heavier In ions, due to the choice of incoming x-ray wavelength, $\beta$-branch waves are absorbed slightly less than $\alpha$-branch waves. Consequently, for $\theta<\theta_B$, where $\alpha$-branch waves dominate, a small dip in intensity is found. The peak in intensity occurs where $\beta$-branch waves dominate, at $\theta>\theta_B$. For GaSb, the heavier ions absorb more than the lighter ions for both (200) and (400) reflections, so that both reflections show peaks for $\theta<\theta_B$.

Similar arguments can be made for the case of Bragg geometry, where both the incident and diffracted beams enter and leave the same crystal surface. The diffracted beam profile has an asymmetry, which will be reversed if the sign of $\epsilon$ is reversed.[4]

The sign of $\epsilon$ also plays a role in the formation of contrast in transmission x-ray topographs of strained crystals. The determination of the sense of strain vectors, or Burger's vectors, using contrast asymmetries between $(hkl)$ and $(\bar{h}\bar{k}\bar{l})$ topographs of the strain field, depends on the sign of $\epsilon$.[8] In fact, x-ray topographs of strained crystals provide a convenient method to experimentally determine the sign of $\epsilon$.[8]

## ACKNOWLEDGMENT

We thank Bob Jiminez for invaluable assistance in preparing the experimental samples.

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# Direct-Transition Optical Absorption in PbS, PbSe, and PbTe from Relativistic Augmented-Plane-Wave Functions

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The optical absorption arising from the first five (six in PbTe) direct band-to-band transitions in each of the lead chalcogenides has been calculated from first principles, using the parabolic approximation. The major features of the absorption structure in these materials are accounted for by the direct transitions considered. Within the energy range of these transitions there also occur indirect transitions whose contributions cannot presently be calculated but are second-order and less important to the absorption structure. The direct-transition optical matrix elements, effective masses, and energy differences (threshold energies) were obtained from the results of relativistic augmented-plane-wave energy-band calculations whose only fit to experiment was to the value of the forbidden gap. All of the electric-dipole transitions which contribute occur at the point $L$. An indication of the applicability of relativistic augmented-plane-wave results to determinations of optical absorption in semiconductors is provided by comparing calculation with experiment. When the above parameters are employed in the theory of Elliott, calculation and experiment agree to within less than an order of magnitude. At the forbidden gap, where Elliott's theory is exact, calculation and experiment agree to within a factor of 3. The calculated absorption curves demonstrate that a direct-transition threshold energy can be accurately obtained only from the position of a discontinuity in slope, and not from the position of a shoulder or maximum. The agreement between the calculated and experimental curves indicates that the observed absorption in the lead chalcogenides arises predominantly from direct transitions at the point $L$.

## INTRODUCTION

THE wave functions obtained from energy-band calculations have been used to calculate from first principles many electronic properties of solids, but they have not been extensively used to calculate optical absorption coefficients. The determination of a direct band-to-band absorption coefficient requires the optical matrix element, the electron and hole effective masses, and the energy difference. Kane[1] used the results of his $\mathbf{k}\cdot\mathbf{p}$ calculation for InSb to obtain the optical matrix element for the transition across the forbidden gap. This was achieved by a fitting to experimental values of the effective masses in the conduction and valence bands, the forbidden gap, and the spin-orbit splitting. Since this optical absorption is determined by these parameters, one expects agreement with experiment. In fact for several materials[1–4] this procedure has yielded very good agreement. However, Kane's method does not start from first principles and does not furnish the absorption coefficients for the higher-energy direct transitions.

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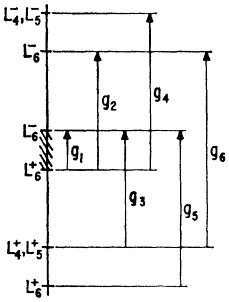

FIG. 1. Electric-dipole transitions contributing to the calculated (RAPW) band-to-band optical absorption in the lead chalcogenides.

The relativistic augmented-plane-wave (RAPW) method provides a first-principle calculation of optical matrix elements, effective masses, and energy differences (i.e., threshold energies) for all direct transitions. In the RAPW method there is no inherent parameter which needs to be fitted to experiment. For each lead chalcogenide, PbS, PbSe, and PbTe, the smallness of the forbidden gap and the sensitivity[5,6] of the conduction-band eigenvalue to the potential outside the "muffin-tin" spheres made it necessary to fit the forbidden gap to experiment. This was the only fitting used. The RAPW functions for the lead chalcogenides[5,6] have yielded effective masses,[6,7] magnetic *g* factors,[6,7] deformation potentials,[6,8] and the magnetic susceptibility and Knight shift in PbTe,[9] all in satisfactory agreement with experiment. Thus, the accuracy of the wave functions has been demonstrated. Comparisons will be made between the calculated and experimental values of the absorption coefficient. These comparisons provide an indication of the applicability of the RAPW results to determinations of optical absorption in semiconductors.

The theory of the absorption coefficient for a direct band-to-band transition in a nondegenerate semiconductor has been given by Elliott,[10] who included the effects of the electron-hole Coulomb interaction. An earlier theory, due to Bardeen, Blatt, and Hall,[11] neglected this interaction. The two theories agree when the energy of the absorbed photon is sufficiently above the threshold energy that the effects of the Coulomb interaction can be neglected. At the threshold, Elliott's theory yields a finite absorption coefficient while Bardeen, Blatt, and Hall's theory gives zero. It is the former which agrees with experiment. However, it is the latter which has customarily been used with Kane's procedure in order to calculate the absorption above the forbidden gap. The energy dependence obtained from Elliott's theory has been applied to experimental data for several materials[12–16] in order to identify direct transitions and to deduce the threshold energy and the magnitude of the electron-hole Coulomb interaction. But it appears that a quantitative comparison of Elliott's theory with experiment has yet to be made. We will make such a comparison for the lead chalcogenides.

The theory used and the calculations made rest on the assumption that the matrix elements of momentum, and therefore the effective masses also, are *k*-independent (parabolic bands). However, there are experimental and theoretical indications that the conduction and valence bands in the lead chalcogenides are nonparabolic. At energies well above the forbidden gap the nonparabolicity leads to inaccuracy in the calculated absorption contribution from the first direct transition. But at these energies the larger contribution from the successively higher-energy direct transitions minimize the effect of this inaccuracy on the calculated total direct absorption coefficient. The use of *k*-dependent momentum matrix elements would have put this calculation beyond the present capabilities.

The compounds PbS, PbSe, and PbTe are of sodium-chloride structure and each has a direct forbidden gap occurring at the point $L$, the zone edge in the [111] direction. For each compound the RAPW calculations indicate that the next several higher-energy direct transitions also occur at $L$ (Fig. 1). We calculate only the first five (six in PbTe) direct electric-dipole-transition contributions to the total band-to-band absorption coefficient. The three highest-energy transitions considered seem to account for the observed absorption maximum (the peak $E_2$ of Cardona and Greenaway[17]), especially in PbS and PbSe. The smallest $\Delta$-$\Delta$ transition and the second- and third-smallest $\Sigma$-$\Sigma$ transitions which occur in this region have not been included in the calculations. These transitions, in addition to direct transitions at $L$, have been identified with $E_2$ by Herman *et al.*[18] in accordance with their band-structure calculations. Similarly, the peak $E_1$ of Cardona and Greenaway[17] seems to be accounted for by direct transitions at $L$, although Herman *et al.* have included also the smallest $\Sigma$-$\Sigma$ transition in this peak. Identification of a given band-theoretical transition with a peak

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in absorption (or reflectivity) is not justified unless it is accompanied by an analysis of the nature of the transition (direct or indirect) and the size of the optical matrix elements and effective masses involved. Unpublished calculations[19] for the lead chalcogenides have indicated that each of the $\Delta$-$\Delta$ and $\Sigma$-$\Sigma$ transitions mentioned above is indirect. An indirect, second-order transition is characterized by a gradual initial rise of absorption coefficient with energy, and a general weakness compared with a direct, first-order transition. Thus smaller absorption contributions should arise from these indirect transitions than from the direct transitions at $L$. Also, any peak arising from the three higher-energy indirect transitions should occur outside the energy range considered here. At the present time, due to insufficient information about the coupling of the lattice and electrons, it is not possible to account for the contribution of indirect transitions in our calculations. Other indirect transitions occur in the energy range considered and have also been neglected. However, we have identified the main features of the absorption structure with direct transitions at $L$. Precisely the same identification has been made by Blomqvist and Nilsson,[20] following their recent experimental study of PbSe.

## CALCULATION OF THE ABSORPTION COEFFICIENT

The theory of Elliott[10] for the absorption coefficient $\alpha_i$ due to a direct electric-dipole transition between bands $c_i$ and $v_i$ in a nondegenerate semiconductor gives

$$\alpha_i=\left[\frac{\pi\beta_i \exp(\pi\beta_i)}{\sinh(\pi\beta_i)}\right]\frac{2e^2(2\mu_i)^{3/2}E_i^{1/2}}{m^2cn_i\omega\hbar^3}|\langle c_i|\hat{\epsilon}\cdot\mathbf{p}|v_i\rangle|^2, \tag{1}$$

where the reduced mass $\mu_i$ of the electron and hole, with its subscript $i$ suppressed, is given by[21]

$$\mu=\frac{3\mu_l\mu_t}{2\mu_l+\mu_t},\quad \text{with } \mu_j=\frac{m_{cj}^*m_{vj}^*}{m_{cj}^*+m_{vj}^*},\quad j=l \text{ or } t. \tag{2}$$

The optical matrix element and reduced mass used are those which pertain at the threshold of the transition $i$. In Eq. (1) $\hbar\omega$ and $\hat{\epsilon}$ are the energy and polarization, respectively, of the absorbed light quantum, $n_i$ is the refractive index, and $E_i$ is $(\hbar\omega-g_i)$, where $g_i$ is the threshold energy. The dimensionless parameter $\beta_i$ is $G_i^{1/2}/E_i^{1/2}$, where $G_i$ is the exciton binding energy $G_i=\mu_i/m\epsilon_0^2$ a.u. ($\epsilon_0$ is the static dielectric constant).

To obtain Eq. (1) Elliott assumed that the optical matrix element and reduced mass for the transition $i$ remain constant as the photon energy increases above the threshold. Because of this assumption the theory is exact only at the threshold. From Eq. (1), after summing over the four $\langle 111\rangle$ ellipsoids in the lead chalcogenides, we obtain the threshold absorption coefficient $\alpha_{i0}$ for the $i$th transition

$$\alpha_{i0}=\frac{4\pi e^2(2\mu_i)^{3/2}G_i^{1/2}}{m^2cn_ig_i\hbar^2}\,\frac{4|\langle c_i|\mathbf{p}|v_i\rangle|^2}{3}. \tag{3}$$

TABLE I. Room-temperature values of the forbidden gap $g_1$, refractive index $n_1$, and static dielectric constant $\epsilon_0$.

| | $g_1$ (eV) | $n_1$ | $\epsilon_0$ |
|---|---|---|---|
| PbS | 0.42[a] | 4.35[b] | 174.4[c] |
| PbSe | 0.29[d] | 5.05[b] | ≈250[e] |
| PbTe | 0.32[d] | 5.95[b] | 412±40[f] |

[a] R. B. Schoolar and J. R. Dixon, Phys. Rev. **137**, A667 (1965).

[b] Reference 22.

[c] J. N. Zemel, in *Physics of Semiconductors*, edited by M. Hulin (Academic Press Inc., New York, 1964), p. 1061.

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Since the optical absorption coefficients of PbS, PbSe, and PbTe have generally been measured at room temperature, our calculations employ the room-temperature value for each forbidden gap, refractive index, and static dielectric constant (Table I). The refractive index varies only slightly over the energy range of interest,[22,23] so all the $n_i$'s are taken equal to $n_1$. The

TABLE II. RAPW results for direct-transition threshold energies $g$ and effective masses $m^*$ at room temperature, and for squares of optical matrix elements $|\langle c|\mathbf{p}|v\rangle|^2$.

| $i$ | $g$[a] (Ry) | $m_{ct}^*$ | $m_{cl}^*$ | $m_{vt}^*$ | $m_{vl}^*$ | $\|\langle c\|\mathbf{p}\|v\rangle\|^2$ ($10^{-38}$ g$^2$ cm$^2$ sec$^{-2}$) |
|---|---|---|---|---|---|---|
| | | | PbS | | | |
| 1 | ··· | 0.158 | 0.166 | 0.163 | 0.249 | 0.504 |
| 2 | 0.138 | 0.171 | 0.645 | 0.163 | 0.249 | 1.627 |
| 3 | 0.207 | 0.158 | 0.166 | 0.365 | −1.79 | 1.593 |
| 4 | 0.200 | 0.203 | 0.694 | 0.163 | 0.249 | 1.901 |
| 5 | 0.211 | 0.158 | 0.166 | 0.444 | −2.174 | 1.377 |
| | | | PbSe | | | |
| 1 | ··· | 0.085 | 0.157 | 0.084 | 0.227 | 0.679 |
| 2 | 0.110 | 0.128 | 0.633 | 0.084 | 0.227 | 1.817 |
| 3 | 0.150 | 0.085 | 0.157 | 0.218 | −2.44 | 1.835 |
| 4 | 0.169 | 0.158 | 0.629 | 0.084 | 0.227 | 2.263 |
| 5 | 0.171 | 0.085 | 0.157 | 0.293 | −3.571 | 1.536 |
| | | | PbTe | | | |
| 1 | ··· | 0.047 | 0.322 | 0.049 | 0.764 | 1.312 |
| 2 | 0.078 | 0.099 | 0.445 | 0.049 | 0.764 | 1.194 |
| 3 | 0.091 | 0.047 | 0.322 | 0.111 | −12.5 | 2.135 |
| 4 | 0.122 | 0.116 | 0.511 | 0.049 | 0.764 | 2.371 |
| 5 | 0.137 | 0.047 | 0.322 | 0.208 | 20.0 | 1.005 |
| 6 | 0.145 | 0.099 | 0.445 | 0.111 | −12.5 | 2.353 |

[a] In PbS $g_6=0.315$ a.u., and in PbSe $g_6=0.239$ a.u.

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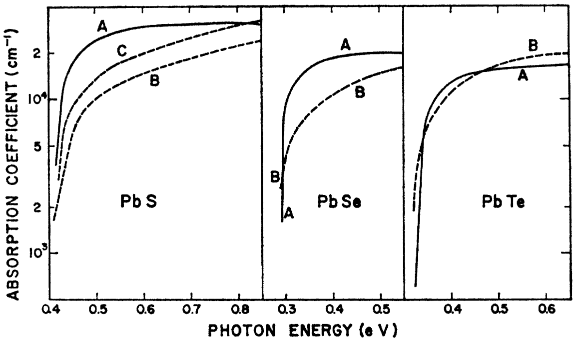

FIG. 2. Room-temperature absorption edge in the lead chalcogenides (photon energies $g_1$ to $\gtrsim 2g_1$). Curve A was obtained from first-principles (RAPW) calculation, curves B and C from experiment (Refs. 24 and 25, respectively).

calculated values for the direct-transition threshold energies and effective masses (Table II) also correspond to room temperature. The calculated optical matrix elements (Table II) are temperature-independent. The threshold absorption coefficients and exciton binding energies are found to be largest in PbS and smallest in PbTe (Table III).

## COMPARISONS WITH EXPERIMENT

The only quantities which can be calculated exactly from Elliott's theory[10] are the threshold absorption coefficients given by Eq. (3). At the forbidden gap where one transition occurs alone, $\alpha_{10}$ is explicitly available from experiment. At the higher-energy thresholds additional direct transitions are superposed, so that the threshold coefficients are not directly available. Hence the only exact comparison between theory and experiment is of the value of $\alpha_{10}$ (Table IV). However, if the optical matrix element and reduced mass for each transition $i$ do not vary as the photon energy increases above the threshold energy $g_i$, which Elliott assumes, then his theory provides other useful comparisons with experiment.

The fundamental absorption edge (Fig. 2) has received the most attention experimentally.[24,25] Theoretically, the absorption rises from its threshold value $\alpha_{10}$ at energy $g_1$ to its maximum value $\alpha_{10}g_1^{1/2}/4\pi G_1^{1/2}$ at energy $2g_1$. Between these energies is a region, $g_1 \gg E_1 \gg G_1$, in which $\alpha_1^2$ depends linearly on $E_1$, and where the calculated value of the differential coefficient

$$\frac{d\alpha_1^2}{dE_1} = \frac{2^9 e^4 \mu_1^3 |\langle c_1|\mathbf{p}|v_1\rangle|^4}{3^2 m^4 c^2 n_1^2 \omega^2 \hbar^6} \tag{4}$$

can be compared (Table V) with a very accurately determined experimental value.[24,25] This comparison has the advantages that Eq. (4) depends on high powers of the optical matrix element and reduced mass, and also is independent of the static dielectric constant. Theoretically, the extrapolation of the straight line portion of $\alpha_1^2(E_1)$ to zero yields $g_1$. The experimental values of the forbidden gap (Table I) which underlie our calculations were obtained[24,25] from such an extrapolation.

TABLE III. Room-temperature threshold absorption coefficients $\alpha_{i0}$ and direct exciton binding energies $G_i$, determined by optical matrix elements and reduced masses obtained from RAPW calculations.

| | PbS | | PbSe | | PbTe | |
|---|---|---|---|---|---|---|
| $i$ | $\alpha_{i0}$ ($10^3$ cm$^{-1}$) | $G_i$ ($10^{-6}$ eV) | $\alpha_{i0}$ ($10^3$ cm$^{-1}$) | $G_i$ ($10^{-6}$ eV) | $\alpha_{i0}$ ($10^3$ cm$^{-1}$) | $G_i$ ($10^{-6}$ eV) |
| 1 | 3.8 | 38 | 1.6 | 11 | 0.61 | 2.7 |
| 2 | 3.7 | 45 | 1.3 | 14 | 0.31 | 3.7 |
| 3 | 3.8 | 56 | 1.4 | 17 | 0.50 | 3.8 |
| 4 | 3.4 | 48 | 1.2 | 15 | 0.44 | 3.9 |
| 5 | 3.5 | 59 | 1.1 | 18 | 0.20 | 4.3 |
| 6 | ... | ... | ... | ... | 0.85 | 6.0 |

TABLE IV. Calculated and experimental values of $\alpha_{10}$, the absorption coefficient at the forbidden gap. Units are $10^3$ cm$^{-1}$.

| | PbS | PbSe | PbTe |
|---|---|---|---|
| Calculated | 3.8 | 1.6 | 0.61 |
| Experimental | 3[a] | 2.7[b] | 1.9[b] |

[a] Reference 25, Fig. 4.  [b] Reference 24, Fig. 11.

The calculated band-to-band absorption coefficients for the transitions $i>1$ (Fig. 3) cannot individually be compared with experiment, but the superposed or total direct band-to-band absorption coefficient $\alpha = \Sigma_i \alpha_i$ may usefully be compared with experimental data[17] for the energy range from $g_1$ to $\gtrsim g_5$ (Fig. 3). At each

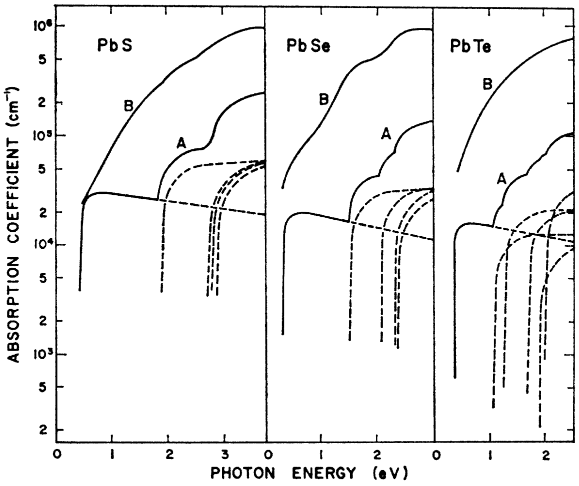

FIG. 3. Room-temperature optical absorption in the lead chalcogenides, for photon energies $g_1$ to $\gtrsim g_5$. Curve A is the total direct band-to-band absorption obtained from first-principles (RAPW) calculation, and its individual components ($i=1,\cdots,6$) are shown. Curve B is the absorption determined experimentally by Cardona and Greenaway (Ref. 17). For PbSe the recent data of Blomqvist and Nilsson (Ref. 20) are similar to but below Cardona and Greenaway's.

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[25] R. B. Schoolar and J. R. Dixon, Phys. Rev. **137**, A667 (1965).

threshold energy $g_i$ above the forbidden gap there is a discontinuity in the slope of the calculated curve for $\alpha$.

## DISCUSSION

From Tables IV and V, and from Figs. 2 and 3, one sees that calculation and experiment[26] agree to within less than an order of magnitude. At the forbidden gap, where Elliott's theory is exact, calculation and experiment agree to within a factor of 3. It should be noted that Cardona and Greenaway regard their values of $\alpha$ as only approximate,[27] because of extrapolations beyond 25 eV of reflectivities used in their Kramers-Kronig analyses.

The theory for the total direct band-to-band absorption coefficient $\alpha$ shows, as illustrated by Fig. 3, that as the photon energy increases above the forbidden gap the threshold of each successively higher-energy transition is uniquely identified (to within the exciton binding energy $G_i$, i.e., to within less than $6\times10^{-5}$ eV in these compounds) by a discontinuity in the slope of $\alpha$. It is apparent that a threshold energy above the forbidden gap cannot be read directly from the position of a shoulder or maximum in the calculated curve for $\alpha$. Further, except in the energy region $g_1$ to $g_2$, the calculated value of $\alpha$ at a given energy is comprised of contributions from more than one transition. Therefore the shoulders and maximum of the calculated curve generally occur at positions different from the maxima of the component $\alpha_i$ curves when $i > 1$.

The experimental curve for $\alpha$ (Fig. 3) contains, in addition to the direct contributions already discussed, indirect-transition contributions. These may further displace a direct-transition shoulder or maximum, and also produce additional shoulders or maxima. Therefore the threshold of a direct transition above the forbidden gap can be accurately read only from a discontinuity in slope, and not from a shoulder or maximum, in the experimental curve for $\alpha$.

TABLE V. Calculated and experimental values of the slope $d\alpha_1^2/dE_1$ in the intermediate energy region $g_1 \gg E_1 \gg G_1$. Units are $10^9$ cm$^{-2}$ eV$^{-1}$.

| | PbS | PbSe | PbTe |
|---|---|---|---|
| Calculated | 9.5 | 5.7 | 3.4 |
| Experimental | 1.8[a] | 1.0[b] | 1.5[b] |

[a] Reference 25, Fig. 5. [b] Reference 24, Fig. 10.

These considerations argue against the tentative identification, by Cardona and Greenaway,[17] of an observed shoulder and maximum in $\alpha$ (Fig. 3) with the threshold energies of transitions between $\Sigma_1$ and $\Sigma_4$, and between $\Delta_1$ and $\Delta_1$, respectively (Ref. 17, Fig. 20). Cardona and Greenaway state that for each of these transitions only a single point in $k$ space is involved. In other words, they assume that these two transitions are direct, although the APW calculations indicate otherwise.[5,6,17,19] The curve of $\alpha$ calculated from first principles (Fig. 3) satisfactorily accounts for the shoulder and maximum observed in the experimental curve. The five or six direct transitions contributing to the calculated curve do not include the $\Sigma_1$-$\Sigma_4$ and $\Delta_1$-$\Delta_1$ transitions postulated by Cardona and Greenaway.

## CONCLUSIONS

The calculated optical absorption arising from the first five (six in PbTe) direct band-to-band transitions in each of the lead chalcogenides agrees closely with experiment. Such agreement establishes the applicability of the results of RAPW energy-band calculations to determinations of optical absorption in semiconductors. The calculated absorption curves demonstrate that a direct-transition threshold energy can be accurately obtained only from the position of a discontinuity in slope, and not from the position of a shoulder or maximum. The agreement between the calculated and experimental curves indicates that the observed absorption in the lead chalcogenides arises predominantly from direct transitions at the point $L$.

## ACKNOWLEDGMENTS

We are grateful to Professor G. W. Pratt, Jr., for the RAPW programs used, and to M. A. Gilleo and D. E. Hill for counsel.

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[26] The specimens used by Scanlon (see Ref. 24) and by Schoolar and Dixon (Ref. 25) had room-temperature carrier concentrations which were nondegenerate. We assume that the same was true for the specimens of Cardona and Greenaway (Ref. 17), so that the theory of Elliott is apposite to all the experimental measurements we have cited.

[27] M. Cardona and D. L. Greenaway (private communication), cited in Ref. 25 as Ref. 11.