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## An investigation of photoconductivity in tellurium at low temperatures

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During an investigation of the photoconductivity spectra of tellurium in the 1.6-4.2K temperature range peculiarities have been discovered which indicate the existence of allowed states within the forbidden band near the bottom of the conduction band. The mobility of non-equilibrium electrons and its temperature dependence have been determined. It is shown that the rate of recombination of non-equilibrium carriers is described by a combination of terms linear and quadratic in the concentration.

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The phenomenon of photoconductivity in tellurium is characterized by very specific spectral and relaxation peculiarities which make the interpretation of the experimental results difficult. In preceding investigations at the temperature of liquid nitrogen (see, for example, <sup>[1-3]</sup>) the presence of a maximum near the intrinsic absorption edge, the position of which depends on the polarization of the exciting light, was revealed, and the non-linear character of the recombination of the non-equilibrium carriers was pointed out. Experiments at the temperature of liquid helium<sup>[4]</sup> led to the discovery of the existence of an additional maximum in the photoconductivity spectrum situated at energies less than the width of the forbidden band and differing markedly in its

characteristics from the remaining parts of the spectrum.

Since the study of this peculiarity has opened up the possibility of clearing up the question of the existence of allowed energy states within the forbidden band, we have carried out a detailed investigation of photoconductivity in samples of tellurium with a hole concentration  $p_0 = 2 \cdot 10^{14} - 2 \cdot 10^{16} \text{ cm}^{-3}$  in the temperature range 1.6-4.2 K.

### EXPERIMENTAL RESULTS

The work was carried out in the spectral band 3.5-4.2  $\mu\text{m}$  using a diffraction-grating monochromator. The tellurium samples were placed directly in liquid helium,

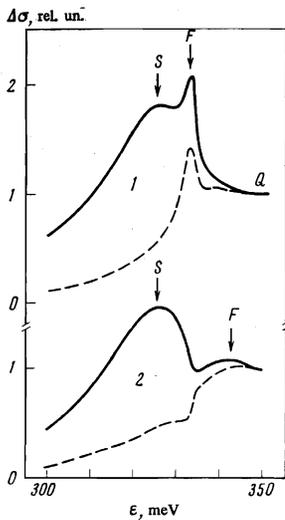


FIG. 1. Photoconductivity of tellurium for steady (continuous line) and modulated illumination (dashed line), 1— $E \perp C_3$ ; 2— $E \parallel C_3$ ,  $T = 4.2$  K,  $p_0 = 7 \cdot 10^{14}$   $\text{cm}^{-3}$ .

and the current was passed in the direction of the  $C_3$  trigonal axis of the crystal. The photoconductivity spectra were recorded using the modulation technique, and also by the potentiometric arrangement with steady illumination of the sample, customarily used in galvanomagnetic measurements, which permits reliable recording of a relative change of  $\sim 10^{-4}$  in the conductivity.

In the photoconductivity spectra under steady illumination (Fig. 1) three characteristic portions are clearly visible: the maxima  $S$  and  $F$  and the portion  $Q$  which is weakly dependent on energy. The position of the maximum  $F$  is essentially dependent on the polarization of the light, while the maximum  $S$  is situated in both cases at identical energies  $\sim 325$  meV, which is less than the width of the forbidden band  $\epsilon_g = 335$  meV.<sup>[5]</sup> The height of the maximum  $S$  decreases rapidly with increase in the modulation frequency (dashed line in Fig. 1),<sup>[4]</sup> and consequently, carrier recombination occurs in this part of the spectrum with a time constant greater than at the maximum  $F$ .

In view of the complexity of the phenomenon, the use of the normal methods of investigating relaxation properties (such as, for example, the  $\tau$ -meter method) at helium temperatures proved to be impossible. The following simple method proved to be the most convenient. For each sample the photoconductivity signal  $\Delta\sigma_{st}$  was recorded for steady illumination and then the amplitude-

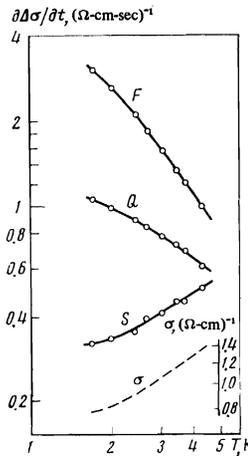


FIG. 3. Temperature dependence of the dark conductivity  $\sigma$  and the photoconductivity  $\partial\Delta\sigma/\partial t$  for different regions of the spectrum,  $p_0 = 7 \cdot 10^{14}$   $\text{cm}^{-3}$ .

frequency dependence of the photoconductivity signal was recorded, from which the value of  $\partial\Delta\sigma/\partial t$  at infinitely high modulation frequency was found. The time constant was defined as

$$\tau = \Delta\sigma_{st} / 2 \frac{\partial\Delta\sigma}{\partial t} \quad (1)$$

The spectral dependence of  $\tau$  for two light polarization directions is shown in Fig. 2. The arrows indicate the positions of the maxima in the photoconductivity spectra. It is evident that each of the regions of the spectrum  $S$ ,  $F$ , and  $Q$  is characterized by its own time constant  $\tau_S$ ,  $\tau_F$ , and  $\tau_Q$ . Moreover, there are parts of the spectrum with contributions from the different regions, for which  $\tau$ , as determined by the method indicated above, assumes a certain intermediate value.

The difference between the maxima  $S$  and  $F$  is determined not only by the difference in time constant. The photoconductivity signal in these regions of the spectrum have sharply differing temperature dependences (Fig. 3). The very similar nature of the temperature curves for the photoconductivity at the maximum  $S$  and the dark conductivity  $\sigma$  should be noted.

The values of  $\tau_F$ ,  $\tau_S$ , and  $\tau_Q$  do not give exhaustive information on the relaxation processes in tellurium, since these processes have a non-linear character and  $\tau$  depends on the concentration of non-equilibrium carriers. Figure 4 shows the dependence of the reciprocal

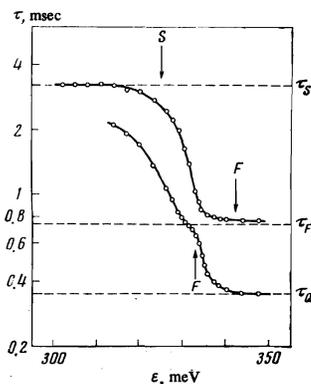


FIG. 2. Spectral dependence of the time constant  $\tau$  for  $E \parallel C_3$  (upper curve) and  $E \perp C_3$  (lower curve) polarization,  $T = 1.7$  K,  $p_0 = 7 \cdot 10^{14}$   $\text{cm}^{-3}$ .

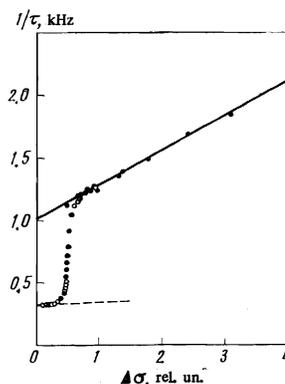


FIG. 4. Relationship between the the photoconductivity signal  $\Delta\sigma_{st}$  and the reciprocal of the time constant  $1/\tau$ ,  $T = 1.7$  K,  $p_0 = 7 \cdot 10^{14}$   $\text{cm}^{-3}$ ,  $E \parallel C_3$ .

lifetime  $1/\tau$  on  $\Delta\sigma_{st}$ . For a fixed value of the excitation quantum energy lying in the region of the maximum  $F$ , the experimental points fit a straight line well (black circles, Fig. 4). The concentration of non-equilibrium carriers at the same time varied with change in the intensity of the exciting illumination. However, the concentration can also be varied by another method, by varying the coefficient of absorption (the sample is illuminated with photons of various energies) at constant intensity (open circles, Fig. 4). So long as the energy of the exciting quantum corresponds to the region of the maximum  $F$ , the experimental points lie on the aforementioned straight line, and then, with decrease in energy, they assume a constant value which characterizes the lifetime at the maximum  $S$ .

## DISCUSSION

In accordance with our preceding paper,<sup>[3]</sup> we shall describe the properties of the non-equilibrium carriers in tellurium by a single rate equation:

$$\frac{\partial n}{\partial t} - D \frac{\partial^2 n}{\partial x^2} + R = kI(t)e^{-kx} \quad (2)$$

with the boundary conditions  $(\partial n/\partial x)_{x=0,b} = 0$ . The light propagates along the  $x$  axis,  $D$  is the coefficient of diffusion,  $I$  is the light intensity,  $k$  is the absorption coefficient,  $n(x, t)$  is the concentration of non-equilibrium carriers, while  $R$  is their rate of recombination, and  $b$  is the thickness of the sample.

The quantity measured is the photoconductivity averaged over the volume of the sample

$$\Delta\sigma(t) = \frac{e\mu}{l} \int n dV, \quad (3)$$

where  $e$  is the electron charge,  $\mu$  is the sum of the moduli of the mobilities of photoelectrons  $\mu_e$  and photoholes  $\mu_h$ . From (2) and (3) one can determine the absolute magnitude of  $\partial\Delta\sigma/\partial t$  at an infinitely high modulation frequency:

$$\frac{\partial\Delta\sigma}{\partial t} = \frac{e\mu l(1 - e^{-kb})}{2b}. \quad (4)$$

The above relationships will be used in the sections below when discussing the basic peculiarities of the photoconductivity observed in the present work.

a) *Mobilities*. At the present time Te is known exclusively as a  $p$ -type semiconductor having an extrinsic conductivity range (below 250 K) containing no equilibrium electrons. Consequently, to study the momentum-relaxation mechanisms for electrons in the conduction band in the low temperature region it is necessary to make use of non-equilibrium carriers. Using expression (4) and the value of the hole mobility  $\mu_h$  found from measurements of the dark conductivity  $\sigma$ , we have succeeded in determining the value of the electron mobility  $\mu_e$  in the temperature range investigated (Fig. 5). In this way information on the kinetic properties of electrons in tellurium in the region of extrinsic conductivity has evidently been obtained for the first time. The data for  $\mu_h$  are in good agreement with the results of other

work<sup>[6]</sup> and provide evidence that in the temperature range 1.5–4.2 K the momentum relaxation for holes takes place in the main on account of scattering by ionized impurities. It would appear that scattering by ionized impurities must also be dominant even for carriers of lower mass, such as electrons, i.e.,  $\mu_e$  ought to increase with increase in temperature. However, the results presented in Fig. 5 indicate that in all the samples the electron mobility decreases with increase in temperature.

In accordance with (4), with increase in the absorption coefficient the quantity  $\partial\Delta\sigma/\partial t$  ought to increase like  $1 - e^{-kb}$ . In fact, as is evident in Fig. 1 ( $E \perp C_3$ ), the signal increases with increase in energy (with increase in  $k$ ). However, on going from the maximum  $F$  towards the region  $Q$  a decrease in the signal takes place. This fact is not difficult to explain if one assumes that  $\mu$  depends on  $x$ . In that case  $\mu$  must be put under the integral sign in expression (3). As a result the quantity

$$\mu_{\text{eff}} = \mu(x) e^{-kx} dV / \int e^{-kx} dV \quad (5)$$

enters in (4) in place of  $\mu$ . For large values of  $k$  (the region  $Q$ ),  $\mu_{\text{eff}}$  is determined by the value of  $\mu(x)$  at the surface. The fall in the signal mentioned above means that in the layer near the surface the mobility of the carriers is less than in the interior. This is quite natural since on nearing the surface the number of defects increases, which also leads to a reduction in  $\mu_{\text{eff}}$ .

b) *The maximum S*. The occurrence of photoconductivity at energies less than  $\varepsilon_g$  (the maximum  $S$ , Fig. 1) means that there are allowed states within the forbidden band of Te. Since the maximum  $S$  is situated at energies 10–15 meV lower than  $\varepsilon_g$ , it cannot be due to any states above the top of the valence band, inasmuch as at helium temperatures such states would be completely free and the rate of generation of non-equilibrium carriers from them would be equal to zero. Consequently, one can speak only of levels (localized states, a narrow band, etc.) situated beneath the bottom of the conduction band. In this case, for the transitions leading to the oc-

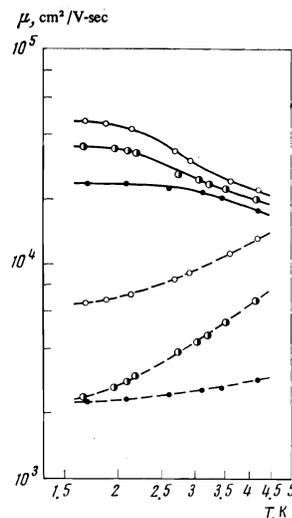


FIG. 5. The temperature dependence of the electron  $\mu_e$  (continuous line) and hole  $\mu_h$  (broken line) mobilities for samples with impurity concentrations equal to  $8 \cdot 10^{14} \text{ cm}^{-3}$  ( $\circ$ ),  $1.6 \cdot 10^{15} \text{ cm}^{-3}$  ( $\bullet$ ), and  $1.4 \cdot 10^{16} \text{ cm}^{-3}$  ( $\bullet$ ).

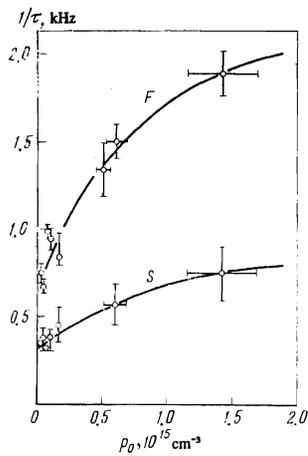


FIG. 6. Relationship between the reciprocal of the time constant and the impurity concentration.

currence of the maximum S, a photohole is formed in the valence band and a photoelectron at levels below the conduction band. It is possible that these levels are also the cause of the heavy electrons with a mass  $0.7m_0$  observed in cyclotron-resonance experiments with external illumination.<sup>[7]</sup> It is natural to suppose that the mobility of such photoelectrons is very small. This explains the noted coincidence of the temperature dependences of the dark conductivity  $\sigma$  and of the quantity  $\partial\Delta\sigma/\partial t$  for the maximum S (Fig. 3). In fact, if  $\mu_e \ll \mu_h$ , then it follows from (4) that  $\partial\Delta\sigma/\partial t$ , as also  $\sigma$ , becomes proportional to  $\mu_h$ .

c) *Time constants.* Up to this point we have been discussing results obtained at very large modulation frequencies and which for this reason did not depend on the form of the recombination term  $R$  in (2). Let us now examine the stationary solution of this equation. This solution is simple to derive in the case of a thin sample ( $kb \ll 1$ ). In this event the reciprocal lifetime determined from formula (1) is equal to  $1/\tau = R(n_{st})/n_{st}$ , where  $n_{st}$  is the steady-state value of the concentration of non-equilibrium carriers. Since  $\Delta\sigma_{st}$  is proportional to  $n_{st}$ , the linear dependence of  $1/\tau$  on  $\Delta\sigma_{st}$  (Fig. 3) means that  $R$  can be presented in the form:

$$R = n/\tau_0 + \gamma n^2, \quad (6)$$

where  $\tau_0$  is the lifetime of non-equilibrium carriers at zero light intensity. In the general case a linear dependence of  $1/\tau$  on  $\Delta\sigma_{st}$  is obtained only for  $kb \ll 1$ , whereas for a real sample  $kb \sim 1$ . However, calculation of this dependence, neglecting the diffusion term, gives a curve whose deviation from a straight line is less than the

scatter of the experimental points.

At the temperature of liquid nitrogen  $R$  also has the form (6),<sup>[3]</sup> but with a somewhat different value of  $1/\tau_0$  and  $\gamma$ . Thus

$$\gamma(1,6K) = 2-8 \cdot 10^{-10} \text{ cm}^3/\text{сек}, \quad \gamma(77K) = 1-5 \cdot 10^{-11} \text{ cm}^3/\text{сек}.$$

Figure 6 shows plots of the reciprocal lifetime  $1/\tau_0$  for the maxima S and F vs the concentration of the equilibrium carriers  $p_0$ . These curves do not pass through zero. The cause of this behavior may be the presence of external unmodulated light that excites non-equilibrium carriers. In this case, owing to the quadratic term in  $R$  (6), the probability of recombination differs from zero even when  $1/\tau_0$  is equal to zero. For this type of explanation it is necessary that the intensity of the external illumination be equal to  $3.1 \times 10^{13}$  photons/cm<sup>2</sup> · sec. An estimate of the intensity of black-body radiation of a temperature 293 K gives a value of  $2.7 \times 10^{13}$  photons/cm<sup>2</sup> · sec. Only photons with wavelengths for which the volume of the sample is illuminated were taken into account for this purpose.

It should be noted that allowance for states below the bottom of the conduction band requires the use of three equations to describe the properties of the non-equilibrium carriers. Our use of a single rate equation (2) can be justified by the fact that all the measurements were carried out in regions of the spectrum for which  $\tau$  does not depend on energy (Fig. 2).

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