Infrared Optical Properties of Single Crystals of Tellurium*

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The fundamental optical absorption and photoconductivity of single crystals of tellurium has been investigated. Tellurium crystals exhibit dichroism in the infrared, i.e., the absorption constant depends on the polarization of the incident radiation. At 300°K for radiation polarized perpendicular to the C axis the absorption edge, located by means of an arbitrary criterion, is at 3.82 microns (0.324 ev); for the case of polarization parallel to the C axis the same criterion locates the second edge at 3.29 microns (0.374 ev). The difference between absorption constants survives at wavelengths beyond the edges and is ascribable to the effective masses of the carriers, which depend on their direction of motion relative to the crystal axis. The variation of the energy gaps with temperature has been observed to be -2×10^{-5} ev/°C, i.e., the energy gaps decrease with increasing temperature. Comparison is made with existing theories. The photoconductivity which is barely detectable at room temperature is considerably enhanced by a reduction of the temperature to 90°K. The spectral response indicates the presence of two peaks corresponding in position to the absorption edges. Measurements of the dependence of photoresponse on voltage, light intensity, and shuttering speed indicate that the photoresponse is at least partially in conformity with a monomolecular model. Selenium-tellurium alloys containing 2.7 percent and 11 percent selenium by weight and therefore possessing a considerably reduced lattice volume show a shift of photoconductivity and transmission toward shorter wavelengths, i.e., larger energy gaps.

I. INTRODUCTION

THIS investigation is concerned with the infrared optical properties of single crystals of tellurium, and in particular with the effects of temperature, of the addition of selenium, and of the crystalline anisotropy on the transmission and photoconductivity of the element.

The optical properties of semiconductors have proven to be an important tool in the determination of the band structure appropriate to these materials.[1–3] From the location of the fundamental absorption edge and the corresponding threshold of photoconductivity it is possible to establish the width of the forbidden energy gap; the value so obtained is in reasonable agreement with the values determined by measuring the conductivity as a function of temperature in the intrinsic range.[4] Furthermore the movement of these thresholds when the lattice volume is changed is directly related to the change in energy gap due to the dilation.

Other information can be extracted from the absorption beyond the edge, i.e., from the absorption of radiation whose energy is too low to induce direct transitions from the filled to the conduction band. It is postulated that such residual absorption is due to the free conduction electrons in the material, and consequently some of the properties of these electrons can be inferred from this absorption.

II. SOME GENERAL PROPERTIES OF TELLURIUM (AND SELENIUM)

Tellurium occupies the fifty-second place in the periodic table, its ground state being $5s^25p^4$. It belongs to the VIb group, which comprises in order of increasing atomic number the insulators oxygen and sulfur, the semiconductors selenium and tellurium, and the metal polonium.[5]

Selenium and tellurium share a peculiar hexagonal crystal structure, illustrated in Fig. 1.[6] The atoms are arranged in spiral chains which are oriented along the C axis, each atom sharing covalent bonds with its two nearest neighbors in the chain. The chains are held together by a combination of Van Der Waals and metallic binding. Every third atom is directly above another atom in its chain, so that looking down the C axis a chain appears triangular in shape. The hexagonal lattice is finally achieved by locating a chain at the center and at each of the six corners of the hexagon. This hexagonal structure is readily revealed in tellurium by cleaving a crystal, since the relatively weak binding between chains generates planes of easy cleavage parallel to the C axis.

Because of the difference in atomic radii the lattice constants of selenium are smaller than those of tellurium as shown in Table I.[7]

The similarities between selenium and tellurium suggest that the two elements might form a complete series of solid solutions for all concentrations, and indeed corroborating evidence can be found in the

* This work was supported by contracts with the U. S. Office of Naval Research. The work on Te-Se alloys was supported by an Air Force contract.
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[1] *Semiconducting Materials* (Butterworths Publishing Company, London, 1951), p. 132.
[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, London, 1940), Chap. V.
[3] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. XVII.
[4] K. Lark-Horovitz and K. W. Meissner, Phys. Rev. 76, 1530 (1949); M. Becker and H. Y. Fan, Phys. Rev. 76, 1530 (1949).

[5] A. von Hippel, J. Chem. Phys. 16, 372 (1948).
[6] Landolt-Bornstein Phys.-Chem. Tabellen (Julius Springer, Berlin, 1929), 5. Aufl. 1. Erg.-Bd, p. 394.
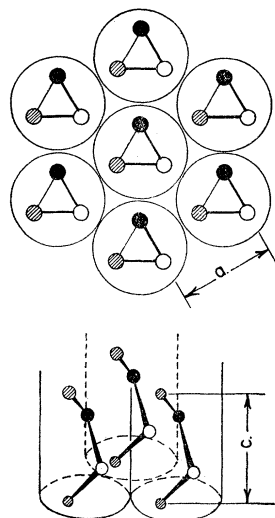[7] E. Grison, J. Chem. Phys. 19, 1109 (1951).

Fig. 1. The crystal structure of tellurium and selenium. Similarly shaded atoms are at the same level in neighboring chains and above each other in the same chain (after Grison).

literature.[7] The most recent x-ray investigation indicates that both lattice constants decrease in a linear fashion as selenium is added to tellurium. The volume of the crystal lattice is reduced, thus markedly affecting the properties of the material. Part of this investigation is consequently devoted to a preliminary study of two alloys of selenium and tellurium.

The electrical properties of tellurium have undergone an intensive investigation in recent years by the groups at Purdue University and at Tôhoku University in Japan.[8,9] An analysis of the available data by Fukuroi indicates that the thermal energy gap is 0.34 ev,[10] which suggests that the fundamental optical absorption ought to begin at a wavelength of about 3.6 microns. Thus tellurium should possess a photoconductive threshold farther in the infrared than any other element with the possible exception of grey tin.[11]

As for the optical properties of tellurium, early investigators reported that the conductivity of tellurium was unaffected by radiation.[12] The existence of a photoconductive effect in tellurium films was reported by Bartlett,[13] although he does not discuss spectral sensitivity except to remark that the wavelength of the exciting radiation had to be less than 4500A. The presence of a photovoltaic effect was observed by Bergmann and Hausler who indicated that the effect was too small to have its spectral dependence established.[14]

Recently Moss[15] observed photoconductivity in evaporated films of tellurium at 195°K and at 90°K.

[8] Fukuroi, Tanuma, and Tobisawa, Sci. Repts. Research Inst. Tôhoku Univ. A1, 373 (1951).
[9] V. E. Bottom, Science 115, 570 (1952).
[10] T. Fukuroi, Sci. Repts. Research Inst. Tôhoku Univ. A3, 175 (1951).
[11] T. S. Moss, Proc. Phys. Soc. (London) A64, 590 (1951).
[12] L. Gmelin, Gmelins Handbuch der Anorganischen Chemie, Tellur (Verlag Chemie, Berlin, 1940), Vol. 11, p. 215.
[13] P. S. Bartlett, Phys. Rev. 26, 247 (1925).
[14] L. Bergmann and J. Hausler, Z. Physik 100, 50 (1936).
[15] T. S. Moss, Proc. Phys. Soc. (London) A62, 264 (1949).

The spectral response reached a maximum at 1.1 microns while the photoconductive threshold lay at about 3.5 microns. The shift of threshold with temperature was 2×10^{-4} ev/°C.[16] Subsequently, he also published data on the transmission of such films. The absorption constant at 1 micron was 10^5 cm^{-1}; it falls to 5×10^4 cm^{-1} at 3 microns. He reported that transmission measurements were possible on bulk samples although he does not indicate whether he used single crystals.[17]

III. EXPERIMENTAL ARRANGEMENT

A. Preparation of the Samples

Much of the work on transmission has been performed using single crystals of tellurium kindly supplied to us by the Anaconda Copper Refining Company. These appear to have been grown unintentionally from the melt, their dimensions varying up to a maximum of about 2 cm×1 cm×0.2 cm. The crystals are prepared for use by grinding and polishing them according to metalographic techniques and subsequently by optical techniques. Spectroscopic analysis of the samples failed to indicate any impurities although a determination of the Hall coefficient as a function of temperature indicated that the impurity concentration was about 10^{18}/cc. The samples were barely in the intrinsic range at room temperature.[18] Uniformity of the samples was established by probing their surface to determine the resistivity from a plot of the potential drop versus distance from an electrode. The resistivity was about 0.3 ohm-cm parallel to the C axis.

These crystals were however unsuitable for measurement of photoconductivity. Because of their dimensions, their resistance was so small that the change in voltage across the sample was not detectable, viz., with an incident energy of 10^{-4} watt and a wavelength of 3 microns the rms change in voltage across a sample was less than 10^{-6} volt with a dc bias of 4.5 volts. Consequently in order to obtain samples of a size suitable for measuring photoconductivity and in general to improve on the purity of the tellurium it was necessary to produce single crystals. These were obtained using an adaptation of the Bridgman technique.[19] Crystals of random orientations and dimensions varying in diameter from about 0.2 mm to 1.5 cm, were successfully produced. The orientation of the crystals was determined by visual examination after the ends had been cleaved and the crystals had been etched by concentrated HNO_3.

TABLE I. Lattice constants of Te and Se in angstroms.

	C	A	C/A
Se	4.944	4.337	1.14
Te	5.912	4.495	1.32

[16] T. S. Moss, Phys. Rev. 79, 1011 (1950).
[17] T. S. Moss, Proc. Phys. Soc. (London) B65, 62 (1952).
[18] A. Nussbaum (private communication).
[19] P. A. Bridgman, Proc. Am. Acad. Sci. 60, 305 (1925).

The crystals were spectroscopically analyzed; again no impurities were indicated. The measurement of the Hall coefficient and the conductivity indicated that the impurity concentration was about 10^{15}/cc in the exhaustion region.[18]

The samples were further prepared for photoconductive experiments by etching in nitric acid. Electrical contact to the sample was provided by electroplating nickel to the ends and soldering copper leads to the nickel.

B. Apparatus

The source of monochromatic radiation was a Beckman infrared monochromator equipped with rock salt optics; it was used in conjunction with a Nernst glower. Most of the measurements were made with radiation interrupted at the rate of 10 cps. The radiation emerging from the monochromator was incident on a plane mirror set at 45 deg to the face of the instrument so that the beam was deflected outward through a polarizer onto a front surface spherical mirror. The latter in turn formed an image of the slit on the sample
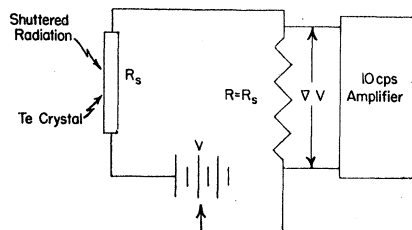
FIG. 2. Circuit used to measure photocoductivity.

whose photoconductivity or optical absorption was being measured. When the optical absorption was under observation, the radiation transmitted by the sample was collected by an elliptical mirror. The mirror formed an image on the target of a Perkin-Elmer radiation thermocouple whose output was fed into a suitable amplifier.

On the other hand the photoconductivity was observed using the simple series circuit of Fig. 2. Due to the radiation the resistance of the sample changes by an amount ΔR. The resulting change in voltage ΔV across the fixed resistor R, when expressed in terms of the constant dc voltage across the sample V, the change in conductivity $\Delta\sigma$, and the dark conductivity σ, is given by:

$$\Delta V = -V\Delta\sigma/\sigma.$$

This signal ΔV is normalized to constant incident energy by using the output of the radiation thermocouple to provide a normalization curve. It is the ratio of ΔV to the output of the thermocouple $V_{\text{T.C.}}$ which is recorded as the relative photoresponse.

The transmission polarizer was constructed following the method of Elliott et al.[20] It consisted of five unsup-

[20] Elliott, Ambrose, and Temple, J. Opt. Soc. Am. **38**, 212 (1948).
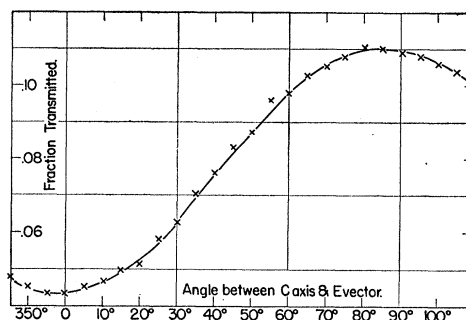
FIG. 3. Transmission of a typical Te crystal plotted vs angle between the C axis and E vector of the incident polarized radiation. $\lambda = 5$ microns.

ported films of amorphous selenium about 50 microns thick mounted so that the radiation to be polarized was incident on the films at Brewster's angle.

IV. OPTICAL ABSORPTION: EXPERIMENTAL RESULTS

The transmission of a typical crystal as function of the angle between the C axis and the plane of vibration of the electric vector for a wavelength beyond the absorption edge, viz., 5 microns, is shown in Fig. 3. The transmission is largest when the plane of polarization is perpendicular to the C axis; it is smallest when the plane of polarization is parallel to the C axis. Figure 4 shows the transmission as a function of λ for these extreme positions. It is evident that the threshold of transmission as well as the transmission in the region beyond the edge depends markedly on polarization. For an angle intermediate between the two extreme polarizations the transmission is as shown in Fig. 5. The results shown in Fig. 5 can be computed from those shown in Fig. 4 in the conventional way, i.e., by resolving the incident radiation into two components one parallel to, and the other perpendicular to the C axis and adding the resulting transmissions vectorially. Thus the plane of electric vibration always experiences a rotation toward the direction perpendicular to the C axis.
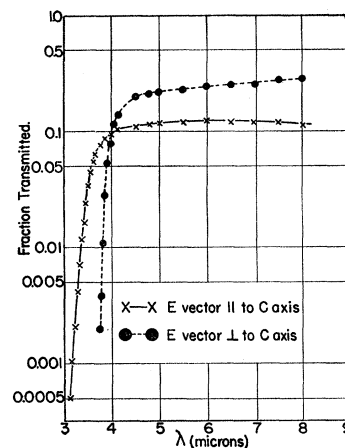
FIG. 4. Transmission plotted vs wavelength for a typical Te crystal showing the effect of polarizing the incident radiation.
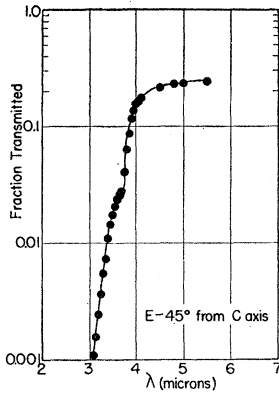
FIG. 5. Transmission of Te crystal plotted vs λ (microns) for E vector making an angle of 45° with the C axis.

In order to determine the value of the absorption constant, i.e., to separate the absorption from the reflection loss, the transmission of a number of samples, of differing thickness was determined as a function of wavelength (Fig. 6). The results are analyzed according to the expression:

$$I/I_0 = (1-R)^2 e^{-Kx},$$

where I_0 and I are the incident and transmitted intensities, respectively, K is the absorption constant, x is the thickness of the sample, and R is the reflection loss at a surface. From a plot of $\ln(I/I_0)$ vs x, both K and $(1-R)^2$ can be determined. The results for K are shown in Fig. 7. It is evident that there are two separate absorption edges dependent on the polarization of the incident radiation, and that even beyond the edge the
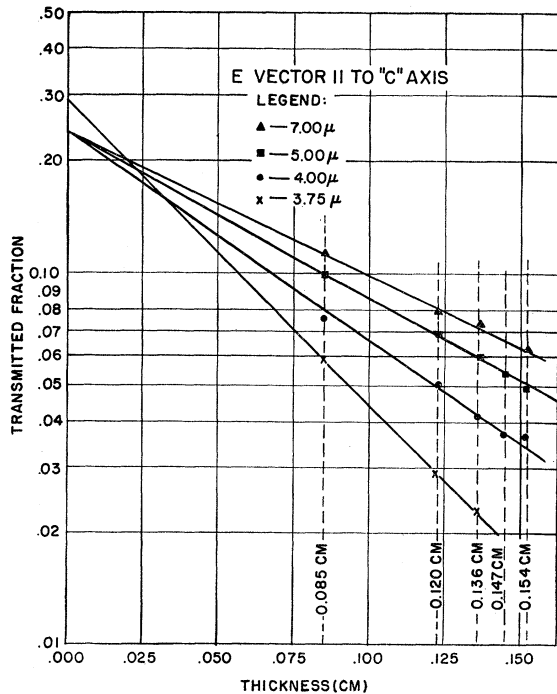

FIG. 6. Transmission of Te crystals plotted vs thickness in cm, E vector parallel to the C axis.

absorption is different for each direction of polarization. Thus tellurium exhibits dichroism in the infrared.

Because a satisfactory theory of the absorption edge has not been developed, somewhat arbitrary criteria must be used for the location of this edge. If that value of wavelength for which the transmission has fallen to, say, 20 percent of its value in the transparent region is chosen, the two edges are 3.91 microns (which corresponds to 0.316 ev) for E perpendicular to the C axis and at 3.45 microns (0.358 ev) for E parallel to the C axis. If the point where the transmission is 5 percent of its long wavelength value is used, these edges are at 3.82 microns (0.324 ev) and 3.29 microns (0.374 ev).

The dependence of transmission on temperature is illustrated in Fig. 8, where the transmission is plotted against λ for E parallel to the C axis. The results indicate
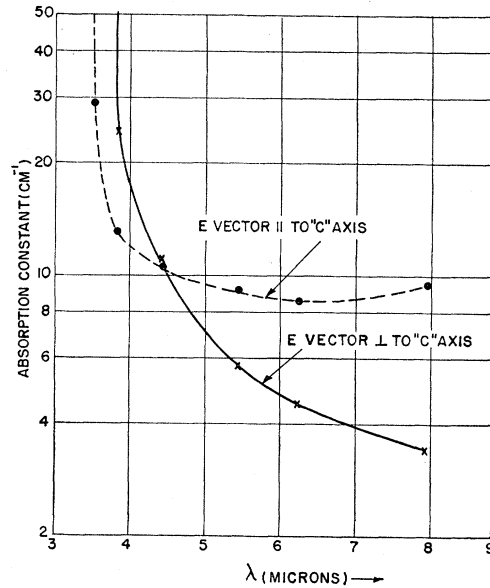

FIG. 7. Absorption constants (cm⁻¹) plotted vs (microns) for Te crystals.

that the edge shifts by an amount approximately -2×10^{-5} ev/°C between 100°K and 300°K and -5×10^{-5} ev/°C between 300°K and 400°K, independent of the criterion used to locate the edge. These shifts were barely detectable, i.e., they were at the limit of resolution available in our optical system. The absorption edge for E perpendicular to the C axis shifted by approximately the same amount.

V. PHOTOCONDUCTIVITY: EXPERIMENTAL RESULTS

The dependence of photoconductive response on temperature, voltage, light intensity, shuttering speed, wavelength, and polarization has been examined.

(A) Temperature

With the particular circuit chosen to measure photoconductive response, the signal ΔV is proportional to

the ratio $\Delta\sigma/\sigma$ as indicated above. Consequently ΔV is expected to be largest at 90°K where σ has decreased by a factor of 18 to 25, depending on the purity of the sample, from its room temperature value. In Table II we have tabulated $(\Delta V/V)V_{\text{T.C.}}$, i.e., the response per volt at constant incident energy, the resistance of the sample, and the ratio $\Delta\sigma_T/\Delta\sigma_{302°}$ at four temperatures. The wavelength chosen was 3.6 microns.

Because of the enhanced response in the low-temperature region most measurements of the spectral dependence were limited to these temperatures, where it was possible to work with smaller band widths.

(B) Voltage

The response for a given light intensity proved to be a linear function of the voltage. In spite of shielding the contacts, there was a residual photovoltaic effect which persisted after the voltage across the sample had vanished. At 100°K its magnitude was 6 μv as compared to a signal of 200 μv with a 1-volt bias across the sample. No saturation of the response was observed. Attempts to increase the voltage toward saturation ended in destruction of the samples which melted away.

TABLE II. Photoresponse vs temperature, at a wavelength of 3.6 microns.

Temp., °K	$(\Delta V/V)V_{\text{T.C.}}$ volts	Resistance ohms	$\Delta\sigma_T/\Delta\sigma_{302°}$
302	0.78×10^{-6}	20.7	1.00
273	2.33×10^{-6}	29.9	2.20
195	$14.4\ \times10^{-6}$	122.0	3.10
100	$56.7\ \times10^{-6}$	295.0	5.16

(C) Shuttering Speed

A large-diameter disc which contained twenty openings was driven by a variable-speed motor to provide a means of interrupting the incident radiation at various frequencies. White light of high intensity was focused on the sample and the signal generated across a series resistor was fed into a wide band amplifier and read off a (Ballantine) ac voltmeter. For the range of shuttering speeds available, i.e., up to 1000 cps the photoresponse was independent of shuttering speed at 300°K and at 90°K.

(D) Light Intensity

The light intensity was reducible by means of a set of grey filters which consisted of wire screens of different meshes. The results indicated that at 90°K the response was linear with light intensity, L_0, for $\lambda = 3.6$ microns, and is proportional to $\sqrt{L_0}$ for $\lambda = 2.2$ microns. At 300°K the response was approximately linear with light intensity when white light was used.

(E) Spectral Response and Polarization

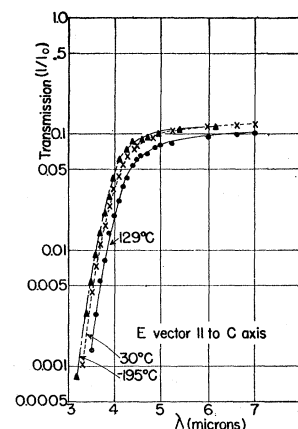In order to improve its accuracy, much of the data on spectral sensitivity was gathered by continuously

FIG. 8. Transmission of Te crystal plotted vs (microns) at three temperature E vector parallel to the C axis.

scanning the spectrum with the help of an automatic wavelength drive attached to the monochromator. The amplified signal, after rectification, was fed into an automatic recorder. A constant slit width was maintained throughout a run; its size was chosen so as to yield a maximum resolution in the region of the photoconductive threshold.

The results at 100°K will be discussed first since at this temperature the enhanced photoconductivity permitted the use of a band width of no more than 0.05 micron for all wavelengths on the curve. The normalized photoresponse is shown in Fig. 9. The most remarkable feature of these curves is the appearance of two separate maxima at wavelengths just short of the threshold. An average of thirty trials on five samples at 100°K places the maxima at 3.24 microns (0.381 ev) and at 3.72 microns (0.332 ev) while the threshold of photoconductivity (that value of the wavelength for which the normalized response has fallen to one-half its maximum value) lies at 4.02 microns (0.307 ev). These values should be compared to the positions of the absorption edges as given above, viz., 3.27 microns (0.377 ev) and 3.77 microns (0.328 ev).

The coexistence of the two maxima was ascribed to the unpolarized quality of the incident radiation. Consequently for subsequent experiments the radiation was polarized. It was expected that by analogy with the transmission there would be only one maximum for
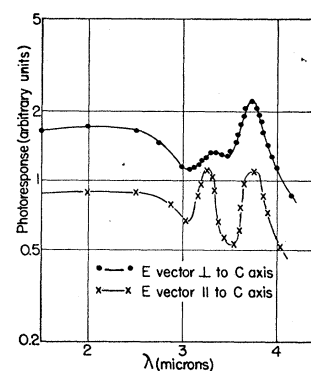

FIG. 9. Photoresponse plotted vs λ for Te crystal at 90°K.

each of two settings of the polarizer 90° apart and that two separate threshold wavelengths would be observed. These expectations were only partly realized (Fig. 9). In all of our runs the same long wavelength threshold persisted for all settings of the polarizer, i.e., $\lambda_{\frac{1}{2}}=4.02$. microns. Rotation of the polarizer did however affect the relative heights of the two maxima. In general the 3.24-micron maximum never exceeded that at 3.72 microns; at very best they were equal. However on some samples the 3.24-micron peak practically disappeared leaving only the one at longer value of wavelengths.

There are a number of possible explanations of this behavior. First of all, the thin needle crystals were oriented by visual examination and may never have been so oriented that the plane of polarization had no components perpendicular to the C axis. Furthermore the "crystals" may have consisted of more than one crystal, these being oriented at small angles to each other.

At the sublimation temperature of $CO_2(195°K)$ the smallest practicable band width at the photoconductive threshold was 0.25 micron, so that the results obtained at this temperature are not as conclusive as those at 100°K. Here again two separate maxima appeared and their average positions were at 3.30 microns (0.374 ev) and 3.75 microns (0.329 ev). The threshold was at 3.94 microns. Comparing results at these two temperatures, the threshold of photoconductivity shifted by 7×10^{-5} ev/°C while the positions of the maxima shifted by -7×10^{-5} ev/°C and -3×10^{-5} ev/°C. The shifting of the maxima was in the same direction as the motion of the absorption edges. On the other hand the thresholds moved in the opposite direction. However, closer examination indicated that the shape of the curve near the threshold had changed with the temperature, so that different criteria for the location of the threshold yielded shifts of different signs as well as different magnitudes. It was concluded therefore that the position and shifting of the maxima bear a closer connection to the same properties of the absorption edges, and consequently to that of the energy gap.

VI. DISCUSSION OF THE EXPERIMENTAL RESULTS

(A) Anisotropy, General Discussion

The anisotropic character of a crystal lattice manifests itself in an anistropy of its mechanical, electrical, magnetic, optical, and photoelectric properties. Thus, in the case of tellurium, anisotropy of some of the mechanical properties, the electrical conductivity, the diamagnetic susceptibiltiy, and the thermal conductivity has been reported by other workers. The experiments described above indicate the anisotropy of optical absorption and of one of the photoelectric effects, viz., photoconductivity. Other work in this laboratory (to be reported soon) indicates that the anisotropy extends to the index of refraction.

Because the electrical conductivity, the index of refraction, and the optical absorption for wavelengths longer than those at the absorption edge depend on the properties of the conduction electrons in a relatively simple fashion, the theory of these properties should indicate what effect anisotropy has on them and what correlations can be expected between them.

Thus the electrical conductivity σ is given by the expression

$$\sigma = neb = ne^2\tau/m^*,$$

where n is the number of carriers, e is the electronic charge, b is their mobility, τ is the mean lifetime between collisions, and m^* is the effective mass. In an anisotropic crystal, $1/m^*$ and consequently b and σ are tensor quantities which tensor reduces to three diagonal components for a hexagonal lattice. The ratio of σ parallel to, and perpendicular to, the C axis, as reported by Bottom, is 1.9.[9]

Secondly the classical Drude-Zener theory of the optical absorption caused by free carriers in solids leads to the following expression for the absorption constant K:

$$K = \frac{2\pi\mu_0 c}{N}\sigma_{dc}\left[\frac{\gamma^2}{\gamma^2+\nu^2}\right],$$

where σ_{dc} is the dc conductivity, ν is the frequency of the exciting radiation, N is the index of refraction, and $\gamma = e/2\pi m^* b$. From this expression it is possible to compute the value of K, say parallel to the C axis, using these values: $\sigma_{dc}=0.3$ ohm^{-1} cm^{-1}, $N=4.8$, $\lambda=5$ microns. The result is 8.9×10^{-3} cm^{-1} compared to a measure value of ~20 cm^{-1}. Such a discrepancy in magnitude between theory and experiment has also been observed in germanium and silicon.[11]

In the case of an anisotropic lattice σ_{dc}, N, and consequently K are tensors and the analysis leads to the following result:

$$(NK)_{11}/(NK)_{33} = (\sigma_{dc})_{11}/(\sigma_{dc})_{33}.$$

Here the subscripts 11 and 33 refer to quantities perpendicular to the C axis and parallel to it, respectively. Since $\sigma_{dc}\propto b\propto 1/m^*$, the theory predicts that by measuring the optical constants of an anisotropic crystal, it should be possible to arrive at a value for the ratio of effective masses therein. In the case of tellurium, the ratio N_{11}/N_{33} as measured by Miss P. Hartig in this laboratory is 0.78 for $\lambda=5$ microns. Furthermore Bottom measured the ratio $(\sigma_{dc})_{11}/(\sigma_{dc})_{33}$ as 0.52. Thus the theory predicts that $K_{11}/K_{33}<1$ which is in agreement with the results shown in Fig. 7. Closer quantitative comparison is not possible because the values of the absorption constant shown in Fig. 7, do not appear to be in accord with the Drude-Zener theory, viz, K is not proportional to λ^2 in the range of wavelengths shown, which was limited by the available equipment. An extension of the observation to longer

wavelengths is necessary before one can make any conclusive comparison with the theory.

(B) Anisotropy and the Energy Gaps of Tellurium

The location of the optical absorption edge of a semiconductor corresponds closely to the longest wavelength of radiation energetically capable of exciting an electron from the filled to the conduction band. Theory, however, does not indicate what criterion should be used for the exact location of this edge on the experimental curve. Consequently the exact evaluation of the gap width is not possible from transmission data. In the case of tellurium the significant fact is that no matter what criterion is used for the location of the absorption edge, there are two separate edges, each corresponding to a different value of the energy gap.

The presence of two gap widths was inferred from the transmission of the sample without correcting for the reflection loss; this procedure is questionable. However, even after such correction, two edges remain, as shown in Fig. 7. Furthermore, photoconductivity offers a means of observing the dependence of the absorption constant on wavelength for a large value of $K(>100 \text{ cm}^{-1})$ so that the existence of two maxima in the dependence of photoresponse on the wavelength indicates that the two edges do not coalesce for values of K larger than those shown in Fig. 7. Thus the experiments demonstrate that the minimum energy required to induce an optical transition from the filled to the conduction band is a function of the polarization of the incident radiation. The probability of such a transition is proportional to $|\langle\psi_i\boldsymbol{\xi}\cdot\boldsymbol{\nabla}\psi_f\rangle|^2$ where ψ_i and ψ_f are the wave functions of the initial and final states, respectively, $\boldsymbol{\xi}$ is a unit vector parallel to the electric vector of the exciting radiation, and $\boldsymbol{\nabla}$ is the operator representing the instantaneous momentum of the electron. Thus the experimental results imply that if the electrons are all in the same initial state, changing the direction of $\boldsymbol{\xi}$ will induce transitions into final states of different minimum energies. This in turn suggests a multiplicity of bands which are less than 0.4 ev above the valence band. Further speculation on the significance of the optical selection rules must be deferred, however, until a satisfactory band model becomes available.[21] Such a band model must also explain the anomolous double reversal in the sign of the Hall coefficient reported by Bottom and Fukuroi.

(C) Variation of the Energy Gap with Temperature

The dependence on the lattice parameter of the forbidden gap between the valence and the conduction bands can be studied experimentally in a number of ways. One of the most direct is an observation, as a function of pressure, of the conductivity of an intrinsic semiconductor at two temperatures. Then since $\sigma=\sigma_\infty\exp(-E_G/2KT)$, where we assume that σ_∞ is relatively insensitive to temperature, we can solve for E_G:

$$E_G=[2K\ln(\sigma_2/\sigma_1)]\left[\frac{1}{T_2}-\frac{1}{T_1}\right]^{-1}.$$

Such an experiment was performed by Bridgman, whose results were analyzed by Bardeen[22],[23] to yield the following value for the slope of the line relating energy gap to pressure in tellurium:

$$\partial E_G/\partial P)_T=-1.6\times10^{-5}\text{ ev}-\text{cm}^2/\text{kg.}$$

Thermodynamically, temperature is equivalent to pressure in changing the lattice parameter, and for changing temperature the result is

$$\partial E_G/\partial T)_P=1.7\times10^{-4}\text{ ev/}^\circ\text{C,}$$

where we have used Bridgman's values of the thermal expansion coefficient and for the compressibility[23] to convert from one set of parameters to the other.

Bardeen and Shockley[24] have related this shift in lattice parameter to the mobilities of holes and electrons, so that from an experimental determination of the mobilities and the elastic constants of the material it is possible to determine the variation of energy gap with dilation of the lattice. Fukuroi[10] has used their results to compute this variation and his result is

$$\partial E_G/\partial P)_T=-2.2\times10^{-5}\text{ ev}-\text{cm}^2/\text{kg,}$$

which is in fair agreement with Bridgman's result. He used values of the mobility and the effective mass ratios for holes and electrons determined at Tôhoku University. However he did not take into account the anistropy of the tellurium lattice.

Now there is another way of obtaining information about changes in the gap width of a semiconductor, viz., by measuring the shift in the fundamental absorption band under the influence of pressure and of temperature. No measurements of the movement of the absorption edge with pressure have been made for an elementary semiconductor, but it would be expected that since a pure compression would be involved the results should agree with the movement of the energy gap determined by a Bridgman type experiment. Measurements of the shift of the edge with temperature had been made, however, notably in germanium and silicon, and the results so obtained did not agree quantitatively with the value measured by other methods.[1]

[21] By using group theory, H. B. Callen has made a qualitative theoretical analysis of the energy band structure of a tetragonal crystal composed of atoms whose ground state is $5s^25p^4$. There is a close analogy between such a hypothetical solid and tellurium, so that this model successfully explains many of the properties of tellurium discussed in this paper. The results are being prepared for publication. Work is also in progress to extend this treatment to a lattice having the spiral chain structure of tellurium.

[22] J. Bardeen, Phys. Rev. 75, 1777 (1949).
[23] P. W. Bridgman, Proc. Am. Acad. Sci. 60, 366 (1925).
[24] J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).

Fan[25] has proposed an explanation for this discrepancy based on the fact that temperature not only affects the volume of the lattice, but also increases thermal vibrations. The interaction between the new spectrum of lattice vibrations and the conduction electrons will result in a shift of the valence and the conduction bands with a consequent decrease of the forbidden band between them. Fukuroi[26] used Fan's results to compute the magnitude of this effect in tellurium and the result was -0.68×10^{-4} ev/°C. However, it should be emphasized that the expression he used was applicable to the diamond lattice and modification must be made before it is applied to the anisotropic tellurium lattice. Addition of these two terms yields a value of approximately 1.0×10^{-4} ev/°C as compared to the experimentally determined shift of approximately -3×10^{-5} ev/°C.

The effect of lattice contraction on the energy gap is quite solidly established by Bridgman's experiment and Hall's confirmation thereof in the lower pressure range.[27] Consequently, in order that there be closer conformity between theory and experiment, it is necessary that the negative, i.e., the Fan term, be of a larger absolute value. Fan found this same difficulty in germanium, where theory and experiment would agree if the effective mass of the electron were reduced by a factor of 3.0. In the case of tellurium, such agreement would result if the effective mass were reduced by a factor of 3.5. There is no experimental basis for such an assumption.

(D) Photoconductivity: Discussion

All of our measurements of photoconductivity were made with shuttered radiation partly to avoid the effects of background radiation and consequent drifting, but mostly to take advantage of the relative ease of amplifying the resulting signal. In the case of tellurium we are dealing with a high dark-current semiconductor, in which the photoconductivity is a small perturbation on the dark current. Under these conditions the rate of change of carrier concentration while the sample is uniformly illuminated by light of intensity L_0 is given by

$$dn(t)/dt=\alpha L_0-BNn(t),$$

where $n(t)$ is the density of photoelectrons, N is the density of carriers in the dark $[N\gg n(t)]$, α is a constant which is related to the excitation efficiency, and B is a constant which expresses the probability for recombination of the electron and a hole in the filled band.

This equation can be solved for $n(t)$, and since experimentally we measure the rms voltage due to the shuttered light, we will ignore the transient terms and compute the rms value of $n(t)$. The result is:

$$n_{\rm rms}=\frac{\alpha L_0}{\sqrt{2}}\left[\frac{1}{(BN)^2+\omega^2}\right]^{\frac{1}{2}},$$

[25] H. Y. Fan, Phys. Rev. **82**, 900 (1951).
[26] T. Fukuroi, Sci. Repts. Research Inst. Tôhoku Univ. **A3**, 175 (1951).
[27] H. Hall (private communication from the author).

and the measured

$$\Delta V_{\rm rms}=\frac{ebRAV}{l}n_{\rm rms},$$

where e is the electron charge, b is the mobility, R is the resistance of the matching resistor, l is the length of the sample, V is the voltage impressed across it, and A is the cross-sectional area. Thus the so-called monomolecular model predicts that the ac response should be directly proportional to V and L_0, and either insensitive to the shuttering frequency or else inversely proportional to it, depending on whether $BN\gg\omega$ or $BN\ll\omega$, respectively.

Our experiments at 300°K indicate that $\Delta V_{\rm rms}\propto VL_0$ and that it is insensitive to shuttering speeds up to 1000 cps for a square-wave input.

At 90°K the photosignal was large enough to permit its observation on an oscilloscope. Here again the response followed the shape of the signal up to the highest shuttering speeds available, viz., 1000 cps. The time-constant or the photoconductive process is therefore shorter than 10^{-3} sec.

Using monochromatic light, $\Delta V_{\rm rms}$ is proportional to L_0 for $\lambda=3.6$ microns, i.e., in the vicinity of the absorption edge, whereas it is proportional to $L_0^{\frac{1}{2}}$ for $\lambda=2.2$ microns, i.e., in the region where absorption takes place within the surface layer. Thus the surface has different photoconductive properties from the bulk material. The experiments therefore indicate that at 90°K the bulk material photoconductivity is in accord with the monomolecular model, while the surface follows either a bimolecular process or else it exhibits complications due to trapping.

The difference in the properties of the surface and of the volume can be used to explain qualitatively the presence of a maximum in photoresponse at the absorption edge. There may be a larger number of traps in the surface layer which would decrease the sensitivity as the absorption was confined to a greater degree in the surface material.

An alternative explanation for the existence of the maximum is afforded by a model similar to Fassbender's,[28] where the optical absorption is included in the analysis of the resulting photocurrent. In this case we modify the basic monomolecular equation by writing

$$L_0=a_0Ke^{-Kz},$$

where L_0 is the light absorbed in a thickness dz, a_0 is the intensity of the incident radiation, K is the absorption constant, and z is the sample thickness. The analysis leads to the result that the total number of electrons liberated by radiation of wavelength λ is

$$N(\lambda)=\frac{a_0K(\lambda)}{B}[1-e^{-K(\lambda)D}],$$

[28] J. Fassbender, Ann. Physik **5**, 33 (1949).

where D is the total thickness of the sample. It is necessary to assume some functional relation between K and λ. Reasonable considerations suggest that at the absorption edge $K = \gamma/\lambda$, where γ is a constant, while in the short wavelength region $K = $ const. These assumptions lead to a maximum response at the absorption edge, if the response is proportional to $L_0^{\frac{1}{2}}$. This condition is fulfilled, at least partially, in tellurium.

An explanation for the temperature dependence of the photoresponse shown in Table III, is based on the observation that, although each incident photon liberates a pair of carriers, the observed photocurrent depends on the number of times these liberated carriers traverse the circuit before they experience recombination. Thus the ratio of photocurrent to photon current, Q, is not necessarily unity. In our case, Q was about 0.1 for $\lambda = 2$ microns at 90°K. Rose[29] shows that the measured increment in the current ΔI, is related to the photon current F, through the expression

$$\Delta I = eQF = (e\tau/T_r)F,$$

where e is the electronic charge, τ is the lifetime of the carriers, and T_r is their transit time between electrodes, which is related to the mobility b, the voltage V, and sample length l, thus

$$T_r = l^2/bV.$$

Therefore the ratio $\Delta\sigma_T/\Delta\sigma_{302°}$ recorded in Table III, which is essentially $\Delta I_T/\Delta I_{302°}$, is given by

$$\Delta\sigma_T/\Delta\sigma_{302°} = (\tau b)_T/(\tau b)_{302°}.$$

This expression is greater than unity, since the mobility is greater at the lower temperature, whereas τ should not change very much. This is in qualitative agreement with our experimental results, although quantitative comparison is not feasible since none of the quantities on the right side of the equation is known.

VII. THE OPTICAL PROPERTIES OF TELLURIUM-SELENIUM ALLOYS

As mentioned previously, we have also examined the photoconductivity and optical transmission of two alloys of tellurium and selenium. Our main purpose was to observe the spectral sensitivity of these properties and to observe the magnitude of the photoconductive effect.

Single crystals of alloys containing 2.7 percent selenium by weight, (hereafter referred to as alloy No. 1) and 11 percent selenium by weight (hereafter alloy No. 2) were grown in a manner similar to that used for growing tellurium crystals. The selenium was obtained from the Canadian Copper Refining Company and their spectroscopic analysis indicated about 7 parts/million impurities. The alloy No. 1 crystals looked very much like Te, although the alloy No. 2 had lost much of the

FIG. 10. Photoresponse of alloy No. 2 (89 Te-11 Se) plotted *vs* λ (cm^{-1}).
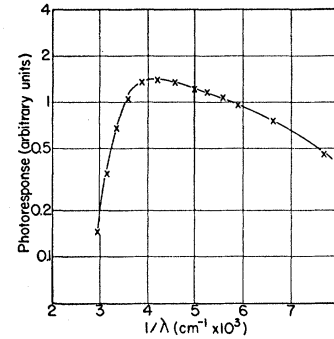
metallic luster characteristic of Te. Uniformity of an alloy No. 2 crystal was established by probing the surface to determine a plot of the potential drop against distance from an electrode. The resistivity as computed from the slope of this curve was 4.1 ohm-cm as compared to 0.6 ohm-cm for tellurium. This is in qualitative agreement with the results of Haken[30] for the resistivity of these alloys. The resistivity of alloy No. 1 was 0.75 ohm-cm. Measurement of the Hall constant and conductivity leads to values of 150 cm^2/volt sec for the mobility in alloy No. 1 and 25 cm^2/volt sec in alloy No. 2 at 300°K.

The transmission of alloy No. 1 exhibits two absorption edges as in tellurium, but these have shifted to shorter wavelengths and are now located (at 300°K) at $\lambda_{1/5} = 3.29\mu$ (0.375 ev) for E parallel to the C axis and at $\lambda_{1/5} = 3.57\mu$ (0.346 ev) for E perpendicular to the C axis as compared to 3.45μ (0.358 ev) and 3.91μ (0.316 ev) for the corresponding quantities in tellurium. The photoconductivity at 90°K exhibited two peaks at 3.33μ (0.372 ev) and 3.59μ (0.344) and the threshold of photoconductivity was at 3.75μ (0.330 ev).

The photoconductivity of alloy No. 2 is shown in Fig. 10. It was impossible to decide whether two peaks and two edges existed since the maximum photoresponse and the absorption coincide in location with the position of the atmospheric absorption band between 2.6 and 3.0 microns. The data shows however that the response has virtually disappeared at 3.1 microns and the maximum photoresponse occures at about $\lambda = 2.8$ microns.

Thus the reduction of lattice parameter accompanying the addition of selenium to tellurium increases the energy gap of the resulting alloy over that of pure tellurium. This conclusion is in agreement with the values for energy gap of the alloys derived by plotting $\ln\sigma$ *vs* reciprocal temperature by Mr. Nussbaum of this laboratory and is in qualitative agreement with the unpublished results of H. Hall,[31] who found that the gap increased with addition of selenium up to concentrations of 30 percent.

The author gratefully acknowledges the advice and

[29] A. Rose, RCA Rev. **12**, 362 (1951).

[30] W. Haken, Ann. Physik **32**, 330 (1910).
[31] H. Hall (private communication).

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Variation of the l-Type Doubling Constant in HCN

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Microwave measurements on six transitions between the l-type doublets of HCN show that the l-type doubling constant depends on rotational angular momentum J as follows:

$$q = 224.471 - 0.002613J(J+1) \text{ Mc/sec.}$$

MICROWAVE transitions directly between the two levels of HCN, which have been split by l-type doubling, have been reported[1] and a variation noticed in the value of the l-type doubling constant q with the rotational quantum number J. However, discrepancies in the nature of this variation and uncertainties[1,2] in its functional dependence on J stimulated the present measurement of l-type doubling in HCN for a number of different values of J.

Measured frequencies for microwave transitions between the l-doubled levels of HCN in the first excited

bending mode ($v_2 = 1$) for a wide range of values of J are listed in Table I. These frequencies are expected to have the form

$$\nu = qJ(J+1) = [q_{J=0} - \epsilon J(J+1)]J(J+1). \quad (1)$$

The small quantity ϵ is expected to be of the order $q(B/\omega_2)^2 \approx 10^{-5}q$, where B is the rotational constant and ω_2 the bending frequency. It is shown in Table I that the measured frequencies can be fitted fairly well to an expression of the form (1) with $q_{J=0} = 224.471$ and $\epsilon = 0.002614$. The form (1) and the positive sign of ϵ are in accordance with calculations of Nielsen.[3]

These results are essentially in agreement with those of Weatherly and Williams,[2] although these authors did not measure enough transitions to determine critically the dependence of q on J. Evaluation of ϵ from the earlier measurements of Shulman and Townes[1] is inaccurate apparently because misidentification of frequency markers gave errors in some of the measured frequencies which were multiples of 30 Mc/sec.

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TABLE I. Transitions between l-type doublets of HCN in excited bending mode ($v_2 = 1$) for various rotational states, and the l-type doubling constant q.

J	Frequency ν in Mc/sec	$q = \dfrac{\nu}{J(J+1)}$	$q = 224.471 - 0.002614J(J+1)$
6	9423.3	224.365	224.361
8	16147.8	224.274	224.283
9	20181.4	224.238	224.236
10	24660.4	224.185	224.184
11	29585.1	224.129	224.126
12	34953.5	224.061	224.063

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[1] R. G. Shulman and C. H. Townes, Phys. Rev. 77, 421 (1950).
[2] T. L. Weatherly and D. Williams, Phys. Rev. 87, 517 (1952).

[3] H. H. Nielsen (private communication).