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Intrinsic Optical Absorption in Tellurium*

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Measurements of intrinsic optical absorption have been made at 100 and 300°K by transmission techniques, covering a range of absorption coefficient from 0.01 cm^{-1} to 1000 cm^{-1} for radiation polarized $\mathbf{E}\parallel\mathbf{C}$, and to 5000 cm^{-1} for $\mathbf{E}\perp\mathbf{C}$. These results suggest that the edge is set by vertical transitions, the transition being allowed for the polarization $\mathbf{E}\perp\mathbf{C}$ but forbidden for $\mathbf{E}\parallel\mathbf{C}$. Absorption above the intrinsic threshold is apparently influenced by electron-hole interaction, as postulated by Elliott. In the actual edge region, absorption falls off exponentially with decreasing photon energy, the steepness at 300°K being 197 eV^{-1} for $\mathbf{E}\parallel\mathbf{C}$ and 267 eV^{-1} for $\mathbf{E}\perp\mathbf{C}$. The steepness for each polarization increases by only 14% on cooling to 100°K.

INTRODUCTION

IN a number of semiconductors, it has been possible to derive important information about the energy band structure from measurements of the shape of the intrinsic absorption edge. This shape is controlled in some materials (e.g., gallium arsenide,[1] indium antimonide[2]) by direct (vertical) band-to-band transitions. For some other semiconductors (notably germanium[3,4] and silicon[5,6]), transitions involving photons of energy smaller than the intrinsic gap E_i can occur by simultaneous absorption of lattice vibrational phonons. Our measurements of optical absorption in tellurium as a function of photon energy, polarization, and temperature, indicate that the absorption edge here is probably set by vertical transitions, though several features of the band structure must remain in doubt.

The elemental semiconductor tellurium exists as an optically uniaxial positive crystal, which exhibits birefringence,[7,8] dichroism,[9] and optical activity.[10] As has been discussed elsewhere (see, for instance, the review by Blakemore *et al.*[11]), the trigonal crystal structure of tellurium consists of spiral chains, each spiral having three atoms per turn. Figure 1 shows how the chains are stacked parallel to each other with corresponding atoms in each chain forming plane hexagonal nets.

Many electrical and thermal properties of tellurium are anisotropic, depending on the orientation with respect to the **C** direction (the axis of the chains in Fig. 1); and the **C** direction is of course also the optic axis. The two important radiation orientations for optical absorption studies are $\mathbf{E}\parallel\mathbf{C}$ and $\mathbf{E}\perp\mathbf{C}$, where **E** denotes the electric vector of incident electromagnetic radiation.

Dichroism of the absorption edge in tellurium was very apparent from the transmission measurements of Loferski.[9] It seemed likely to Loferski that the actual edge energy might be different for the two polarizations (0.32 eV for $\mathbf{E}\perp\mathbf{C}$ but 0.37 eV for $\mathbf{E}\parallel\mathbf{C}$). His data covered a limited range of absorption coefficient, from ~10 cm^{-1} to ~100 cm^{-1}; but this rather restricted evidence helped to trigger a number of theories, including those of Callen,[12] Gáspár,[13] Reitz,[14] and Asendorf.[15] These various theories (which were arranged to explain also the electrical properties of tellurium) all assumed that intrinsic optical excitation for $\mathbf{E}\perp\mathbf{C}$ and $\mathbf{E}\parallel\mathbf{C}$ must either stem from two distinct valence

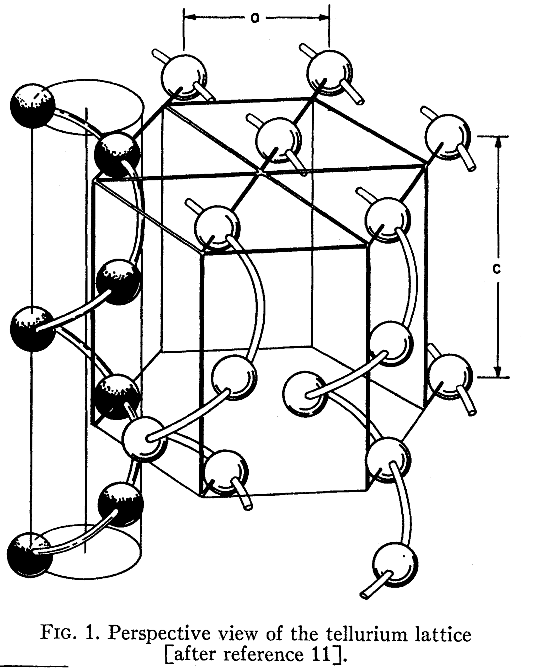

FIG. 1. Perspective view of the tellurium lattice [after reference 11].

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[1] T. S. Moss and T. D. F. Hawkins, Infrared Phys. **1**, 111 (1961).

[2] C. Hilsum and A. C. Rose-Innes, *Semiconducting III-V Compounds* (Pergamon Press, New York, 1961).

[3] G. G. Macfarlane and V. Roberts, Phys. Rev. **97**, 1914 (1955).

[4] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957).

[5] G. G. Macfarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).

[6] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **111**, 1245 (1958).

[7] P. Hartig and J. J. Loferski, J. Opt. Soc. Am. **44**, 17 (1954).

[8] R. S. Caldwell and H. Y. Fan, Phys. Rev. **114**, 664 (1959).

[9] J. J. Loferski, Phys. Rev. **93**, 707 (1954).

[10] K. C. Nomura, Phys. Rev. Letters **5**, 500 (1960).

[11] J. S. Blakemore, D. Long, K. C. Nomura, and A. Nussbaum, in *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1962), Vol. 6.

[12] H. B. Callen, J. Chem. Phys. **22**, 518 (1954).

[13] R. Gáspár, Acta. Phys. Acad. Sci. Hung. **7**, 289 (1956).

[14] J. R. Reitz, Phys. Rev. **105**, 1233 (1957).

[15] R. H. Asendorf, thesis, University of Pennsylvania, 1956 (unpublished).

bands or must generate electrons in two distinct conduction bands. Appropriate selection rules for the two polarizations were formulated. Unfortunately, even the multiple-valence-band models could not be reconciled with the data of Caldwell and Fan[8] on the long wavelength intraband transitions of free holes in tellurium. (See reference 11.)

Dresselhaus[16] has proposed that the intrinsic absorption in tellurium results from vertical transitions involving only one valence band and conduction band. The variation of absorption edge shape with polarization is then to be interpreted as the consequence of a polarization-dependent matrix element. Dresselhaus suggested that transitions are allowed when $\mathbf{E}\perp\mathbf{C}$; whereas those for $\mathbf{E}\|\mathbf{C}$ are rather forbidden close to the extremum.[17] The expectation of Dresselhaus that a single pair of bands is responsible for the totality of intrinsic absorption edge behavior is supported by the measurements we have attempted to make of $K_\perp$ and $K_\|$ over a wide range. In a preliminary report on our data,[18] it was noted that $K_\perp$ and $K_\|$ had been measured over the four decades from 1000 cm^{-1} to 0.1 cm^{-1} and that the resulting curves showed every sign of a common energy origin. The more recent experiments[19] in which we have been able to measure lower values of absorption coefficient (see Fig. 2) reinforce this conclusion of a common energy origin for all intrinsic transitions.

EXPERIMENTAL

The magnitude of intrinsic optical absorption can be deduced from transmission, reflection, and photoconductance measurements. However, the curves of Fig. 2 are based exclusively on our transmission data. The transmission measurements were made using a Perkin-Elmer model 112 double-pass single-beam monochromator with NaCl optics. Plane polarized light was obtained with a stack of ten AgCl plates, arranged to make the E vector of the emergent radiation parallel to the instrument base (thus taking advantage of the 30% monochromator polarization). The samples were mounted in a cryostat with NaCl windows, and runs could conveniently be made from about 100 to 300°K.

For a plane parallel-sided sample of thickness b, the fraction of monochromatic radiation transmitted at normal incidence is

$$\left(\frac{I_t}{I_0}\right)=\frac{(1-R)^2\exp(-Kb)}{1-R^2\exp(-2Kb)}. \tag{1}$$

Thus, calculation of K for any chosen photon energy requires a knowledge of the sample thickness, the transmittance, and the reflectivity R. For absorption which is not too strong [say $K\lesssim 1000$ cm^{-1}], R is related very simply to the refractive index, which is anisotropic in tellurium, but which has been measured[7,8] as a function of $h\nu$ for both principal polarizations. Then if samples with surfaces of good quality are used, a wide range of absorption coefficient can be explored by transmission techniques on thick and thin slices.

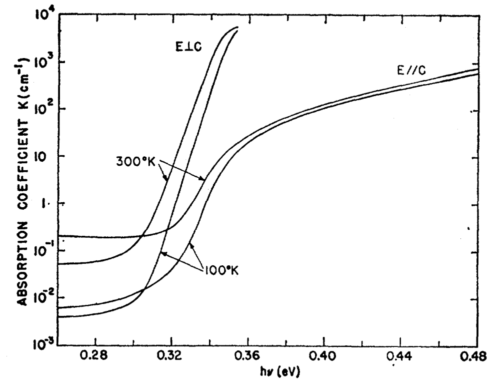

FIG. 2. Absorption coefficient as function of photon energy for the two main polarizations at 100 and 300°K.

We have made such measurements on some 60 samples, covering a range of thickness from 11 μ to 2.2 cm. For most samples, the front and rear surfaces were $(10\bar{1}0)$ planes, and plane polarized light was used to make measurements with $\mathbf{E}\|\mathbf{C}$ and $\mathbf{E}\perp\mathbf{C}$. A second group of samples was prepared with surfaces parallel to (0001). In this case, radiation travels *along* the optic axis, and is *automatically* polarized $\mathbf{E}\perp\mathbf{C}$.

In the early stages of our investigation, samples showed an undesirably low fractional transmittance beyond the intrinsic absorption edge, a spectral region in which (I_t/I_0) should tend towards $(1-R)/(1+R)$. (This amounts to a maximum transmittance of some 30% for $\mathbf{E}\|\mathbf{C}$ and of 39% for $\mathbf{E}\perp\mathbf{C}$.) The evidence showed that lapped and optically polished surfaces were contributing to extensive additional absorption. We now know that these preparation procedures create massive dislocation arrays,[20] and that transmission samples must be prepared in a different way. The procedure we have developed starts by cleaving (at 77°K) a parallel-sided slice. Only those slices with mirror-like finish, free from steps, are proceeded with. Selected slices are then individually chemically polished to the desired thickness, using a mixture of 3 parts water, 1 part concentrated hydrochloric acid, and one part Cr_2O_3 (by weight). This oxidation-reduction reaction usually yields an excellent optical finish.

It is possible to deduce the absorption coefficient from reflectivity data at several angles of incidence. This reflection method, as used by Avery[21] and others, is

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[16] G. Dresselhaus, Phys. Rev. **105**, 135 (1957).

[17] The matrix element presumably is then proportional to $(\mathbf{k}-\mathbf{k}_e)$, where $\mathbf{k}_e$ is the position of the extremum in the reduced zone.

[18] K. C. Nomura and J. S. Blakemore, Bull. Am. Phys. Soc. **5**, 62 (1960).

[19] J. S. Blakemore and K. C. Nomura, Bull. Am. Phys. Soc. **7**, 221 (1962).

[20] J. S. Blakemore, J. W. Schultz, and K. C. Nomura, J. Appl. Phys. **31**, 2226 (1960).

[21] D. G. Avery and P. L. Clegg, Proc. Phys. Soc. (London) **B66**, 512 (1953).

useful primarily in the spectral region of very strong intrinsic absorption. We have attempted to extend the upper limit of our absorption measurements in tellurium by reflective techniques, but cannot report any significant results from this approach.

At the other end of the scale, photoconductive techniques[22] should permit the measurement of a very small intrinsic absorption coefficient K_i in the presence of an appreciable[23] free carrier absorption contribution K_f. We have monitored the photoconductive response of a number of tellurium samples well down into the long-wavelength tail (for incident radiation of the two principal polarizations), but do not have any data which reliably extends the lower limit of intrinsic absorption below the point reached in transmission measurements.

Data for most samples was secured at only two temperatures, 100 and 300°K. However, the copper finger to which the sample was attached could be maintained at any desired temperature above that of the liquid nitrogen reservoir, and a limited number of runs were made at temperatures intermediate between 100 and 300°K. Figures 3 and 4 summarize the results of such runs, in plotting iso-absorption curves for absorption levels of 20 cm^{-1} and 5 cm^{-1}. Not enough information has been accrued on very thin samples to plot corresponding curves for higher levels of absorption.

DISCUSSION

The primary question to be answered is that of whether the curves in Fig. 2 are the consequence of direct or of indirect transitions between valence band and conduction band. At the time of Loferski's early work, intrinsic transitions were expected to occur only between states of the same wave vector. However, the intervening years have seen the development of the suggestion by Bardeen *et al.*[24] that "nonvertical" transitions can occur by absorption or emission of a phonon. The success of Macfarlane and Roberts in explaining the lower portions of the absorption edges in germanium[3] and silicon[5] in this manner is well known; also their subsequent elaborations to include the separate branches of the lattice vibrational spectrum and the modifications due to electron-hole interaction.[4,6] This subject has been discussed very completely by McLean.[25]

These successes with Ge and Si have encouraged the application of indirect absorption models to a variety of semiconductors, including lead sulfide,[26] silicon carbide,[27] and magnesium silicide and germanide.[28] The success has not been unanimous; thus data on InSb were at first analyzed[29] in terms of indirect transitions, yet it now seems clear that vertical transitions set the edge in this material, with slight assistance from indirect processes involving optical photons of zero wave vector.[30]

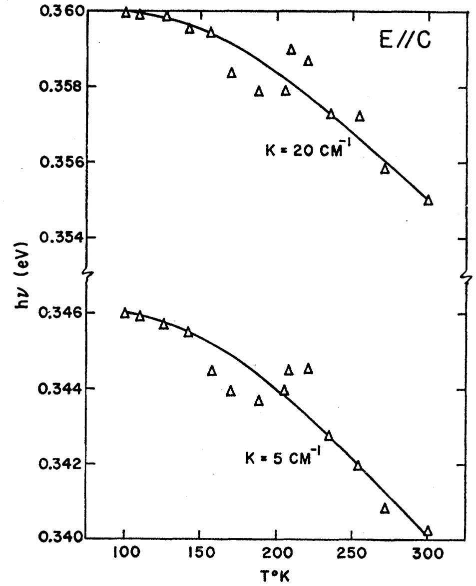

FIG. 3. Iso-absorption curves for $K=5$ cm^{-1} and 20 cm^{-1} over the temperature range 100–300°K, when $\mathbf{E}\|\mathbf{C}$.

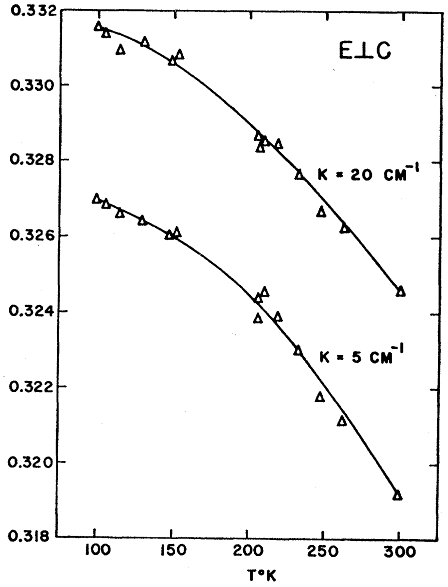

FIG. 4. Iso-absorption curves for $K=5$ cm^{-1} and 20 cm^{-1} over the temperature range 100–300°K, when $\mathbf{E}\perp\mathbf{C}$.

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[22] T. S. Moss and T. D. H. Hawkins, Phys. Rev. Letters **1**, 129 (1958).

[23] Note however that analysis after the style of reference 21 presupposes that bK_f is small compared with unity.

[24] J. Bardeen, F. J. Blatt, and H. Hall, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956).

[25] T. P. McLean, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5.

[26] W. W. Scanlon, Phys. Rev. **109**, 47 (1958).

[27] W. J. Choyke and L. Patrick, Phys. Rev. **105**, 1721 (1957).

[28] P. Koenig, D. W. Lynch, and G. C. Danielson, J. Phys. Chem. Solids **20**, 122 (1961).

[29] V. Roberts and J. E. Quarrington, J. Electronics and Control **1**, 152 (1955).

[30] W. P. Dumke, Phys. Rev. **108**, 1419 (1958).

In our attempts to understand optical absorption in tellurium, it became speedily apparent that the data could not fit the conventional picture of vertical transitions. For it is conventionally to be expected (see, for instance, Dresselhaus[16] or Moss[31]) that direct absorption should vary as $(h\nu - E_i)^{1/2}$ for allowed transitions, and as $(h\nu - E_i)^{3/2}$ for forbidden ones. This was patently not the case, and led us to inspect the indirect absorption approach. A second reason for doing so was that the complex galvanomagnetic properties of tellurium[11,32] are indicative of bands with multiple extrema. Two recent band models[33,34] for tellurium attempt to account for the magnetoresistive behavior by postulating a twelve ellipsoid conduction band, with another set of twelve ellipsoids for the uppermost valence band. Note that for such models, indirect transitions will dominate the absorption edge *unless* the twelve conduction band minima coincide in **k** space with the valence band maxima.

As previously reported,[18] our initial attempts to fit data on tellurium to an indirect absorption model were crowned with apparent success. Thus data for **E**⊥**C** (see Fig. 5) can be fitted tolerably well by expressions of the form

$$Kh\nu = \sum_i A_i (h\nu - B_i)^2, \qquad (2)$$

using four or more terms to optimize the fit. For the "forbidden" polarization **E**‖**C** (Fig. 6), we expect a summation over terms varying as $(h\nu - B_i)^3$, and here again an apparently plausible fit can be contrived. Yet further analysis along these lines proved frustrating. Exciton effects should make the expression for indirect absorption more complicated, with appreciable steps in the absorption curves as the thresholds of the various processes are reached. This fine structure is very evident in germanium[4] and silicon.[6] However, the appearance of fine structure in our curves for tellurium has always been negated by more detailed study of the particular spectral region with a variety of samples. The more extensive our data, the smoother do the $K - h\nu$ curves appear.

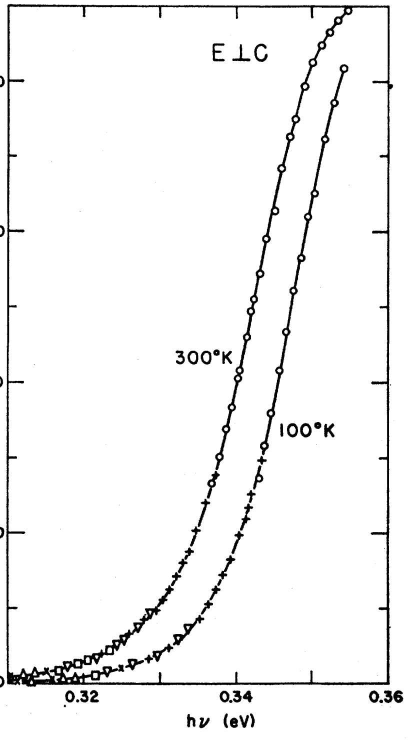

FIG. 5. Presentation of data for **E**⊥**C** in a form appropriate for comparison with a model of allowed indirect transitions.

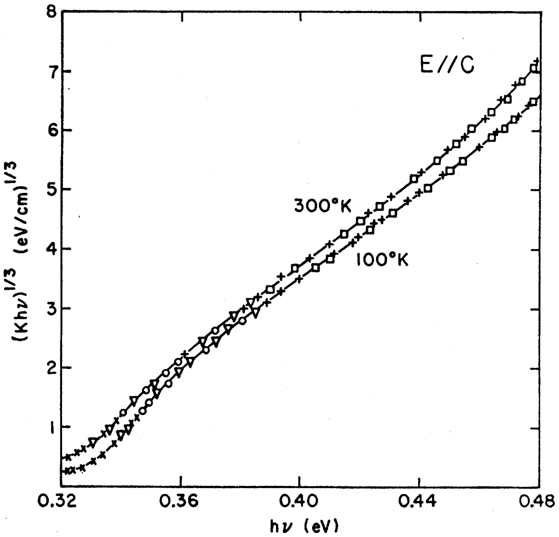

FIG. 6. Presentation of data for **E**‖**C** in a form appropriate for comparison with a model of forbidden indirect transitions.

Moreover, the temperature dependence of the curves is quite inappropriate for indirect transitions. For a process involving emission of a phonon with energy $k\theta$ should have an amplitude varying as $[1 - \exp(-\theta/T)]^{-1}$, while a process involving phonon absorption should vary as $[\exp(\theta/T) - 1]^{-1}$. We found that for neither polarization did the absorption edge show the required change of shape on cooling to 100°K. Instead, the main effect is that of a lateral shift to higher energies, just as would be expected for *direct* transitions.

A re-examination of our results in terms of direct transitions has been greatly encouraged by the theoretical work of Elliott[35] on the modifications brought about by considering the Coulomb interaction between electron and hole. These modifications are fully reviewed by McLean[25]; absorption is grossly affected not only in

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[31] T. S. Moss, *Optical Properties of Semiconductors* (Academic Press Inc., New York, 1959).

[32] H. Roth, J. Phys. Chem. Solids **8**, 525 (1959).

[33] A. Nussbaum and R. J. Hager, Phys. Rev. **123**, 1958 (1961).

[34] C. Rigaux, Compt. rend. **253**, 81 (1961).

[35] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

the small spectral range of bound exciton states, but also for photon energies as high as (E_i+100E_{ex}). The $\mathbf{k}=000$ direct transition in germanium has been found[36] to be in accordance with Elliott's model.

On the basis of this modified direct absorption model, the absorption coefficient for an allowed transition should rise abruptly from zero to a finite value K_a at the threshold $h\nu=E_i$. The behavior through the spectrum should fit

$$Kh\nu=K_aE_i\left\{1-\exp\left[-\left(\frac{4\pi^2E_{ex}}{h\nu-E_i}\right)^{1/2}\right]\right\}^{-1},\quad h\nu\geq E_i \qquad (3)$$
$$=0,\qquad h\nu<E_i.$$

Similarly, Elliott finds for a forbidden vertical transition that

$$Kh\nu=K_b(h\nu+E_{ex}-E_i)\left\{1-\exp\left[-\left(\frac{4\pi^2E_{ex}}{h\nu-E_i}\right)^{1/2}\right]\right\}^{-1},\quad h\nu\geq E_i \qquad (4)$$
$$=0,\qquad h\nu<E_i$$

where K_b depends on the rate at which the matrix element departs from zero as $\mathbf{k}$ moves from the location of the extremum.

According to this theory, the absorption edge itself should be infinitely steep; but in practice we can expect that secondary effects will always provide an edge of finite slope. At this point, Fig. 7 reminds us that the tellurium absorption edges are essentially exponential, a form of behavior found in many semiconductors. Thus Moser and Urbach[37] noted that AgCl and AgBr had absorption edges of the form

$$K_i\approx A/\{1+\exp[(E^*-h\nu)/kT]\}, \qquad (5)$$

over the temperature range 100 to 600°K. For some other materials, this must be generalized to

$$K_i\approx A/\{1+\exp[\alpha(E^*-h\nu)]\}, \qquad (6)$$

where the steepness α may be considerably larger than $(1/kT)$. For gallium arsenide at room temperature, Moss and Hawkins[1] find a steepness three times larger than $(1/kT)$. With indium arsenide,[38] the steepness is some $(4/kT)$ both at 300 and 78°K. The edge in indium antimonide is similarly steep and exponential, and it is interesting to note that the three III–V compounds just cited are all ones for which the band structure is sufficiently well known[2] to assert that the fundamental edge *is* set by vertical transitions. In contract, a much shallower and nonexponential edge is found for gallium phosphide,[39] in which the conduction and valence band extrema do not coincide.

Thus a very steep and exponential absorption edge should probably be taken as a sign of a direct transition.

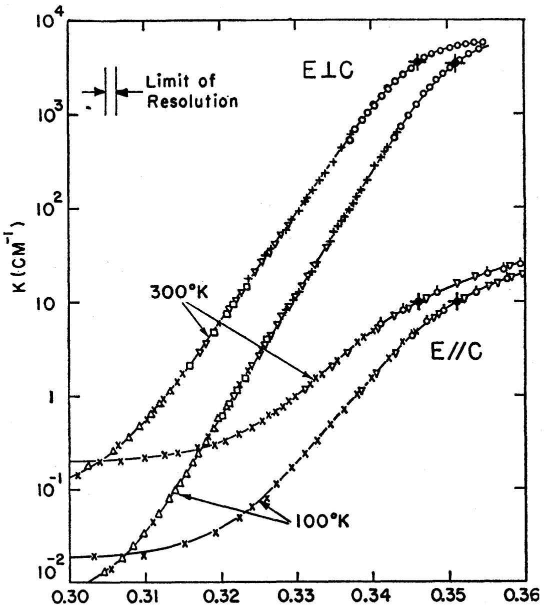

FIG. 7. The data for $K_\perp$ and $K_{\parallel}$ in the spectral region of exponential absorption edge.

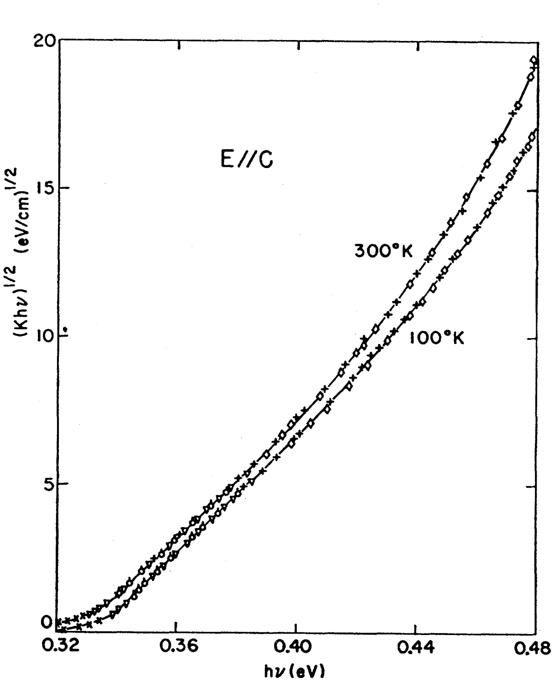

FIG. 8. Data on $K_{\parallel}$ plotted to show comparison with Eq. (8).

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[36] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Proc. Phys. Soc. (London) **71**, 863 (1958).

[37] F. Moser and F. Urbach, Phys. Rev. **102**, 1519 (1956).

[38] J. R. Dixon and J. M. Ellis, Phys. Rev. **123**, 1560 (1961).

[39] W. G. Spitzer, M. Gershenzon, C. T. Frosch, and D. F. Gibbs, J. Phys. Chem. Solids **11**, 339 (1959).

Factors contributing to the finite slope of the edge must include:

(a) Exciton states—though the exponential behavior usually extends over an energy range much larger than E_{ex}.

(b) Phonon-assisted transitions involving absorption of zero-wave-vector optical phonons, as discussed by Dumke[30] for InSb. This mechanism carries implications about the permissible temperature dependence of the steepness.

(c) Lattice disorders, which have been suggested[40,41] as a cause of a tailing-off of states into the forbidden gap.

No single and decisive explanation of the "Urbach effect" is recognized at this time.

The data of Fig. 7 can be fitted to the form of Eq. (6) in a very satisfactory manner up to $K \sim 3400$ cm^{-1} for **E**$\perp$**C** and to $K \sim 10$ cm^{-1} for **E**$\|$**C**. The required values of E^* are 0.346 eV at 300°K and 0.351 eV at 100°K. From the curves of Figs. 3 and 4, we should expect that the quantity E^* (which must be closely related to the intrinsic gap energy E_i) probably varies in a nonlinear manner with temperature. The values of A and α required to fit Eq. (6) are given in Table I. The effectiveness of this fit depends to some extent on a correct allowance for free carrier absorption, but minor changes in this would not obscure the main result; that the steepness increases only by some 14% on cooling from room temperature to 100°K. The steepness is of course already very considerable at room temperature; it will be noted from Table I that the steepness at 300°K for **E**$\perp$**C** is almost seven times as large as $(1/kT)$.

In the upper reaches of the curves in Fig. 7, heavy markers indicate the positions of

$$\begin{aligned} K_{\perp} &= 3400 \text{ cm}^{-1} \text{ at } h\nu = E^*, \\ K_{\parallel} &= 10 \text{ cm}^{-1} \text{ at } h\nu = E^*. \end{aligned} \qquad (7)$$

According to Elliott's theory[35], we might expect data for **E**$\perp$**C** to satisfy Eq. (3) at higher energies, and that for **E**$\|$**C** to accord with the form of Eq. (4). Now it has not proved practicable to extend absorption data for **E**$\perp$**C** beyond about 5000 cm^{-1}, thus a check of Eq. (3) is not possible at this time. [Macfarlane *et al.*[36] appear to have found good agreement between Eq. (3) and their germanium data. Their resolution was good enough to see the peak of the exciton band just below $h\nu = E_i$. With the resolution at our command, this cannot be expected in the present work.]

TABLE I. Values of A and α required to fit Eq. (6).

	E$\perp$**C**	**E**$\|$**C**
A	6800 cm^{-1}	20.0 cm^{-1}
α_{300}	267 eV^{-1}	197 eV^{-1}
α_{300}	302 eV^{-1}	225 eV^{-1}

We do, however, have data on $K_{\parallel}$ for almost two decades beyond the supposed edge. According to Eq. (4), $(K_{\parallel} h\nu)$ should at first be a linear function of $h\nu$, but at sufficiently high energies should vary as $(h\nu - E_i)^{3/2}$. In practice our high absorption data does not fit this anticipated dependence, but rather is in accordance (see Fig. 8) with

$$(K_{\parallel} h\nu) = \frac{9000(h\nu - 0.327)^2}{1 - f(h\nu)} \text{ eV/cm} \quad \text{at} \quad 300°\text{K}. \qquad (8)$$

We have not yet found the most appropriate analytic form for the function $f(h\nu)$, but this is a quantity which is much smaller than unity until $h\nu$ exceeds 0.42 eV. For the data at 100°K, the principal effect is a 0.005 eV shift to higher energies, with perhaps some slight change in the form needed for $f(h\nu)$.

A modification of Eq. (4) to make the initial variation of $(K_{\parallel} h\nu)$ other than the first power of $(h\nu + E_{ex} - E_i)$ seems quite plausible. Deviations from parabolic band shape, or a nonlinear variation of matrix element with $(\mathbf{k} - \mathbf{k}_c)$ could produce such a modification. (The analysis of III-V compounds such as GaAs is similarly complicated[1] by nonparabolic band corrections.) Thus it seems reasonable to anticipate that attempting a fit in terms of the Elliott model for electron-hole-interaction modified direct transitions should ultimately be successful. Other kinds of information on the band structure of tellurium should be able to provide an expression more concrete than Eq. (8) for absorption parallel to the **C** axis above the intrinsic threshold, and an analogous expression for **E**$\perp$**C**.

ACKNOWLEDGMENTS

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[40] R. H. Parmenter, Phys. Rev. **97**, 587 (1955).

[41] H. L. Fritsch and S. P. Lloyd, Phys. Rev. **120**, 1175 (1960).