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109

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PECULIARITIES OF THE PHOTOCONDUCTIVITY IN CADMIUM SELENIDE

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Peculiarities of the photoconductivity in single crystals of cadmium selenide excited by red light of $\lambda = 7740$ A and by x-rays are considered. The first case corresponds to linear conductivity with a quantum yield $\beta^* = \text{const}$ and $\tau = \text{const}$, and the second case to nonlinear photoconductivity for which $\beta^* = \beta^*(L, J_{ph}, t)$ and $\tau = \tau(L, J_{ph})$. A two stage excitation scheme is proposed in order to explain the irregularities observed in the photoconductivity of single-crystal CdSe.

CADMIUM selenide as well as cadmium sulfide belong to those semiconducting materials with electron conductivity, which show a considerable internal photoeffect under the action of visible light as well as of other types of ionizing irradiation. From this point of view, CdSe can be quite effectively utilized for the preparation of photoresistors, whose integral sensitivity is measured in tens of amperes per lumen. With a resistance in the dark of more than 10^{14} ohms, changes in resistivity by a factor of $10^6 - 10^8$ are observed. The characteristics of the photoresistance are determined both by the technique of preparation as well as by the intrinsic properties of the semiconductor, whose internal photoeffect shows a number of peculiarities.

During the investigation of the properties of the added photoconductivity of single crystal CdSe, it was noted that the qualitative features of the internal photoeffect were similar for irradiation by visible light and by x-rays. This similarity shows up both in the statistical properties (current-voltage characteristics, nature of the light, variation of the sensitivity with applied bias, etc.) as well as in the transients in the photocurrent on switching the excitation in and out. The latter refers to the shape of the curve $J_{ph}(t)$ (Ref. 1), which determines the general features in the evolution of the process. Thus it is found that on approximating the rise and decay curves of the photocurrent by exponential functions, the time constants of these processes show the same dependence on the intensity of excitation, on the bias applied to the sample, on the temperature, etc., independent of whether the conductivity is stimulated by irradiation in the visible part of the spectrum or by x-rays. It was noted, however, that quantitatively the processes of excitation and decay of the photocurrent are substantially different in the two cases. Also, the detailed shapes of the curves prove to be different.

The samples investigated were single crystals

of cadmium selenide obtained by deposition directly from the vapor phase in a stream of argon, analogous to the growth of CdS single crystals.[2] Platinum contacts were applied to opposite ends of the sample by cathodic sputtering, after first cleaning the semiconductor surface by electron bombardment, in such a fashion that the distance between the electrodes was about 2 mm. The contacts obtained were not ohmic, but the contact barrier was small and did not appreciably affect the current-voltage characteristics of the sample, as will be shown below. The CdSe crystals grown by this technique showed a maximum photoeffect in the red region of the spectrum at $\lambda = 7700$ A (Fig. 1) and at the same time were very sensitive to x-rays.

It was noted that the kinetics of the photoconductivity of single crystals of CdSe are markedly dependent on the nature of the exciting irradiation,

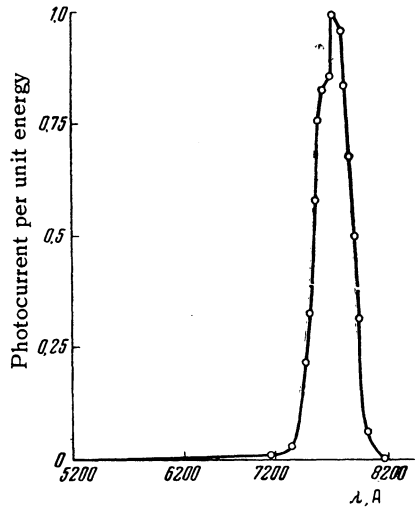

FIG. 1. Spectral sensitivity of single crystal cadmium selenide.

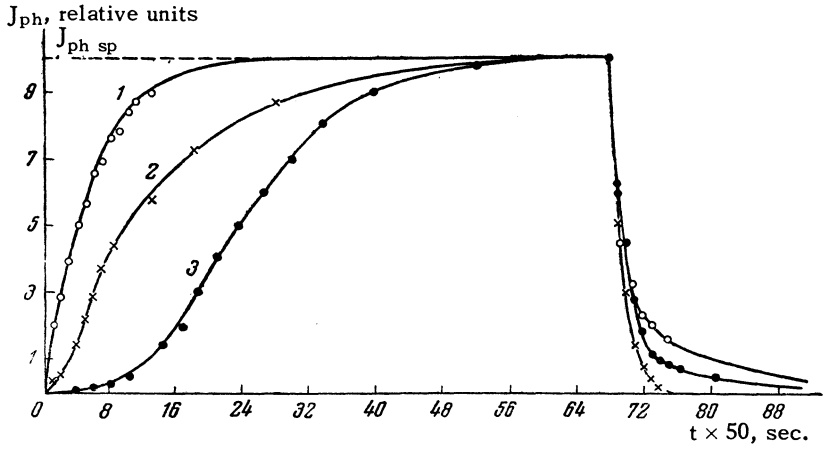

FIG. 2. Oscillograms of the photocurrent in single crystal CdSe excited by radiation of different types: 1 – $\lambda = 7740$ A, 2 – $\lambda = 7160$ A, 3 – x-rays of 50 kv max. energy.

i.e., the parameters of the excitation and decay processes of the photocurrents under otherwise identical conditions are functions of λ. This is illustrated by Fig. 2, which shows oscillograms of the photocurrent when the sample is excited with square light pulses at two different values of λ and by x-rays with a maximum energy of 50 kv. The value of the resultant photocurrent was the same for all three curves and equal to 1 μa with a bias of $U_{ph} = 13$ v applied to the sample.

From an analysis of the oscillograms shown above it follows that, of the three excitation processes studied, only the first case corresponds to a linear shape where $J_{ph}(t)$ varies exponentially with time. The second and third curves show a marked deviation from linearity in the initial rise of the photocurrent. An analysis of the initial stage shows that it corresponds to a parabolic time dependence of the photocurrent, where $J_{ph} \sim t^2$.

Thereafter the parabola degenerates into an exponential whose time constant is, however, larger by about an order of magnitude than the time constant which characterizes Curve 1. The relaxation processes do not show such a characteristic dependence on λ: As a rule, the decay of the photocurrent is exponential, with approximately equal values for the time constants of all three curves, except for the tail of the decay curves which amounts to only 10 – 15% of $J_{ph\ sp}$.

The mismatch in the shape of the curves shown above cannot be explained by a different concentration of current carriers forming in the active volume of the crystal, since the greatest deviation from linearity in the initial stages of the curves is observed under excitation by weakly absorbed light which penetrates uniformly throughout the whole crystal ($\lambda = 7740$ A and x-rays). The deviation from linearity in the photocurrent rise curve is in

this case a consequence of different mechanisms of excitation of the photoconductivity in CdSe when the crystal is illuminated by x-rays and by light of long wavelength, corresponding to the maximum of the spectral characteristics of the photocurrent.

The formal kinetic equation for the photocurrent, which determines J_{ph} as a function of t, may be presented in the form

$$dJ_{ph}/dt + TJ_{ph} = \beta^* L, \quad (1)$$

where T is defined as a quantity inversely proportional to the time constant τ for the rise or decay of the photocurrent, and β^* is a coefficient proportional to the quantum yield β and related to parameters of the photoresistance such as the mobility μ, the absorption coefficient k', the magnitude of the applied bias U_{ph} and the distance d between the electrodes by the relationship

$$\beta^* = \beta\mu e k' U_{ph}/d^2. \quad (2)$$

In the general case T and β^* may depend upon the intensity of illumination L, the current carrier concentration and the time, i.e., $T(L, J_{ph}, t)$ and $\beta^*(L, J_{ph}, t)$. In this case the kinetics of the photoconductivity will obviously be non-linear. The rise and decay curves of the photocurrents may then have different shapes with values of T differing by an order of magnitude. The condition that T and β^* are constants obviously corresponds to the linear case.

It follows from Eq. (1) that the initial stage of the rise of the photocurrent when $t \ll \tau$ is determined by

$$J_{ph} = \beta^* L t. \quad (3)$$

Every deviation from linearity in the relationship (3) is caused by the time dependence of the quantum yield $\beta^* = \beta(t)$. Expanding this expression into a series and taking into account only terms of the first order of magnitude, in the assumption that the term of zero order is equal to zero, we obtain $J_{ph} \sim t^2$; this is indeed observed experimentally under excitation by strongly absorbed light and by x-rays. Curve 1 of Fig. 2 corresponds to the condition $\beta^* = \text{const}$.

On the other hand, when the photocurrent is measured after a long interval of time, i.e., when $t \gg \tau$, it proves to be proportional to the product $\beta^*\tau$. Then the lux-ampere characteristics of the sample must be determined by a relationship of the form

$$J_{ph} = \beta^* \tau L, \quad (4)$$

where β^* and τ may themselves be functions of L, in agreement with the above.

Proceeding in the same manner as in the treatment of the time dependence of the photocurrent in the initial stage of the rise curve, it is not difficult to show that the relationship (4) of the photocurrent with $\beta^*(L)$ and $\tau(L)$ must lead to a nonlinear curve with increasing slope for $J_{ph}(L)$. This nonlinearity should be particularly marked at low intensities of illumination when the concentration of photoelectrons is small, and should change with increasing L first to a linear relationship and then to a nonlinear relationship with decreasing slope. In the case of single crystals of CdSe such a behavior of the light characteristics corresponds to excitation by x-rays as illustrated in Fig. 3. In the

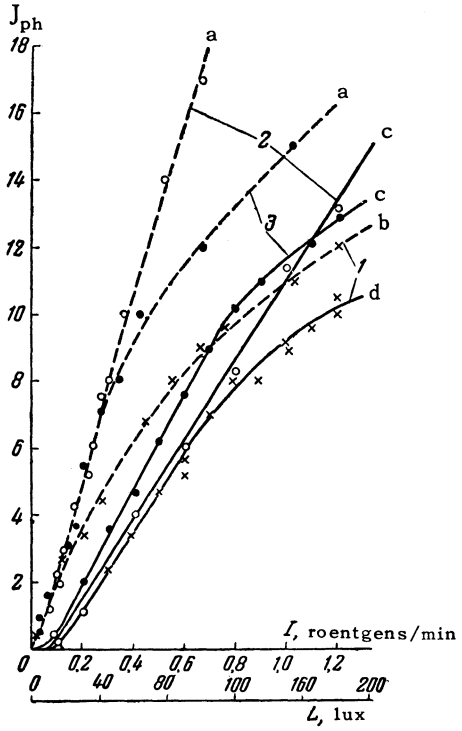

FIG. 3. Light characteristics of single crystal CdSe. The dashed curves correspond to excitation by white light, the full curves correspond to excitation by x-rays. The abscissa gives L in lux for curves a and b; the ordinate for a – $J_{ph} \times 2.10^5$ amp, for b – $J_{ph} \times 10^6$ amp. The abscissa gives I in roentgens/minute for curves c and d; the ordinate for c – $J_{ph} \times 10^5$ amp, for d – $J_{ph} \times 2 \times 10^7$ amp. 1 – $U_{ph} = 0.2$; 2 – $U_{ph} = 15$; 3 – $U_{ph} = 100$ v.

diagram the full curves represent $J_{ph}(I)$ under excitation by x-rays of intensity I, and the dashed curves represent $J_{ph}(L)$ under excitation by non-dispersed white light and with different biases applied to the sample.

Starting from the shape of the spectral characteristics of CdSe shown in Fig. 1 one may conclude that the characteristics of the photocurrent pro-

duced in this experiment by excitation with white light should be close to those of Curve 1, Fig. 2. Analysis of the curve $J_{ph}(L)$ showed that in this case the dependence of the photocurrent on the intensity of illumination at low values of L is linear and that it curves downwards in the region of large values of L; whereas under excitation by x-rays $J_{ph} \sim I^3$ at low intensity I, and changes first to a proportional relationship on increasing I and thereafter to a nonlinear relationship with decreasing slope. From the curves shown in Fig. 3 it follows that the nonlinearity of $J_{ph}(L)$ or $J_{ph}(I)$ in the region of intermediate and large intensities of the exciting irradiation depends also on the magnitude of the bias applied to the sample, particularly for low values of U_{ph}. At large values of U_{ph} (of the order of hundreds of volts) the curvature of the light characteristics is caused by the heating of the sample by photocurrents. In the present paper this part of the curves is not discussed further.

The above discussion leads to the conclusion that excitation by x-rays produces an essentially nonlinear curve also in the case of the statistical characteristics, whereas excitation by light in the visible part of the spectrum close to the maximum sensitivity gives an approximately linear curve. This renders evidence of the different mechanisms of the internal photoeffect in the two cases.

The variation of β^* and τ with L should obviously show up in the kinetics of the photoconductivity, mainly in the rise of the photocurrent. From this point of view, the investigated case of single crystals of CdSe appears typical, as is illustrated by the oscillograms of $J_{ph}(t)$ in Fig. 4. The oscillograms were taken under different x-ray intensities increasing from Curve 1 to Curve 4. It follows from the curves shown that the nonlinearity mentioned above, which is caused by variations of β^* and τ with L, appears only at small levels of excitation. The process becomes linear for large values of I and for large carrier concentrations in the crystal (Curves 3 and 4). This refers not only to the variation of β^* and τ with I, but also to the variation of these parameters with time. Indeed, on increasing the level of excitation the quantum yield β^* no longer depends on the time, giving evidence of the transition from a "bimolecular" to a "monomolecular" process.[3,4]

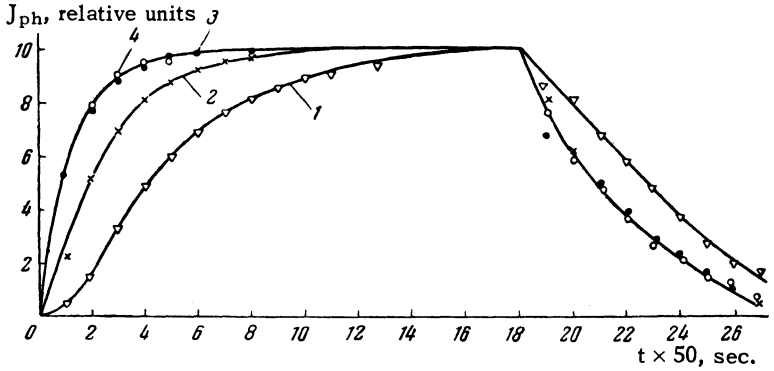

FIG. 4. Oscillograms of excitation and decay of photocurrents in single crystal CdSe for different x-ray intensities, expressed in roentgens/min: 1 – 25; 2 – 125; 3 – 250; 4 – 375. Curves 3 and 4 coalesce.

Some useful information on the hypothetical structure may be obtained from a consideration of the I–V characteristics, as is well known.[5] For CdSe single crystals these characteristics curve upwards in the absence of light and are for the most part linear under illumination regardless of the wavelength of the exciting light (Fig. 5). Such a variation of J_{ph} with U_{ph} may be explained by the presence of electron traps close to the bottom of the conduction band with quite low life times for the electrons. Consequently their role in determining the kinetics of the photoconductivity is negligibly small and did not show up in the preceding experiments. These levels should be unoccupied in darkness and are filled under illumination. The space charge localized in these traps under illumination displaces the Fermi level in the semiconductor. As a result the metal-semiconductor contact does not block the current and the $J_{ph}(U_{ph})$ curve becomes linear. This is confirmed by the temperature dependence of the photocurrent and of the dark current in single crystal CdSe as shown in Fig. 6. The temperature variation of the photocurrent was measured under illumination by red light of wavelength $\lambda = 7740$ A (Curve 1) and by x-rays (Curve 2). In accordance with expectations, at relatively low temperatures until the appearance of an appreciable dark conductivity $J_{ph}(T°) \sim \exp(T_c/T°)$ independent of the wavelength of the exciting illumination, where T_c is a constant for the given range T°.

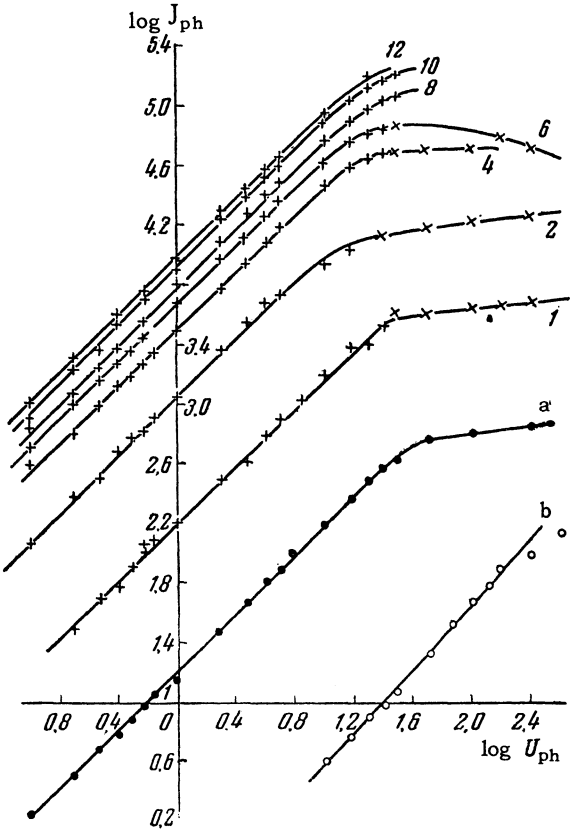

FIG. 5. Current-voltage characteristics of single crystal CdSe. Numbers placed besides the curves correspond to the flux in ma of the x-ray tube at a generating voltage of 50 kv. a – excitation with visible light; b – dark current.

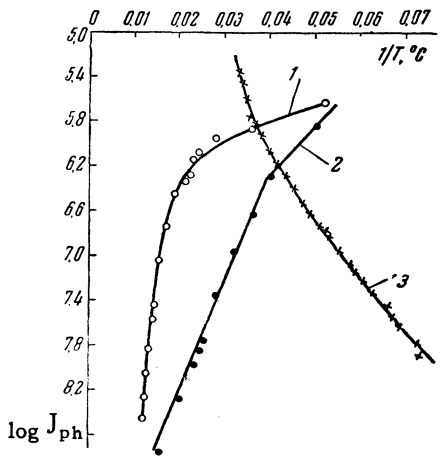

FIG. 6. Temperature dependence of the photocurrent and of the dark current in single crystal CdSe. 1 – excitation with λ = 7740 A, 2 – excitation with x-rays, 3 – dark current (for curve 3 the units of the abscissa are $1/T \times 10$).

The experimental results concerning the photoconductivity of single crystals of CdSe discussed above makes it plausible to adopt the transition scheme shown in Fig. 7. The scheme is based on a two stage mechanism for the excitation of the

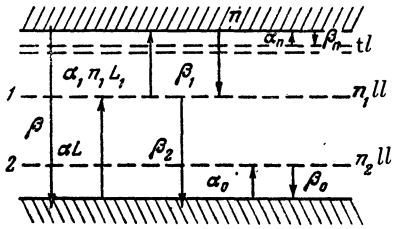

FIG. 7. Model of the proposed optical transitions in single crystal CdSe.

photoconductivity (αL and $\alpha_1 n_1$L). As shown by Lashkarev[6] and Tolstoi,[4] the presence of such a transition causes β^* to be a function of L, J_{ph}, t and τ to be a function of L, J_{ph}. Moreover, the different character of the excitation and decay curves of the photocurrent follows from the formal treatment of a two-stage excitation. The rise curves of the photocurrent are found to depend on L, but not the decay curves. In this connection it is worth noting that the excitation process takes a longer time than the decay. These general conclusions are in good agreement with the experimental data given in the present paper.

In the scheme of Fig. 7, tl are the electron traps. As mentioned above, they do not affect the photoconductivity and play a part only in the dependence of J_{ph} on U_{ph}. The localized electron levels are marked "ll". Level 1 should be nearer the bottom of the conduction band and level 2 nearer the top of the valence band. In agreement with this scheme, the capture cross-section of level 1 for electrons is less than the capture cross-section of level 2 for electrons. For this reason level 1 may be regarded as sparsely populated by electrons, and level 2 as almost completely occupied by electrons.

Recombination from the band onto level 1 is more probable than excitation for low excitation intensities and low current carrier concentrations within the band. In this case the solution of the kinetic equations for the postulated transition scheme leads to[4] $J_{ph} \sim t^2$ for the processes taking place at the beginning of the rise curve; this is observed experimentally. For increasing excitation, the ejection $\alpha_1 n_1$L becomes more probable than recombination onto this level. The analysis shows that in this case $J_{ph} \sim$ L and $\tau \sim 1/L$. At large levels of excitation, partial saturation[4] must occur as a result of the two stage optical transitions.

The transition scheme shown in Fig. 7 corresponds to excitation by x-rays and strongly absorbed light. Under excitation by red light of wavelength λ = 7740 A, the transition αL should be considered as the primary transition, leading to a change in conductivity. However, such a transition suggests the possibility of conduction by local levels;[4] this has yet to be confirmed.

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110

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MEASUREMENT OF THE MASS OF 660 Mev PROTONS

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Measurements of the momentum p and velocity v of 660-Mev protons were conducted in the external beam of the synchrocyclotron. The mass $m_1 = p/v$ was compared with the value computed in accord with the relativistic relation $m_2 = m_0[1 - (v^2/c^2)]^{-1/2}$. Both mass values are in agreement within the limits of the experimental error. The observed relative deviation was $\Delta m/m = 0.004\,(1 \pm 0.6)$.

INTRODUCTION

THE accuracy with which the theory of relativity, now a classic one, describes high-velocity effects, as well as possible deviations from the theoretical predictions, may be rightly questioned. The existence of such deviations can, of course, be rejected from purely theoretical considerations requiring the preservation of the internal completeness of the basic theory. The decisive answer, however, indisputably belongs to the experiment. The large experimental material available confirms, on the whole, the existence of relativistic effects in nature but contains little data with respect to the degree of accuracy of the theoretical predictions. It is often claimed that the successful operation of cyclic high-energy particle accelerators gives an accurate confirmation of the relativistic dependence of the mass on velocity. Farago and Janossy,[1] however, having analyzed the corresponding experimental material, have concluded that the relativistic relation is confirmed to a considerably lesser extent than it is generally assumed. Quantitative results from accelerators now in operation are indefinite to a few percent. It was found in direct experiments with electrons[1] that the experimental error is rather large (2 — 10%). Grove and Fox[2] carried out an experiment with protons, using a 140-inch synchrocyclotron. They determined the equilibrium orbit for 385-Mev protons and measured the angular frequency on the orbit. The results are in agreement with the relativistic law of the variation of mass. An analysis of the data is, however, rendered difficult by the complex motion of protons inside the accelerator on the one hand, and by the scant information provided by the authors on the other.

The purpose of our work was to compare the proton mass calculated according to the relativistic relation $m_2 = m_0[1 - (v^2/c^2)]^{-1/2}$ (from the measured value of v) with the value $m_1 = p/v$ found from the measured proton momentum and velocity. The measurements were conducted in an external beam of protons of about 660 Mev, which made it considerably easier to determine the possible errors.

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