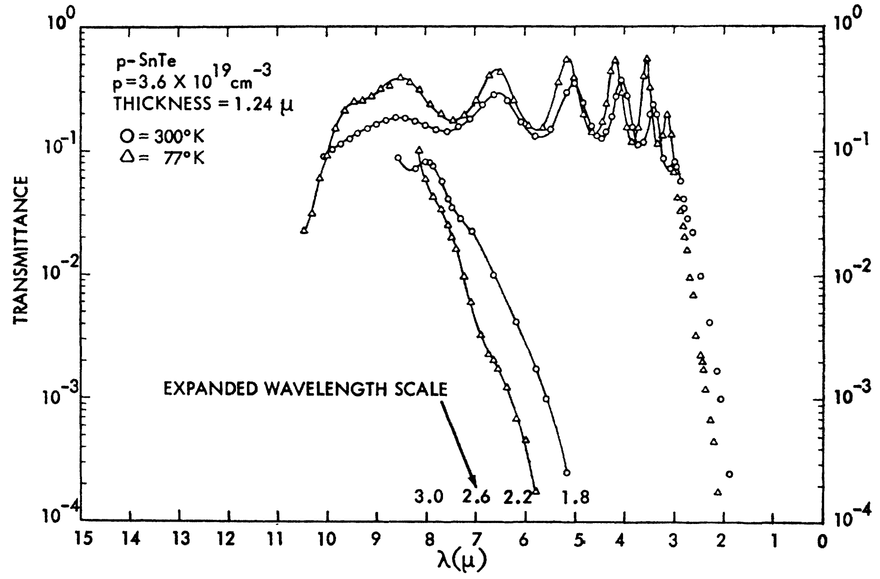

FIG. 1. Transmittance versus wavelength at 300 and 77°K. The oscillations are the result of interference phenomena in the film. The short-wavelength data are also shown on an expanded wavelength scale.

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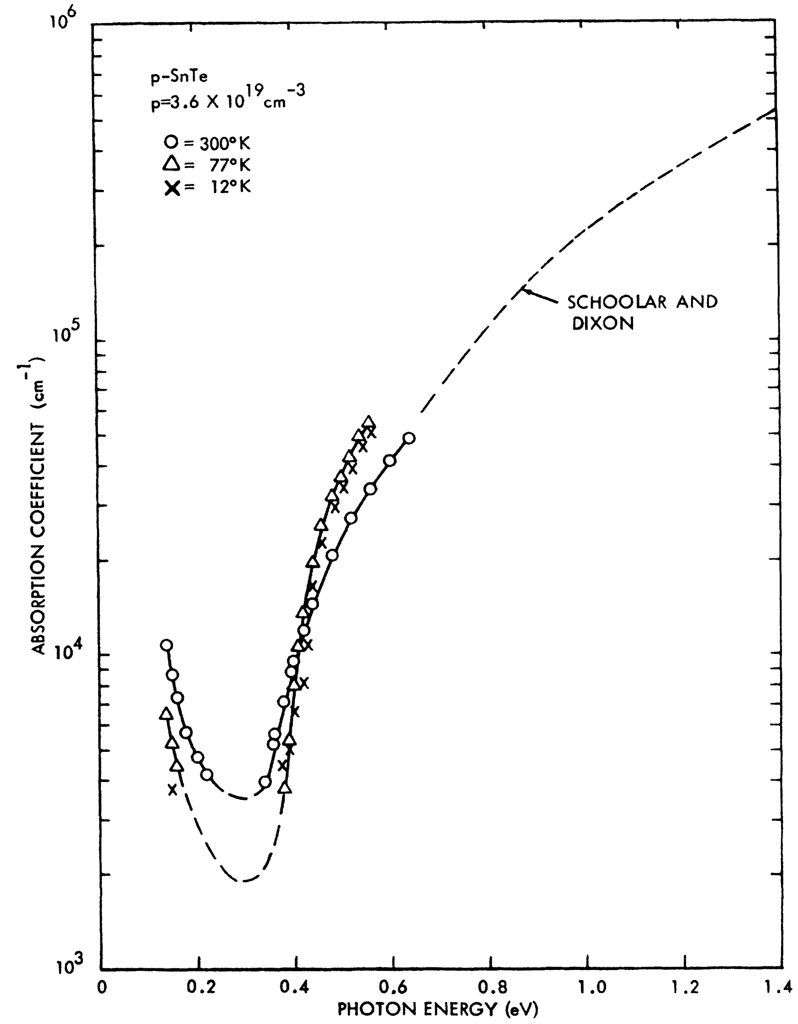

FIG. 2. Absorption coefficient at 300, 77, and 12°K. The data from 0.7 to 1.4 μ were taken on the same film by Schoolar and Dixon (see Ref. 11).

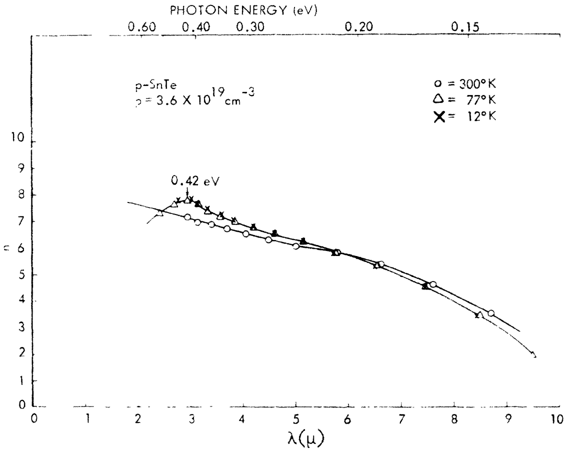

FIG. 3. Wavelength dependence of the index of refraction at 300, 77, and 12°K.

on the low-energy side of the minima is due to free carriers. Schoolar and Dixon[11] have shown that both the magnitude and energy dependence of this absorption at room temperature are in good agreement with values calculated using classical free-carrier dispersion theory, and values of the optical mobility and electric-susceptibility mass determined from reflectivity measurements.[14]

Figure 3 shows the temperature dependence of the dispersion of the refractive index. An interesting feature of the 77 and 12°K data is the peak which occurs at 0.42 eV. A similar peak has been observed in PbS.[26] The PbS results first confirmed the calculations of Stern,[27] which showed that such a peak should be present in the spectral region where the absorption coefficient increases rapidly because of the onset of bound-carrier absorption. The observation of this peak in SnTe at low temperatures, but not at room temperature, is

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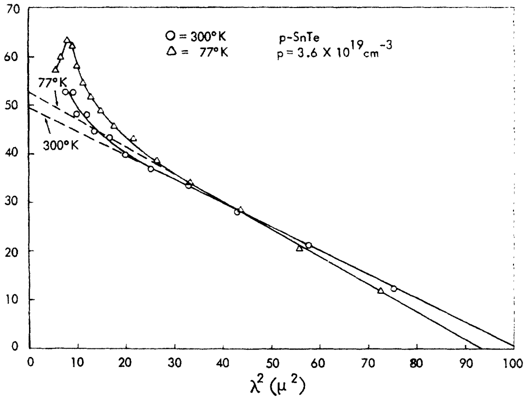

FIG. 4. The square of the refractive index versus the wavelength squared at 300 and 77°K. The slope and the intercept of the long-wavelength data extrapolated to $\lambda=0$ determine m_s and ϵ_∞, respectively.

probably due to the sharper absorption edge at low temperatures.

III. ANALYSIS

A. Free-Carrier Absorption

In the spectral region governed by free carriers, the complex dielectric constant $\tilde{\epsilon}$ can be written

$$\tilde{\epsilon}=n^2-k^2+i(2nk)=\epsilon_\infty-\frac{4\pi pe^2}{m_s}\frac{1}{\omega^2+\gamma^2}\left(1-i\frac{\gamma}{\omega}\right), \qquad (3a)$$

where ϵ_∞ is the optical dielectric constant, p is the carrier concentration, m_s is the free-carrier electric-susceptibility effective mass, ω is the angular photon frequency, and γ is the damping coefficient. If $n^2 \gg k^2$ and $\omega^2 \gg \gamma^2$, the real part of $\tilde{\epsilon}$ becomes

$$n^2=\epsilon_\infty-(pe^2/\pi c^2 m_s)\lambda^2, \qquad (3b)$$

where λ is the wavelength. Figure 4 is a plot of the real part of $\tilde{\epsilon}$ versus λ^2 in a spectral region where the above inequalities hold. Over the part of this wavelength region governed by free carriers, Eq. (3b) is valid, and therefore a straight line results. Its slope can be used to determine m_s, while the intercept, obtained by extrapolation to $\lambda=0$, gives ϵ_∞. The values for m_s and ϵ_∞ obtained in this way at 300, 77, and 12°K are given in Table I. The room-temperature values are in good agreement with those obtained from reflectivity data.[14]

TABLE I. Temperature dependence of the susceptibility effective mass m_s and the optical dielectric constant ϵ_∞. The uncertainty in the absolute values of these numbers is about 10%, but their relative uncertainty is only 2%.

Temperature (°K)	m_s	ϵ_∞
300	0.066	49
77	0.057	52
12	0.057	52

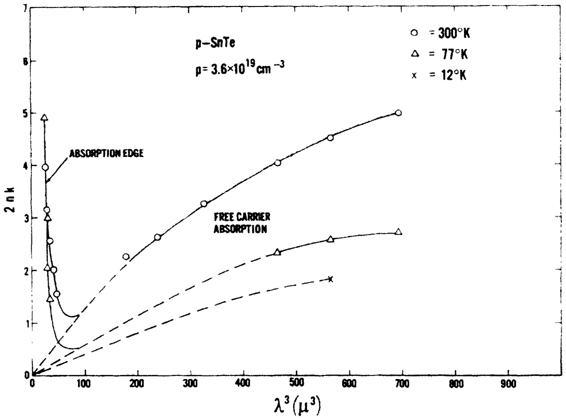

FIG. 5. Imaginary part of the dielectric constant versus the wavelength cubed. The absence of a linear region in the long-wavelength free-carrier contribution shows that the data in this region are not completely described by simple classical dispersion theory.

The positive temperature coefficient of m_s is a persistent feature of SnTe at all hole concentrations thus far investigated. We will discuss this point in more detail in Sec. IV.

For the condition $\omega^2 \gg \gamma^2$, the imaginary part of Eq. (3a) reduces to

$$2nk=(pe^2\gamma/2\pi^2c^3m_s)\lambda^3. \qquad (3c)$$

Figure 5 shows $2nk$ plotted against λ^3. The free-carrier contribution is given by the data on the long-wavelength side of the minima. These data do not exhibit the linear dependence expected from Eq. (3c). Thus, they are not completely described by the simple classical dispersion theory on which this equation is based. One possible explanation is that the assumption of an energy independent γ is not justified. However, since values of γ computed from Eq. (3c) for wavelengths in this range vary by less than a factor of 2, we will assume that they are reasonable estimates. Table II shows the temperature dependence of γ for $\lambda=8.27$ μ ($\omega=2.28\times10^{14}$ sec^{-1}). Also shown are the optical relaxation time τ_{opt} and the optical mobility μ_{opt} defined by

$$\tau_{\text{opt}}=1/\gamma, \qquad (4a)$$

and

$$\mu_{\text{opt}}=e\tau_{\text{opt}}/m_s. \qquad (4b)$$

Approximate values of the dc bulk mobilities are listed

TABLE II. Temperature dependence of the damping coefficient γ, the optical relaxation time τ_{opt} and the optical mobility μ_{opt} at $\lambda=8.27$ μ ($\omega=2.28\times10^{14}$ sec^{-1}). dc bulk mobilities are given for comparison.

Temp (°K)	γ (10^{14} sec^{-1})	τ_{opt} (10^{-14} sec)	μ_{opt} (cm^2/V sec)	$\mu_{\text{bulk}}{}^{\text{dc}}$ (cm^2/V sec)
300	0.315	3.17	840	1200
77	0.154	6.50	2000	3900
12	0.109	9.17	2800	9000

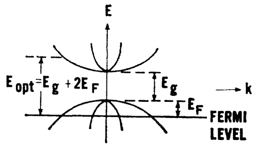

FIG. 6. Simple "mirror" bands shown for two directions in k space. E_{opt} is the optical gap that is determined by a measurement of the threshold of the low-temperature bound-carrier absorption.

for comparison. They were obtained by extrapolating data from bulk samples which had hole concentrations greater than 5×10^{19} cm^{-3}.

B. Bound-Carrier Absorption

1. Optical Gap

The threshold for vertical transitions in a degenerate semiconductor occurs at a photon energy which is larger than the smallest direct gap. We will call this threshold the optical gap (E_{opt}). If E_{opt} is measured at low temperatures, it can be defined more accurately because of the sharp cutoff of the Fermi-Dirac distribution function. For simple conduction and valence bands

$$E_{\mathrm{opt}}=E_g+xE_F\,, \tag{5}$$

where E_g is the energy separation between the conduction-band minimum and the valence-band maximum, E_F is the Fermi level relative to the top of the valence band in a p-type semiconductor, and $x\geq 1$.

A band model for which $x=2$ and the conduction and valence bands are mirror images of one another, is shown in Fig. 6. This model is a good approximation to the bands at the L points in PbTe.

The smallest value of E_{opt}, for a given set of values of E_g and E_F, occurs when $x=1$. This is an extreme case in which a dispersion curve of the conduction band is flat.

The bound-carrier absorption coefficients (α_{bc}) of our SnTe film are shown in Fig. 7. They were deduced from Eq. (2) and the bound-carrier contribution to $2nk$. The latter was obtained by subtracting out the free-carrier contribution indicated by the dashed lines in Fig. 5. The α_{bc} data do not extend to zero because, as Fig. 2 shows, some of the smaller absorption coefficients were not determined. However, the photon energy corresponding to the lowest bound-carrier absorption obtained is an upper limit to E_{opt}. At 12 and 77°K this upper limit is 0.38 eV, slightly larger than the tunneling gap of 0.30±0.05 eV which Esaki and Stiles[15] attribute to the thermal gap between the conduction and valence bands. Since both gaps were perturbed by strain at low temperatures due to the difference in thermal expansion coefficients of SnTe and the substrate on which it is deposited, we have tried to estimate the size and effect of these strains for each case.

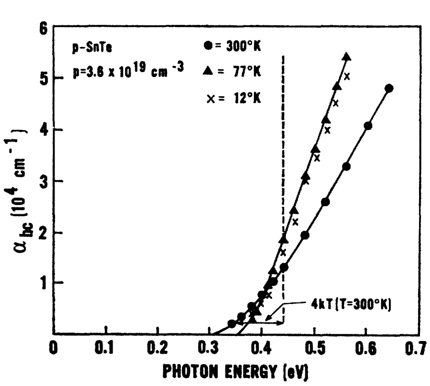

FIG. 7. Bound-carrier absorption coefficient of SnTe at 300, 77, and 12°K. The data at photon energies greater than 0.44 eV (to the right of the vertical line) are unmodified by the Fermi-Dirac distribution function, and are therefore characteristic of the combined densities of states in the valence and conduction bands.

Mitchell, Palik, and Zemel[18] found that lead-salt films, epitaxially deposited on NaCl substrates, are in a state of compression at low temperatures, and that the energy gap (E_g) in PbTe for example, is *decreased* by about 0.02 eV because of the strain at 4.2°K. For our SnTe film, we can expect an *increase* of about this amount in the energy gap at the L point because the thermal-expansion coefficient is the same in both materials,[22,28] but the calculated value of the deformation potential[29] is equal in magnitude, but opposite in sign, to that of PbTe.[30] This confirms the idea that the ordering of the bands which determines the gap in SnTe, is opposite to that in PbTe.

The tunneling junctions studied by Esaki and Stiles were deposited on fused quartz.[31] They neglected the effect of strain in the interpretation of their results. However, an estimate of the pure dilatational component can be made. Since the thermal-expansion coefficient of quartz is negligible compared to that of SnTe, only the thermal-expansion data of SnTe are needed. Using the data in Ref. 22, we calculate that the SnTe films measured by Esaki and Stiles are under a tension of about 1.2% at 4.2°K. (Since their films were polycrystalline, we will assume that the shear component of the strain did not significantly affect their results.) For the deformation potential −2.9 eV calculated by Rabii,[29] a tension of 1.2% will decrease the energy gap at the L point by about 0.03 eV.

We therefore conclude that for unstrained material,

$$\text{Optical Gap (Upper Limit)}=0.36\text{ eV},$$
$$\text{Tunneling Gap}=0.33\pm0.05\text{ eV}.$$

Let us now consider the implications of these values.

The band calculations for SnTe[6–8] indicate that it is a direct-gap semiconductor with the gap being at or near the L points. Shubnikov-de Haas studies of the Fermi surface of p-type SnTe[4,5] clearly show that the valence-band extrema lie on lines in ⟨111⟩ directions. Thus, it is reasonable to assume that the optical gap is the energy required for transitions from the Fermi

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level across a direct gap near the L points. If we also assume that, in the region investigated, the bands are simple like those shown in Fig. 6, we can relate the optical gap (E_{opt}) to the smallest direct gap (E_g) and to the Fermi level (E_F) according to Eq. (5). The band calculations suggest that a reasonable choice for x is 2 (mirror bands). If we identify E_g with the tunneling gap, we find that the upper limit for E_F is 0.04 eV. This value is a factor of 4 smaller than the corresponding value for PbTe,[32] in spite of the fact that the electric-susceptibility effective mass in PbTe[32] is about twice as large as that in SnTe.[14]

Similar calculations, using values of E_{opt} deduced from optical-absorption data obtained by Schoolar and Dixon[11] at higher carrier concentrations, also result in values of E_F that are surprisingly small.

At the carrier concentrations thus far investigated, it would be easier to understand the values obtained for the optical gaps if the smallest direct gap were considerably less than the tunneling gap.

2. *Temperature Dependence of the Absorption Edge*

Since the difference between the 77 and 12°K data in Fig. 7 is probably within our experimental error, we will not distinguish between the results at these two temperatures. We will also neglect strain effects, because their consideration would not alter the conclusions based on the results to be described here. Band calculations by Lin *et al.*[6], Herman *et al.*,[7] and Rabii[29] indicate that contributions to the absorption coefficient by direct transitions from subsidiary valence bands should require photon energies greater than about 0.9 eV. We will assume therefore, that all of our absorption data result from direct transitions between the principal valence and conduction bands.

An upper limit for the photon energy that is required to produce transitions from the Fermi level can be obtained by adding an energy of $2kT$ to the photon energy at which we obtain our smallest, but still relatively large, bound-carrier absorption coefficient. Thus, the energy interval $4kT$ shown in Fig. 7 corresponds to the photon energy range over which we might expect the absorption coefficient at 300°K to be modified by thermal broadening around the Fermi level. The effect of thermal broadening on the absorption coefficient at 77 or 12°K can be neglected, since it is barely observable on this scale. Thus for photon energies *greater than 0.44 eV*, the temperature dependence of the absorption edge is a consequence of the temperature dependences of the corresponding direct gaps.

This dependence shows that the temperature coefficients of these gaps are *positive*. This is a surprising result because the tunneling gap measured by Esaki and Stiles[17] has a negative temperature coefficient. The signs of two results are not necessarily inconsistent, however, because we are investigating states considerably removed from the band edge. It is obvious from Fig. 7 that a nonuniform shift of the edge results from lowering the temperature. We have used this shift to compute temperature coefficients for the direct gaps at each of several photon energies. The results are plotted in Fig. 8 as a function of the photon energy of the data at 300°K. The temperature coefficient $\Delta E/\Delta T$ was evaluated by dividing the temperature difference (300−77)°K into the corresponding photon energy difference at a given absorption level. All of the data shown down to the lowest bound-carrier absorption coefficients obtained are plotted. For the reasons described above, the points below about 0.44 eV are questionable. However, it is interesting that these data, as well as the behavior of the data at photon energies larger than 0.44 eV, suggest that states sufficiently near the band edge will have a negative temperature coefficient. The point at $\Delta E/\Delta T = -2\times10^{-4}$ eV/°K is the temperature coefficient of the tunneling gap reported by Esaki and Stiles.[17] We have placed this point at a photon energy of 0.2 eV, the value of the tunneling gap at 300°K (Ref. 16).

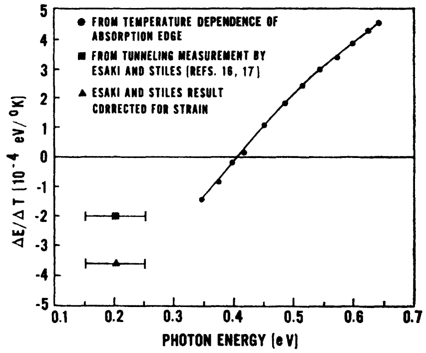

FIG. 8. Temperature coefficients of the direct gaps that lie in the photon energy range investigated. Values for $\Delta E/\Delta T$ were obtained from the data in Fig. 7 by dividing the temperature difference (300−77)°K into the corresponding photon energy difference at given absorption levels. The abscissa is the photon energy of the absorption data at 300°K.

The point at -3.6×10^{-4} eV/°K was obtained by correcting their value for strain. The error bars shown in Fig. 8 are those quoted for the tunneling gap at 4.2°K, since no uncertainty was specified for the room-temperature gap.

IV. BAND STRUCTURE

Figure 9 presents E-versus-k curves passing through the L points of the zone. Figure 9(a) describes the situation for PbTe. In this case, the L point is the lowest point in the conduction band and the highest point in the valence band, so that the figure is appropriate for all directions in k space. The character of the states is predominantly L_6^- in the conduction band and L_6^+ in the valence band.[33,34] Decreasing the temperature decreases the separation between the conduction and valence bands at all points near L.

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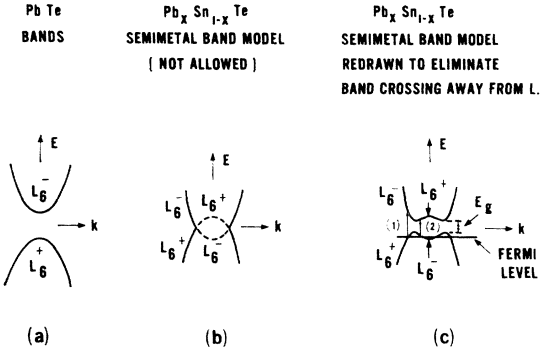

FIG. 9. Energy bands for $Pb_xSn_{1-x}Te$ near the L points of the Brillouin zone. (a) Bands for PbTe ($x=1$). (b) Hypothetical semimetallic model for an alloy. (c) Semimetallic model redrawn to eliminate band crossing away from the L point. We propose that a model of this general nature is also applicable to SnTe ($x=0$).

Optical-transmission[19] and laser-emission[20] studies have shown that adding SnTe to PbTe also moves the conduction and valence bands closer together in the neighborhood of L. Dimmock *et al.*[20] suggested that when a sufficient fraction of PbTe has been replaced by SnTe, the L_6^- and L_6^+ energy levels will cross. Then the effect of lowering the temperature is to move the two levels at L further apart, rather than closer together.

It might be postulated that the band crossing would lead to a semimetallic model such as is sketched in Fig. 9(b). Again, the k vector may represent any direction through L. But the symmetry of the wave functions involved does not allow the two bands to cross except at the point L itself.

One possible way of redrawing the "uncrossed" bands is shown in Fig. 9(c). We propose that a complexity of this general nature is responsible for the observed behavior of SnTe. Rabii[8] originally proposed that the valence band of SnTe had this form along the $\langle 111 \rangle$ directions in k space on the basis of an augmented-plane-wave (APW) band calculation which he carried out. A more refined APW calculation supplemented by a $\mathbf{k}\cdot\mathbf{p}$ perturbation calculation centered on the L points, now suggests that Fig. 9(c) applies along any transverse k vector lying on the $\{111\}$ zone faces.[29] If it does not apply in the $\langle 111 \rangle$ directions, then toroidal Fermi surfaces would be generated at the Fermi level shown in Fig. 9(c). At larger hole concentrations, Fermi surfaces with multiple extremal cross sections would evolve. These have been observed in Shubnikov–de Haas studies.[4,5]

A new and very pertinent feature of this model is the manner in which the energies of direct transitions change with temperature. The transition labeled (1) in Fig. 9(c) would retain the positive temperature coefficient, characteristic of PbTe, while that labeled (2) would acquire a negative value.

In three dimensions, this band-crossing model might be described as follows: Adding SnTe to PbTe, or lowering the temperature, brings the conduction and valence bands closer together until they finally touch at L. Beyond that point, we may define a "boundary surface" (*not*, in general, a constant-energy surface), which grows in size as more SnTe is added or as the temperature is lowered further. Inside of this surface, the temperature coefficient for the direct transitions is negative, while outside it is still positive.

In general terms, we would say that for SnTe having the carrier concentration investigated here, the Fermi surface and the boundary surface described above are comparable in size. It is easy to imagine that such a model would cause constant-energy surfaces and direct optical gaps to evolve in a complicated fashion as a function of carrier concentration and temperature.

In terms of this model, we would attribute our observance of the positive temperature coefficients of the direct gaps to the predominance of transitions of type (1) over those of type (2) [see Fig. 9(c)]. The smaller the energy of the transition, the nearer its k value approaches the boundary surface. Hence, this model also explains why the magnitude of the temperature coefficient decreases with decreasing photon energy (see Fig. 8).

Tunneling measurements can determine energy differences between *empty* states near band extrema. The general nature of the model we have been discussing makes it clear that the gap in SnTe measured by the tunneling experiments could have a negative temperature coefficient.

The positive temperature coefficient of the electric-susceptibility effective mass m_s (Table I) is of course linked to the temperature dependence of the direct gaps. It constitutes further evidence that transitions of type (1) predominate at the hole density of our film.

Some temperature dependence of m_s can result from thermal redistribution of carriers in a nonparabolic model. However, detailed calculations[35] suggest that this effect will usually be much smaller than that associated with the changes in the direct gaps. In addition, measurements of m_s on samples with higher hole concentrations[36] reveal that the positive temperature coefficient is present up to a hole density of 1.2×10^{21} cm^{-3}.

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[35] J. R. Dixon (private communication).

[36] R. F. Bis (private communication).